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Protonation of Cp<sup>\*</sup>M(dppe)H hydrides: peculiarities of the osmium congener

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The interaction between Cp<sup>\*</sup>OsH(dppe) (**1**) and a series of proton donors (HA) of increasing strength (indole, CFH<sub>2</sub>CH<sub>2</sub>OH (MFE), CF<sub>3</sub>CH<sub>2</sub>OH (TFE), (CF<sub>3</sub>)<sub>2</sub>CHOH (HFIP), *p*-nitrophenol, and HBF<sub>4</sub>·Et<sub>2</sub>O) has been investigated experimentally by variable temperature IR and NMR spectroscopies in solvents with different coordinating abilities (alkanes, dichloromethane and their mixtures) and computationally at the DFT/B3PW91 level using different models. Both the IR and NMR spectroscopic data for the interaction with weak proton donors are conform to the criteria of M-H...H-A bond formation. Theoretical calculations, however, indicate an asymmetric bifurcated interaction with a significant contribution from the metal atom, which is greater than that previously found for the corresponding Fe system. The basicity factor of **1** (*E*<sub>j</sub> = 1.47) is greater than those of the Ru (1.39) and Fe (1.35) congeners, in agreement with previous studies on other compound families. The kinetic product of proton transfer, *cis*-

[Cp<sup>\*</sup>Os(H)<sub>2</sub>(dppe)]<sup>+</sup>X<sup>-</sup>, which is selectively obtained at low temperatures, irreversibly rearranges to *trans*-[Cp<sup>\*</sup>Os(H)<sub>2</sub>(dppe)]<sup>+</sup>X<sup>-</sup> upon warming to > 230 K. The latter compound with X = BF<sub>4</sub><sup>-</sup> has been crystallographically characterized. The activation enthalpy of the isomerization process ( $\Delta H^\ddagger = 21.5 \pm 1.0$  kcal mol<sup>-1</sup>), obtained from kinetics investigation by <sup>1</sup>H NMR in the 240–260 K range, is identical within experimental error to those previously reported for the M(η<sup>2</sup>-H<sub>2</sub>)<sup>+</sup>BF<sub>4</sub><sup>-</sup> → *trans*-M(H)<sub>2</sub><sup>+</sup>BF<sub>4</sub><sup>-</sup> isomerization process of the iron and ruthenium analogues. The activation entropy ( $\Delta S^\ddagger = 12 \pm 4$  e.u.), on the other hand, is greater than for the lighter metals, following the order Fe < Ru < Os. The mechanism of proton transfer and trends in the energetics of the various steps upon changing the metal atom nature are discussed.

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## Introduction

Proton transfer to transition metal hydrides continues to attract attention<sup>[1, 2]</sup> because of its fundamental importance in many areas, from homogeneous catalysis<sup>[3, 4]</sup> to H<sub>2</sub> biogenesis.<sup>[5, 6]</sup> It results in the formation of cationic dihydride and/or dihydrogen complexes.<sup>[7–10]</sup> The latter may also be kinetic protonation products giving ultimately the dihydride.<sup>[11–15]</sup> In the case of half-sandwich cyclopentadienyl metal dihydride complexes the hydride ligands could occupy different coordination sites, being in *cisoid* (as shown for instance in **I** and **II** of Chart 1) or *transoid* position (**IV**) and the specific *cisoid* case results in a possible dichotomy between classical (**II**) dihydride and nonclassical (**III**) dihydrogen complexes. Structure **I** was shown *e.g.* for compounds [Cp<sup>\*</sup>Mo(PMe<sub>3</sub>)<sub>2</sub>LH<sub>2</sub>]<sup>+</sup> (L = CO, Cp<sup>\*</sup> = Cp<sup>\*</sup>,<sup>[16]</sup> L = PMe<sub>3</sub>, Cp<sup>\*</sup> = Cp,<sup>[17]</sup> Cp<sup>\*</sup>,<sup>[18]</sup>), [Cp<sup>\*</sup>W(PMe<sub>3</sub>)<sub>2</sub>(CO)H<sub>2</sub>]<sup>+</sup>,<sup>[19]</sup> and [Cp<sup>\*</sup>Mo(dppe)(CO)H<sub>2</sub>]<sup>+</sup>.<sup>[20]</sup> For group 8 complexes of type [Cp<sup>\*</sup>ML<sub>2</sub>H<sub>2</sub>]<sup>+</sup>, structure **IV** is typical of all metals (L<sub>2</sub> = 2 PR<sub>3</sub> or bidentate diphosphine),<sup>[7, 8, 12, 15, 21]</sup> whereas structure **II** was only

demonstrated spectroscopically at low temperature for a few osmium compounds.<sup>[21–23]</sup> These structures are usually referred as *trans* and *cis*; this notation will be used herein as well. The *cis* (**II**) and dihydrogen complex (**III**) could be seen as resulting from protonation of the neutral precursors (C<sub>5</sub>R<sub>5</sub>)MHL<sub>2</sub> on the same side (*syn*) as the hydride ligand, whereas the *trans* (**IV**) structure results from proton attack at the opposite side (*anti*).

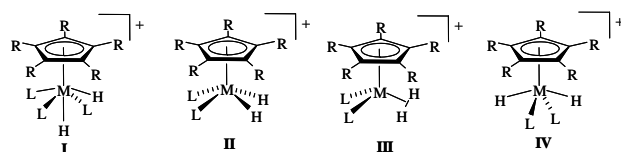
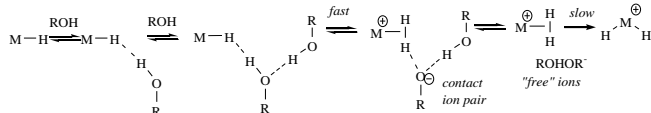


Chart 1.

The metal influence on the properties and relative stability of dihydrogen and dihydride tautomers of Group 8 metal hydrides is known for complexes of several types such as MH<sub>4</sub>L<sub>3</sub>, [MH<sub>3</sub>L<sub>4</sub>]<sup>+</sup>, [MH<sub>3</sub>(PP)<sub>2</sub>]<sup>+</sup>, [MCl(H<sub>2</sub>)(PP)<sub>2</sub>]<sup>+</sup>, [MH(H<sub>2</sub>)(PP)<sub>3</sub>]<sup>+</sup>, and [CpMH<sub>2</sub>(PP)]<sup>+</sup> (L = phosphines or monophosphites, CO; PP = chelating phosphines; PP<sub>3</sub> = P(CH<sub>2</sub>CH<sub>2</sub>PR<sub>2</sub>)<sub>3</sub>).<sup>[24, 25]</sup> The relative stability of the dihydrogen form decreases when the metal is replaced successively by a heavier metal in the same group. The same trend was found for the (η<sup>2</sup>-H<sub>2</sub>) ligand acidity. A few exceptions to this general trend have been noted, which could be related to the strong H–H interaction.<sup>[24, 25]</sup> The osmium analogues usually have the least tendency to form dihydrogen complexes. In some cases they give cationic *cis*-dihydride **II** (Chart 1) upon protonation without the observation of a dihydrogen complex

intermediate.<sup>[21-23]</sup> For example, the result of CpMH(dppe) protonation depends on the metal (Fe, Ru, Os) and temperature. In the case of iron the low temperature protonation by HBF<sub>4</sub> yields [CpFe(η<sup>2</sup>-H<sub>2</sub>)(dppe)]<sup>+</sup>, which remains non-classical up to room temperature but slowly loses H<sub>2</sub>.<sup>[14, 15]</sup> For osmium the same reaction at 198 K yields mixture of *cis*-[CpOs(H)<sub>2</sub>(dppe)]<sup>+</sup> and *trans*-[CpOs(H)<sub>2</sub>(dppe)]<sup>+</sup> in a 1:3 ratio, which changes to 1:70 upon warming to room temperature.<sup>[21]</sup> Protonation of the ruthenium congener was reported only at room temperature to yield a 1:2 mixture of [CpRu(η<sup>2</sup>-H<sub>2</sub>)(dppe)]<sup>+</sup> and *trans*-[CpRuH<sub>2</sub>(dppe)]<sup>+</sup>.<sup>[26]</sup>

For the recently studied series of Group 8 Cp\*M(dppe)H complexes (M = Fe,<sup>[15, 27, 28]</sup> Ru,<sup>[29]</sup> Os<sup>[23]</sup>), the low temperature protonation by strong acids (195 K, CD<sub>2</sub>Cl<sub>2</sub>) yields (η<sup>2</sup>-H<sub>2</sub>) (Fe, Ru) or *cis*-(H)<sub>2</sub> (Os) complexes as kinetic products of *syn* protonation. For all three metals they convert into the corresponding *trans*-dihydrides upon warming. The use of weak proton donors allowed establishing the following proton transfer mechanism for M = Fe and Ru (Scheme 1):



Scheme 1. Mechanism of proton transfer to Cp\*MH(dppe) (M = Fe, Ru)

After the reversible dihydrogen bond formation the proton transfer occurs with participation of a second proton donor molecule. The irreversible isomerization [Cp\*M(η<sup>2</sup>-H<sub>2</sub>)(dppe)]<sup>+</sup> → *trans*-[Cp\*M(H)<sub>2</sub>(dppe)]<sup>+</sup> occurs upon ion pair dissociation. The enthalpy of dihydrogen bond formation and proton transfer increases from iron to ruthenium, whereas the activation parameters for the subsequent isomerization are very similar. The theoretical study of the dihydrogen – dihydride transformation mechanism for M = Fe showed that it involves a ligand reorganization without intermediates.<sup>[30]</sup> Notably, no stationary point was found corresponding to a putative *cis*-dihydride isomer. The present work aims at shining more light on the mechanism of proton transfer to Cp\*Os(dppe)H.

## Results

### Interaction with weak proton donors: characterisation of the hydrogen-bonded intermediate.

In order to investigate the mechanism of the protonation of Cp\*OsH(dppe), **1**, in more details, its interaction with different proton donors was studied by IR (ν<sub>OH</sub> and ν<sub>OSH</sub>) and NMR spectroscopies in the 190–300 K temperature range. According to our well-established protocol,<sup>[31]</sup> the following set of OH and NH proton donors was used: CFH<sub>2</sub>CH<sub>2</sub>OH (MFE), CF<sub>3</sub>CH<sub>2</sub>OH (TFE) and (CF<sub>3</sub>)<sub>2</sub>CHOH (HFIP), indole. In the presence of excess hydride in any solvent used (CH<sub>2</sub>Cl<sub>2</sub>, alkanes or their mixtures), the IR spectra of MFE and TFE in the ν<sub>OH</sub> region show a typical picture of hydrogen bond formation. The intensity decrease of the alcohol ν<sub>OH</sub><sup>free</sup> band is accompanied by the appearance of a new broad low frequency ν<sub>OH</sub><sup>bonded</sup> bands typical of hydrogen bonded OH (Table 1).

As expected, the interaction with the more fluorinated alcohol – TFE – is stronger than with MFE, as indicated by the greater band

shift Δν<sub>OH</sub> = ν<sub>OH</sub><sup>free</sup> - ν<sub>OH</sub><sup>bonded</sup>. The interaction enthalpies were obtained using Iogansen's empirical correlation (Equation 1).<sup>[32, 33]</sup> Analysis of the temperature dependence of the H-bond formation constants for TFE gives ΔH° = -6.1 kcal mol<sup>-1</sup> and ΔS° = -19.7 e.u. The basicity factor E<sub>j</sub> = 1.47 obtained by Equation 2 can be compared with those found for the Ru (1.39)<sup>[29]</sup> and Fe (1.35)<sup>[27]</sup> analogues. These data show the expected basicity increase on descending the group, similarly to the PP<sub>3</sub>MH<sub>2</sub> hydride series (PP<sub>3</sub> = P(CH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>3</sub>, M = Fe, Ru, Os).<sup>[34]</sup> However, the E<sub>j</sub> range is narrower for the Cp\*MH(dppe) series than for the PP<sub>3</sub>MH<sub>2</sub> series (1.12–1.67).

Table 1. Parameters of the hydrogen-bonding between Cp\*OsH(dppe) and MFE or TFE in CH<sub>2</sub>Cl<sub>2</sub>.

ROH	P <sub>i</sub> <sup>[a]</sup>	ν <sub>OH</sub> (free), cm <sup>-1</sup>	ν <sub>OH</sub> (bonded), cm <sup>-1</sup>	Δν, cm <sup>-1</sup>	ΔH° <sup>[b]</sup> kcal mol <sup>-1</sup>	E <sub>j</sub> <sup>[c]</sup>
MFE	0.74	3614	3338	276	-5.0	1.47
TFE	0.89	3592	3229	363	-6.0	1.47

[a] Acidity factors of proton donors.<sup>[35]</sup> [b] Calculated by Equation 1, mean error ± 0.4 kcal mol<sup>-1</sup> [c] Basicity factor as defined in Equation 2, ΔH<sub>II</sub>° = -4.6 kcal mol<sup>-1</sup> for CH<sub>2</sub>Cl<sub>2</sub>.<sup>[35]</sup>

$$\Delta H = 18\Delta\nu/(\Delta\nu + 720) \quad (1)$$

$$E_j = \Delta H_{ij}/(\Delta H_{11}P_i) \quad (2)$$

The IR spectrum of **1** in the Os-H stretching vibration region was studied in the presence of proton donors in different solvents. The ν<sub>MH</sub> band of the hydride complex **1** (2033 cm<sup>-1</sup>, Δν<sub>1/2</sub> = 56 cm<sup>-1</sup> at 200K) is quite symmetric as shown in Figure 1 and partially overlaps on the low frequency side with a dppe ligand overtone. Its intensity decreases as the temperature increases (ε = 84 and 63 L mol<sup>-1</sup> cm<sup>-1</sup> at 200 and 250 K, respectively). Titration of **1** by TFE in hexane at 200K causes the ν<sub>OSH</sub> band intensity to increase when using up to 4 equiv of the proton donor. However, no ν<sub>OSH</sub> band shift was observed under these conditions. Further addition of the proton donor causes an intensity decrease, explained by the proton transfer (see Figure S1). When the same study was carried out in the more polar dichloromethane, only the ν<sub>OSH</sub> band decrease due to protonation was observed with any amount of proton donor. No low-frequency shifts/shoulders expected for a dihydrogen-bonded adducts were revealed. A similar behavior was observed for the Ru analogue in these solvents.<sup>[29]</sup>

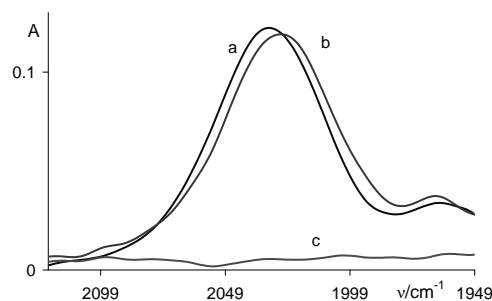


Figure 1. IR spectra (ν<sub>OSH</sub> region) of Cp\*OsH(dppe) (**1**) (0.017 M) (a), **1** in the presence of indole (5 equiv) (b). Methylcyclopentane-dichloromethane 2:1 v/v mixture, 190 K. Spectrum of indole (0.085 M) (c) is shown for comparison.

In the case of the Ru system, use of a 2:1 v/v hexane (or methylcyclopentane)-dichloromethane mixture revealed a low-frequency ν<sub>MH</sub> shoulders in the presence of MFE or TFE,

evidencing *syn* addition with formation of a dihydrogen-bonded adduct. In the case of osmium, on the other hand, only a band intensity increase and no low-frequency shoulder were observed under these conditions. However, a low-frequency shift (of  $-5\text{ cm}^{-1}$ ) became observable in the presence of the weaker proton donor indole (5 equiv) (Figure 1), also suggesting *syn* addition of the proton donor for this metal.

The low temperature NMR study of **1** in the presence of excess TFE in  $\text{CD}_2\text{Cl}_2$  shows the expected changes for dihydrogen bond formation:<sup>[31]</sup> the hydride resonance shifts upfield ( $\Delta\delta = -0.05$  and  $-0.07$  with 2.7 and 4.5 equiv. TFE respectively, see Figure S2). The  $^{31}\text{P}\{^1\text{H}\}$  resonance shifts by  $-0.4$  and  $-0.5$  ppm. The  $T_{1\text{min}}$  value of the hydride resonance substantially decreases upon proton donor addition, being 270 ms at 230 K (500 MHz) in the presence of 2.7 equiv of TFE (vs. 850 ms at 220 K for **1**). The presence of *cis*- $[\text{Cp}^*\text{Os}(\text{H})_2(\text{dppe})]^+$ , *cis*-**1H**<sup>+</sup> (6% and 20% for 2.7 and 4.5 equiv of TFE), is evident from the appearance of a virtual triplet signal at  $-13.32$  ppm in the  $^1\text{H}$  NMR spectrum (having a  $T_1$  of ca. 270 ms at 200 K). Much smaller  $\Delta\delta$  values were found for the interaction between **1** and MFE (3 and 7 equiv):  $-0.005$  and  $-0.011$  for  $^1\text{H}$  and  $-0.03$  and  $-0.06$  for  $^{31}\text{P}\{^1\text{H}\}$  (see Figure S3). Both the IR and NMR spectroscopic data obtained for the interaction of  $\text{Cp}^*\text{OsH}(\text{dppe})$  with proton donors as well as those obtained earlier for the iron and ruthenium congeners are conform to the criteria of  $\text{M}-\text{H}\cdots\text{H}-\text{A}$  bond formation.<sup>[31]</sup>

### Interaction with *p*-nitrophenol – ion pairing in *cis*- $[\text{Cp}^*\text{Os}(\text{H})_2(\text{dppe})]^+\text{X}^-$

The equilibrium resulting from the interaction between  $\text{Cp}^*\text{OsH}(\text{dppe})$  and *p*-nitrophenol (PNP,  $P_i = 1.27$ ) was investigated with the aim to get data about ion pairs formed as the result of proton transfer. Following the approach developed in our laboratories,<sup>[28, 29, 36]</sup> UV-visible spectra were recorded for  $\text{CH}_2\text{Cl}_2$  solutions of PNP (0.001 M) in the presence of **1** at ratios from 1:0.1 to 1:2 at 200 K. As expected the spectra show wide overlapping bands resulting from various forms of phenol and the hydride complex (both free and hydrogen bonded) (Figure 2 and Scheme 2). The absence of free phenolate is signalled by the absence of a band at 430 nm.

Band decomposition yields three bands with maxima at 312, 346, and 386 nm. The first two are assigned to free PNP and to the dihydrogen bonded complex  $[\text{Cp}^*(\text{dppe})\text{OsH}]\cdots\text{HOC}_6\text{H}_4\text{NO}_2$ . The band at 386 nm is attributed to a hydrogen-bonded phenolate ion, since this is blue-shifted from the free  $\text{ArO}^-$  band by 44 nm. The anion appears to be present in the form of a homoconjugate ion on the basis of a titration experiment. Upon increasing the amount of **1** at constant PNP concentration at 200 K, the bands at 346 nm and 386 nm grow in intensity whereas the free phenol band at 312 nm decreases (Figure 2, top). Plotting the intensity at 390 nm vs the  $\text{Cp}^*\text{OsH}(\text{dppe})$  mole fraction (Figure 2, bottom) gives a break

point for a mole fraction of 0.33, indicating a 1:2 binding stoichiometry for the ionic species, *cis*- $[\text{Cp}^*(\text{dppe})\text{Os}(\text{H})_2]^+[\text{ArOHOAr}]^-$ . The same ion pair composition was shown previously for the cationic dihydrogen complexes of iron and ruthenium,  $[\text{Cp}^*(\text{dppe})\text{M}(\eta^2\text{-H}_2)]^+[\text{ArOHOAr}]^-$ . The 14 nm blue-shift of this band relative to free  $[\text{ArOHOAr}]^-$  suggests<sup>[37]</sup> further hydrogen bonding of the homoconjugated anion with the cationic dihydrogen complex,  $[\text{Cp}^*(\text{dppe})\text{OsH}_2]^+\cdots[\text{ArOHOAr}]^-$ . Note that on descending the group both bands attributed to the hydrogen bonded complex and ion pair shift slightly to longer wavelengths; the hydrogen bonded complex band appears at 340, 342 and 346 nm and that of the ion pair is at 380, 384 and 386 nm for Fe, Ru and Os, respectively. This is in agreement with an increase of hydride proton accepting ability and weakening of hydrogen bonding within the ion pair on going down the Group.

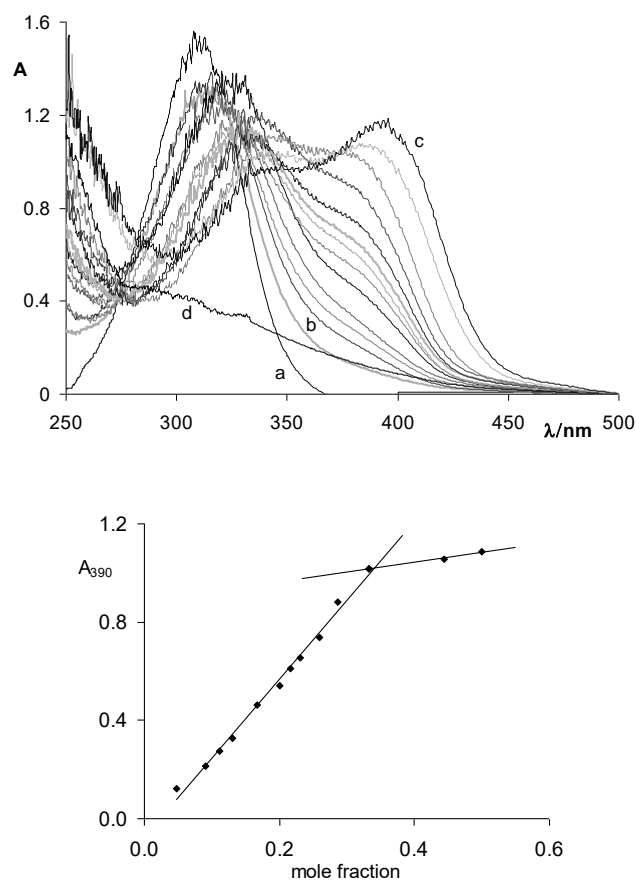
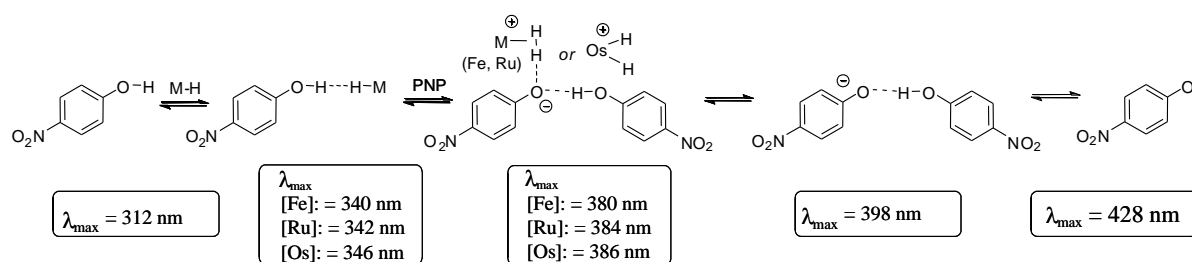


Figure 2. UV-visible spectra (top) of PNP (0.002 M, a) in the presence of 0.05 (b) to 1.0 (c) equiv  $\text{Cp}^*\text{OsH}(\text{dppe})$  (**1**) and corresponding titration plot (bottom).  $\text{CH}_2\text{Cl}_2$ , 200 K. Mole fraction =  $c(\mathbf{1})/(c(\mathbf{1}) + c(\text{PNP}))$ . The spectrum of **1** (0.0023 M, d) is also given for comparison.



Scheme 2. Summary of UV-visible absorption frequencies of various forms of PNP and its conjugate anion.

## Protonation by HBF<sub>4</sub>·Et<sub>2</sub>O: characterisation of *cis*- and *trans*-[Cp\*Os(dppe)H<sub>2</sub>]<sup>+</sup>

We have shown recently<sup>[23]</sup> that *cis*-[Cp\*Os(dppe)H<sub>2</sub>]<sup>+</sup> is the kinetic product (193 K) when protonating **1** with HBF<sub>4</sub>·Et<sub>2</sub>O, then irreversibly transforming into the *trans*-isomer upon warming (above 233 K). Both *cis*- and *trans*-1H<sup>+</sup> were characterized by NMR-spectroscopy in CD<sub>2</sub>Cl<sub>2</sub>. In this contribution, we complete the characterisation of these complexes by an IR study and by structural analysis of *trans*-1H<sup>+</sup>BF<sub>4</sub><sup>-</sup>.

Addition of ca. 1 equiv HBF<sub>4</sub>·Et<sub>2</sub>O to the solution of **1** in CH<sub>2</sub>Cl<sub>2</sub> at 200 K causes the complete disappearance of the Os-H stretching band of **1** (Table 2) and the appearance of two new bands at 2126 and 2177 cm<sup>-1</sup> belonging to *cis*-1H<sup>+</sup> in the IR spectrum (Table 2, Figure 3). These two bands were attributed to the symmetric ν<sup>s</sup> and asymmetric ν<sup>as</sup> OsH<sub>2</sub> stretching vibrations on the basis of the theoretical calculations (Table S1). This spectrum remains essentially unchanged so long the temperature remains below 230 K. At higher temperatures, slow conversion to the *trans*-dihydride complex (*trans*-1H<sup>+</sup>) occurs, eventually yielding two new bands at 2053 and 2102 cm<sup>-1</sup> (Figure 3, spectrum c).

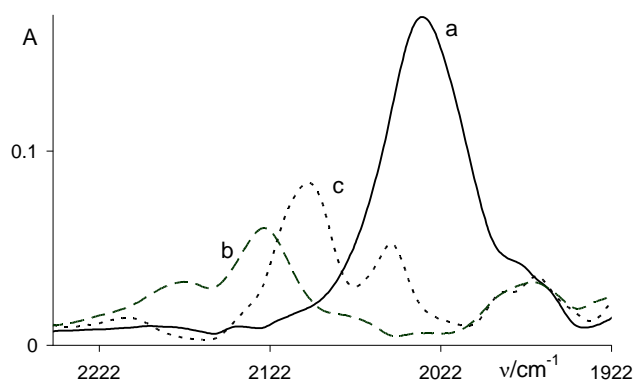


Figure 3. IR spectra (ν<sub>OsH</sub> region) of Cp\*Os(dppe)H (**1**, 0.017 M) (a); *cis*-1H<sup>+</sup> generated *in situ*<sup>[38]</sup> by mixing **1** and ca. 1 equiv. HBF<sub>4</sub>·Et<sub>2</sub>O (b) and *trans*-1H<sup>+</sup>, obtained from (b) after warming to 298 K and cooling back (c). CH<sub>2</sub>Cl<sub>2</sub>, 200 K, l = 1.2 mm.

Table 2. IR spectroscopic parameters of the ν<sub>MH</sub> and ν<sub>MH2</sub> bands of Cp\*MH(dppe) hydrides and their protonation products, [Cp\*MH<sub>2</sub>(dppe)]<sup>+</sup>, in CH<sub>2</sub>Cl<sub>2</sub> at 200 K.

M	Cp*MH(dppe)		<i>trans</i> -[Cp*M(H) <sub>2</sub> (dppe)] <sup>+</sup>			
	ν <sub>MH</sub> (Δν <sub>1/2</sub> ) <sup>[a]</sup>	ε <sup>[b]</sup>	ν <sup>s</sup> <sub>MH2</sub> (Δν <sub>1/2</sub> ) <sup>[a]</sup>	ε <sup>[b]</sup>	ν <sup>as</sup> <sub>MH2</sub> (Δν <sub>1/2</sub> ) <sup>[a]</sup>	ε <sup>[b]</sup>
Fe	1844 (48)	12	1940 (40)	4		
Ru	1918 (58)	34	2002 (56)	14	1968 (26)	8
Os	2033 (56)	83	2102 (40)	41	2053 (24)	25
			2126 (55) <sup>[c]</sup>	16 <sup>[c]</sup>	2177 (85) <sup>[c]</sup>	29 <sup>[c]</sup>

[a] in cm<sup>-1</sup> [b] molar absorption coefficient in L mol<sup>-1</sup> cm<sup>-1</sup> [c] *cis*-H<sub>2</sub>

Careful reinvestigation of the previously reported<sup>[29]</sup> IR spectrum of *trans*-[Cp\*Ru(H)<sub>2</sub>(dppe)]<sup>+</sup> complex revealed two ν<sub>RuH2</sub> bands at 1968 and 2002 cm<sup>-1</sup> (see Figure S4 and Tables 2 and S1), whereas only the stronger one was previously described. On the other hand the IR spectrum of *trans*-[Cp\*Fe(H)<sub>2</sub>(dppe)]<sup>+</sup> complex features only one band at 1940 cm<sup>-1</sup>. This can be explained by the lower intensity of the ν<sup>s</sup><sub>FeH2</sub> band and by the decrease of the difference

between ν<sup>s</sup><sub>MH2</sub> and ν<sup>as</sup><sub>MH2</sub> (Table 2 and Table S1) on ascending the group (Δν = ν<sup>s</sup><sub>MH2</sub> - ν<sup>as</sup><sub>MH2</sub> = 51 cm<sup>-1</sup> for Os and 35 cm<sup>-1</sup> for Ru) leading to bands superposition for Fe. Another interesting feature is a decrease of the band shift upon protonation on descending the group. Taken as the difference between the starting hydride ν<sub>M-H</sub> band and the higher intensity ν<sub>MH2</sub> band of the *trans*-dihydride, the band shift Δν = 100, 86 and 71 cm<sup>-1</sup> for M = Fe, Ru and Os, respectively.

The molecular structure of *trans*-[Cp\*Os(dppe)(H)<sub>2</sub>]<sup>+</sup>BF<sub>4</sub><sup>-</sup> was determined by single crystal X-ray analysis (Figure 4); the main geometrical parameters are collected in Table 3. The two hydrides were located and fully refined with isotropic thermal parameter. The coordination geometry around osmium can be described as a distorted four-legged piano stool. The two hydride atoms are in transoid position with an H(1)-Os(1)-H(2) angle much larger than that for *trans*-[Cp\*Fe(dppe)(H)<sub>2</sub>]<sup>+</sup>BF<sub>4</sub><sup>-</sup> (133(3)° vs. 110.5°),<sup>[15]</sup> whereas the Os-H bonds and Fe-H bonds are identical within the experimental error (1.45(3)-1.42(4) Å vs. 1.48-1.50 Å).<sup>[15]</sup> Relative to the iron analogue, the P(1)-M-P(2) angle is smaller (87.11(3)° vs. 90.73(8)°), whereas the Os-P and Os-CNT distances are slightly longer (2.2841(9)-2.2836(9) Å and 1.888(2) Å vs. 2.170(2)-2.166(2) Å and 1.728(6) Å).

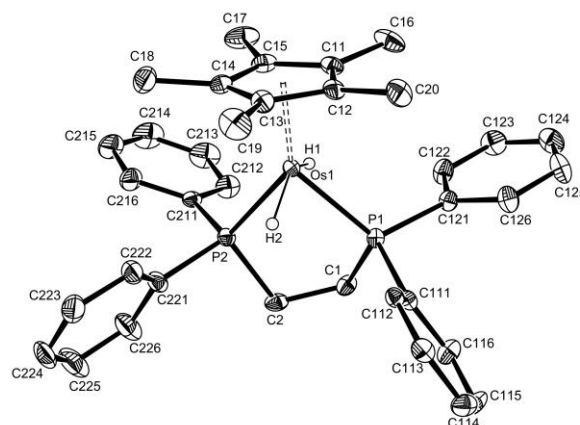


Figure 4. Molecular structure of *trans*-[Cp\*Os(dppe)(H)<sub>2</sub>]<sup>+</sup>BF<sub>4</sub><sup>-</sup> (30% probability level).

## Kinetic study on the “*cis-trans*” isomerization

The previously reported <sup>1</sup>H NMR study of the *cis/trans* isomerization of 1H<sup>+</sup> was limited to 250 K, giving the rate constant  $k = 3.15 \pm 0.02 \cdot 10^{-4} \text{ s}^{-1}$ .<sup>[23]</sup> We have now carried out a variable temperature study in order to obtain the activation parameters.<sup>[39]</sup> An example of the <sup>1</sup>H NMR monitoring is shown in Figure 5.

The data obtained at each temperature gave an excellent fit to the first order rate law yielding the isomerization rate constants reported in Figure 6. The Eyring analysis of the rate constants (Figure S5) yields the activation parameters ΔH<sup>‡</sup> = 21.5 ± 1.0 kcal mol<sup>-1</sup> and ΔS<sup>‡</sup> = 12 ± 4 e.u. The activation enthalpy value is identical, within experimental error, to those found for the iron (ΔH<sup>‡</sup> = 21.6 ± 0.8 kcal mol<sup>-1</sup>)<sup>[30]</sup> and ruthenium (ΔH<sup>‡</sup> = 20.9 ± 0.8 kcal mol<sup>-1</sup>)<sup>[29]</sup> M(η<sup>2</sup>-H<sub>2</sub>)<sup>+</sup> → *trans*-M(H)<sub>2</sub><sup>+</sup> isomerization process, whereas the entropy values tend to increase on descending the group (ΔS<sup>‡</sup> = 5 ± 3 e.u. for Fe and ΔS<sup>‡</sup> = 9 ± 3 e.u. for Ru) resulting in the increase of the isomerization rate constant in the order  $k_{\text{Fe}} < k_{\text{Ru}} < k_{\text{Os}}$  at any given temperature.

Table 3. Key bond lengths (Å) and angles (deg) for hydride **1** and its protonation products *cis*-**1H**<sup>+</sup> and *trans*-**1H**<sup>+</sup> according to the single crystal X-ray data and the DFT B3PW91 calculations on model Cp\*OsH(dhpe) (**1<sub>t</sub>**) and real (**1**) complexes.<sup>[a]</sup>

	<b>1</b>		<i>cis</i> - <b>1H</b> <sup>+</sup>		<i>trans</i> - <b>1H</b> <sup>+</sup>			
	X-ray <sup>[b]</sup>	DFT	DFT	DFT	DFT	X-ray	DFT	DFT
		<b>1<sub>t</sub></b>	<b>1</b>	<i>cis</i> - <b>1<sub>t</sub>H</b> <sup>+</sup>	<i>cis</i> - <b>1H</b> <sup>+</sup>		<i>trans</i> - <b>1<sub>t</sub>H</b> <sup>+</sup>	<i>trans</i> - <b>1H</b> <sup>+</sup>
Os-H	1.56	1.635	1.627	1.615	1.602	1.45(3)	1.638	1.628
				1.619	1.610	1.42(4)	1.641	1.631
Os-CNT	1.90(3)	1.936	1.955	1.952	1.977	1.888(2)	1.931	1.945
Os-P(1)	2.2357(9)	2.253	2.264	2.321	2.345	2.2841(9)	2.315	2.330
Os-P(2)	2.2302(10)	2.252	2.267	2.319	2.371	2.2836(9)	2.310	2.324
∠H-Os-H				61.3	62.8	133(2)	134.4	132.3
∠CNT-Os-H	119(3)	122.2	119.8	116.4	111.6	111(2)	112.1	114.6
				119.7	120.0	116(2)	113.5	113.1
∠CNT-Os-P(1)	134.0(4)	132.4	133.3	126.1	127.5	136.04(5)	136.8	136.9
∠CNT-Os-P(2)	135(2)	132.7	134.0	127.1	130.3	136.34(5)	136.8	135.1
∠P(1)-M-P(2)	78.0(2)	83.7	85.2	81.3	81.3	87.11(3)	86.4	87.9

[a] See computational section for details. [b] Data from ref. [29].

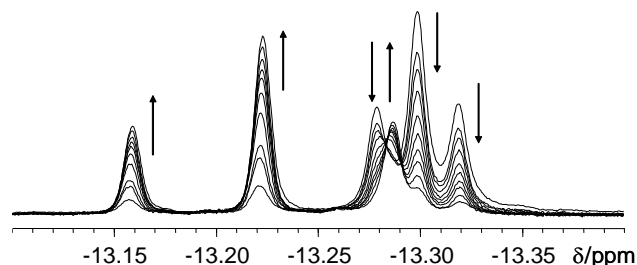


Figure 5. <sup>1</sup>H NMR (500 MHz) monitoring (hydride region) of the *cis*-**1H**<sup>+</sup> → *trans*-**1H**<sup>+</sup> isomerization at 250K, CD<sub>2</sub>Cl<sub>2</sub>. *c*(*cis*-**1H**<sup>+</sup>) = 0.017 M.

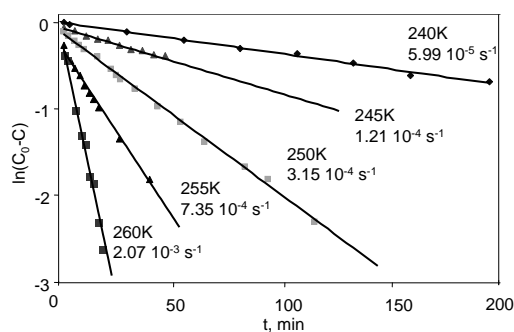


Figure 6. Logarithmic plots of the hydride resonance (-13.17 ppm) appearance for *trans*-[Cp\*Os(dppe)(H)<sub>2</sub>]<sup>+</sup>BF<sub>4</sub><sup>-</sup>. Temperatures and the corresponding rate constants are indicated near to the lines.

The isotope effect in the isomerization process was investigated using CF<sub>3</sub>SO<sub>3</sub>X (X = H, D) at 250 K, yielding the rate constants  $k_H = 2.48 \pm 0.05 \cdot 10^{-4} \text{ s}^{-1}$  and  $k_D = 1.86 \pm 0.04 \cdot 10^{-4} \text{ s}^{-1}$ . The kinetic isotope effect  $k_{HH}/k_{HD} = 1.33$  compares to 1.24 previously reported for iron,<sup>[30]</sup> suggesting a similar intramolecular mechanism for the two isomerization processes. No scrambling of the *cis*-**1D**<sup>+</sup> compound with *cis*-**1H**<sup>+</sup> and *cis*-[Cp\*Os(dppe)(D)<sub>2</sub>]<sup>+</sup> was observed and the isomerization produced *trans*-**1D**<sup>+</sup> selectively, indicating that the initial protonation process is irreversible and that the isomerization is intramolecular.

## Computational study

The computational analysis of hydrogen bonding and proton transfer was carried out at the DFT/B3PW91 level, using HFIP as proton donor and the model complex Cp\*OsH(dhpe) (**1<sub>t</sub>**), where the phenyl rings of the dppe ligand are replaced by H atoms. A

similar study on the Fe analogue was previously reported using either 1 or 2 HFIP molecules, although using a different method (B3LYP) and the simpler CpFeH(dhpe) model.<sup>[28]</sup> Our study started with the analysis of the H-bonding and proton transfer to the *syn* site. The optimized geometries of the hydrogen bonded complexes Cp\*(dhpe)OsH...[HFIP]<sub>x</sub> (x = 1, 2) and of the proton transfer product, *cis*-**1H**<sup>+</sup>...[(CF<sub>3</sub>)<sub>2</sub>CHO...H...OCH(CF<sub>3</sub>)<sub>2</sub>]<sup>-</sup>, are depicted in Figure 7.

As expected the formation of *syn*-**1<sub>t</sub>**·HFIP entails the lengthening of the O-H and Os-H bonds relative to the isolated compounds by  $\Delta r(\text{OH}) = 0.024 \text{ Å}$  and  $\Delta r(\text{Os-H}) = 0.006 \text{ Å}$ . The

(Os)H...H(O) distance is quite short, but the overall geometry of the Os-H...HO fragment (Os...H distance 2.924 Å,  $\angle \text{Os}\cdots\text{H}-\text{O} = 158^\circ$ ,  $\angle \text{H}\cdots\text{H}-\text{O} = 152^\circ$ ) indicates an asymmetric bifurcated interaction with a contribution from the metal atom. Similar structural features were found for the hydrogen bonded adducts of complex Cp\*WH<sub>3</sub>(dppe).<sup>[40]</sup> The Os...H(O) and (Os)H...H(O) distances shorten while the Os-H and O-H bonds elongate upon binding of the second alcohol molecule in agreement with stronger binding in the *syn*-**1<sub>t</sub>**·(HFIP)<sub>2</sub> adduct. The minimum for the *syn*-**1<sub>t</sub>**·HFIP adduct is found 10.7 kcal mol<sup>-1</sup> below the isolated reactants, whereas addition of the second alcohol molecule brings it further down to -21.3 kcal mol<sup>-1</sup>. The formation energy of the latter complex considerably exceeds the sum of the formation energies for the **1<sub>t</sub>**·HFIP adduct and the HFIP dimer (-7.5 kcal mol<sup>-1</sup>) due to a cooperative effect, which was calculated as  $\Delta E_{\text{coop}} = \Delta E(\mathbf{1}_t(\text{HFIP})_2) - \Delta E(\mathbf{1}_t \cdot \text{HFIP}) - \Delta E((\text{HFIP})_2) = -4.5 \text{ kcal mol}^{-1}$ . As expected,<sup>[41]</sup> consideration of the solvent by means of single point CPCM calculations lowers all the formation energies, the *syn*-**1<sub>t</sub>**·(HFIP)<sub>2</sub> adduct being found only -3.5 kcal mol<sup>-1</sup> below the reactants in CH<sub>2</sub>Cl<sub>2</sub> (see the energy profile in Figure S6).

Proton transfer was only investigated starting from the 1:2 adduct, *syn*-**1<sub>t</sub>**·(HFIP)<sub>2</sub>, because when using only 1 HFIP molecule the proton transfer product did not afford a local minimum and reverted back to the H-bonded adduct, like for the previously published Fe system.<sup>[28]</sup> The proton transfer transition state, *syn*-**TS** (Figure 7), features an almost fully formed Os-H bond, with a distance between the hydride ligand and the incoming proton (1.315 Å) far above that typical of (η<sup>2</sup>-H<sub>2</sub>) complexes. The most stable configuration of the *cis*-**1<sub>t</sub>H**<sup>+</sup>...[(CF<sub>3</sub>)<sub>2</sub>CHO...H...O-CH(CF<sub>3</sub>)<sub>2</sub>]<sup>-</sup> ion pair (*syn*-**1<sub>t</sub>IP**) features a quite symmetrical cation-anion arrangement with two (Os)H...O hydrogen bonds (Figure 7). The distance between the two hydride ligands is 1.552 Å. Thus, formation of the *cis*-dihydride complex occurs via the direct *syn* protonation of the metal atom assisted by the interaction with the hydride ligand. No minimum for an (η<sup>2</sup>-H<sub>2</sub>) complex could be found. The transition state *syn*-**TS** is above *syn*-**1<sub>t</sub>**·(HFIP)<sub>2</sub> by 13.8 kcal mol<sup>-1</sup> in the gas phase and 10.2 kcal mol<sup>-1</sup> in dichloromethane. The product ion pair is 4.0 kcal mol<sup>-1</sup> higher than *syn*-**1<sub>t</sub>**·(HFIP)<sub>2</sub> adduct in the gas phase and 0.5 kcal mol<sup>-1</sup> lower in dichloromethane. Thus, the *syn* proton transfer is rendered favourable by the solvent effect in CH<sub>2</sub>Cl<sub>2</sub>. The full energetic profile for hydrogen bonding and proton transfer in the gas phase and in CH<sub>2</sub>Cl<sub>2</sub> solution is available in the Supporting Information (Figure S6).



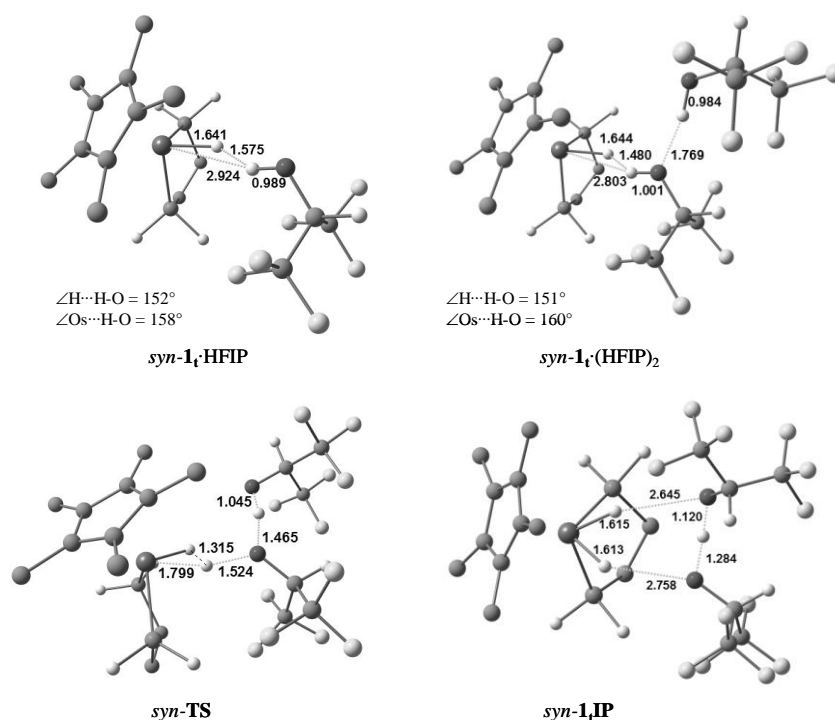


Figure 7. Optimized geometries of the hydrogen bonded, transition state, and final ion pair complexes related to the *syn* proton donor addition to **1<sub>t</sub>**, with selected bond distances in Å. Hydrogen atoms of the Cp\* ligand and of the ethylene backbone are removed for clarity.

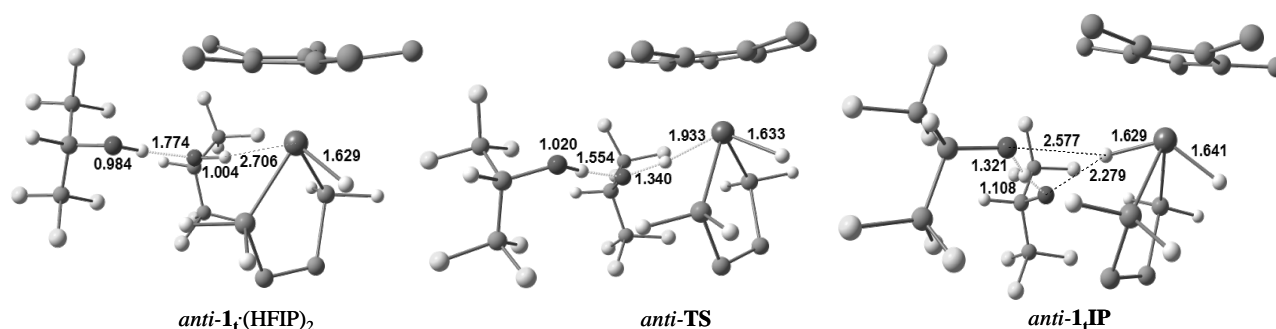


Figure 8. Optimized geometries of the hydrogen bonded, transition state, and final ion pair complexes related to the *anti* proton donor addition to **1<sub>t</sub>**, with selected bond distances in Å. Hydrogen atoms of the Cp\* ligand and of the ethylene backbone are removed for clarity.

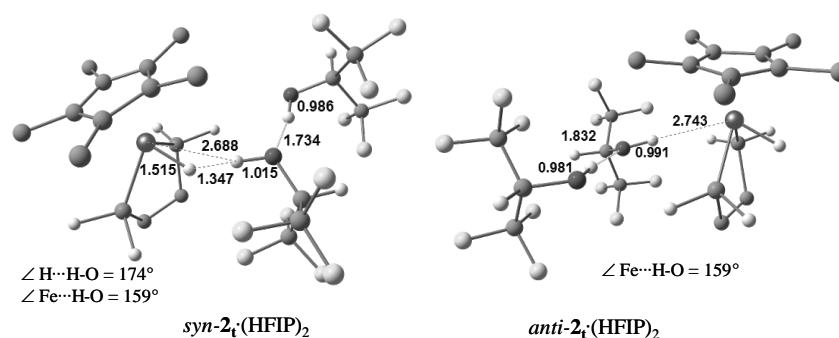


Figure 9. Optimized geometries of the hydrogen bonded complexes between Cp\*FeH(dhpe) (**2<sub>t</sub>**) and two HFIP molecules, with selected bond distances in Å. Hydrogen atoms of the Cp\* ligand and of the ethylene backbone are removed for clarity.

The *anti* addition has only been studied for the more favourable 1:2 adduct, *anti-1<sub>t</sub>*(HFIP)<sub>2</sub>. As already found for the Fe analogue,<sup>[28]</sup> this hydrogen-bonded adduct is less energetically

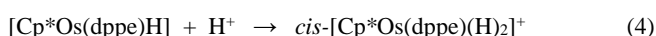
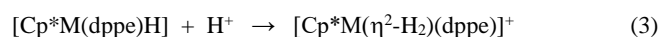
favourable than the corresponding *syn-1<sub>t</sub>*(HFIP)<sub>2</sub>. Its optimized geometry is shown in Figure 8 and its relative energy is included in Figure S6. The most relevant structural change is the shortening of

the Os-H distance ( $\Delta r(\text{Os-H}) = -0.006 \text{ \AA}$ ). The *anti* protonation to yield *trans*-**1H**<sup>+</sup>[R<sup>F</sup>O<sup>−</sup>⋯H<sup>+</sup>⋯OR<sup>F</sup>]<sup>−</sup> features a transition state, *anti*-**TS** at 6.7 kcal mol<sup>−1</sup> (in the gas phase) and 4.8 kcal mol<sup>−1</sup> (in dichloromethane) above the corresponding metal-bound hydrogen bonded adduct, *anti*-**1r**⋯(HFIP)<sub>2</sub>. Since the energetically preferred adduct is the dihydrogen bonded complex *syn*-**1r**⋯(HFIP)<sub>2</sub>, the latter can be regarded as the system “resting state”. Hence, the proton transfer barrier becomes almost identical for the two pathways in dichloromethane (Figure S6).

For comparison, the two protonation pathways for the iron analogue were reinvestigated using the same computational level (B3PW91) and model [Cp\*FeH(dhpe)] (**2i**) as for the Os system. The complete energy profiles for hydrogen bond formation and proton transfer, for both *syn* and *anti* additions, are provided in the Supporting Information (Figure S7). In spite of the lower E<sub>j</sub>, **2i** gave slightly greater formation energies for the more stable *syn*-**2r**⋯(HFIP)<sub>2</sub> adduct (Figure 9), −22.4 kcal mol<sup>−1</sup> in gas phase and −4.2 kcal mol<sup>−1</sup> in CH<sub>2</sub>Cl<sub>2</sub> relative to the isolated reactants, than the osmium analogue. The transition state for the *syn* protonation to yield the nonclassical kinetic protonation product, [Cp\*Fe(η<sup>2</sup>-H<sub>2</sub>)(dhpe)]<sup>+</sup>⋯[R<sup>F</sup>O<sup>−</sup>⋯H<sup>+</sup>⋯OR<sup>F</sup>]<sup>−</sup>, *syn*-**2iP**, is above **2r**⋯(HFIP)<sub>2</sub> by 7.6 kcal mol<sup>−1</sup> in the gas phase and by 4.9 kcal mol<sup>−1</sup> in dichloromethane, both being *ca.* half those of the related osmium system. On the other hand, the *anti* protonation to yield *trans*-**2H**<sup>+</sup>[R<sup>F</sup>O<sup>−</sup>⋯H<sup>+</sup>⋯OR<sup>F</sup>]<sup>−</sup>, *anti*-**2iP**, is characterized by a higher activation barrier, reaching 12.3 kcal mol<sup>−1</sup> in the gas phase and 9.7 kcal mol<sup>−1</sup> in dichloromethane relative to the corresponding *anti*-**2r**⋯(HFIP)<sub>2</sub> local minimum (Figure S7), which corresponds to 20.2 kcal mol<sup>−1</sup> and 18.0 kcal mol<sup>−1</sup>, respectively, from the “resting state” *syn*-**2r**⋯(HFIP)<sub>2</sub> (Figure S7).

The last point addressed by the computational study is the *cis/trans* isomerization mechanism for **1H**<sup>+</sup>. This study was carried out on both the model [Cp\*OsH<sub>2</sub>(dhpe)]<sup>+</sup> (**1iH**<sup>+</sup>) and the full [Cp\*OsH<sub>2</sub>(dppe)]<sup>+</sup> system, without consideration of the counterion. The optimized geometries of the model and full *trans* systems are in close correspondence with the experimentally observed structure (Table 3), the only major discrepancy being the Os-H distances which are notoriously underestimated in X-ray structural determinations. It is also notable that the experimental bond distances are better matched by the model system, although the discrepancy between model and full systems is small. The bond angles are quite close to the experiment for both systems. For comparison, the calculations were also carried out for the neutral precursor **1** (and for the model **1i**), and compared with those of the previously reported<sup>[23]</sup> X-ray structure in Table 3.

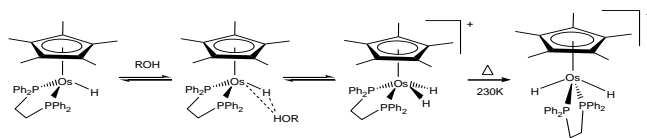
The model cation **1iH**<sup>+</sup> gives nearly the same gas-phase energy (E<sub>s</sub>) for the two isomers (just 0.8 kcal mol<sup>−1</sup> in favour of *cis*-**1iH**<sup>+</sup>), but the *trans* isomer becomes preferred by 6 kcal mol<sup>−1</sup> for the full system **1H**<sup>+</sup>, in agreement with the essentially quantitative isomerization. For comparison, the energy difference between the *syn* and *anti* protonation products for the Ru and Fe systems, [Cp\*M(η<sup>2</sup>-H<sub>2</sub>)(dppe)]<sup>+</sup> and *trans*-[Cp\*M(dppe)(H)<sub>2</sub>]<sup>+</sup>, is 4.9 kcal mol<sup>−1</sup> and 3.1 kcal mol<sup>−1</sup>, respectively, in favor of the *anti* isomer. The optimized geometries of these four complexes, reported here for the first time, are available in the SI. The proton affinity of these hydrides, calculated as −ΔH(298 K) for the kinetically controlled *syn* protonation reactions 3 and 4, is 258.6 kcal mol<sup>−1</sup> for Fe, 257.3 kcal mol<sup>−1</sup> for Ru and 263.4 kcal mol<sup>−1</sup> for Os, placing the basicity of the Os complex higher than that of the Fe and Ru analogues in agreement with experiment.<sup>[42]</sup>



The transition state for the *cis/trans* isomerization of **1H**<sup>+</sup> displays a similar geometry to that previously reported for the related non-classical complex of iron (Figure S8) and is located at 25.5 kcal mol<sup>−1</sup> above *cis*-**1iH**<sup>+</sup> in the gas phase (25.1 kcal mol<sup>−1</sup> in dichloromethane).<sup>[30]</sup> The isomerization proceeds in a single step by migration of one hydride ligand from one side to the other of the metal coordination sphere with concomitant tilt of the phosphine ligands. The isomerization barrier is slightly lower than that reported for the [Cp\*Fe(η<sup>2</sup>-H<sub>2</sub>)(dhpe)]<sup>+</sup> isomerization in the gas phase (28.9 kcal mol<sup>−1</sup>).<sup>[30]</sup> This is in agreement with the slow rate measured experimentally for the osmium system (see above), similar to that of the corresponding Fe system.<sup>[30]</sup>

## Discussion

The overall process of proton transfer to Cp\*OsH(dppe) (**1**) can be rationalized as shown in Scheme 3. It parallels the mechanism established for the protonation of the Cp\*MH(dppe) complexes of Fe and Ru (Scheme 1), with a kinetically controlled *syn* addition followed by slow isomerization to the thermodynamically more stable *trans* isomer, which corresponds to the expected product of *anti* addition.

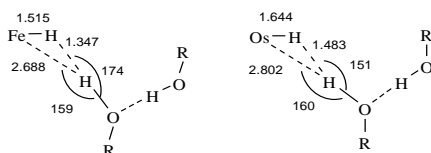


Scheme 3. Proposed mechanism of interaction between **1** and ROH proton donors.

The first step for all three metals is formation of a hydrogen-bonded adduct with two proton donor molecules, since a 1:1 adduct does not have sufficient thermodynamic drive to complete the proton transfer step. Also common to the three metals is the site preference, the *syn* adduct being more stable than direct bonding to the metal site opposite to the hydride ligand. The hydride basicity in hydrogen bonding (E<sub>j</sub>) increases on going down the group in agreement with expectations based on previous studies on other compound families (see Introduction). However, the range is narrower (1.35–1.47 on going from Fe to Os) than for the only other investigated family of Group 8 hydride complexes, PP<sub>3</sub>MH<sub>2</sub> (1.12–1.67 range).<sup>[34]</sup>

A striking difference between the PP<sub>3</sub>MH<sub>2</sub> and Cp\*MH(dppe) families is that dihydrogen bonding always leads to a nonclassical (dihydrogen complex) product for the former, whereas a change occurs in the latter: nonclassical product for Fe and Ru; classical *cis* dihydride for Os. The geometrical analysis of the dihydrogen bonded adducts reveals an asymmetric bifurcated structure with the increasing impact of the M⋯HO interaction on going from iron to osmium (see Scheme 4). Consequently, the increasing importance of the direct metal participation in hydrogen bonding for the osmium system leads the proton transfer toward the direct formation of the classical *cis*-**1H**<sup>+</sup>, without involvement of a non-classical intermediate. Despite its classical nature, *cis*-**1H**<sup>+</sup> exists as an ion pair stabilized by hydrogen bonding with the homoconjugated [R<sup>F</sup>O<sup>−</sup>⋯H<sup>+</sup>⋯OR<sup>F</sup>]<sup>−</sup> anion similarly to the [Cp\*(dppe)M(η<sup>2</sup>-H<sub>2</sub>)]<sup>+</sup>[R<sup>F</sup>O<sup>−</sup>⋯H<sup>+</sup>⋯OR<sup>F</sup>]<sup>−</sup> ion pairs of Fe<sup>[28]</sup> and Ru.<sup>[29]</sup>





Scheme 4. Comparison of H-bonding parameters for *syn*-Cp\*MH(dppe)-(HFIP)<sub>2</sub> with M = Fe and Os.

A similar trend had been previously reported for the [Cp\*MH<sub>3</sub>(dppe)] (M = Mo, W) pair of compounds.<sup>[40]</sup> Although in neither case could a nonclassical intermediate of kinetically controlled protonation at a hydride site be experimentally observed,<sup>[40, 43]</sup> calculations on the simplified [CpMH<sub>3</sub>(dhpe)] models revealed a distinct local minimum for a dihydrogen complex [CpMH<sub>2</sub>(H<sub>2</sub>)(dppe)]<sup>+</sup> in the molybdenum case but none along the proton transfer pathway for the tungsten system.<sup>[40]</sup> The maximum energy point for the preferred protonation pathway in the [Cp\*WH<sub>3</sub>(dppe)] system has a dihydrogen character, with a H...H distance of 1.102 Å.<sup>[40]</sup> For the presently investigated [Cp\*OsH(dppe)] complex, on the other hand, the H...H distance is much longer (1.315 Å in *syn*-TS, see Figure 7). On the basis of these distances, it is arguable that assistance by the hydride ligand for the direct proton transfer to the metal is greater for CpWH<sub>3</sub>(dppe)<sup>[40]</sup> than for compound **1**.

It is interesting to understand what factors orient the proton transfer directly toward the metal (with a greater or smaller assistance by a hydride ligand) to form a classical product, or produce a well-defined non-classical local minimum. Whenever lone pairs are available on the metal site, they can compete with the high-energy electrons in the M-H bond(s) as hydrogen bonding sites and the resulting interaction may have component from both types of electron density (bifurcation). For the same structural type, it seems clear from the results obtained so far that the electron density increase associated to a change of metal from the lighter to the heavier member of the same group increases the aptitude of the metal lone pairs to serve as proton acceptors to a greater extent relative to the M-H bonding electrons. However, the details of the coordination sphere play also an important role for systems based on the same metal, as shown by proton transfer to the metal for **1** and to the hydride site for OsH<sub>2</sub>(PP<sub>3</sub>).

For the specific Cp\*MH(dppe) family, comparison of the two barriers for the *syn* and *anti* protonations, the second one leading directly to the *trans* protonation product, leads to interesting considerations. The calculated barriers relative to the “resting state” *syn*-[Cp\*MH(dppe)]·(HFIP)<sub>2</sub> for the Fe and Os systems in dichloromethane solution are compared in Figure 10. The relative energies of the isomeric protonation products shown by these calculations are incorrect (the *trans* product is more stable in the real system) but correct trends were obtained by running calculations on the full system, as shown above in the Results section. The interesting comparisons concern the barriers toward *syn* and *anti* protonation for the same metal (*syn* much faster than *anti* for the Fe system; similar barriers for the Os system), and the barriers for the same type of process (*syn* or *anti*) as the metal changes from Fe to Os (*syn*: faster for Fe than for Os; *anti*: slower for Fe than for Os). The *anti* pathway is easier to analyze because it gives the same product for both metals, whereas the *syn* pathway gives a classical dihydride product for Os and a dihydrogen complex for Fe. For the *anti* protonation, a lower barrier of the Os system is easily rationalized by invoking the greater metal basicity and the more diffuse character of the metal lone pairs, yielding

greater thermodynamic stability to the protonation product and a more product-like character to the transition state. In both cases, the metal changes formal oxidation state from II to IV during the process. For the *syn* attack, on the other hand, the Fe complex protonation yields a non-classical product with little involvement of the metal lone pair at the transition state level and the metal formal oxidation state remains II throughout the process. The low metal rehybridization required for this process leads to a very low activation barrier. *Syn* protonation of the osmium system leads instead to a classical product with a change of formal oxidation state and a metal rehybridization, entailing a reaction barrier similar to that of the *anti* pathway. It is important to recollect that, although the sterically encumbered complex **1** shows a kinetically preferred *syn* protonation pathway leading to *cis*-**1H**<sup>+</sup>, less sterically encumbered complexes of the same family yield a mixture of *cis* and *trans* isomers under kinetically controlled conditions,<sup>[21, 22]</sup> in agreement with similar barriers for the protonation of both sites.

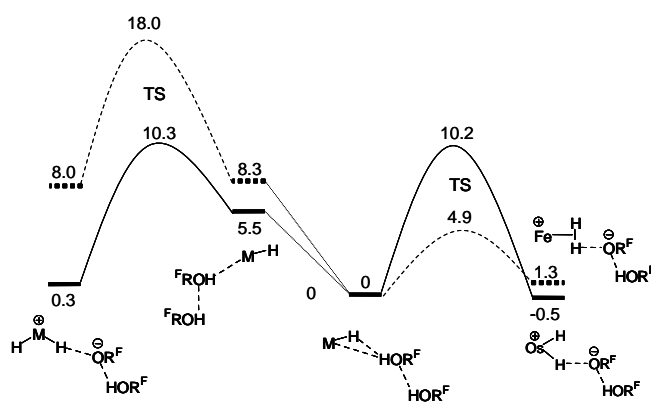


Figure 10. Energy profiles for *syn* (right) and *anti* (left) proton transfer to Cp\*MH(dppe) in dichloromethane (Os – solid lines, Fe – dashed lines). Energies (in kcal mol<sup>-1</sup>) are relative to the “resting state”, *syn*-Cp\*MH(dppe)·(HFIP)<sub>2</sub>.

## Conclusions

This work has revealed a large metal atom participation in the “dihydrogen bonding” to Cp\*OsH(dppe) and has confirmed that direct proton transfer to a metal lone pair may be a favored process in the presence of a hydride ligand, although the latter provides assistance to this process. In this case the proton approaches the metal along a trajectory featuring a fleeting proton-hydride contact. As the result, the classical dihydride complex *cis*-[Cp\*(dppe)Os(H)<sub>2</sub>]<sup>+</sup> is formed at low temperatures. Its fate, however, is similar to that of lighter non-classical congeners, the [Cp\*(dppe)M(η<sup>2</sup>-H<sub>2</sub>)]<sup>+</sup> complexes of iron and ruthenium, with transformation into the thermodynamically more stable *trans*-[Cp\*(dppe)M(H)<sub>2</sub>]<sup>+</sup>.

## Experimental Section

The hydride **1** was prepared as previously described.<sup>[23]</sup> All samples were prepared under a dry argon atmosphere using standard Schlenk techniques. The solvents used were purified by refluxing over Na (hexane, methylcyclohexane) or CaH<sub>2</sub> (CH<sub>2</sub>Cl<sub>2</sub>) and distilled prior to use under a dry argon atmosphere. The NMR solvents (Aldrich) were degassed by three freeze-pump-thaw cycles, and then vacuum transferred at room temperature.

The IR measurements were performed on an “Infracol 801” FT-IR spectrometer using CaF<sub>2</sub> cells of 0.04 – 0.22 cm path length. The UV measurements were performed on Specord M-40 and Varian Cary 5 spectrophotometers. Low-temperature

measurements were carried out using a Carl Zeiss Jena cryostat under a stream of liquid nitrogen. The accuracy of the experimental temperature adjustment was  $\pm 1$  K. The cryostat modification allows operating under an inert atmosphere and a reagents transfer (premixed either at low or at room temperature) directly into the cell pre-cooled to the required temperature.

The  $^1\text{H}$  and  $^{31}\text{P}\{^1\text{H}\}$  data were collected with a Bruker AV500 spectrometer, operating at 500.3 MHz and 202.5 MHz, respectively. The temperature was calibrated using a methanol chemical shift thermometer; the accuracy and stability was  $\pm 1$  K. All samples were allowed to equilibrate at every temperature for at least 3 min. The spectra were calibrated with the residual solvent resonance ( $^1\text{H}$ ) and with external 85%  $\text{H}_3\text{PO}_4$  ( $^{31}\text{P}$ ). The conventional inversion-recovery method (180- $\tau$ -90) was used to determine the variable-temperature longitudinal relaxation time  $T_1$ . Standard Bruker software was used for the calculation of the longitudinal relaxation time.

**Crystallographic study.** *trans*- $[\text{Cp}^*\text{Os}(\text{dppe})(\text{H})_2]^+\text{BF}_4^-$  was crystallized from dichloromethane by slow evaporation. A single crystal was mounted under inert perfluoropolyether at the tip of a glass fibre and cooled in the cryostream of a Bruker APEX2 CCD diffractometer. Data were collected using monochromatic  $\text{MoK}\alpha$  radiation ( $\lambda = 0.71073$ ). The structure was solved by direct methods (SIR97)<sup>[44]</sup> and refined by least-squares procedures on  $F^2$  using SHELXL-97.<sup>[45]</sup> All H atoms attached to carbon were introduced in calculation in idealised positions and treated as riding models. The absolute structure was determined by refining the Flack's parameter.<sup>[46]</sup> The drawing of the molecules was realised with the help of ORTEP32.<sup>[47]</sup> Crystal data and refinement parameters are shown in Table 4.

The crystallographic data have been deposited with the Cambridge Crystallographic Data Center (CCDC 754974). Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk) or <http://www.ccdc.cam.ac.uk>).

Table 4. Crystal data and structure refinement parameters for *trans*- $[\text{Cp}^*\text{Os}(\text{dppe})(\text{H})_2]^+\text{BF}_4^-$ .

Empirical formula	$\text{C}_{36}\text{H}_{41}\text{OsP}_2\text{B}_4\text{F}_4$
Formula weight	812.64
Temperature, K	180(2)
Wavelength, Å	0.71073
Crystal system	Monoclinic
Space group	$P2_1(1)$
a, Å	11.0513(7)
b, Å	13.8528(8)
c, Å	11.9523(7)
$\alpha$ , °	90
$\beta$ , °	113.272(3)
$\gamma$ , °	90
Volume, Å <sup>3</sup>	1680.92(17)
Z	2
D (calcd), Mg/m <sup>3</sup>	1.606
Abs. coeff., mm <sup>-1</sup>	3.935
F(000)	808
Crystal size, mm <sup>3</sup>	0.123 x 0.099 x 0.079
Theta range, °	2.49 to 29.20°
Reflts collected	45979
Unique reflts [R(int)]	8865 (0.0439)
Completeness, %	99.7 %
Abs. correction	Multi-scan
Max. / min. transmission	1.0 and 0.788
Refinement method	$F^2$
Data / restr. / param.	8865 / 1 / 410
Goodness-of-fit on $F^2$	0.978
R, wR2 [ $I > 2\sigma(I)$ ]	0.0263, 0.0395
R, wR2 (all data)	0.0367, 0.0415
Resid. density, e.Å <sup>-3</sup>	0.733 / -0.528
Absolute structure	-0.005(4)

**Computational details.** Calculations were performed with the Gaussian03<sup>[48]</sup> package at the DFT/B3PW91 level.<sup>[49-51]</sup> Effective core potentials (ECP) were used to represent the innermost electrons of the osmium, ruthenium and iron atoms as well as the

electron core of the phosphorous atoms.<sup>[52, 53]</sup> The basis set for the Os, Ru, Fe and P atoms was that associated with the pseudopotential,<sup>[52, 53]</sup> with a standard double- $\zeta$  LANL2DZ contraction, supplemented in the case of P with a set of d-polarization functions.<sup>[54]</sup> The carbon and hydrogen atoms of the  $\text{Cp}^*$  and dppe ligands together with the atoms of the proton donor molecules (C, F, H) that are not involved in hydrogen bonds were described with a 6-31G basis set.<sup>[55]</sup> The phenyl substituents in case of dppe ligand were also described with 6-31G basis set. The hydridic hydrogen atom and the hydrogen and oxygen atoms of the proton donor molecules involved in hydrogen bonding were described with a 6-31G(d,p) set of basis functions.<sup>[56]</sup>

The structures of the reactants, intermediates, transition states, and products were fully optimized without any symmetry restriction. Transition states were identified by having one imaginary frequency in the Hessian matrix. IRC calculations were carried out in both directions starting from the located transition states. No scaling factor was applied to the calculated frequencies since the optimization was run in the gas phase and the IR spectra were measured in solution.

Solvent effects were taken into account by using the CPCM continuum representation of the solvent,<sup>[57, 58]</sup> using standard options.<sup>[48]</sup> The solvation free energies were computed in dichloromethane ( $\epsilon = 8.93$ ) using the gas phase optimized geometries.

**Supporting Information** (see footnote on the first page of this article): IR and NMR spectra,  $\nu_{\text{MH}}$  and  $\nu_{\text{MH}_2}$  frequencies calculated and xyz coordinates of all optimized structures.

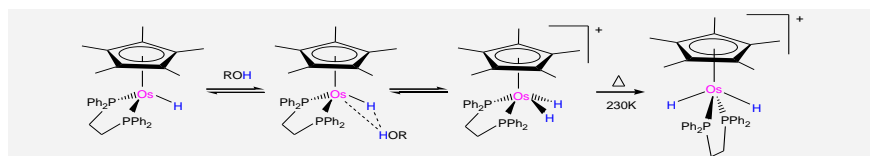
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- [39] The *cis-trans* isomerization reaction for [Cp\*OsH<sub>2</sub>(dppe)]<sup>+</sup>BF<sub>4</sub><sup>-</sup> could be studied by IR monitoring of the increase of the ν<sub>OH</sub> band of *trans*-1H<sup>+</sup> at 2102 cm<sup>-1</sup>. In this way the rate constant *k*<sub>250K</sub> = 3.43 ± 0.03·10<sup>-4</sup> s<sup>-1</sup> was obtained by plotting ln(A<sub>0</sub> - A<sub>t</sub>) versus time *t* (compare to 3.15 ± 0.02·10<sup>-4</sup> s<sup>-1</sup> from NMR at 250 K).
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Large metal atom participation in the “dihydrogen bonding” to  $\text{Cp}^*\text{OsH}(\text{dppe})$  makes the direct proton transfer to a metal a favored process in the presence of a hydride ligand, yielding *cis*- $[\text{Cp}^*(\text{dppe})\text{Os}(\text{H})_2]^+$  at low temperatures.

Similarly to lighter non-classical congeners, the  $[\text{Cp}^*(\text{dppe})\text{M}(\eta^2\text{-H}_2)]^+$  complexes of iron and ruthenium, it transforms into the thermodynamically more stable *trans*- $[\text{Cp}^*(\text{dppe})\text{M}(\text{H})_2]^+$  upon warming.

**P. A. Dub, O. A. Fillipov, G. A. Silant'ev, N. V. Belkova,\* J.-C. Daran, L. M. Epstein, R. Poli,\* and E. S. Shubina\*** ... Page No. – Page No.

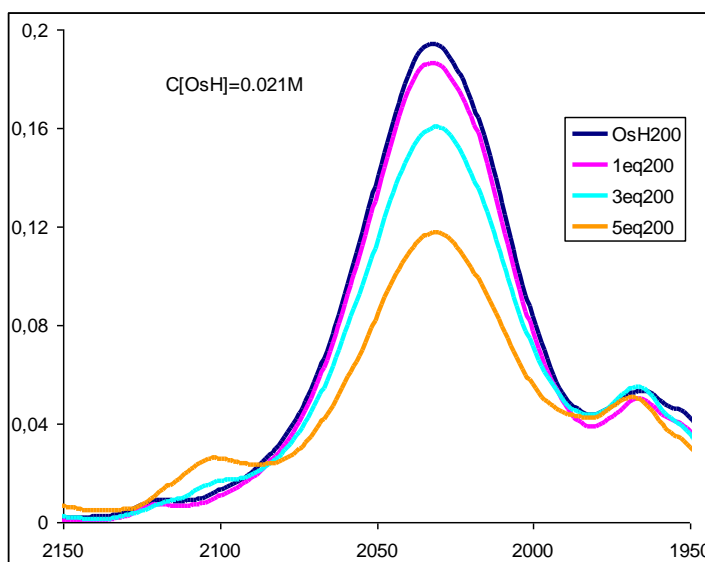
Protonation of  $\text{Cp}^*\text{M}(\text{dppe})\text{H}$  hydrides: peculiarities of the osmium congener

**Keywords:** Osmium / Hydrido ligand / Proton transfer / Hydrogen bonding / DFT calculations

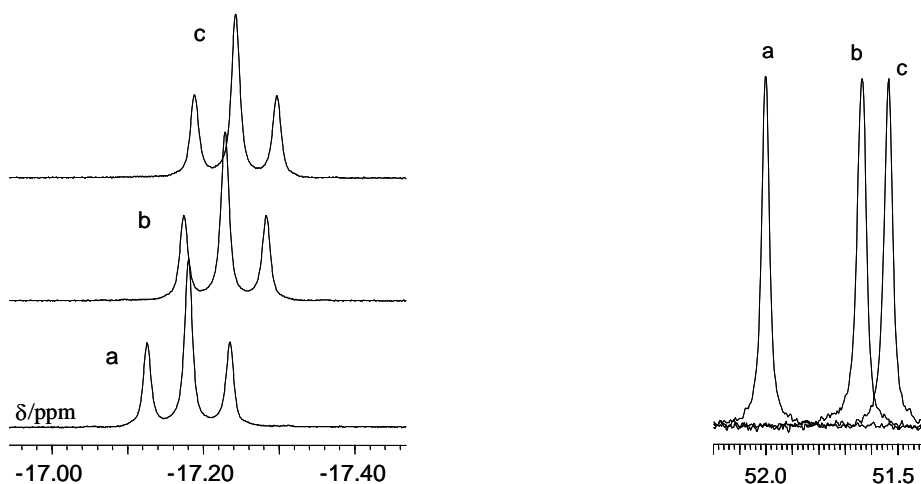
# Protonation of Cp\*M(dppe)H hydrides: peculiarities of the osmium congener

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Jean-Claude Daran,<sup>[b]</sup> Lina M. Epstein,<sup>[a]</sup> Rinaldo Poli,<sup>\*,[b,c]</sup> and Elena S. Shubina<sup>\*,[a]</sup>

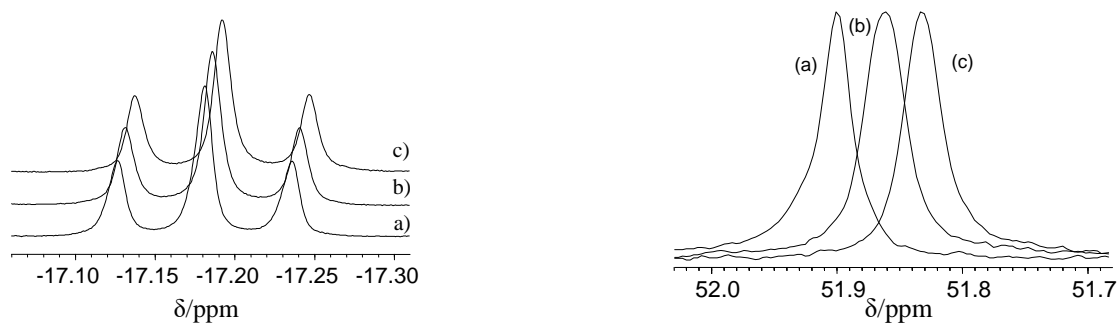
## Supporting Information



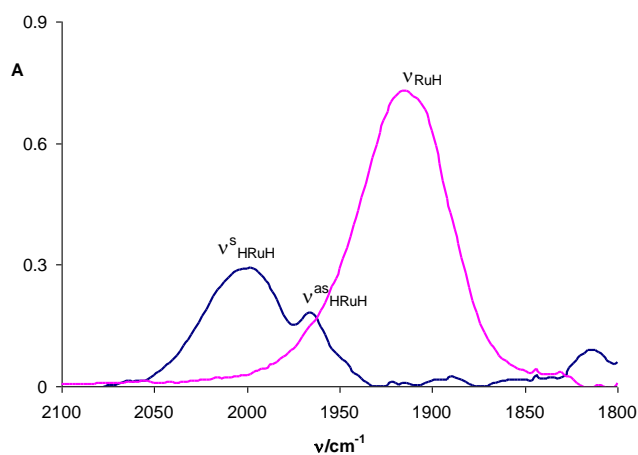
**Figure S1.** IR spectra of Cp\*Os(dppe)H (**1**) in the presence of increasing amount of TFE. Hexane-CH<sub>2</sub>Cl<sub>2</sub> 2:1 v/v mixture, 200 K.



**Figure S2.** <sup>1</sup>H NMR (500 MHz, hydride region) and <sup>31</sup>P{<sup>1</sup>H} (202.5 MHz) spectrum of **1** (a), **1** in the presence of 2.7 (b) and 4.5 (c) equiv TFE. CD<sub>2</sub>Cl<sub>2</sub>, 200K, c(**1**) = 3.3·10<sup>-2</sup> M.



**Figure S3.**  $^1\text{H}$  (500 MHz) (hydride region, left) and  $^{31}\text{P}\{^1\text{H}\}$  NMR (202.5 MHz, right) NMR spectra of **1** (a), **1** in the presence of 3 equiv (b) or 7 equiv MFE (c).  $\text{CD}_2\text{Cl}_2$ , 200K.  $c(\mathbf{1}) = 3.3 \cdot 10^{-2} \text{ M}$ .



**Figure S4.** IR spectra ( $\nu_{\text{RuH}}$  region) of  $\text{Cp}^*\text{Ru}(\text{dppe})\text{H}$  (0.026 M) and *trans*- $[\text{Cp}^*\text{Ru}(\text{dppe})(\text{H})_2]^+\text{BF}_4^-$  after the subtraction of  $\text{Cp}^*\text{RuHCl}(\text{dppe})$ .  $\text{CH}_2\text{Cl}_2$ , 200 K,  $l = 1.2 \text{ mm}$ .



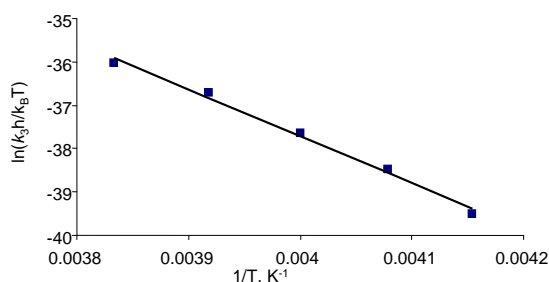
**Table S1.** Frequencies ( $\nu_{\text{MH}}$  or  $\nu_{\text{MH}_2}$  in  $\text{cm}^{-1}$ ) and intensities ( $A$  in  $10^4 \text{ L mol}^{-1}\text{cm}^{-2}$ ) of MH stretching vibrations calculated for  $[\text{Cp}^*\text{MH}(\text{dppe})]$  and  $\text{trans}-[\text{Cp}^*\text{M}(\text{H})_2(\text{dppe})]^+$  and their dhpe models.

$[\text{Cp}^*\text{MH}(\text{dhpe})]$			$\text{trans}-[\text{Cp}^*\text{M}(\text{H})_2(\text{dhpe})]^+$			
M	$\nu_{\text{MH}}$	A	$\nu_{\text{MH}_2}^s$	A	$\nu_{\text{MH}_2}^{\text{as}}$	A
Fe	1867	1.14	1990	0.63	2005	0.16
Ru	1971	1.38	2005	0.78	1970	0.12
Os	2093	0.84	2117	0.49	2065	0.05
			2155 <sup>a</sup>	0.25 <sup>a</sup>	2187 <sup>a</sup>	0.001 <sup>a</sup>
$[\text{Cp}^*\text{MH}(\text{dppe})]$			$\text{trans}-[\text{Cp}^*\text{M}(\text{H})_2(\text{dppe})]^+$			
M	$\nu_{\text{MH}}$	A	$\nu_{\text{MH}_2}^s$	A	$\nu_{\text{MH}_2}^{\text{as}}$	A
Fe	1920	1.12	2022	0.40	2062	0.18
Ru	2007	1.31	2069	0.55	2034	0.31
Os	2141	0.82	2169	0.41	2122	0.14
			2129 <sup>b</sup>	0.12 <sup>b</sup>	2257 <sup>b</sup>	0.18 <sup>b</sup>

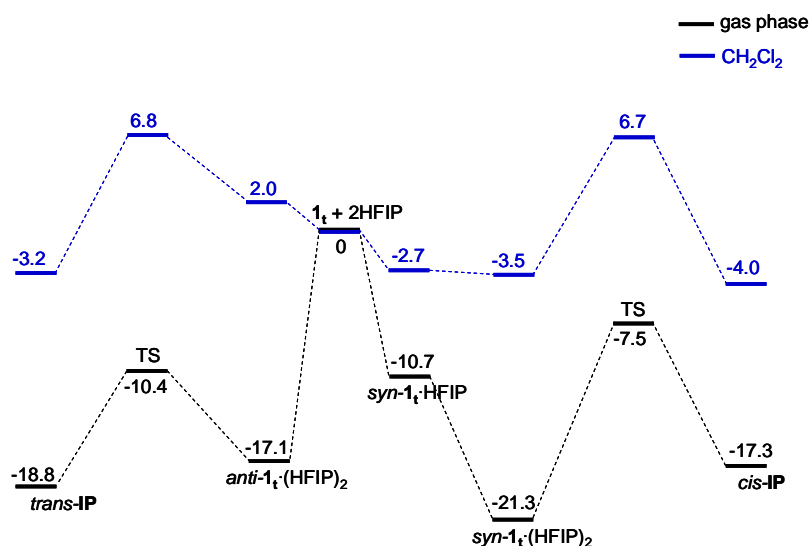
<sup>a</sup>  $\text{cis}-[\text{Cp}^*\text{Os}(\text{H})_2(\text{dhpe})]^+$

<sup>b</sup>  $\text{cis}-[\text{Cp}^*\text{Os}(\text{H})_2(\text{dppe})]^+$

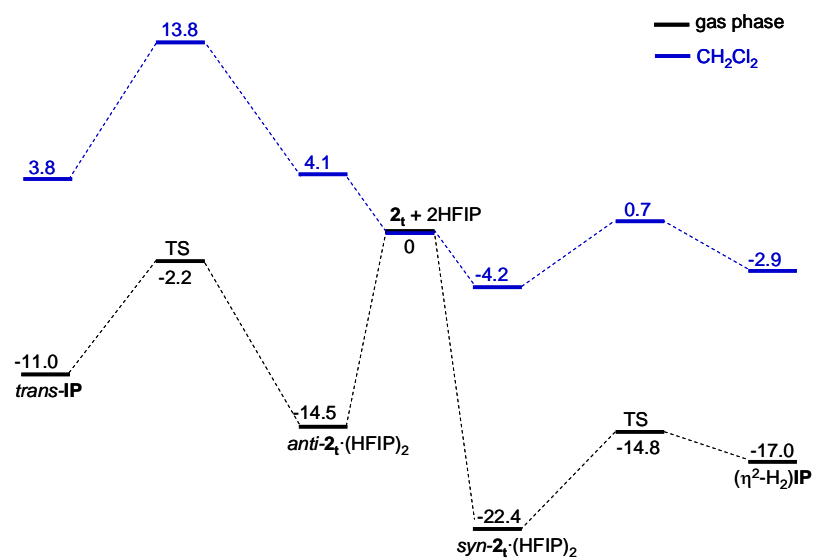
The calculated frequencies of the Os-H stretching vibrations match the experimental observations (Table 2, main text) with experimental to calculated ratio of  $> 0.97$



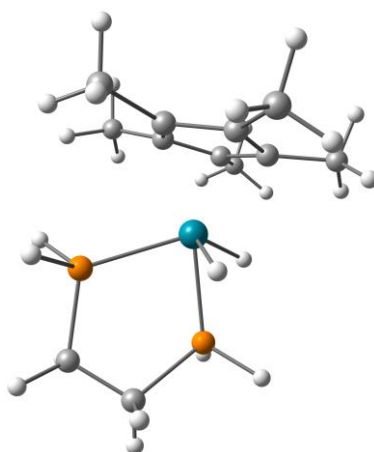
**Figure S5.** Eyring plot for the isomerization rate constant  $k_3$ .



**Figure S6.** Energy profile for the hydrogen bonding and proton transfer between  $\text{Cp}^*\text{OsH}(\text{dhpe})$  ( $\mathbf{1_t}$ ) and HFIP. Energies (in  $\text{kcal mol}^{-1}$ ) are relative to isolated  $\mathbf{1_t}$  and HFIP.



**Figure S7.** Energy profile for the hydrogen bonding and proton transfer between  $\text{Cp}^*\text{FeH}(\text{dhpe})$  ( $2_t$ ) and two molecules of HFIP. Energies (in  $\text{kcal mol}^{-1}$ ) are relative to isolated  $2_t$  and HFIP.



**Figure S8.** Transition state for the *cis*- to *trans*- $[\text{Cp}^*\text{OsH}_2(\text{dhpe})]^+$  isomerization.

**Table S2.** xyz coordinates of all optimized structures.

<b>a. free species</b>				1	-0.565906000	1.918324000	2.748580000
Cp*Os(dhpe)H E=-575.694341100				1	1.133386000	0.918256000	-0.468634000
6	-1.311765000	-1.465036000	-0.068221000	6	2.302676000	-1.780585000	-0.981747000
6	-0.701866000	-1.434719000	1.232639000	1	3.088550000	-1.301419000	-0.390555000
6	0.738462000	-1.614837000	1.059334000	1	2.560654000	-2.844429000	-1.083449000
6	0.995275000	-1.775658000	-0.349893000	1	2.327785000	-1.334109000	-1.980051000
6	-0.257414000	-1.664275000	-1.061207000	6	1.724399000	-1.634416000	2.156825000
76	0.119736000	0.325326000	0.001235000	1	1.402728000	-1.114452000	3.065890000
15	-1.041088000	1.902852000	-1.109538000	1	1.910115000	-2.683177000	2.430243000
6	-1.349079000	3.447689000	-0.067980000	1	2.681611000	-1.198950000	1.852295000
1	-0.574603000	2.513067000	-2.324921000	6	-1.442680000	-1.465077000	2.576207000
1	-2.371887000	1.649580000	-1.585872000	1	-2.425297000	-0.987102000	2.508783000
6	-0.165768000	3.644186000	0.890500000	1	-1.597929000	-2.489137000	2.944872000
1	-1.508857000	4.325025000	-0.704821000	1	-0.870533000	-0.928454000	3.341040000
1	-2.271549000	3.264402000	0.497678000	6	-2.822337000	-1.534631000	-0.309199000
1	-0.419523000	4.303033000	1.728263000	1	-3.072837000	-1.044736000	-1.256459000
15	0.410559000	1.961939000	1.522125000	1	-3.182242000	-2.571329000	-0.375452000
1	0.688763000	4.084449000	0.361219000	1	-3.396083000	-1.036770000	0.479149000
1	1.685104000	2.351371000	2.057789000	6	-0.499330000	-1.722337000	-2.508151000
1	-0.250272000	1.900303000	2.799624000	1	0.317138000	-1.260950000	-3.073152000
1	1.425980000	0.988760000	-0.724248000	1	-0.543692000	-2.782471000	-2.797001000
6	2.320980000	-2.097466000	-0.964922000	1	-1.432748000	-1.256157000	-2.841586000
1	3.143676000	-1.663920000	-0.389944000	HFIP E=-789.322984605			
1	2.474202000	-3.185015000	-1.007611000	8	8.651224000	0.489130000	-11.074275000
1	2.393062000	-1.707564000	-1.983807000	6	8.667873000	-0.844616000	-10.632764000
6	1.729042000	-1.817285000	2.163538000	1	9.681354000	-1.254165000	-10.525767000
1	1.454607000	-1.250730000	3.058836000	6	8.012521000	-0.954647000	-9.259146000
1	1.788066000	-2.877580000	2.450098000	6	7.983615000	-1.665335000	-11.716437000
1	2.732328000	-1.497405000	1.867236000	9	8.740218000	-1.628287000	-12.870105000
6	-1.409956000	-1.380720000	2.549638000	9	6.724782000	-1.204940000	-12.018067000
1	-2.392933000	-0.909446000	2.457075000	9	7.876791000	-2.989282000	-11.327760000
1	-1.561197000	-2.389796000	2.959326000	9	6.669555000	-0.668170000	-9.263537000
1	-0.841816000	-0.808088000	3.290788000	9	8.188750000	-2.203249000	-8.700616000
6	-2.778512000	-1.444278000	-0.361987000	9	8.638545000	-0.033010000	-8.421635000
1	-2.990328000	-0.945393000	-1.313341000	1	9.188096000	1.012363000	-10.466000000
1	-3.182587000	-2.464356000	-0.428229000	HFIP dimer E=-1578.65797852			
1	-3.334276000	-0.913966000	0.416981000	8	8.572624000	0.522208000	-11.017665000
6	-0.468263000	-1.940015000	-2.517816000	6	8.642900000	-0.815121000	-10.608026000
1	0.388196000	-1.614822000	-3.115751000	1	9.669220000	-1.184050000	-10.499653000
1	-0.614131000	-3.015005000	-2.700172000	6	7.978296000	-0.969306000	-9.241792000
1	-1.350735000	-1.419078000	-2.901861000	6	7.994484000	-1.658378000	-11.698999000
Cp*Fe(dhpe)H E=-608.008435119				9	8.733858000	-1.554208000	-12.858741000
6	-1.352514000	-1.493640000	-0.031758000	9	6.706284000	-1.265286000	-11.977513000
6	-0.737410000	-1.467676000	1.256218000	9	7.964410000	-2.996469000	-11.341934000
6	0.702749000	-1.529044000	1.068335000	9	6.646238000	-0.645061000	-9.238259000
6	0.959386000	-1.615851000	-0.342707000	9	8.118607000	-2.242095000	-8.729599000
6	-0.300227000	-1.568436000	-1.032444000	9	8.611662000	-0.106104000	-8.334686000
26	-0.052114000	0.191928000	0.109049000	6	12.507522000	2.280392000	-10.536005000
15	-1.095168000	1.655244000	-1.055935000	6	12.006526000	1.577621000	-9.281123000
6	-1.067500000	3.353986000	-0.232024000	1	12.380212000	2.146781000	-8.421572000
1	-0.662251000	1.992231000	-2.382236000	6	12.504930000	0.145832000	-9.116740000
1	-2.489388000	1.584427000	-1.401377000	8	10.599253000	1.588444000	-9.367019000
6	0.102427000	3.405381000	0.766116000	1	9.384742000	0.969663000	-10.729240000
1	-1.011328000	4.159496000	-0.972183000	9	12.139870000	3.607583000	-10.499009000
1	-2.021295000	3.457548000	0.300971000	9	11.978556000	1.721946000	-11.679427000
1	-0.027728000	4.200098000	1.508715000	9	13.883010000	2.220522000	-10.618880000
15	0.249699000	1.717267000	1.575545000	9	12.168982000	-0.660488000	-10.187134000
1	1.049541000	3.577720000	0.241673000	9	13.863482000	0.077733000	-8.929826000
1	1.495331000	1.878956000	2.267372000				

9	11.890787000	-0.387854000	-7.989785000	15	0.435901000	2.036388000	1.596844000
1	10.209616000	1.236554000	-8.552659000	1	1.122472000	3.806344000	0.093691000
<b>b. [Cp*Os(dhpe)H<sub>2</sub>]<sup>+</sup> : minima and isomerisation TS</b>				1	1.785239000	2.116677000	2.036210000
<i>cis</i> -[Cp*Os(dhpe)H <sub>2</sub> ] <sup>+</sup> E=-576.112439335				1	-0.219472000	2.251189000	2.840294000
6	-1.553338000	-1.831078000	0.143226000	1	1.034184000	1.001749000	-0.507921000
6	-0.763314000	-1.678359000	1.355553000	6	2.277981000	-1.735532000	-0.936597000
6	0.599327000	-1.361747000	0.962341000	1	3.056576000	-1.265680000	-0.331366000
6	0.646390000	-1.281128000	-0.470073000	1	2.535576000	-2.797393000	-1.043747000
6	-0.686899000	-1.559615000	-0.988647000	1	2.308385000	-1.285430000	-1.931246000
76	-0.917942000	0.324721000	0.272062000	6	1.681677000	-1.743077000	2.195129000
15	-0.276499000	2.006398000	-1.193384000	1	1.328896000	-1.329058000	3.142794000
6	-0.058372000	3.652836000	-0.340799000	1	1.907160000	-2.804060000	2.364666000
1	0.966956000	1.835176000	-1.872966000	1	2.620098000	-1.245895000	1.936507000
1	-1.087295000	2.327762000	-2.313978000	6	-1.491857000	-1.784467000	2.597086000
6	0.547420000	3.411635000	1.048228000	1	-2.502603000	-1.371549000	2.564765000
1	0.565487000	4.317126000	-0.947385000	1	-1.574727000	-2.853022000	2.834237000
1	-1.054404000	4.105005000	-0.261798000	1	-0.962216000	-1.303207000	3.423187000
1	0.440297000	4.287696000	1.695531000	6	-2.854028000	-1.817489000	-0.308652000
15	-0.279476000	1.922732000	1.826628000	1	-3.149306000	-1.380220000	-1.265989000
1	1.616884000	3.180111000	0.971294000	1	-3.083277000	-2.890095000	-0.350354000
1	0.654258000	1.549754000	2.836462000	1	-3.481363000	-1.373290000	0.467714000
1	-1.270823000	2.500857000	2.664818000	6	-0.504133000	-1.788331000	-2.491688000
1	-2.257594000	0.786309000	-0.511015000	1	0.281622000	-1.275563000	-3.052505000
6	1.875516000	-1.094986000	-1.300189000	1	-0.457939000	-2.852942000	-2.755528000
1	2.631273000	-0.492470000	-0.789460000	1	-1.468241000	-1.408038000	-2.837897000
1	2.327775000	-2.070920000	-1.520191000	1	-1.621800000	0.902644000	0.932366000
1	1.655029000	-0.620369000	-2.260364000	<i>cis-trans</i> isomerisation TS E=-576.071762005			
6	1.767108000	-1.267779000	1.890534000	6	-1.768570000	0.061719000	-1.208215000
1	1.479887000	-0.885423000	2.874067000	6	-1.336986000	1.249855000	-0.514728000
1	2.199215000	-2.264947000	2.046816000	6	-1.371848000	0.976430000	0.936201000
1	2.559233000	-0.627539000	1.493706000	6	-1.735604000	-0.381681000	1.112229000
6	-1.211530000	-2.033506000	2.738293000	6	-1.941457000	-0.981236000	-0.230724000
1	-2.280476000	-1.854816000	2.874474000	76	0.254813000	-0.362079000	-0.163591000
1	-1.024407000	-3.097589000	2.932342000	15	2.135156000	-1.679507000	0.094316000
1	-0.679014000	-1.461077000	3.502199000	6	3.689912000	-0.769532000	-0.374641000
6	-2.953844000	-2.350510000	0.071874000	1	2.464025000	-2.231096000	1.367502000
1	-3.476914000	-1.984135000	-0.814456000	1	2.203336000	-2.869609000	-0.676974000
1	-2.944149000	-3.447054000	0.027082000	6	3.624839000	0.643081000	0.218236000
1	-3.539664000	-2.057126000	0.945997000	1	4.565407000	-1.322851000	-0.018252000
6	-1.035648000	-1.777763000	-2.427497000	1	3.725722000	-0.739285000	-1.469599000
1	-0.432557000	-1.156709000	-3.095315000	1	4.335483000	1.320900000	-0.264167000
1	-0.857671000	-2.825313000	-2.703259000	15	1.883932000	1.300217000	0.035253000
1	-2.086861000	-1.557040000	-2.626189000	1	3.852911000	0.627273000	1.290427000
1	-2.248474000	0.639754000	1.132399000	1	1.781175000	2.231275000	1.109357000
<i>trans</i> -[Cp*Os(dhpe)H <sub>2</sub> ] <sup>+</sup> E=-576.113676016				1	1.993722000	2.238263000	-1.033934000
6	-1.398718000	-1.615802000	-0.028443000	1	0.145486000	-1.809106000	0.563735000
6	-0.777535000	-1.605032000	1.295255000	6	-2.050175000	-0.049589000	-2.671573000
6	0.659024000	-1.606055000	1.113487000	1	-1.416004000	0.616213000	-3.261184000
6	0.927688000	-1.608264000	-0.307217000	1	-1.894923000	-1.067180000	-3.036128000
6	-0.336504000	-1.619536000	-1.015353000	1	-3.095529000	0.221707000	-2.868271000
76	-0.270506000	0.317777000	0.215761000	6	-2.547123000	-2.323839000	-0.489502000
15	-1.109242000	1.967297000	-1.166484000	1	-2.260363000	-3.054623000	0.270568000
6	-1.023317000	3.599248000	-0.250484000	1	-3.642658000	-2.250183000	-0.483690000
1	-0.476256000	2.237033000	-2.410873000	1	-2.245040000	-2.720581000	-1.461604000
1	-2.460964000	1.926272000	-1.604193000	6	-2.020462000	-1.066065000	2.409983000
6	0.206579000	3.653776000	0.678199000	1	-3.080168000	-0.943795000	2.670594000
1	-1.012619000	4.433891000	-0.958834000	1	-1.817360000	-2.138567000	2.361364000
1	-1.949049000	3.672599000	0.333769000	1	-1.427746000	-0.649680000	3.228050000
1	0.123274000	4.485577000	1.385084000	6	-1.200669000	2.607618000	-1.129447000
				1	-0.544341000	3.263152000	-0.549597000
				1	-0.811007000	2.556277000	-2.149374000

1	-2.182849000	3.095756000	-1.175446000	<i>syn</i> -Cp*OsH(dhpe)·(HFIP) <sub>2</sub> E=-2154.37417594		
6	-1.201960000	1.999182000	2.011753000	6	-7.394308000	-0.659831000 -10.480307000
1	-2.164443000	2.483422000	2.223697000	6	-6.837931000	-0.004565000 -11.635437000
1	-0.842985000	1.554531000	2.943398000	6	-7.640860000	-0.377111000 -12.796242000
1	-0.504330000	2.791562000	1.725323000	6	-8.704041000	-1.231479000 -12.336870000
1	0.770372000	-0.725188000	-1.658741000	6	-8.566240000	-1.402935000 -10.892585000
<b>c. Hydrogen bonded complexes of 1<sub>t</sub> with HFIP</b>				76	-8.982386000	0.791808000 -11.342284000
<i>syn</i> -Cp*OsH(dhpe)·HFIP E=-1365.03438009				15	-11.209631000	1.050722000 -11.634205000
6	-7.686253000	-0.997126000	-10.749461000	6	-11.670354000	2.828624000 -12.048472000
6	-6.955207000	-0.142603000	-11.653007000	1	-11.884179000	0.327117000 -12.674700000
6	-7.571200000	-0.259016000	-12.972002000	1	-12.180764000	0.783639000 -10.615040000
6	-8.687018000	-1.159144000	-12.862718000	6	-10.547950000	3.456192000 -12.887818000
6	-8.770175000	-1.616049000	-11.476439000	1	-12.638496000	2.867829000 -12.559483000
76	-9.116145000	0.642478000	-11.536559000	1	-11.771125000	3.352932000 -11.089902000
15	-11.317112000	0.934030000	-11.957820000	1	-10.611884000	4.549722000 -12.898961000
6	-11.769745000	2.747032000	-12.200089000	15	-8.882948000	2.888165000 -12.203949000
1	-11.902863000	0.333478000	-13.124762000	1	-10.601726000	3.101263000 -13.924712000
1	-12.365460000	0.549961000	-11.058159000	1	-8.035182000	3.150629000 -13.328568000
6	-10.582719000	3.482076000	-12.839696000	1	-8.504004000	4.048677000 -11.458445000
1	-12.682588000	2.839412000	-12.798615000	1	-9.375856000	1.476122000 -9.900270000
1	-11.978042000	3.150848000	-11.201272000	6	-9.685524000	-1.958819000 -13.200881000
1	-10.661794000	4.567638000	-12.714194000	1	-9.885665000	-1.417296000 -14.130493000
15	-8.981248000	2.835617000	-12.076267000	1	-9.302533000	-2.952834000 -13.469783000
1	-10.532347000	3.266506000	-13.914630000	1	-10.643352000	-2.103869000 -12.690712000
1	-8.031021000	3.274473000	-13.055096000	6	-7.308534000	-0.053658000 -14.218816000
1	-8.717540000	3.879263000	-11.134006000	1	-6.907674000	0.960169000 -14.320343000
1	-9.578595000	1.121290000	-10.036388000	1	-6.550919000	-0.746134000 -14.612404000
6	-9.519381000	-1.677570000	-13.992415000	1	-8.190112000	-0.125791000 -14.862671000
1	-9.569375000	-0.961313000	-14.818063000	6	-5.543496000	0.746781000 -11.677293000
1	-9.101896000	-2.614182000	-14.387497000	1	-5.359041000	1.283791000 -10.743197000
1	-10.546563000	-1.885564000	-13.675135000	1	-4.700368000	0.060563000 -11.841937000
6	-7.028534000	0.333343000	-14.234235000	1	-5.530750000	1.482071000 -12.487463000
1	-6.590258000	1.321590000	-14.061468000	6	-6.773987000	-0.707762000 -9.120441000
1	-6.240306000	-0.303993000	-14.659421000	1	-7.518171000	-0.867562000 -8.337999000
1	-7.809687000	0.447134000	-14.991747000	1	-6.056705000	-1.539057000 -9.069047000
6	-5.657212000	0.544373000	-11.361036000	1	-6.233745000	0.210447000 -8.879337000
1	-5.582305000	0.843850000	-10.313152000	6	-9.337551000	-2.361507000 -10.039257000
1	-4.808945000	-0.121079000	-11.578513000	1	-10.353399000	-2.508233000 -10.418628000
1	-5.531923000	1.445288000	-11.969138000	1	-8.849767000	-3.346862000 -10.010546000
6	-7.307966000	-1.300343000	-9.333982000	1	-9.422924000	-2.000149000 -9.010497000
1	-8.183070000	-1.552436000	-8.729602000	1	-8.455302000	1.910759000 -8.826553000
1	-6.618892000	-2.156088000	-9.302831000	8	-8.207824000	1.975524000 -7.858843000
1	-6.816291000	-0.452910000	-8.852611000	6	-7.847364000	3.263616000 -7.447240000
6	-9.661024000	-2.704851000	-10.964096000	1	-7.654134000	3.214029000 -6.372712000
1	-10.613105000	-2.734801000	-11.502885000	6	-6.538133000	3.688180000 -8.105425000
1	-9.186132000	-3.690214000	-11.078907000	6	-8.987889000	4.261758000 -7.634162000
1	-9.890294000	-2.567915000	-9.903383000	9	-10.144478000	3.762735000 -7.075899000
1	-8.725322000	1.483390000	-8.763356000	9	-9.256508000	4.526649000 -8.967895000
8	-8.518743000	1.404488000	-7.799097000	9	-8.708431000	5.467671000 -7.019933000
6	-8.086803000	2.608117000	-7.248854000	9	-6.629845000	3.737524000 -9.485693000
1	-7.885000000	2.425655000	-6.188023000	9	-6.119742000	4.929710000 -7.666746000
6	-6.761354000	3.071501000	-7.850566000	9	-5.546642000	2.778152000 -7.795815000
6	-9.184002000	3.669802000	-7.292640000	9	-9.320768000	2.209146000 -4.701422000
9	-10.276060000	3.236912000	-6.569139000	9	-11.076415000	0.853737000 -4.471883000
9	-9.618948000	3.927358000	-8.581839000	6	-9.715064000	0.942178000 -4.289361000
9	-8.772630000	4.872197000	-6.744192000	9	-9.467687000	0.853101000 -2.932461000
9	-6.880275000	3.476823000	-9.168773000	6	-9.012405000	-0.158749000 -5.082181000
9	-6.208185000	4.121069000	-7.139699000	8	-9.328012000	-0.081150000 -6.437935000
9	-5.848778000	2.031856000	-7.820589000	1	-8.954148000	0.734284000 -6.842988000
				1	-9.405588000	-1.108225000 -4.705547000
				6	-7.502866000	-0.198704000 -4.851203000
				9	-6.939674000	-1.207439000 -5.604092000
				9	-7.184632000	-0.441157000 -3.528725000

9	-6.884134000	0.988668000	-5.217730000	9	-5.710819000	-1.316607000	-16.920216000
				9	-5.785588000	-1.066101000	-19.132427000
				9	-7.589705000	-1.780964000	-18.025665000
<i>anti</i> -Cp*OsH(dhpe) $\cdot$ (HFIP) <sub>2</sub> E= -2154.36761761				<b>d. 1<sub>t</sub> protonation by HFIP</b>			
6	-8.759734000	0.405189000	-11.038251000	<i>syn</i> -TS	E=-2154.35231606		
6	-8.080035000	0.119835000	-12.278116000	6	-7.213656000	-0.657265000	-10.465040000
6	-8.563530000	-1.147168000	-12.788890000	6	-6.851128000	-0.034747000	-11.716638000
6	-9.579769000	-1.622536000	-11.879897000	6	-7.797374000	-0.475478000	-12.735569000
6	-9.703744000	-0.676108000	-10.786702000	6	-8.741486000	-1.358667000	-12.096783000
76	-10.346016000	0.407009000	-12.652758000	6	-8.402101000	-1.462028000	-10.693059000
15	-12.527197000	0.086087000	-13.178297000	76	-8.908066000	0.741819000	-11.111248000
6	-13.241617000	1.635141000	-13.977341000	15	-11.114200000	1.196612000	-11.503030000
1	-13.049931000	-0.957286000	-14.005434000	6	-11.425266000	3.039469000	-11.488828000
1	-13.482656000	-0.090278000	-12.124761000	1	-11.727787000	0.790692000	-12.733875000
6	-12.192668000	2.330694000	-14.859828000	1	-12.136812000	0.722324000	-10.630421000
1	-14.141834000	1.385736000	-14.549194000	6	-10.290237000	3.742166000	-12.249335000
1	-13.537193000	2.286483000	-13.146182000	1	-12.408657000	3.276750000	-11.908336000
1	-12.420399000	3.394952000	-14.984724000	1	-11.416665000	3.335408000	-10.433410000
15	-10.462242000	2.125498000	-14.133549000	1	-10.212975000	4.795326000	-11.963302000
1	-12.172604000	1.880388000	-15.855959000	15	-8.653702000	2.872769000	-11.896204000
1	-9.663987000	2.244564000	-15.315755000	1	-10.461505000	3.695701000	-13.331436000
1	-10.209708000	3.457287000	-13.664035000	1	-8.003896000	2.996460000	-13.164770000
1	-11.114481000	1.551472000	-11.784320000	1	-7.902605000	3.859611000	-11.210944000
6	-10.248440000	-2.960002000	-11.952177000	1	-9.600396000	0.925796000	-9.650062000
1	-10.426023000	-3.265915000	-12.985681000	6	-9.821229000	-2.126370000	-12.792827000
1	-9.623655000	-3.728695000	-11.476226000	1	-10.224806000	-1.575689000	-13.647509000
1	-11.213532000	-2.955326000	-11.437335000	1	-9.425480000	-3.078299000	-13.171393000
6	-7.903785000	-1.944373000	-13.869270000	1	-10.650356000	-2.360575000	-12.119441000
1	-7.477952000	-1.307287000	-14.646997000	6	-7.686130000	-0.209802000	-14.204112000
1	-7.077924000	-2.535060000	-13.444812000	1	-7.249633000	0.773557000	-14.404543000
1	-8.590029000	-2.643876000	-14.348531000	1	-7.042267000	-0.956757000	-14.688919000
6	-6.939604000	0.899782000	-12.855476000	1	-8.662014000	-0.243931000	-14.697673000
1	-6.963175000	1.944328000	-12.531694000	6	-5.605275000	0.760419000	-11.954591000
1	-5.979935000	0.474895000	-12.528702000	1	-5.346400000	1.364056000	-11.080883000
1	-6.954379000	0.887645000	-13.949006000	1	-4.759528000	0.091482000	-12.164120000
6	-8.436306000	1.520015000	-10.093076000	1	-5.708597000	1.435091000	-12.809824000
1	-9.307645000	1.803421000	-9.496261000	6	-6.409777000	-0.618249000	-9.205616000
1	-7.636639000	1.222130000	-9.400223000	1	-7.021548000	-0.849304000	-8.332777000
1	-8.099840000	2.414305000	-10.625375000	1	-5.595786000	-1.354465000	-9.261004000
6	-10.486722000	-0.880631000	-9.527484000	1	-5.974539000	0.367721000	-9.031829000
1	-11.390415000	-1.470560000	-9.707491000	6	-9.039630000	-2.366497000	-9.685403000
1	-9.888483000	-1.411927000	-8.773305000	1	-10.072351000	-2.604459000	-9.956957000
1	-10.800834000	0.072995000	-9.093293000	1	-8.487257000	-3.313316000	-9.612384000
1	-10.349393000	-0.550737000	-15.183609000	1	-9.056145000	-1.898914000	-8.697340000
8	-9.950952000	-0.689176000	-16.094950000	1	-8.486445000	1.621890000	-9.599531000
6	-10.694213000	-1.444313000	-17.012997000	8	-8.045316000	1.952537000	-8.178696000
1	-10.055391000	-1.588205000	-17.888044000	6	-7.912120000	3.193415000	-7.610739000
6	-11.011847000	-2.837865000	-16.479464000	1	-7.890630000	3.150354000	-6.510582000
6	-11.928319000	-0.696555000	-17.516762000	6	-6.569629000	3.809250000	-8.005808000
9	-11.589325000	0.597875000	-17.857493000	6	-9.092833000	4.117039000	-7.935906000
9	-12.936904000	-0.619035000	-16.567832000	9	-10.292609000	3.447608000	-7.778776000
9	-12.459343000	-1.296156000	-18.640297000	9	-9.090469000	4.591295000	-9.252089000
9	-11.673846000	-2.798000000	-15.264091000	9	-9.137572000	5.235063000	-7.120899000
9	-11.792934000	-3.560032000	-17.359723000	9	-6.367453000	3.853312000	-9.380860000
9	-9.842425000	-3.546131000	-16.285635000	9	-6.409304000	5.106392000	-7.536383000
9	-8.952520000	0.380405000	-19.097300000	9	-5.535720000	3.055332000	-7.484037000
9	-8.133317000	2.401736000	-18.630996000	9	-9.714186000	2.158653000	-5.165820000
6	-7.779534000	1.099334000	-18.900777000	9	-11.336378000	0.709962000	-5.658621000
9	-7.083991000	1.090922000	-20.093635000	6	-10.110227000	0.835507000	-5.039742000
6	-6.952534000	0.535311000	-17.747235000	9	-10.307691000	0.597111000	-3.688536000
8	-7.612504000	0.683136000	-16.526793000	6	-9.114130000	-0.146336000	-5.658516000
1	-8.441401000	0.153344000	-16.492963000				
1	-6.038702000	1.135674000	-17.701072000				
6	-6.508958000	-0.909279000	-17.967592000				



8	-9.049386000	-0.020803000	-7.034140000	1	-8.819730000	0.113868000	-6.114032000
1	-8.628543000	0.869722000	-7.382615000	6	-9.823772000	-1.650212000	-6.708495000
1	-9.503593000	-1.143208000	-5.415461000	6	-10.733268000	0.187940000	-5.214618000
6	-7.731473000	-0.082513000	-5.010092000	9	-9.562107000	-2.427339000	-5.591136000
9	-6.908111000	-1.037902000	-5.577741000	9	-8.814802000	-1.935872000	-7.627459000
9	-7.776166000	-0.341854000	-3.649834000	9	-11.002865000	-2.108121000	-7.263031000
9	-7.112635000	1.144802000	-5.174735000	9	-10.259988000	-0.349640000	-4.025888000
<i>syn-1<i>h</i>P</i>				9	-12.038156000	-0.235829000	-5.369342000
E=-2154.36795874				9	-10.763443000	1.564758000	-5.040710000
6	-7.073433000	-1.614726000	-11.372198000	<i>anti-TS</i>			
6	-6.682831000	-0.549406000	-12.280649000	E=-2154.35689154			
6	-7.736035000	-0.406756000	-13.274632000	6	-8.766250000	0.397065000	-11.130443000
6	-8.771075000	-1.350223000	-12.969017000	6	-8.014832000	0.085632000	-12.321410000
6	-8.381176000	-2.091764000	-11.781174000	6	-8.474180000	-1.188455000	-12.827142000
76	-8.515344000	0.082558000	-11.095972000	6	-9.533222000	-1.657275000	-11.962473000
15	-10.766167000	0.481289000	-10.711677000	6	-9.717759000	-0.681700000	-10.902524000
6	-11.145844000	2.267917000	-10.358771000	76	-10.273142000	0.329382000	-12.833295000
1	-11.629626000	0.177166000	-11.811250000	15	-12.496109000	0.079264000	-13.263246000
1	-11.438263000	-0.219105000	-9.680694000	6	-13.158394000	1.658823000	-14.037749000
6	-10.196040000	3.163288000	-11.162799000	1	-13.044491000	-0.945490000	-14.079326000
1	-12.197498000	2.483843000	-10.572887000	1	-13.395300000	-0.063280000	-12.162042000
1	-10.954745000	2.408443000	-9.291226000	6	-12.109264000	2.321558000	-14.949162000
1	-10.133026000	4.161407000	-10.721424000	1	-14.077906000	1.446626000	-14.593073000
15	-8.487972000	2.397585000	-11.201957000	1	-13.412423000	2.319170000	-13.199767000
1	-10.524355000	3.260590000	-12.205103000	1	-12.323539000	3.387313000	-15.082756000
1	-7.966671000	2.938774000	-12.418259000	15	-10.365474000	2.101740000	-14.281102000
1	-7.725181000	3.127716000	-10.266138000	1	-12.116425000	1.857008000	-15.937694000
1	-8.855080000	-0.346014000	-9.575902000	1	-9.581432000	2.185931000	-15.463407000
6	-9.999712000	-1.599747000	-13.784299000	1	-10.077935000	3.403799000	-13.766081000
1	-10.333632000	-0.696969000	-14.303817000	1	-11.045197000	1.516924000	-12.019891000
1	-9.802360000	-2.366384000	-14.545340000	6	-10.172947000	-3.008614000	-12.026360000
1	-10.830904000	-1.957880000	-13.170026000	1	-10.279723000	-3.356301000	-13.055436000
6	-7.680588000	0.487722000	-14.472622000	1	-9.563222000	-3.744199000	-11.483535000
1	-7.137405000	1.413890000	-14.262550000	1	-11.167509000	-3.005467000	-11.571382000
1	-7.161314000	-0.013650000	-15.300468000	6	-7.796806000	-1.984389000	-13.893301000
1	-8.679727000	0.758810000	-14.825452000	1	-7.321164000	-1.343717000	-14.636818000
6	-5.340076000	0.111483000	-12.328685000	1	-7.014265000	-2.610539000	-13.440277000
1	-4.895582000	0.183975000	-11.332963000	1	-8.488946000	-2.641510000	-14.417940000
1	-4.650578000	-0.461500000	-12.963361000	6	-6.854543000	0.860090000	-12.862874000
1	-5.400069000	1.124877000	-12.736034000	1	-6.900534000	1.912262000	-12.567579000
6	-6.219788000	-2.222371000	-10.304253000	1	-5.910142000	0.450418000	-12.478481000
1	-6.825290000	-2.610374000	-9.482069000	1	-6.822301000	0.815435000	-13.954608000
1	-5.628918000	-3.051890000	-10.714984000	6	-8.501260000	1.541463000	-10.202465000
1	-5.526089000	-1.491625000	-9.880865000	1	-9.399816000	1.827443000	-9.649246000
6	-9.091426000	-3.277858000	-11.205909000	1	-7.728153000	1.270508000	-9.470347000
1	-10.162718000	-3.253598000	-11.424358000	1	-8.151476000	2.425690000	-10.742474000
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1	-8.980745000	-3.320711000	-10.119960000	1	-11.463697000	-1.447958000	-9.899595000
1	-7.663705000	0.615380000	-9.833501000	1	-10.010355000	-1.384285000	-8.893488000
8	-8.959628000	2.406395000	-8.184024000	1	-10.894710000	0.101454000	-9.277033000
1	-9.283815000	3.165742000	-6.269334000	1	-10.348358000	-0.322062000	-14.652157000
6	-7.240744000	3.263209000	-6.802138000	8	-10.030737000	-0.606635000	-15.922714000
6	-9.126999000	4.721289000	-7.677835000	6	-10.693227000	-1.388297000	-16.855765000
9	-10.476706000	4.725501000	-8.004577000	1	-10.045901000	-1.581412000	-17.722697000
9	-8.943041000	5.712118000	-6.728065000	6	-11.045762000	-2.774423000	-16.317678000
9	-6.879112000	4.187912000	-5.832930000	6	-11.917101000	-0.674710000	-17.437313000
6	-8.715629000	3.329129000	-7.201861000	9	-11.583526000	0.612847000	-17.820899000
9	-8.448269000	5.127751000	-8.823788000	9	-12.967488000	-0.554478000	-16.529738000
9	-6.383126000	3.444595000	-7.875702000	9	-12.424262000	-1.308894000	-18.556184000
9	-6.965680000	2.006854000	-6.274931000	9	-11.785848000	-2.741081000	-15.145473000
1	-9.634558000	1.392801000	-7.777308000	9	-11.767408000	-3.528141000	-17.229492000
8	-10.291119000	0.519203000	-7.530263000	9	-9.891393000	-3.487309000	-16.038228000
6	-9.845470000	-0.152500000	-6.413680000	9	-9.010401000	0.308111000	-19.056253000

9	-8.528010000	2.316750000	-18.210986000
6	-7.972255000	1.132626000	-18.648389000
9	-7.214251000	1.421885000	-19.769355000
6	-7.123815000	0.510752000	-17.538620000
8	-7.765466000	0.513656000	-16.308632000
1	-8.645668000	-0.001856000	-16.285801000
1	-6.233838000	1.145563000	-17.457930000
6	-6.609397000	-0.883401000	-17.895350000
9	-5.700245000	-1.298257000	-16.940998000
9	-5.966570000	-0.913019000	-19.119598000
9	-7.622081000	-1.828881000	-17.932961000

**anti-1<sub>IP</sub>**

E= -2154.37020262

6	1.039167000	2.059888000	4.576798000
6	0.267688000	1.680253000	5.745989000
6	0.484054000	2.672376000	6.774489000
6	1.379030000	3.676449000	6.247055000
6	1.735373000	3.298282000	4.882620000
76	-0.473352000	3.705371000	4.917086000
15	-1.230016000	4.156367000	2.787507000
6	-3.025052000	4.657232000	2.874931000
1	-0.612478000	5.200133000	2.038725000
1	-1.233357000	3.111613000	1.832032000
6	-3.336240000	5.410365000	4.182490000
1	-3.300769000	5.254873000	2.000240000
1	-3.586542000	3.717286000	2.851094000
1	-4.414651000	5.421044000	4.366771000
15	-2.468255000	4.627843000	5.647592000
1	-2.983110000	6.447985000	4.131709000
1	-2.465494000	5.696253000	6.589478000
1	-3.441048000	3.784649000	6.233579000
1	-0.266568000	5.328581000	4.792462000
6	1.986956000	4.799907000	7.026816000
1	1.300115000	5.183664000	7.785966000
1	2.895418000	4.458203000	7.541134000
1	2.264472000	5.634835000	6.378602000
6	-0.035853000	2.606872000	8.175479000
1	-1.005286000	2.104005000	8.222116000
1	0.659582000	2.044406000	8.812866000
1	-0.150939000	3.603378000	8.610636000
6	-0.519067000	0.415941000	5.880047000
1	-0.974893000	0.126555000	4.930026000
1	0.139684000	-0.398601000	6.210984000
1	-1.325948000	0.512332000	6.609180000
6	1.151196000	1.238201000	3.332358000
1	1.588434000	1.813902000	2.511455000
1	1.792189000	0.363613000	3.503465000
1	0.160466000	0.889679000	3.019633000
6	2.789633000	3.949757000	4.043774000
1	2.804975000	5.033903000	4.185008000
1	3.783390000	3.561784000	4.305033000
1	2.629956000	3.758468000	2.979212000
1	-1.716190000	2.717387000	4.550622000
8	-3.839901000	1.931866000	4.290370000
6	-5.029872000	1.307661000	4.613356000
1	-5.287301000	0.478099000	3.942972000
6	-4.932420000	0.709462000	6.015566000
6	-6.158797000	2.325952000	4.490935000
9	-6.206573000	2.835107000	3.206837000
9	-5.991384000	3.415268000	5.341871000
9	-7.403787000	1.787342000	4.764342000
9	-4.631987000	1.657105000	6.987120000
9	-6.097886000	0.076542000	6.416042000

9	-3.922440000	-0.234467000	6.055985000
6	-3.586964000	0.649802000	0.826837000
6	-2.525549000	0.062179000	1.761621000
1	-1.648222000	-0.107555000	1.109722000
6	-2.903252000	-1.337127000	2.259461000
8	-2.247268000	0.902130000	2.800219000
1	-3.209190000	1.357072000	3.583665000
9	-3.178389000	1.905468000	0.394528000
9	-4.819100000	0.820381000	1.441393000
9	-3.802536000	-0.110302000	-0.312546000
9	-4.044209000	-1.343946000	3.051711000
9	-3.121788000	-2.244330000	1.231565000
9	-1.873578000	-1.847718000	3.030868000

**e. Hydrogen bonded complexes and protonation of 2<sub>t</sub> with HFIP**

*syn*-Cp\*FeH(dhpe)-(HFIP)<sub>2</sub> E=-2186.69011339

6	-7.018993000	-0.458562000	-10.683333000
6	-6.691532000	0.133023000	-11.954175000
6	-7.662091000	-0.343418000	-12.921747000
6	-8.603552000	-1.174767000	-12.240011000
6	-8.212446000	-1.237927000	-10.841590000
26	-8.622395000	0.779580000	-11.383352000
15	-10.697456000	0.937090000	-10.799726000
6	-11.315212000	2.689642000	-11.062654000
1	-11.723228000	0.182814000	-11.464417000
1	-11.179544000	0.691792000	-9.475334000
6	-10.696454000	3.231299000	-12.362612000
1	-12.409477000	2.727684000	-11.084282000
1	-10.975145000	3.273308000	-10.200903000
1	-10.736477000	4.324520000	-12.410054000
15	-8.924495000	2.599011000	-12.508285000
1	-11.238669000	2.838387000	-13.232212000
1	-8.755669000	2.670590000	-13.930240000
1	-8.181578000	3.785543000	-12.216201000
1	-8.364764000	1.784276000	-10.279091000
6	-9.721006000	-1.945484000	-12.868920000
1	-10.100010000	-1.449344000	-13.768227000
1	-9.388738000	-2.951308000	-13.162238000
1	-10.565567000	-2.072525000	-12.183139000
6	-7.617747000	-0.093366000	-14.396215000
1	-7.142172000	0.863484000	-14.634393000
1	-7.038556000	-0.877747000	-14.902792000
1	-8.618531000	-0.085021000	-14.840392000
6	-5.472330000	0.948418000	-12.252621000
1	-5.194714000	1.576259000	-11.400794000
1	-4.610789000	0.307935000	-12.490068000
1	-5.630107000	1.613007000	-13.108672000
6	-6.194454000	-0.359399000	-9.439213000
1	-6.796334000	-0.468233000	-8.533984000
1	-5.435292000	-1.154271000	-9.426555000
1	-5.669063000	0.596251000	-9.374794000
6	-8.845491000	-2.101972000	-9.795019000
1	-9.911771000	-2.258663000	-9.990811000
1	-8.371793000	-3.093838000	-9.768637000
1	-8.758724000	-1.667997000	-8.795087000
1	-8.219970000	1.828270000	-8.940951000
8	-8.205623000	1.889933000	-7.927506000
6	-7.813358000	3.145271000	-7.448998000
1	-7.888046000	3.113859000	-6.358974000
6	-6.347716000	3.420229000	-7.775900000
6	-8.757329000	4.253166000	-7.912687000
9	-10.068998000	3.863628000	-7.712195000

9	-8.624250000	4.549066000	-9.260837000	6	-8.604196000	4.447711000	-8.189329000
9	-8.557515000	5.423075000	-7.208472000	9	-9.955028000	4.408340000	-7.875892000
9	-6.085591000	3.357023000	-9.133336000	9	-8.530737000	4.555251000	-9.575368000
9	-5.951088000	4.667743000	-7.329492000	9	-8.102779000	5.625798000	-7.665282000
9	-5.548338000	2.481187000	-7.158345000	9	-6.017399000	3.378661000	-9.183308000
9	-9.787209000	2.295076000	-5.004877000	9	-5.804282000	4.302806000	-7.164052000
9	-11.740932000	1.229369000	-4.908268000	9	-5.811091000	2.088171000	-7.380270000
6	-10.392342000	1.091601000	-4.663551000	9	-10.162898000	2.181832000	-5.518738000
9	-10.228151000	0.916116000	-3.302924000	9	-11.579875000	0.623922000	-6.248274000
6	-9.834924000	-0.075769000	-5.477074000	6	-10.513368000	0.847703000	-5.395212000
8	-9.982563000	0.159737000	-6.842440000	9	-10.977414000	0.660620000	-4.104902000
1	-9.366853000	0.868543000	-7.143801000	6	-9.370272000	-0.105447000	-5.741764000
1	-10.442706000	-0.949430000	-5.221758000	8	-9.044659000	-0.058268000	-7.086796000
6	-8.395736000	-0.431115000	-5.105749000	1	-8.758666000	0.879466000	-7.430698000
9	-7.911794000	-1.396513000	-5.965126000	1	-9.744266000	-1.109824000	-5.507802000
9	-8.305806000	-0.935032000	-3.822370000	6	-8.138644000	0.088187000	-4.857145000
9	-7.545553000	0.661985000	-5.185908000	9	-7.181750000	-0.850115000	-5.184310000
TS <i>syn</i> -Cp*FeH(dhpe) <sub>2</sub> E=-2186.67804531				9	-8.431209000	-0.071094000	-3.512572000
6	-7.126228000	-0.615230000	-10.597137000	9	-7.561525000	1.339086000	-5.007146000
6	-6.669184000	0.069027000	-11.791931000	<i>syn</i> -2 $\mu$ -IP E=-2186.68149712			
6	-7.606544000	-0.211352000	-12.843406000	6	-7.245880000	-0.966132000	-10.461154000
6	-8.678396000	-1.003214000	-12.297663000	6	-6.411796000	-0.133435000	-11.301226000
6	-8.355496000	-1.276897000	-10.909974000	6	-7.083836000	0.061877000	-12.551519000
26	-8.558830000	0.830038000	-11.221993000	6	-8.342572000	-0.662436000	-12.500127000
15	-10.536318000	0.916638000	-10.260275000	6	-8.414770000	-1.321174000	-11.225467000
6	-11.363885000	2.556634000	-10.595909000	26	-8.281929000	0.804297000	-10.962707000
1	-11.515230000	0.007293000	-10.771579000	15	-10.153789000	0.940364000	-9.806546000
1	-10.778819000	0.707059000	-8.877299000	6	-10.885133000	2.649282000	-9.907723000
6	-11.051152000	2.965101000	-12.046251000	1	-11.226379000	0.120391000	-10.280946000
1	-12.442000000	2.503364000	-10.412352000	1	-10.250656000	0.614821000	-8.427518000
1	-10.935640000	3.270035000	-9.885276000	6	-10.674165000	3.216739000	-11.324087000
1	-11.231930000	4.031022000	-12.217717000	1	-11.943841000	2.638525000	-9.628551000
15	-9.265327000	2.511370000	-12.433988000	1	-10.334638000	3.236626000	-9.167625000
1	-11.680318000	2.401355000	-12.746984000	1	-10.618864000	4.307986000	-11.299756000
1	-9.301550000	2.457602000	-13.861047000	15	-9.079152000	2.549111000	-12.063032000
1	-8.621714000	3.779522000	-12.329016000	1	-11.493056000	2.923795000	-11.991337000
1	-7.801127000	1.956352000	-10.475305000	1	-9.472015000	2.310398000	-13.415445000
6	-9.804802000	-1.613824000	-13.069756000	1	-8.295208000	3.706908000	-12.286359000
1	-10.086000000	-1.000859000	-13.932300000	1	-7.435106000	1.927902000	-10.276863000
1	-9.529384000	-2.607494000	-13.450004000	6	-9.296436000	-0.843333000	-13.637763000
1	-10.700220000	-1.742137000	-12.452611000	1	-9.306376000	0.025214000	-14.303632000
6	-7.454193000	0.177830000	-14.279709000	1	-9.017507000	-1.714039000	-14.247007000
1	-6.916563000	1.124124000	-14.395174000	1	-10.321630000	-1.002602000	-13.288895000
1	-6.882743000	-0.589922000	-14.818742000	6	-6.530187000	0.781852000	-13.740821000
1	-8.420745000	0.275110000	-14.783831000	1	-5.879588000	1.609794000	-13.444786000
6	-5.377737000	0.812963000	-11.924609000	1	-5.934139000	0.098205000	-14.360512000
1	-5.144062000	1.372152000	-11.014579000	1	-7.320541000	1.189992000	-14.378451000
1	-4.544951000	0.122693000	-12.117637000	6	-5.064745000	0.399605000	-10.927581000
1	-5.408388000	1.531421000	-12.749587000	1	-4.985629000	0.575556000	-9.851568000
6	-6.384493000	-0.703625000	-9.303123000	1	-4.279762000	-0.315412000	-11.208511000
1	-7.058363000	-0.802644000	-8.449004000	1	-4.847959000	1.347102000	-11.428004000
1	-5.717194000	-1.577176000	-9.310377000	6	-6.881602000	-1.484322000	-9.105481000
1	-5.768993000	0.180475000	-9.127134000	1	-7.768590000	-1.774511000	-8.534281000
6	-9.118315000	-2.173508000	-9.985668000	1	-6.236420000	-2.369942000	-9.185189000
1	-10.173089000	-2.250731000	-10.269070000	1	-6.348657000	-0.733992000	-8.515854000
1	-8.701694000	-3.189796000	-10.012808000	6	-9.478080000	-2.282015000	-10.797939000
1	-9.069316000	-1.817121000	-8.952661000	1	-10.440509000	-2.069157000	-11.272160000
1	-8.188510000	1.800876000	-9.663903000	1	-9.194734000	-3.304780000	-11.080642000
8	-8.455396000	2.072610000	-8.238105000	1	-9.627236000	-2.275558000	-9.713735000
6	-7.909329000	3.195595000	-7.656276000	1	-7.801875000	1.523282000	-9.611792000
1	-8.062723000	3.216539000	-6.567383000	8	-8.170908000	4.273453000	-9.709358000
6	-6.391981000	3.251603000	-7.849493000	6	-7.380026000	5.400693000	-9.569026000

1	-7.028579000	5.560541000	-8.542509000	8	-10.009353000	-0.749305000	-16.084448000
6	-6.127773000	5.268369000	-10.434311000	6	-10.819712000	-1.510914000	-16.941869000
6	-8.222344000	6.616599000	-9.939700000	1	-10.230026000	-1.693301000	-17.843148000
9	-9.233254000	6.789307000	-9.015471000	6	-11.140428000	-2.877932000	-16.349201000
9	-8.829342000	6.478040000	-11.180276000	6	-12.054865000	-0.732706000	-17.391080000
9	-7.486641000	7.790178000	-9.972680000	9	-11.680409000	0.515791000	-17.846221000
9	-6.408335000	5.261980000	-11.796774000	9	-12.965291000	-0.534877000	-16.364282000
9	-5.216371000	6.284840000	-10.212430000	9	-12.713746000	-1.375666000	-18.417598000
9	-5.483475000	4.074647000	-10.158423000	9	-11.849123000	-2.782796000	-15.164327000
9	-8.307092000	5.044934000	-6.434974000	9	-11.877771000	-3.651594000	-17.221695000
9	-10.023882000	3.691440000	-6.004291000	9	-9.968062000	-3.555715000	-16.075355000
6	-8.647910000	3.805597000	-5.910031000	9	-9.143894000	-0.064715000	-19.292445000
9	-8.338292000	3.839008000	-4.557678000	9	-8.409630000	2.036696000	-19.144888000
6	-7.986961000	2.642619000	-6.657269000	6	-8.000510000	0.727266000	-19.244576000
8	-8.378752000	2.613894000	-7.961589000	9	-7.346581000	0.580686000	-20.451213000
1	-8.171497000	3.648893000	-8.833807000	6	-7.108593000	0.367929000	-18.057626000
1	-8.291799000	1.740225000	-6.094784000	8	-7.724280000	0.680073000	-16.844011000
6	-6.459525000	2.672650000	-6.540788000	1	-8.508297000	0.112803000	-16.683656000
9	-5.920181000	1.567491000	-7.189879000	1	-6.215673000	0.994664000	-18.142480000
9	-6.001298000	2.622892000	-5.233398000	6	-6.628632000	-1.081275000	-18.074317000
9	-5.893538000	3.794670000	-7.128681000	9	-5.742200000	-1.291442000	-17.040662000
<i>anti</i> -Cp*FeH(dhpe)·(HFIP) <sub>2</sub> E= -2186.67758673				9	-5.988716000	-1.412943000	-19.251179000
6	-8.915207000	0.392628000	-10.911872000	9	-7.682368000	-1.971301000	-17.904032000
6	-8.101524000	0.331525000	-12.092280000	TS <i>anti</i> -Cp*FeH(dhpe)·(HFIP) <sub>2</sub> E= -2186.65798079			
6	-8.421463000	-0.893887000	-12.801558000	6	-8.851550000	0.456915000	-11.218832000
6	-9.453258000	-1.561085000	-12.068992000	6	-8.077358000	0.148651000	-12.389598000
6	-9.780133000	-0.759616000	-10.907828000	6	-8.490961000	-1.144511000	-12.877352000
26	-10.154431000	0.393439000	-12.624327000	6	-9.529791000	-1.630266000	-12.008074000
15	-12.265877000	0.172775000	-12.968473000	6	-9.758410000	-0.642501000	-10.983059000
6	-12.917543000	1.778294000	-13.697661000	26	-10.164088000	0.221561000	-12.852882000
1	-12.969489000	-0.801976000	-13.753069000	15	-12.268430000	-0.070909000	-13.173100000
1	-13.123517000	0.046732000	-11.828558000	6	-12.964592000	1.520405000	-13.879451000
6	-11.879126000	2.364577000	-14.672232000	1	-12.880122000	-1.081043000	-13.963719000
1	-13.883968000	1.624465000	-14.189207000	1	-13.094636000	-0.235155000	-12.018623000
1	-13.070580000	2.454189000	-12.848698000	6	-11.924753000	2.224315000	-14.773934000
1	-12.016664000	3.443232000	-14.804893000	1	-13.886503000	1.323030000	-14.435237000
15	-10.131909000	1.978823000	-14.081160000	1	-13.215049000	2.147943000	-13.016123000
1	-11.980307000	1.899206000	-15.657684000	1	-12.133566000	3.296543000	-14.852181000
1	-9.436672000	2.034888000	-15.334120000	15	-10.181884000	1.943684000	-14.148673000
1	-9.682781000	3.266018000	-13.639770000	1	-11.948321000	1.809234000	-15.783526000
1	-10.807400000	1.546906000	-11.928454000	1	-9.411740000	2.092075000	-15.334618000
6	-10.001529000	-2.925227000	-12.349301000	1	-9.851387000	3.203366000	-13.557435000
1	-9.834211000	-3.228426000	-13.384472000	1	-10.906100000	1.299428000	-12.146000000
1	-9.512894000	-3.670875000	-11.706154000	6	-10.166010000	-2.982100000	-12.077860000
1	-11.077695000	-2.986084000	-12.157038000	1	-10.240895000	-3.341516000	-13.105539000
6	-7.635863000	-1.447552000	-13.948872000	1	-9.573981000	-3.712781000	-11.509521000
1	-7.279469000	-0.661084000	-14.619278000	1	-11.174743000	-2.979073000	-11.652965000
1	-6.749905000	-1.984467000	-13.579518000	6	-7.775015000	-1.940527000	-13.918076000
1	-8.216335000	-2.152139000	-14.548894000	1	-7.337972000	-1.305010000	-14.689561000
6	-7.002470000	1.282011000	-12.454536000	1	-6.957252000	-2.505762000	-13.447527000
1	-7.211062000	2.296341000	-12.098737000	1	-8.431086000	-2.655263000	-14.413292000
1	-6.048096000	0.968294000	-12.008223000	6	-6.955190000	0.963936000	-12.951720000
1	-6.854165000	1.333708000	-13.538020000	1	-7.047880000	2.021242000	-12.683354000
6	-8.836624000	1.437444000	-9.842945000	1	-5.991148000	0.611647000	-12.559267000
1	-9.791833000	1.550088000	-9.321944000	1	-6.919095000	0.891223000	-14.042432000
1	-8.076962000	1.171571000	-9.094412000	6	-8.677965000	1.658694000	-10.344924000
1	-8.569687000	2.415919000	-10.253430000	1	-9.598111000	1.902580000	-9.806214000
6	-10.736067000	-1.144381000	-9.823272000	1	-7.890792000	1.484242000	-9.598671000
1	-11.554869000	-1.759875000	-10.210776000	1	-8.390886000	2.542321000	-10.923175000
1	-10.234879000	-1.726083000	-9.036406000	6	-10.683010000	-0.781465000	-9.815893000
1	-11.183083000	-0.264536000	-9.348949000	1	-11.563492000	-1.382489000	-10.063667000
1	-10.361424000	-0.613804000	-15.167653000	1	-10.177778000	-1.274979000	-8.974307000

1	-11.037386000	0.192222000	-9.463787000	1	-11.424370000	-0.792137000	-9.594954000
1	-10.288201000	-0.332837000	-14.514476000	1	-9.942448000	-0.803799000	-8.630943000
8	-10.031803000	-0.598581000	-15.868259000	1	-10.628716000	0.729268000	-9.187403000
6	-10.698943000	-1.371507000	-16.806448000	1	-9.941339000	-0.099897000	-14.084917000
1	-10.074228000	-1.517923000	-17.699247000	8	-10.510037000	-0.755746000	-16.252688000
6	-10.992650000	-2.787442000	-16.310971000	6	-10.889675000	-1.476385000	-17.371061000
6	-11.958873000	-0.677376000	-17.331091000	1	-10.214033000	-1.348449000	-18.225596000
9	-11.663492000	0.619971000	-17.715410000	6	-10.885736000	-2.966555000	-17.037835000
9	-12.973714000	-0.584575000	-16.381446000	6	-12.258844000	-0.982247000	-17.826342000
9	-12.499341000	-1.308061000	-18.435947000	9	-12.211148000	0.373368000	-18.097503000
9	-11.721369000	-2.822935000	-15.130144000	9	-13.240360000	-1.155645000	-16.854276000
9	-11.697008000	-3.536919000	-17.239459000	9	-12.707661000	-1.612568000	-18.972646000
9	-9.810084000	-3.464986000	-16.068343000	9	-11.710028000	-3.277274000	-15.962453000
9	-9.121425000	0.381481000	-19.036352000	9	-11.289152000	-3.758945000	-18.099821000
9	-8.548628000	2.356101000	-18.168431000	9	-9.609821000	-3.368282000	-16.689162000
6	-8.044422000	1.167615000	-18.655020000	9	-9.325208000	0.997249000	-18.760896000
9	-7.325637000	1.462098000	-19.799846000	9	-8.738898000	2.698844000	-17.447574000
6	-7.170805000	0.498672000	-17.593715000	6	-8.242049000	1.599240000	-18.136501000
8	-7.772192000	0.479035000	-16.344090000	9	-7.420493000	2.096110000	-19.136226000
1	-8.664194000	-0.021063000	-16.291890000	6	-7.521415000	0.668641000	-17.156314000
1	-6.267185000	1.115698000	-17.525206000	8	-8.336493000	0.295270000	-16.128489000
6	-6.691518000	-0.892765000	-18.005155000	1	-9.504387000	-0.326880000	-16.333085000
9	-5.771212000	-1.355025000	-17.084812000	1	-6.648577000	1.255367000	-16.812444000
9	-6.075549000	-0.893575000	-19.243531000	6	-6.906376000	-0.547698000	-17.856549000
9	-7.722845000	-1.817755000	-18.052635000	9	-6.211727000	-1.310891000	-16.934542000
				9	-6.005313000	-0.207020000	-18.855833000
				9	-7.855884000	-1.379307000	-18.437278000

*anti-2r*-IP E= -2186.67193130

6	-8.627421000	0.548358000	-11.148847000
6	-7.981841000	0.011319000	-12.321071000
6	-8.580628000	-1.270157000	-12.615571000
6	-9.579529000	-1.535145000	-11.609481000
6	-9.620149000	-0.409693000	-10.711490000
26	-10.049297000	0.259630000	-12.661716000
15	-12.002202000	-0.266488000	-13.421140000
6	-12.648737000	1.210043000	-14.362351000
1	-12.169682000	-1.370086000	-14.293031000
1	-13.065274000	-0.527402000	-12.506150000
6	-11.490832000	2.003061000	-15.000248000
1	-13.354214000	0.879255000	-15.129755000
1	-13.190715000	1.825366000	-13.634034000
1	-11.808098000	3.011735000	-15.282192000
15	-10.013885000	2.057670000	-13.868644000
1	-11.141277000	1.481643000	-15.896518000
1	-8.934186000	2.284986000	-14.757214000
1	-10.096375000	3.332057000	-13.229489000
1	-11.024501000	1.166325000	-12.002205000
6	-10.372989000	-2.796356000	-11.478348000
1	-10.565968000	-3.255113000	-12.452245000
1	-9.824118000	-3.531412000	-10.874561000
1	-11.335723000	-2.624202000	-10.987589000
6	-8.146492000	-2.196771000	-13.704462000
1	-7.825877000	-1.646680000	-14.592657000
1	-7.307952000	-2.816794000	-13.358519000
1	-8.950807000	-2.867466000	-14.014339000
6	-6.866552000	0.620406000	-13.106851000
1	-6.729634000	1.678894000	-12.865112000
1	-5.920233000	0.107903000	-12.889775000
1	-7.068482000	0.529920000	-14.181155000
6	-8.271075000	1.820069000	-10.448352000
1	-9.140685000	2.270107000	-9.960906000
1	-7.512783000	1.636938000	-9.675414000
1	-7.860539000	2.560548000	-11.141028000
6	-10.449761000	-0.311134000	-9.471366000

**f. Cp\*M(dppe)H and their protonation products (M = Fe, Ru, Os)**

Cp*Fe(dppe)H		E= -1531.67297438	
6	-0.795107000	0.892813000	2.514308000
6	0.616163000	1.082570000	2.481946000
6	1.247855000	-0.215428000	2.626921000
6	0.207316000	-1.196864000	2.760392000
6	-1.059075000	-0.525621000	2.662328000
26	0.045302000	-0.234534000	0.862546000
15	-1.520916000	-0.095418000	-0.639033000
15	1.512812000	0.098382000	-0.701020000
6	0.674009000	-0.173369000	-2.369144000
1	-1.375067000	-0.150387000	-3.126911000
1	-0.841384000	1.392684000	-2.457744000
1	1.249041000	0.301741000	-3.173215000
6	-0.778971000	0.306826000	-2.328912000
1	0.710956000	-1.257250000	-2.530733000
1	0.179212000	-1.590191000	0.248881000
1	-1.514811000	-2.826164000	0.404537000
6	0.405507000	-2.650303000	3.061303000
1	1.356134000	-3.021266000	2.665893000
1	0.412212000	-2.826004000	4.146794000
1	-0.392568000	-3.266142000	2.634540000
6	2.711685000	-0.445839000	2.840281000
1	3.317191000	0.291520000	2.304317000
1	2.968515000	-0.364527000	3.906835000
1	3.029441000	-1.435337000	2.500335000
6	1.314785000	2.405320000	2.472099000
1	0.779108000	3.139370000	1.862468000
1	1.393887000	2.812734000	3.490902000
1	2.328238000	2.331784000	2.069518000
6	-1.819619000	1.979186000	2.588205000
1	-2.782426000	1.667531000	2.175031000
1	-1.987717000	2.271845000	3.635328000

1	-1.505827000	2.874010000	2.043177000	1	0.664541000	-1.381929000	-2.531617000
6	-2.405805000	-1.135519000	2.899777000	1	-0.424570000	-1.946821000	0.460958000
1	-2.434660000	-2.189664000	2.607328000	1	0.449353000	-1.938589000	0.418897000
1	-2.681846000	-1.082189000	3.963429000	6	1.278988000	-2.388309000	3.296288000
1	-3.187622000	-0.618903000	2.333824000	1	2.343410000	-2.393893000	3.048541000
6	2.409110000	1.720393000	-0.936660000	1	1.203752000	-2.472708000	4.388676000
6	2.931914000	-1.095985000	-0.920980000	1	0.824689000	-3.289523000	2.872136000
6	-2.876186000	1.184302000	-0.546219000	6	2.693224000	0.401147000	2.667504000
6	-2.506739000	-1.624815000	-1.066041000	1	2.974267000	1.308672000	2.130311000
6	1.823532000	2.771574000	-1.664640000	1	2.947606000	0.555572000	3.724889000
6	2.453106000	4.014693000	-1.771303000	1	3.315846000	-0.419146000	2.298109000
6	3.682959000	4.235804000	-1.145531000	6	0.419090000	2.562930000	2.128572000
6	4.278529000	3.202731000	-0.416634000	1	-0.452839000	3.058329000	1.694847000
6	3.648659000	1.959437000	-0.313721000	1	0.608780000	3.030239000	3.104572000
1	0.870617000	2.622291000	-2.161452000	1	1.278117000	2.777989000	1.487543000
1	1.984161000	4.807723000	-2.346537000	6	-2.398111000	1.126349000	2.638365000
1	4.173162000	5.200910000	-1.227821000	1	-3.223041000	0.494127000	2.300721000
1	5.236984000	3.361153000	0.068926000	1	-2.578176000	1.362347000	3.696476000
1	4.134078000	1.160701000	0.238236000	1	-2.445085000	2.062135000	2.079921000
6	3.964882000	-0.862614000	-1.848313000	6	-1.858714000	-1.934739000	3.226544000
6	4.963254000	-1.816840000	-2.058600000	1	-1.546621000	-2.961318000	3.011341000
6	4.945906000	-3.021143000	-1.347596000	1	-2.021763000	-1.868067000	4.310909000
6	3.921454000	-3.267660000	-0.430382000	1	-2.825096000	-1.766869000	2.742842000
6	2.921159000	-2.312960000	-0.221668000	6	2.429064000	1.559631000	-0.869012000
1	3.992493000	0.069711000	-2.403528000	6	2.971130000	-1.261498000	-0.912473000
1	5.752766000	-1.620637000	-2.778174000	6	-2.726331000	1.359625000	-0.579330000
1	5.723551000	-3.761364000	-1.510565000	6	-2.708103000	-1.472038000	-1.164385000
1	3.898006000	-4.202742000	0.121557000	6	1.797703000	2.667924000	-1.463026000
1	2.110115000	-2.502296000	0.473780000	6	2.450069000	3.899725000	-1.556351000
6	-4.203648000	0.864447000	-0.210601000	6	3.743877000	4.049578000	-1.050335000
6	-5.170994000	1.866296000	-0.076304000	6	4.385427000	2.956607000	-0.462184000
6	-4.830909000	3.205807000	-0.277860000	6	3.737361000	1.721478000	-0.374483000
6	-3.511546000	3.540135000	-0.599288000	1	0.800036000	2.577868000	-1.875179000
6	-2.544006000	2.541056000	-0.720385000	1	1.949556000	4.738226000	-2.029728000
1	-4.487109000	-0.171943000	-0.061815000	1	4.250656000	5.005986000	-1.122582000
1	-6.190431000	1.595804000	0.182602000	1	5.395829000	3.059053000	-0.079994000
1	-5.583112000	3.982400000	-0.179395000	1	4.262211000	0.877246000	0.058369000
1	-3.233608000	4.579734000	-0.745869000	6	3.862488000	-1.132311000	-1.996278000
1	-1.515404000	2.823272000	-0.926309000	6	4.883459000	-2.064302000	-2.185926000
6	-3.458762000	-1.626089000	-2.104345000	6	5.035700000	-3.133117000	-1.295250000
6	-4.150315000	-2.792194000	-2.438518000	6	4.163035000	-3.266102000	-0.213828000
6	-3.904247000	-3.978812000	-1.738947000	6	3.136072000	-2.335379000	-0.025172000
6	-2.962019000	-3.991201000	-0.708330000	1	3.767010000	-0.298966000	-2.685320000
6	-2.267368000	-2.822737000	-0.377158000	1	5.560808000	-1.956145000	-3.026664000
1	-3.669031000	-0.709116000	-2.647598000	1	5.831703000	-3.854993000	-1.444664000
1	-4.879763000	-2.775444000	-3.242978000	1	4.279073000	-4.090676000	0.482007000
1	-4.441856000	-4.885717000	-1.999070000	1	2.462097000	-2.443392000	0.817489000
1	-2.762066000	-4.909657000	-0.164365000	6	-4.111086000	1.192922000	-0.412368000
[Cp*Fe(dppe)( $\eta^2$ -H <sub>2</sub> )] <sup>+</sup> E= -1532.09666700				6	-4.948755000	2.306288000	-0.291127000
6	-1.072975000	0.450322000	2.516125000	6	-4.417706000	3.597193000	-0.335053000
6	0.194789000	1.094164000	2.290448000	6	-3.039242000	3.774415000	-0.493688000
6	1.232271000	0.112677000	2.541532000	6	-2.199601000	2.664814000	-0.607866000
6	0.601345000	-1.134621000	2.838253000	1	-4.541010000	0.198072000	-0.382603000
6	-0.831700000	-0.935312000	2.795152000	1	-6.016824000	2.161023000	-0.166320000
26	0.010083000	-0.505283000	0.869096000	1	-5.070688000	4.458933000	-0.246056000
15	-1.569250000	-0.078358000	-0.713900000	1	-2.619024000	4.774516000	-0.526202000
15	1.565581000	-0.073895000	-0.722108000	1	-1.129526000	2.821384000	-0.703677000
6	0.700331000	-0.296978000	-2.370682000	6	-3.485511000	-1.401295000	-2.338357000
1	-1.310981000	-0.120914000	-3.173494000	6	-4.332603000	-2.451006000	-2.694949000
1	-0.705209000	1.372405000	-2.476749000	6	-4.426080000	-3.586683000	-1.882926000
1	1.302679000	0.133846000	-3.178504000	6	-3.675253000	-3.662021000	-0.708874000
6	-0.714024000	0.285564000	-2.351160000	6	-2.824117000	-2.610798000	-0.352341000
				1	-3.446682000	-0.518636000	-2.969260000



1	-4.921021000	-2.381625000	-3.603941000	1	5.241091000	-4.170925000	-1.578928000
1	-5.083294000	-4.402999000	-2.163359000	1	3.350614000	-4.433238000	0.013498000
1	-3.749244000	-4.535550000	-0.069433000	1	1.791875000	-2.547338000	0.408892000
1	-2.253636000	-2.681415000	0.567397000	6	-4.315634000	0.642568000	-0.133279000
<i>trans</i> -[Cp*Fe(dppe)(H) <sub>2</sub> ] <sup>+</sup> E=-1532.10155981				6	-5.378681000	1.533941000	0.042098000
6	-0.812030000	1.063229000	2.509112000	6	-5.187283000	2.904425000	-0.148948000
6	0.620539000	1.255500000	2.473031000	6	-3.923484000	3.385051000	-0.506154000
6	1.244983000	-0.035587000	2.571541000	6	-2.857021000	2.499538000	-0.670018000
6	0.201093000	-1.027907000	2.635171000	1	-4.485251000	-0.420283000	0.000403000
6	-1.069051000	-0.348119000	2.611476000	1	-6.356128000	1.153726000	0.320276000
26	0.012092000	0.095481000	0.805233000	1	-6.015123000	3.593656000	-0.020380000
15	-1.606253000	-0.028787000	-0.674954000	1	-3.767374000	4.448749000	-0.653585000
15	1.564180000	0.155787000	-0.744997000	1	-1.877371000	2.896601000	-0.918471000
6	0.630134000	-0.014796000	-2.364900000	6	-3.339630000	-1.726512000	-2.128131000
1	-1.405421000	0.115520000	-3.129040000	6	-3.881027000	-2.957877000	-2.498984000
1	-0.852950000	1.587944000	-2.326220000	6	-3.470819000	-4.129602000	-1.852967000
1	1.188885000	0.480302000	-3.167559000	6	-2.515385000	-4.065884000	-0.836638000
6	-0.815868000	0.494281000	-2.286911000	6	-1.969097000	-2.833161000	-0.465726000
1	0.636740000	-1.090259000	-2.579235000	1	-3.676493000	-0.823952000	-2.629400000
1	0.141005000	-1.238813000	0.187709000	1	-4.621991000	-3.003391000	-3.290304000
1	-0.094667000	1.397271000	0.110852000	1	-3.894272000	-5.085546000	-2.142709000
6	0.398866000	-2.481629000	2.925758000	1	-2.193597000	-4.972377000	-0.334439000
1	1.366671000	-2.845518000	2.571906000	1	-1.216947000	-2.784899000	0.314724000
1	0.370153000	-2.648572000	4.011056000	Cp*Ru(dppe)H E=-1502.18871699			
1	-0.383660000	-3.105112000	2.484331000	6	-1.008276000	0.601025000	2.680014000
6	2.707253000	-0.290883000	2.750179000	6	0.314156000	1.143158000	2.603748000
1	3.309583000	0.536920000	2.368319000	6	1.246791000	0.041854000	2.759889000
1	2.939079000	-0.395512000	3.818654000	6	0.492555000	-1.166376000	2.949915000
1	3.036822000	-1.205686000	2.251121000	6	-0.910291000	-0.833615000	2.875558000
6	1.319948000	2.575512000	2.501037000	44	0.027811000	-0.387313000	0.834147000
1	0.724910000	3.356913000	2.021793000	15	-1.543917000	-0.141538000	-0.784853000
1	1.501231000	2.885385000	3.538912000	15	1.528477000	-0.041373000	-0.831540000
1	2.285792000	2.540214000	1.991365000	6	0.690127000	-0.305829000	-2.499262000
6	-1.828059000	2.151103000	2.622922000	1	-1.351598000	-0.284312000	-3.264483000
1	-2.809777000	1.837273000	2.262718000	1	-0.810393000	1.275198000	-2.642066000
1	-1.938252000	2.444973000	3.675617000	1	1.274398000	0.156908000	-3.304206000
1	-1.539198000	3.042189000	2.060416000	6	-0.757201000	0.193199000	-2.477292000
6	-2.405554000	-0.983854000	2.825065000	1	0.715677000	-1.391412000	-2.652572000
1	-2.455951000	-1.993201000	2.408114000	1	0.109091000	-1.874572000	0.235201000
1	-2.616176000	-1.062066000	3.900229000	1	-1.946404000	-2.766817000	0.400781000
1	-3.211063000	-0.395662000	2.377812000	6	1.056557000	-2.502687000	3.323793000
6	2.572082000	1.693949000	-0.890228000	1	2.072398000	-2.634402000	2.938741000
6	2.804889000	-1.198365000	-0.932501000	1	1.103827000	-2.615228000	4.416931000
6	-3.042229000	1.115197000	-0.498592000	1	0.445865000	-3.322300000	2.933293000
6	-2.374179000	-1.651618000	-1.104005000	6	2.727553000	0.178796000	2.939172000
6	2.029754000	2.834084000	-1.509068000	1	3.105972000	1.084911000	2.458217000
6	2.759395000	4.022936000	-1.574370000	1	2.983133000	0.245792000	4.006844000
6	4.037236000	4.094493000	-1.011428000	1	3.272694000	-0.674348000	2.523593000
6	4.583476000	2.970333000	-0.386644000	6	0.677528000	2.594523000	2.534279000
6	3.858206000	1.776811000	-0.325930000	1	-0.118626000	3.181269000	2.065872000
1	1.037171000	2.801242000	-1.947245000	1	0.848142000	3.013179000	3.537678000
1	2.332383000	4.890611000	-2.066708000	1	1.588907000	2.757984000	1.950384000
1	4.603720000	5.018214000	-1.063129000	6	-2.279621000	1.386133000	2.746006000
1	5.576901000	3.017043000	0.047450000	1	-3.127029000	0.822767000	2.345165000
1	4.304560000	0.906031000	0.142717000	1	-2.515813000	1.642706000	3.789023000
6	3.873236000	-1.062753000	-1.840457000	1	-2.215839000	2.319304000	2.180503000
6	4.743787000	-2.130132000	-2.069523000	6	-2.049580000	-1.745397000	3.213532000
6	4.561459000	-3.344371000	-1.400079000	1	-1.811207000	-2.788287000	2.981211000
6	3.499848000	-3.491218000	-0.504183000	1	-2.294776000	-1.696559000	4.285255000
6	2.625370000	-2.425235000	-0.274063000	1	-2.955176000	-1.484902000	2.656800000
1	4.028087000	-0.126791000	-2.366997000	6	2.391666000	1.600114000	-1.026806000
1	5.562302000	-2.013657000	-2.772212000	6	2.977902000	-1.197459000	-1.030081000

6	-2.728054000	1.294551000	-0.666353000	6	2.698995000	0.401332000	2.799329000
6	-2.697165000	-1.549138000	-1.194940000	1	3.001403000	1.254340000	2.188737000
6	1.844586000	2.636598000	-1.804204000	1	2.928153000	0.649578000	3.844776000
6	2.462725000	3.888466000	-1.873449000	1	3.321880000	-0.453902000	2.521913000
6	3.640462000	4.132213000	-1.162150000	6	0.436157000	2.561218000	2.199508000
6	4.198524000	3.111907000	-0.386376000	1	-0.423098000	3.051159000	1.735434000
6	3.582218000	1.859540000	-0.321254000	1	0.602519000	3.042024000	3.173386000
1	0.933765000	2.471357000	-2.369928000	1	1.312368000	2.762508000	1.577460000
1	2.025453000	4.670428000	-2.487456000	6	-2.394359000	1.156249000	2.702649000
1	4.120950000	5.104185000	-1.215828000	1	-3.225910000	0.500510000	2.432826000
1	5.119029000	3.286830000	0.162792000	1	-2.561078000	1.491560000	3.735737000
1	4.039691000	1.069483000	0.265184000	1	-2.441490000	2.036214000	2.059017000
6	3.984254000	-0.976643000	-1.988744000	6	-1.873634000	-1.896310000	3.413611000
6	5.017673000	-1.900789000	-2.158729000	1	-1.578424000	-2.928460000	3.203920000
6	5.063165000	-3.056641000	-1.371463000	1	-2.018354000	-1.813273000	4.499363000
6	4.069523000	-3.284954000	-0.416364000	1	-2.844368000	-1.721264000	2.941599000
6	3.032528000	-2.361402000	-0.248535000	6	2.416068000	1.537556000	-0.927266000
1	3.964502000	-0.076932000	-2.596549000	6	3.010400000	-1.264509000	-1.036367000
1	5.786853000	-1.719190000	-2.903715000	6	-2.706052000	1.322965000	-0.645254000
1	5.868490000	-3.773099000	-1.503596000	6	-2.756778000	-1.496199000	-1.269503000
1	4.098633000	-4.181183000	0.196379000	6	1.798961000	2.643823000	-1.538925000
1	2.243177000	-2.531644000	0.477499000	6	2.432309000	3.888744000	-1.571187000
6	-4.110121000	1.154357000	-0.459498000	6	3.691069000	4.052288000	-0.986590000
6	-4.927460000	2.280349000	-0.307113000	6	4.318574000	2.960205000	-0.381202000
6	-4.379166000	3.563218000	-0.362339000	6	3.690119000	1.712156000	-0.354131000
6	-3.001770000	3.716715000	-0.555343000	1	0.830062000	2.541283000	-2.013314000
6	-2.184517000	2.593619000	-0.693911000	1	1.945698000	4.726796000	-2.059699000
1	-4.553143000	0.165210000	-0.417976000	1	4.182971000	5.018821000	-1.012334000
1	-5.993700000	2.150484000	-0.146413000	1	5.303541000	3.073823000	0.059865000
1	-5.015417000	4.435587000	-0.248682000	1	4.204624000	0.867131000	0.090294000
1	-2.563370000	4.709896000	-0.587758000	6	3.888691000	-1.119378000	-2.128497000
1	-1.110206000	2.722463000	-0.796528000	6	4.944608000	-2.013677000	-2.307987000
6	-3.594400000	-1.489758000	-2.278770000	6	5.146209000	-3.056598000	-1.396584000
6	-4.423077000	-2.573047000	-2.578547000	6	4.288968000	-3.201314000	-0.304156000
6	-4.371032000	-3.732873000	-1.797311000	6	3.226029000	-2.309843000	-0.126046000
6	-3.486442000	-3.802544000	-0.718665000	1	3.756058000	-0.302916000	-2.831635000
6	-2.654030000	-2.718071000	-0.421155000	1	5.611341000	-1.895742000	-3.155876000
1	-3.654902000	-0.589603000	-2.884210000	1	5.969533000	-3.748887000	-1.538017000
1	-5.108470000	-2.512529000	-3.418859000	1	4.444870000	-4.005203000	0.407927000
1	-5.015223000	-4.575248000	-2.030984000	1	2.560351000	-2.423763000	0.723499000
1	-3.438948000	-4.701075000	-0.110625000	6	-4.091793000	1.175607000	-0.468266000
[Cp*Ru(dppe)( $\eta^2$ -H <sub>2</sub> )] <sup>+</sup> E=-1502.60913259				6	-4.907694000	2.299764000	-0.303464000
6	-1.075404000	0.462032000	2.620707000	6	-4.353737000	3.581672000	-0.314419000
6	0.203281000	1.094600000	2.377027000	6	-2.973803000	3.739195000	-0.483129000
6	1.239396000	0.110598000	2.660155000	6	-2.155463000	2.618929000	-0.639772000
6	0.596787000	-1.127224000	2.988605000	1	-4.539002000	0.187978000	-0.466578000
6	-0.841872000	-0.916178000	2.949426000	1	-5.977000000	2.170007000	-0.172139000
44	0.011990000	-0.584751000	0.842451000	1	-4.990081000	4.451863000	-0.192743000
15	-1.580265000	-0.132602000	-0.832110000	1	-2.536258000	4.732396000	-0.491285000
15	1.579377000	-0.110928000	-0.841598000	1	-1.083698000	2.758095000	-0.744651000
6	0.710775000	-0.302112000	-2.492469000	6	-3.490476000	-1.455022000	-2.471622000
1	-1.302496000	-0.172095000	-3.290073000	6	-4.377553000	-2.482169000	-2.797478000
1	-0.735108000	1.333947000	-2.587363000	6	-4.557402000	-3.559830000	-1.923805000
1	1.302116000	0.166653000	-3.287492000	6	-3.854191000	-3.600001000	-0.718303000
6	-0.718053000	0.246539000	-2.464779000	6	-2.961243000	-2.573936000	-0.393610000
1	0.702003000	-1.382490000	-2.683641000	1	-3.387804000	-0.614379000	-3.150712000
1	-0.441674000	-2.143433000	0.393047000	1	-4.929974000	-2.439266000	-3.730392000
1	0.478761000	-2.120724000	0.319222000	1	-5.245343000	-4.358450000	-2.180609000
6	1.271794000	-2.369310000	3.480180000	1	-3.997556000	-4.427450000	-0.031113000
1	2.303775000	-2.439937000	3.126837000	1	-2.423170000	-2.609145000	0.548472000
1	1.303792000	-2.370389000	4.578016000	<i>trans</i> -[Cp*Ru(dppe)(H) <sub>2</sub> ] <sup>+</sup> E= -1502.61690313			
1	0.744893000	-3.275992000	3.169241000	6	-0.812533000	1.036417000	2.704333000

6	0.628698000	1.227754000	2.691905000	6	-2.857225000	2.509193000	-0.708929000
6	1.250185000	-0.069485000	2.796371000	1	-4.519208000	-0.409358000	-0.115209000
6	0.202068000	-1.060966000	2.854388000	1	-6.369897000	1.178288000	0.257179000
6	-1.071263000	-0.380477000	2.809561000	1	-5.999525000	3.622391000	-0.015274000
44	0.020740000	0.070689000	0.830298000	1	-3.743336000	4.467788000	-0.630925000
15	-1.642299000	-0.036448000	-0.778594000	1	-1.873121000	2.900866000	-0.948778000
15	1.591554000	0.143385000	-0.877929000	6	-3.362465000	-1.698751000	-2.273549000
6	0.612675000	-0.059078000	-2.468210000	6	-3.939637000	-2.913584000	-2.644398000
1	-1.417575000	0.140162000	-3.230186000	6	-3.600890000	-4.088927000	-1.964391000
1	-0.828033000	1.583627000	-2.398678000	6	-2.682781000	-4.045006000	-0.913279000
1	1.161129000	0.394487000	-3.302246000	6	-2.100163000	-2.829107000	-0.541716000
6	-0.821536000	0.488333000	-2.379276000	1	-3.647342000	-0.791797000	-2.798785000
1	0.589961000	-1.141420000	-2.646335000	1	-4.653453000	-2.943326000	-3.460978000
1	0.141022000	-1.384466000	0.168647000	1	-4.051724000	-5.032300000	-2.254074000
1	-0.094570000	1.498847000	0.107419000	1	-2.417850000	-4.954223000	-0.383603000
6	0.401436000	-2.518609000	3.128562000	1	-1.378654000	-2.798276000	0.268116000
1	1.348817000	-2.885313000	2.725076000				
1	0.419495000	-2.696095000	4.212372000				
1	-0.404126000	-3.129706000	2.712830000	Cp*Os(dppe)H	E=-1499.36609161		
6	1.711009000	-0.326920000	2.986894000	6	-0.646639000	1.088815000	2.588324000
1	3.316392000	0.487791000	2.582211000	6	0.787963000	1.128124000	2.540865000
1	2.944770000	-0.407581000	4.057055000	6	1.289895000	-0.217870000	2.795113000
1	3.034256000	-1.254790000	2.508034000	6	0.146271000	-1.074125000	3.009265000
6	1.337066000	2.543706000	2.764487000	76	0.075722000	-0.282182000	0.847209000
1	0.746673000	3.344197000	2.312280000	15	-1.534316000	-0.162274000	-0.744328000
1	1.522714000	2.817576000	3.811669000	15	1.520605000	0.069386000	-0.859338000
1	2.301846000	2.518676000	2.251105000	6	0.634051000	-0.053906000	-2.526046000
6	-1.838397000	2.118107000	2.814720000	1	-1.428202000	-0.026114000	-3.230315000
1	-2.784090000	1.832255000	2.348385000	1	-0.912093000	1.477554000	-2.464810000
1	-2.040280000	2.339236000	3.871463000	1	1.175717000	0.519163000	-3.287892000
1	-1.504465000	3.044064000	2.340717000	6	-0.826997000	0.387009000	-2.412618000
6	-2.414429000	-1.009032000	3.007388000	1	0.690816000	-1.114173000	-2.800985000
1	-2.445126000	-2.037123000	2.636296000	1	0.210931000	-1.824629000	0.348201000
1	-2.668275000	-1.036501000	4.075657000	1	-1.561520000	-2.912427000	0.250308000
1	-3.200829000	-0.445813000	2.497416000	6	0.196870000	-2.510189000	3.429733000
6	2.569780000	1.692162000	-1.065264000	1	1.082772000	-3.014955000	3.033911000
6	2.862729000	-1.181399000	-1.043537000	1	0.226985000	-2.590919000	4.525522000
6	-3.061137000	1.122892000	-0.579068000	1	-0.680416000	-3.061479000	3.079468000
6	-2.431270000	-1.644976000	-1.216586000	6	2.721225000	-0.572182000	3.055826000
6	2.101334000	2.762966000	-1.845205000	1	3.401524000	0.008418000	2.425325000
6	2.828613000	3.953397000	-1.924446000	1	2.990530000	-0.372944000	4.103798000
6	4.028639000	4.092153000	-1.221749000	1	2.919388000	-1.630372000	2.862300000
6	4.502118000	3.033762000	-0.440686000	6	1.631501000	2.360964000	2.462635000
6	3.779147000	1.841105000	-0.361481000	1	1.136137000	3.153252000	1.894854000
1	1.173558000	2.676651000	-2.401691000	1	1.842543000	2.750212000	3.469467000
1	2.460880000	4.768236000	-2.539593000	1	2.590083000	2.166728000	1.973674000
1	4.593589000	5.015977000	-1.287001000	6	-1.558769000	2.273477000	2.601578000
1	5.437981000	3.132019000	0.099777000	1	-2.543318000	2.035726000	2.191825000
1	4.168693000	1.018119000	0.229618000	1	-1.704889000	2.632101000	3.631356000
6	3.908552000	-1.040199000	-1.976116000	1	-1.153254000	3.103925000	2.017200000
6	4.825247000	-2.075404000	-2.167260000	6	-2.448004000	-0.742943000	3.146689000
6	4.713172000	-3.259633000	-1.431282000	1	-2.578420000	-1.803597000	2.910656000
6	3.678555000	-3.408147000	-0.504490000	1	-2.701917000	-0.602870000	4.207740000
6	2.756681000	-2.374902000	-0.312310000	1	-3.178719000	-0.184235000	2.554502000
1	4.011123000	-0.122978000	-2.546934000	6	2.433807000	1.692005000	-0.963828000
1	5.626080000	-1.957450000	-2.889774000	6	2.912724000	-1.128981000	-1.186029000
1	5.428985000	-4.061249000	-1.580367000	6	-2.951753000	1.030852000	-0.525353000
1	3.587842000	-4.325927000	0.067464000	6	-2.477967000	-1.696019000	-1.254880000
1	1.946457000	-2.494435000	0.399666000	6	1.720254000	2.858701000	-1.291739000
6	-4.338130000	0.654778000	-0.220962000	6	2.349753000	4.104395000	-1.321335000
6	-5.389004000	1.554037000	-0.014967000	6	3.707257000	4.212054000	-1.001255000
6	-5.180995000	2.926815000	-0.167364000	6	4.425190000	3.065584000	-0.654042000
6	-3.912171000	3.402176000	-0.514618000	6	3.795898000	1.815885000	-0.638713000

1	0.659382000	2.791719000	-1.510234000	1	2.415168000	2.592498000	1.664627000
1	1.781458000	4.990669000	-1.588411000	6	-1.713597000	2.556407000	2.396529000
1	4.197675000	5.180521000	-1.018691000	1	-2.706205000	2.202691000	2.110121000
1	5.478134000	3.139203000	-0.398005000	1	-1.814414000	3.095161000	3.348621000
1	4.370630000	0.932634000	-0.380683000	1	-1.385883000	3.278531000	1.644436000
6	3.765563000	-0.990356000	-2.297745000	6	-2.383217000	-0.332167000	3.559079000
6	4.758484000	-1.938335000	-2.554665000	1	-2.479237000	-1.420585000	3.539607000
6	4.916941000	-3.037171000	-1.702574000	1	-2.520852000	-0.004723000	4.598231000
6	4.076990000	-3.183488000	-0.596189000	1	-3.199719000	0.088461000	2.967935000
6	3.079759000	-2.235846000	-0.342357000	6	2.647086000	1.374457000	-0.767103000
1	3.658884000	-0.135142000	-2.958913000	6	2.550453000	-1.435377000	-1.270553000
1	5.407251000	-1.820616000	-3.417729000	6	-3.214232000	0.809881000	-0.289192000
1	5.689482000	-3.773543000	-1.903218000	6	-2.195669000	-1.560195000	-1.560138000
1	4.193368000	-4.036101000	0.066428000	6	2.266826000	2.659811000	-1.191338000
1	2.403660000	-2.343582000	0.499945000	6	3.183054000	3.714269000	-1.174594000
6	-4.225373000	0.598561000	-0.114264000	6	4.488437000	3.503386000	-0.721275000
6	-5.253460000	1.517196000	0.121886000	6	4.875892000	2.230780000	-0.292029000
6	-5.031080000	2.884719000	-0.056993000	6	3.964647000	1.171026000	-0.318822000
6	-3.767331000	3.329676000	-0.457363000	1	1.256916000	2.848788000	-1.540215000
6	-2.737442000	2.412508000	-0.677231000	1	2.878381000	4.697662000	-1.517905000
1	-4.417907000	-0.461431000	0.012461000	1	5.200075000	4.322134000	-0.710662000
1	-6.228924000	1.160654000	0.439415000	1	5.891308000	2.056859000	0.048821000
1	-5.831286000	3.597180000	0.118386000	1	4.288482000	0.180343000	-0.017041000
1	-3.580958000	4.391371000	-0.590246000	6	3.174635000	-1.404116000	-2.533583000
1	-1.751732000	2.779375000	-0.946099000	6	4.021051000	-2.439514000	-2.930777000
6	-3.390683000	-1.676868000	-2.326989000	6	4.270573000	-3.512925000	-2.068978000
6	-4.068374000	-2.836373000	-2.708585000	6	3.672438000	-3.543660000	-0.807876000
6	-3.850052000	-4.034773000	-2.019567000	6	2.816199000	-2.511303000	-0.410727000
6	-2.953851000	-4.064276000	-0.948790000	1	3.010521000	-0.568758000	-3.206734000
6	-2.272304000	-2.902143000	-0.570513000	1	4.488428000	-2.406492000	-3.909401000
1	-3.586029000	-0.748270000	-2.856217000	1	4.930366000	-4.316531000	-2.378802000
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1	-4.376602000	-4.936835000	-2.316774000	1	2.353887000	-2.546504000	0.570048000
1	-2.780375000	-4.990783000	-0.409298000	6	-4.210499000	0.095129000	0.403620000
<i>cis</i> -[Cp*Os(dppe)(H) <sub>2</sub> ] <sup>+</sup> E=-1499.79703350				6	-5.424266000	0.704962000	0.726328000
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6	0.682265000	1.531362000	2.392144000	6	-4.682931000	2.749352000	-0.333011000
6	1.279426000	0.269344000	2.812558000	1	-3.464478000	2.142834000	-0.656085000
6	0.206525000	-0.599441000	3.245501000	1	-4.044980000	-0.944426000	0.670514000
6	-1.046911000	0.115416000	3.057591000	1	-6.186968000	0.140574000	1.252909000
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6	0.479733000	0.281854000	-2.382507000	1	-2.722330000	2.717839000	-1.198990000
1	-1.533037000	0.920963000	-2.945618000	6	-3.285992000	-1.479936000	-2.448165000
1	-0.745098000	1.966276000	-1.738130000	6	-3.683878000	-2.599900000	-3.179217000
1	1.077428000	0.897239000	-3.062582000	6	-2.998972000	-3.811723000	-3.037107000
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1	-1.007747000	-1.589232000	1.055814000	1	-3.833659000	-0.548938000	-2.557936000
1	0.637269000	-1.732888000	0.784891000	1	-4.530047000	-2.528611000	-3.854753000
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1	0.435597000	-1.744058000	5.036913000	1	-0.668082000	-2.850858000	-0.749965000
1	-0.480812000	-2.574513000	3.770584000	<i>trans</i> -[Cp*Os(dppe)(H) <sub>2</sub> ] <sup>+</sup> E=-1499.80661031			
6	2.738130000	0.034612000	3.050320000	6	-0.811444000	1.046005000	2.703513000
1	3.359098000	0.573411000	2.331554000	6	0.637347000	1.235894000	2.690465000
1	3.015300000	0.384463000	4.053822000	6	1.257846000	-0.063078000	2.813365000
1	2.995142000	-1.026133000	2.989734000	6	0.205721000	-1.051548000	2.881635000
6	1.435469000	2.788675000	2.102581000	6	-1.071088000	-0.372501000	2.826865000
1	0.891726000	3.449106000	1.422755000	76	0.020220000	0.071804000	0.839907000
1	1.594891000	3.339228000	3.040121000	15	-1.639488000	-0.034393000	-0.783964000
				15	1.585850000	0.137316000	-0.885045000

6	0.609317000	-0.050323000	-2.480509000	6	-3.905520000	-2.911275000	-2.684405000
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1	1.158856000	0.407600000	-3.311261000	6	-2.121995000	-2.824571000	-0.534161000
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1	0.131867000	-1.433223000	0.228747000	1	-4.049864000	-5.024860000	-2.277132000
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1	-2.023080000	2.360880000	3.872853000				
1	-1.504508000	3.049878000	2.327941000				
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