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Synthesis and Protonation Studies of Cp*Os(dppe)H: kinetic vs thermodynamic control.

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Summary

The previously undescribed complex $\text{Cp}^*\text{Os}(\text{dppe})\text{H}$ was synthesized starting from either K_2OsX_6 salts or H_2OsBr_6 and characterized together with its precursors $\text{Cp}^*\text{Os}(\text{COD})\text{X}$ ($\text{X} = \text{Cl}, \text{Br}$). Protonation of **1** by $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ was studied in CD_2Cl_2 at 193K and was found to lead exclusively to *cis*- $[\text{Cp}^*\text{Os}(\text{dppe})(\text{H})_2]^+\text{BF}_4^-$, which irreversibly transforms into *trans*- $[\text{Cp}^*\text{Os}(\text{dppe})(\text{H})_2]^+\text{BF}_4^-$ above 230 K.

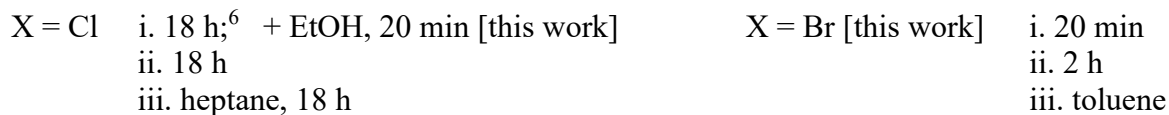
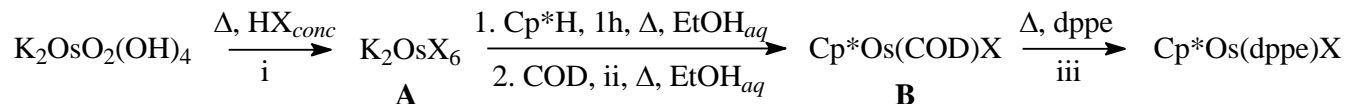
Keywords: osmium, hexahaloosmate(IV), pentamethylcyclopentadienyl ligand, hydrido complexes, protonation

Considerable amount of information has been accumulated since the 80's on proton transfer to transition metal hydrides. Classical polyhydrides may be obtained indirectly through initial, kinetically favored proton transfer at the hydride site, followed by rearrangement of the dihydrogen intermediate to the thermodynamically more stable polyhydride.¹ However, the question of how the nature of the metal center and the electronic and steric properties of the ligands in its coordination sphere affect the choice of the kinetic protonation site (metal or hydride) is not yet fully understood. Thus, for the recently studied Cp*M(dppe)H complexes (M = Fe,² Ru³) proton transfer yields initially (η^2 -H₂)-complexes, which convert quantitatively into the corresponding *trans*-dihydrides upon warming. This isomerization process involves ligand reorganization without intermediates.⁴ Notably, no stationary point was found corresponding to a putative *cis*-dihydride isomer.

From this point of view the protonation of the yet unreported Cp*Os(dppe)H complex would be of special interest because it would complete the series of Group 8 Cp*M(dppe)H complexes and because of the reported⁵ ability of some CpOs(P-P)H complexes [P-P = dpmm, dppe, dppp] to form *cis*-dihydrides [CpOs(P-P)(H)₂]⁺ upon protonation by HBF₄·Et₂O at -78 °C in CD₂Cl₂. Herein, we report the preparation of Cp*Os(dppe)H (**1**) through Cp*Os(COD)X (X = Cl, Br) intermediates and the results of its protonation by HBF₄·Et₂O in CD₂Cl₂. An improved preparation of the K₂OsX₆ precursors is also described.

(a) Synthesis of Cp*Os(dppe)H. An apparently easy synthetic route (“one-pot” procedure, use of non-toxic potassium osmate, K₂OsO₂(OH)₄, and *aqueous* ethanol, higher yield) was reported recently⁶ for the synthesis of some C₅R₅-containing (R = H, Me) osmium complexes (Scheme 1, X = Cl). However, the presumed identity of intermediates **A** and **B** in Scheme 1 was not confirmed. Upon repeating this procedure, we found that the addition of EtOH allows to reduce the reflux time to 20 min for the complete conversion of K₂OsO₂(OH)₄ to species **A**.⁷ In addition, we have confirmed the identity of intermediate **A** as K₂OsCl₆⁸ and **B** as Cp*Os(COD)Cl, **2**⁹ as well as

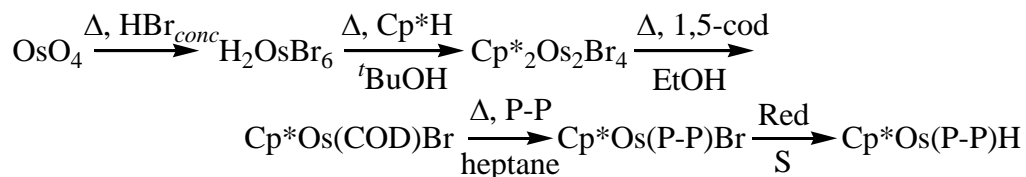
structurally characterized the later by X-ray diffraction (Figure 1). However, compound **2** could not be obtained in acceptable yields in our hands. A significant amount of K_2OsCl_6 , insoluble in EtOH, often remained unreacted.



Scheme 1.

The application of the same strategy to the preparation of the bromide compound, $Cp^*Os(COD)Br$ (**3**), by using HBr instead of HCl (Scheme 1, X = Br) turned to be quite straightforward, faster (ca. 3 h for Br vs 30 h for Cl) and reproducible. The brown-black residue obtained from potassium osmate and conc. HBr corresponds to K_2OsBr_6 . This procedure yields the hexabromoosmate(IV) salt in good yields, being considerably more convenient than those reported in the literature.^{7,10} However the overall route suffers from quite low yield of compound **3**.

Thus, despite the appealing use of the non-toxic potassium osmate as a starting material, both chloro- and bromo- synthetic pathways to $Cp^*Os(dppe)X$ complexes do not appear sufficiently efficient, therefore the original Girolami's protocol^{11,12} (Scheme 2) was used in our further work. However, our improved syntheses of K_2OsX_6 (X = Cl, Br) may become advantageous for other synthetic applications.



Scheme 2.

The new osmium(II) hydride complex Cp*Os(dppe)H (**1**) was obtained as a green-yellow solid in 73% yield by treatment of Cp*Os(dppe)X (with X = either Cl or Br) with MeONa/MeOH. The main NMR spectroscopic features of **1** are given in the Table 1.¹³ Like its ruthenium analogue Cp*Ru(dppe)H,³ compound **1** is not stable in dichloromethane at ambient temperatures undergoing H/Cl exchange with the solvent to yield Cp*Os(dppe)Cl.¹⁴ However, no exchange occurs at measurable rates at low temperatures.

(b) X-ray analyses. The geometry of Cp*Os(COD)X (X = Cl, **2**; Br, **3**) is identical to that of the Cp*Ru(COD)Cl analogue,¹⁵ with the halogen atom and the centers of the two COD double bonds occupying the basal position of a “three-legged piano stool” (Figure 1). Whereas the M-CNT distance is statistically longer for the Os-Cl compound, the M-Cl and M-C (COD) distances are statistically shorter for osmium relative to the Ru analogue.⁸ The reported covalent radii are sensibly similar (Os, 1.28 Å; Ru, 1.26 Å).¹⁶ The longer C-C distances for the coordinated COD double bonds (averages of 1.417(17) Å for Os and 1.388(8) Å for Ru) suggest that Os is capable of stronger M-COD π back-bonding.

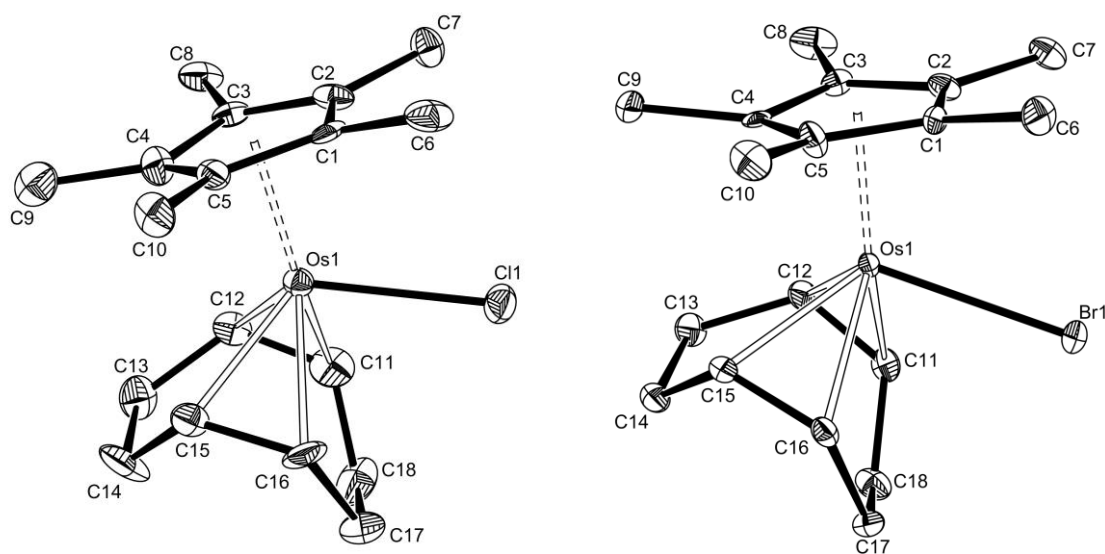


Figure 1. Molecular structures of Cp*Os(COD)Cl (**2**) and Cp*Os(COD)Br (**3**) (30% probability level). Key bond lengths (Å) and angles (deg): **2**, Os-Cl, 2.456(2); Os-CNT, 1.925(4);

Os-C_{av} 2.181(10); CNT-Os-Cl, 110.8(1); Cl-Os-C(11), 79.9(3); Cl-Os-C(12), 115.2(2); Cl-Os-C(15), 119.5(2); Cl-Os-C(16), 81.0(3); **3**, Os-Br, 2.5780(8); Os-CNT, 1.912(4); Os-C_{av} 2.173(9); CNT-Os-Br, 110.7(1); Br-Os-C(11), 78.0(2); Br-Os-C(12), 112.9(3); 122.2(2); Br-Os-C(16), 83.8(2).

Compound Cp*Os(dppe)H (**1**)¹⁷ (Figure 2) also adopts a three-legged piano stool geometry, the H and dppe ligands taking the place of the halogen and COD ligands in the above described structures. Curiously, except for the P-Os-P angle, which is much narrower (by almost 6°), the bond distances and angles are almost identical to those of the previously reported Cp*Ru(dppe)H compound.^{18,8} Another feature of this structure is a short contact (2.32 Å) between Os-H and one ortho-CH proton (bonded to atom C4),¹⁹ which gives rise to the negative ¹H NOE and the cross-peak in the 2D (¹H-¹H) ROESY spectra in solution.⁸

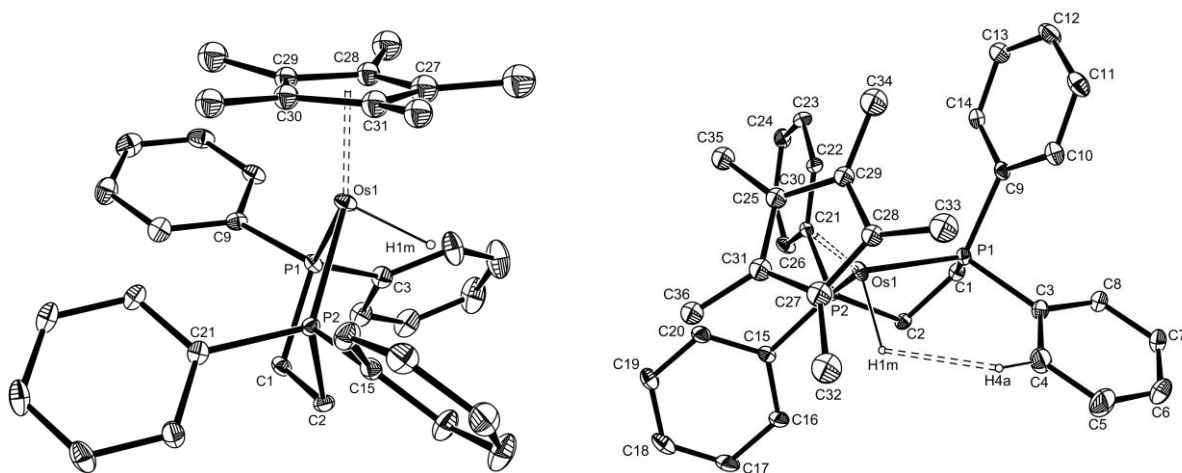


Figure 2. Molecular structure of Cp*Os(dppe)H (**1**) (30% probability level). Key bond lengths (Å) and angles (deg): Os-H 1.56; Os-CNT 1.90(3); Os-P(1) 2.2357(9); Os-P(2) 2.2302(10); CNT-Os-H 119(3); CNT-Os-P(1) 134.0(4); CNT-Os-P(2) 135(2); P(1)-M-P(2) 78.0(2).

(c) Protonation of Cp*Os(dppe)H. The protonation of Cp*Os(dppe)H by strong acids was monitored in CD₂Cl₂ by ¹H and ³¹P{¹H} NMR spectroscopy at low temperatures, where no H/Cl exchange with the solvent occurs. The addition of 1 equiv HBF₄·Et₂O at 193 K led to the complete disappearance of the starting material and to the quantitative appearance of a new poorly resolved triplet resonance at -13.34, which becomes much better resolved at 233 K with ²J_{H-P} = 10 Hz (Figure 3).⁸ Its ²J_{H-P} value, together with the T_{1min} value (186 ms at 220 K and 500 MHz), the overall resonance shape, and temperature-dependent behavior⁸ similar to that reported for the related [CpOs(P-P)H₂]⁺ and [Cp*Ir(dmpm)H₂]²⁺ complexes,^{5,20} suggests the formulation of the new compound as *cis*-[Cp*Os(dppe)(H)₂]⁺BF₄⁻ (*cis*-**1H**⁺, Table 1).²¹ Application of the method of Halpern *et al*²² gives an H-H distance of 1.56 Å in *cis*-**1H**⁺, close to the values of 1.6 Å calculated for *cis*-[CpOs(dppe)(H)₂]⁺ (240 ms at 500 MHz and 218 K)²⁸ and of 1.49 Å derived from T_{1min} data (145 ms at 240K, 500 MHz) for *cis*-[Cp*Ir(dmpm)(H)₂]²⁺.²⁰ On the other hand, much smaller T_{1min} values were measured for the related dihydrogen complexes [Cp*Fe(dppe)(H₂)]⁺ (9.6 ms at 400 MHz)² and [Cp*Ru(dppe)(H₂)]⁺ (19.3 ms at 500 MHz).³

The protonation of **1** by 98% CF₃SO₃D at 200 K led to the appearance of a new triplet resonance at -13.41 ppm (²J_{H-P} = 10 Hz) attributed to the *cis*-[Cp*Os(dppe)(H)(D)]⁺CF₃SO₃⁻ (*cis*-**1D**⁺). Interestingly, besides this resonance the signal of *cis*-**1H**⁺ was also observed.⁸ Correspondingly, two singlets appear in the ³¹P{¹H} spectrum at 41.8 and 41.7 ppm, which were observed as doublet and triplet (*J*_{P-H} = 10 Hz) in non-coupled ³¹P spectra. The chemical shift difference between the hydride signals of two isotopomers is quite high (Δδ = -0.08 ppm), whereas the resonances of other hydrogen atoms are the same for both complexes. The ²H NMR spectrum of the above-mentioned mixture features a single resonance at -13.18 ppm (Δδ = 15 Hz). The 3:1 ratio *cis*-**1D**⁺:*cis*-**1H**⁺ was determined from inverse-gated ³¹P{¹H} spectra.²³

The observation of a simple triplet for the HH'PP' spin system could be rationalized in several different ways: on the basis of a rapid exchange of the two hydride environments; the $J_{HP} = J_{H'P'}$ and $J_{HP'} = J_{H'P}$ could be accidentally degenerate; the J_{PP} could be very large, leading to a virtual triplet; or $J_{HH'}$ could be very large because of quantum mechanical exchange coupling (QMEC) between the two hydride ligands.²⁴ The temperature dependent chemical shift and line broadening for this resonance (see Figure in the Supporting Information) are reminiscent to those of complex *cis*-[CpOs(dppm)H₂]⁺, for which QMEC was shown²⁰ as the responsible cause. The similarity in the structure and NMR behaviour suggest that QMEC could also be operative in *cis*-[Cp*Os(dppe)H₂]⁺.

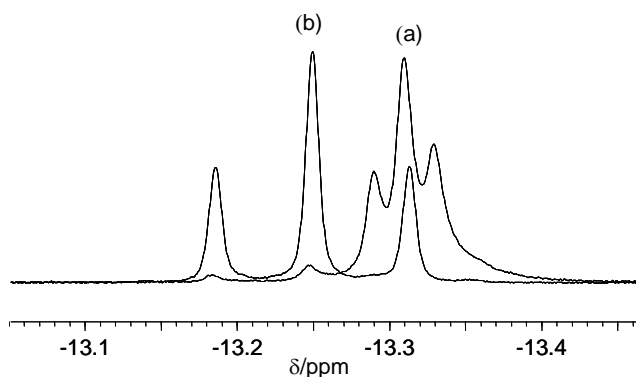


Figure 3. ¹H NMR (500.33 MHz) spectra (hydride region) of [Cp*OsH₂(dppe)]BF₄; 233K, CD₂Cl₂. (a) generated in situ by mixing at 193K, (b) same sample after warming to 298K.

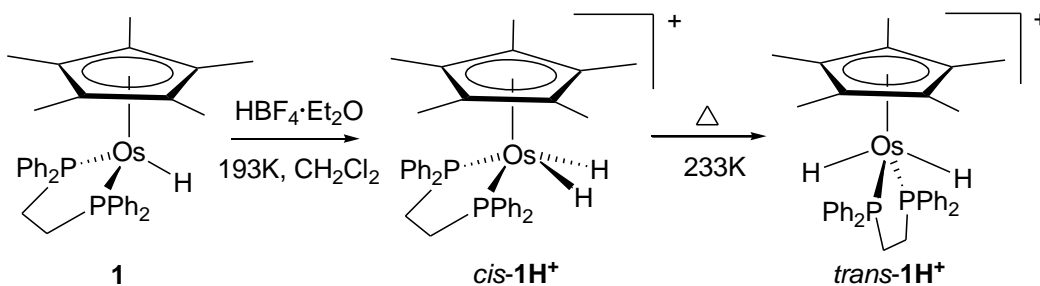
Table 1. Selected NMR (^1H 500.33 MHz, $^{31}\text{P}\{^1\text{H}\}$ 202.5 MHz) data for the $\text{Cp}^*\text{OsH}(\text{dppe})$, *cis*- and *trans*- $[\text{Cp}^*\text{OsH}_2(\text{dppe})]\text{BF}_4$ generated *in situ* in CD_2Cl_2 at 193K.

| | 1 | <i>cis</i> - 1H ⁺ | <i>trans</i> - 1H ⁺ |
|-------------------------------|--|---|--|
| ^1H | -17.19 (t, $^2J_{\text{H-P}} = 27$ Hz, 1 H, Os-H) | -13.34 (bt, $^2J_{\text{H-P}} = 10$ Hz, 2H, Os-H) | -13.32 (t, $^2J_{\text{H-P}} = 35$ Hz, 2H, Os-H) |
| ^1H | 1.92 (s, 15 H, Cp*) | 1.51 (s, 15H, C ₅ Me ₅) | 1.72 (s, 15H, C ₅ Me ₅) |
| ^1H | 1.89-2.06 (2 H, -CH ^A -CH ^A -), 2.08-2.26 (2 H, -CH ^B -CH ^B -) | 2.02-2.25 (m, 2H, -CH ^A -CH ^A -), 2.65-2.88 (m, 2H, -CH ^B -CH ^B -) | 2.32 (vd, $^2J_{\text{H-P}} = 10$ Hz, 4H, -CH ₂ -CH ₂ -) |
| $^{31}\text{P}\{^1\text{H}\}$ | 51.9 (s) | 41.8 (s) | 32.2 (s) |

When the temperature was raised to 293 K, the above described hydride signals of *cis*-**1H**⁺ disappeared and were replaced by a new hydride triplet at δ -13.15 ($^2J_{\text{H-P}} = 35\text{Hz}$), see Figure 3. The signal of *trans*-**1D**⁺ is only slightly shifted to strong field ($\Delta\delta = -0.01$ ppm).⁸ The spectral properties allow the new product to be formulated as *trans*- $[\text{Cp}^*\text{Os}(\text{dppe})(\text{H})_2]\text{BF}_4$, (*trans*-**1H**⁺) (Table 1).²⁵ The relatively large $^2J_{\text{H-P}}$ coupling constant is very similar to those observed for *trans*- $[\text{CpOs}(\text{P-P})(\text{H})_2]^+$ ⁵ and for *trans*- $[\text{CpOs}(\text{LL}')(\text{H})_2]^+$ (LL' = (PR₃)₂, (CO)(PiPr₃)).²⁶ The T_{1min} of *trans*- $[\text{Cp}^*\text{Os}(\text{dppe})(\text{H})_2]^+$ (530 ms at 500 MHz) may be compared with that measured for complex *trans*- $[\text{CpOs}(\text{dppe})(\text{H})_2]^+$ (610 ms at 300 MHz).⁵ Cooling the sample down again to 233 K does not show any further change, showing that the *cis-trans* isomerization is irreversible. When the HBF₄·Et₂O addition (*ca.* 1 equiv) was carried out at room temperature, the nearly quantitative formation of the *trans* isomer was immediately observed; the traces of *cis*-**1H**⁺ completely disappeared within 10 min.²⁷

Thus, the protonation of compound **1** by HBF₄·Et₂O occurs as shown in Scheme 3. Complex *cis*-**1H**⁺ is the kinetic product formed selectively at low temperatures (193 K) and isomerizes

quantitatively to *trans*-**1H**⁺ at higher temperature. We cannot exclude that the minor amount of *trans*-**1H**⁺ observed in the low-temperature protonation process derives from a direct protonation at the metal site, but we consider it more likely that this isomer derives from the isomerization of the *cis* kinetic product due to the occasional warming of the sample during the transfer into the NMR probe. This amount, in fact, was not perfectly reproducible in different experiments but always remained < 2%, see Figure 3. For other related protonation studies, a greater amount of *trans* isomer is obtained directly by low-temperature protonation: the *cis/trans* ratios observed for protonation at -78°C were 24:1 for [CpOs(dppm)H₂]⁺, 1:3 for [CpOs(dppe)H₂]⁺, 1:3 for [CpOs(dppp)H₂]⁺ (changing to 10:1, 1:70 and to 100% *trans*, respectively, upon warming to room temperature).⁵ The 10:1 ratio for the dppm derivative at room temperature was also obtained upon generating the complex by a different route (reaction between CpOs(dppm)Br with Na[BAr^{F*}]₄ under H₂, where Ar^{F*} = 3,5-(CF₃)₂C₆H₃),²⁸ indicating the presence of a reversible equilibrium in that case. Thus, the Cp* system differs from the Cp analogues in two ways: protonation of the monohydride complex yields the *cis* isomer *selectively* at low temperature, and the higher temperature rearrangement to the *trans* isomer is *quantitative*. Our previous results on the kinetics of the (η²-H₂) → (H)₂ isomerization for the Cp*M(dppe)H₂⁺ (M = Fe, Ru) systems^{3,4} revealed that the high activation barrier renders this process too slow at temperatures close to 200 K. At the same time, the proton transfer reaction has a very low activation barrier so the competitive direct proton attack at the metal site can occur at low temperatures to give *trans*-species for the less sterically encumbered complexes. The sterically more crowded coordination sphere, like that in Cp*M(dppe)H, blocks quite efficiently the direct access of the metal site as was shown by calculations of different models for Cp*Fe(dppe)H.²⁹ On the other hand, the *trans*-form is energetically stabilized relative to the *cis* isomer to a greater extent for the Cp* system than for Cp one, for either steric or electronic reasons or both, rendering the isomerization process irreversible like for the Fe and Ru analogues.



Scheme 3.

For all the previously reported examples of [CpOs(P-P)H₂]⁺ complexes, as well as for the [Cp*Os(dppe)H₂]⁺ complex described here, a classical *cis* dihydride structure is generated without the observation of a nonclassical isomer (dihydrogen complex). This behavior is different from that of the Fe and Ru analogues, whose protonation systematically affords dihydrogen complexes as intermediates and *trans*-dihydride isomers as thermodynamically stable products, without the observation of intermediate *cis*-dihydride isomers.^{1d,2,3,29,30} The increase of the relative energy of the metal d electrons upon descending the group destabilizes a dihydrogen structure M(η²-H₂), through a better back-donation to the σ* orbital of the dihydrogen ligand, relative to the classical *cis*-dihydride isomer, and also helps the direct transfer of the proton to the metal.

Though formation of *cis*-dihydride can be formally regarded as a result of proton transfer to the metal atom, it is more likely that the initial proton attack takes place at the hydride site, as it does in the case of (η²-H₂)-complexes formation for the corresponding Fe and Ru complexes.^{1d,2,3} The non-classical (η²-H₂)-like structure could be a transition state for this proton transfer reaction or be generated as a short-lived intermediate, then collapsing to the classical *cis*-dihydride with a very low activation barrier. The latter scenario was found by DFT calculations for the Cp*Mo(dppe)H₃ protonation, although a nonclassical intermediate could not be observed under any experimental conditions.³¹ The former one was suggested for the Cp*W(dppe)H₃ protonation, where the initial H-bonding interaction involves an important contribution from the metal atom.³² The studies of

hydrogen-bonding and proton transfer from weaker acids to Cp*Os(dppe)H are underway aiming to shed more light on the ground state properties of this hydride and the details of the proton transfer mechanism.

In summary, the protonation of the new osmium hydride Cp*Os(dppe)H (**1**) by HBF₄·Et₂O in CD₂Cl₂ was found to lead at low temperatures essentially exclusively to *cis*-[Cp*Os(dppe)(H)₂]⁺BF₄⁻, which then quantitatively transforms into *trans*-[Cp*Os(dppe)(H)₂]⁺BF₄⁻ above 230K. The comparison with the previously reported protonation of less sterically hindered Cp analogues suggests an important difference: a competitive direct proton attack at the metal center, yielding the *trans*-dihydride species, is possible for the sterically less hindered Cp system, but is blocked for the Cp* system.

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Supporting Information Available: Synthetic, spectroscopic, crystallographic, and analytical data, variable temperature NMR spectra, and X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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¹³ The infrared spectrum (Nujol mull) of **1** contains a strong band at 2008 cm⁻¹ due to the Os-H stretch, this frequency being considerably higher than those of the Ru and Fe analogues ($\nu_{\text{RuH}} = 1914 \text{ cm}^{-1}$, $\nu_{\text{FeH}} = 1839 \text{ cm}^{-1}$).

¹⁴ The rate of this exchange is essentially identical to that of the Ru analogue (about 16% in 1 h at 300 K for Os, vs. 15% for Ru), the pseudo-first order rate constant being $7.7 \cdot 10^{-5} \text{ s}^{-1}$ at T = 300 K.

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¹⁶ WebElementsTM, the periodic table on the WWW, URL: <http://www.webelements.com/>.

¹⁷ The Cp* ligand is found disordered with two different orientations with 0.58 and 0.42 occupancies; the position of the hydride ligand was refined in isotropic approximation in riding model. See Supporting Information for further details.

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¹⁹ With normalization of the C-H length to the ideal value of 1.08 Å. This r(H...H) value is certainly overestimated since M-H bond lengths are usually underestimated in X-ray.

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²¹ IR spectra (CH₂Cl₂) at 200 K show full disappearance of the ν_{OSH} band at 2035 cm⁻¹ ($\epsilon/\text{L mol}^{-1}\text{ cm}^{-1} = 84$) of the starting hydride **1** and appearance of two new bands at 2126 ($\epsilon = 29$) and 2177 ($\epsilon = 16$) cm⁻¹ of *cis*-**1H**⁺.

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SYNOPSIS TOC

Synthesis and Protonation Studies of Cp*Os(dppe)H: kinetic vs thermodynamic control.

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The previously undescribed complex Cp*Os(dppe)H was synthesized starting from either K₂OsX₆ salts or H₂OsBr₆ and characterized together with its precursors Cp*Os(COD)X (X = Cl, Br). Protonation of **1** by HBF₄·Et₂O in CD₂Cl₂ at 193K leads exclusively to *cis*-[Cp*Os(dppe)(H)₂]⁺BF₄⁻, which irreversibly transforms into *trans*-[Cp*Os(dppe)(H)₂]⁺BF₄⁻ above 230 K.

