Synthesis and Protonation Studies of Cp*Os(dppe)H: Kinetic versus Thermodynamic Control

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*Summary: The previously undescribed complex Cp*Os(dppe)H was synthesized starting from either K_2OsX_6 salts or H_2OsBr_6 and characterized together with its precursors Cp*Os(COD)X (X = Cl, Br). Protonation of* **1** *by $HBF_4 \cdot Et_2O$ was studied in CD_2Cl_2 at 193 K and was found to lead exclusively to cis-$[Cp^*Os(dppe)(H)_2]^+BF_4^-$, which irreversibly transforms into trans-$[Cp^*Os(dppe)(H)_2]^+BF_4^-$ above 230 K.*

A considerable amount of information has been accumulated since the 1980s 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] Ru[3]) proton transfer yields initially (η^2-H_2)-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 reported[5] ability of some CpOs(P−P)H complexes [P−P = dppm, dppe, dppp] to form *cis*-dihydrides $[CpOs(P-P)(H)_2]^+$ upon protonation by $HBF_4 \cdot Et_2O$ at −78 °C in CD_2Cl_2. 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 $HBF_4 \cdot Et_2O$ in CD_2Cl_2. An improved preparation of the K_2OsX_6 precursors is also described.

(a) Synthesis of Cp*Os(dppe)H. An apparently easy synthetic route ("one-pot" procedure, use of nontoxic potassium osmate, $K_2OsO_2(OH)_4$, and *aqueous* ethanol, higher yield) was reported recently[6] for the synthesis of some C_5R_5-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 reduction of the reflux time to 20 min for the complete conversion of $K_2OsO_2(OH)_4$ to species **A**.[7] In addition, we have confirmed the identity of intermediate **A** as K_2OsCl_6[8] and **B** as Cp*Os(COD)Cl, **2**,[9] as well as structurally characterized the latter 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.

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 out 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 concentrated 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 a quite low yield of compound **3**.

Thus, despite the appealing use of the nontoxic 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.

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Scheme 1

$$K_2OsO_2(OH)_4 \xrightarrow[i]{\Delta,\ HX_{conc}} \underset{\mathbf{A}}{K_2OsX_6} \xrightarrow[2.\ COD,\ ii,\ \Delta,\ EtOH_{aq}]{1.\ Cp^*H,\ 1h,\ \Delta,\ EtOH_{aq}} \underset{\mathbf{B}}{Cp^*Os(COD)X} \xrightarrow[iii]{\Delta,\ dppe} Cp^*Os(dppe)X$$

X = Cl i. 18 h;[6] + EtOH, 20 min [this work] ii. 18 h iii. heptane, 18 h

X = Br [this work] i. 20 min ii. 2 h iii. toluene

Scheme 2

$$OsO_4 \xrightarrow{\Delta,\ HBr_{conc}} H_2OsBr_6 \xrightarrow[^tBuOH]{\Delta,\ Cp^*H} Cp^*_2Os_2Br_4 \xrightarrow[EtOH]{\Delta,\ 1,5\text{-cod}}$$

$$Cp^*Os(COD)Br \xrightarrow[heptane]{\Delta,\ P\text{-}P} Cp^*Os(P\text{-}P)Br \xrightarrow[S]{Red} Cp^*Os(P\text{-}P)H$$

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 Table 1.[13] Like its ruthenium analogue Cp*Ru(dppe)H,[3] compound **1** is not stable in dichloromethane at ambient temperature, 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.

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.[8,18] 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 ^{1}H NOE and the cross-peak in the 2D (^{1}H−^{1}H) ROESY spectra in solution.[8]

(c) Protonation of Cp*Os(dppe)H. The protonation of Cp*Os(dppe)H by strong acids was monitored in CD_2Cl_2 by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy at low temperatures, where no H/Cl exchange with the solvent occurs. The addition of 1 equiv of $HBF_4 \cdot Et_2O$ 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 behavior[8] similar to that reported for the related $[CpOs(P-P)H_2]^+$ and $[Cp^*Ir(dmpm)H_2]^{2+}$ complexes,[5,20] suggests the formulation of the new compound as *cis*-$[Cp^*Os(dppe)(H)_2]^+BF_4^-$ (*cis*-**1H**$^+$, Table 1).[21] Application of the method of Halpern et al.[22] gives an H−H distance of 1.56

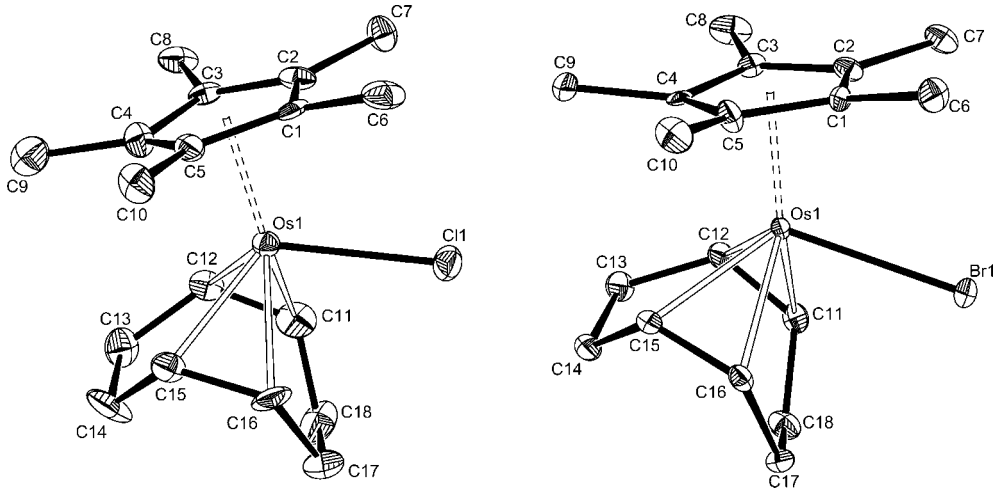


Figure 1. Molecular structures of Cp*Os(COD)Cl (**2**) and Cp*Os(COD)Br (**3**) (30% probability level). Key bond lengths (Å) and angles (deg): **2**, Os−Cl, 2.456(2); Os−CNT, 1.925(4); Os−C_{av} 2.181(10); CNT−Os−Cl, 110.8(1); Cl−Os−C(11), 79.9(3); Cl−Os−C(12), 115.2(2); Cl−Os−C(15), 119.5(2); Cl−Os−C(16), 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).

Table 1. Selected NMR (^{1}H 500.33 MHz, ^{31}P{^{1}H} 202.5 MHz) Data for Cp*OsH(dppe) and *cis*- and *trans*-$[Cp^*OsH_2(dppe)]BF_4$ Generated *in Situ* in CD_2Cl_2 at 193 K

	1	*cis*-**1H**$^+$	*trans*-**1H**$^+$
^{1}H	−17.19 (t, $^2J_{H-P}$ = 27 Hz, 1H, Os−H)	−13.34 (bt, $^2J_{H-P}$ = 10 Hz, 2H, Os−H)	−13.32 (t, $^2J_{H-P}$ = 35 Hz, 2H, Os−H)
^{1}H	1.92 (s, 15H, Cp*)	1.51 (s, 15H, C_5Me_5)	1.72 (s, 15H, C_5Me_5)
^{1}H	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, $^2J_{H-P}$ = 10 Hz, 4H, $-CH_2-CH_2-$)
^{31}P{^{1}H}	51.9 (s)	41.8 (s)	32.2 (s)

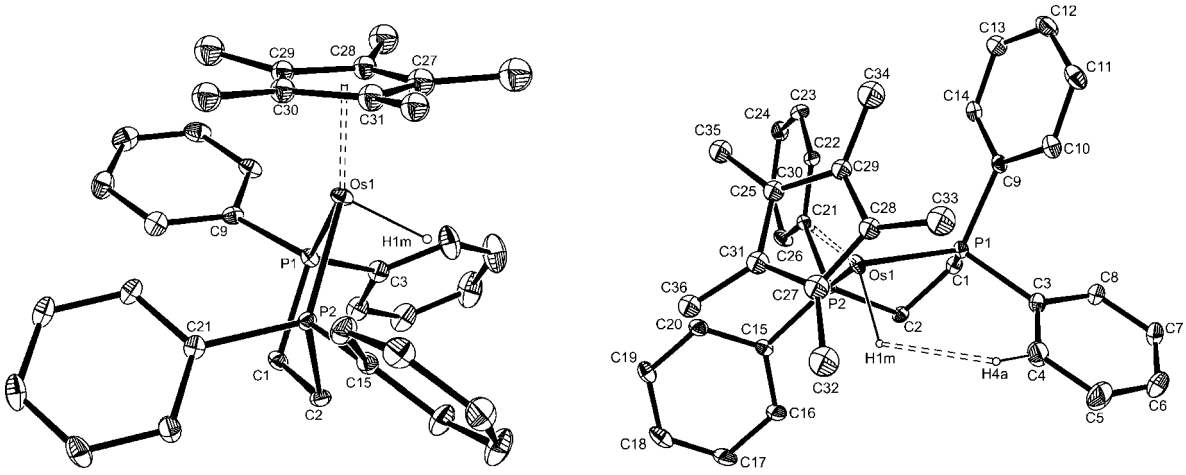


Figure 2. Molecular structure of Cp*Os(dppe)H (**1**) (30% probability level). Key bond lengths (Å) and angles (deg): Os−H 1.56; Os−CNT 1.90(3); Os−P(1) 2.2357(9); Os−P(2) 2.2302(10); CNT−Os−H 119(3); CNT−Os−P(1) 134.0(4); CNT−Os−P(2) 135(2); P(1)−M−P(2) 78.0(2).

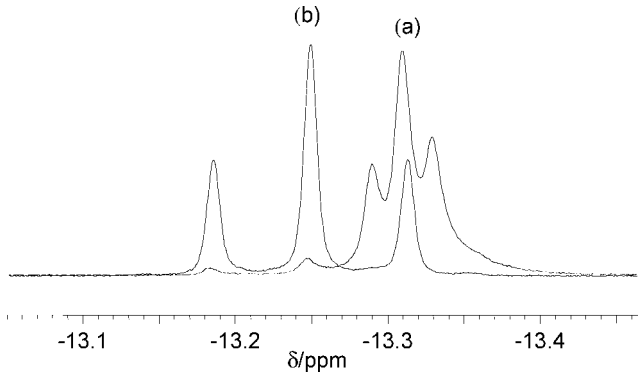


Figure 3. ^{1}H NMR (500.33 MHz) spectra (hydride region) of $[Cp^*OsH_2(dppe)]BF_4$; 233 K, CD_2Cl_2: (a) generated *in situ* by mixing at 193 K, (b) same sample after warming to 298 K.

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 240 K, 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 $[Cp^*Fe(dppe)(H_2)]^+$ (9.6 ms at 400 MHz)[2] and $[Cp^*Ru(dppe)(H_2)]^+$ (19.3 ms at 500 MHz).[3]

The protonation of **1** by 98% CF_3SO_3D at 200 K led to the appearance of a new triplet resonance at −13.41 ppm ($^2J_{H-P}$ = 10 Hz) attributed to *cis*-$[Cp^*Os(dppe)(H)(D)]^+CF_3SO_3^-$ (*cis*-**1D**$^+$). Interestingly, besides this resonance the signal of *cis*-**1H**$^+$ was also observed.[8] Correspondingly, two singlets appear in the $^{31}P\{^1H\}$ specrum at 41.8 and 41.7 ppm, which were observed as a doublet and triplet (J_{P-H} = 10 Hz) in noncoupled ^{31}P spectra. The chemical shift difference between the hydride signals of the two isotopomers is quite high ($\Delta\delta = -0.08$ ppm), whereas the resonances of other hydrogen atoms are the same for both complexes. The ^{2}H NMR spectrum of the above-mentioned mixture features a single resonance at −13.18 ppm ($\Delta\delta$ = 15 Hz). The 3:1 ratio *cis*-**1D**$^+$:*cis*-**1H**$^+$ was determined from inverse-gated $^{31}P\{^1H\}$ 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 the figure in the Supporting Information) are reminiscent of those of complex *cis*-$[CpOs(dppm)H_2]^+$, for which QMEC was shown[20] as the responsible cause. The similarity in the structure and NMR behavior suggests that QMEC could also be operative in *cis*-$[Cp^*Os(dppe)H_2]^+$.

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 ($^2J_{H-P}$ = 35 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*-$[Cp^*Os(dppe)(H)_2]BF_4$ (*trans*-**1H**$^+$) (Table 1).[25] The relatively large $^2J_{H-P}$ coupling constant is very similar to those observed for

(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 (ν_{RuH} = 1914 cm^{-1}, ν_{FeH} = 1839 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 × 10^{-5} s^{-1} at T = 300 K.

(15) Serron, S. A.; Luo, L.; Li, C.; Cucullu; M, E.; Stevens, E. D.; Nolan, S. P. *Organometallics* **1995**, *14*, 5290–5297.

(16) WebElements, the periodic table on the Internet, 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 a riding model. See the Supporting Information for further details.

(18) Guan, H.; Iimura, M.; Magee, M. P.; Norton, J. R.; Zhu, G. *J. Am. Chem. Soc.* **2005**, *127*, 7805–7814.

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

(20) Pons, V.; Heinekey, D. M. *J. Am. Chem. Soc.* **2003**, *125*, 8428–8429.

(21) IR spectra (CH_2Cl_2) at 200 K show full disappearance of the ν_{OsH} band at 2035 cm^{-1} (ε/L mol^{-1} cm^{-1} = 84) of the starting hydride **1** and appearance of two new bands at 2126 (ε = 29) and 2177 (ε = 16) cm^{-1} of *cis*-**1H**$^+$.

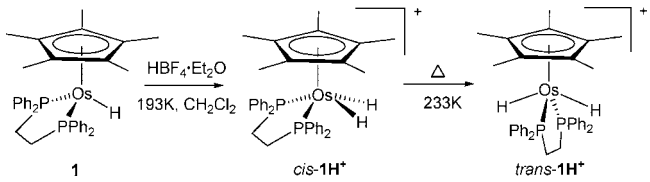
(22) (a) Desrosiers, P. J.; Cai, L.; Lin, Z.; Richards, R.; Halpern, J. *J. Am. Chem. Soc.* **1991**, *113*, 4173–4184. (b) Bayse, C. A.; Luck, R. L.; Schelter, E. J. *Inorg. Chem.* **2001**, *40*, 3463–3467.

(23) The addition of the extra proton could be explained by the exchange of *o*-CH of the phenyl ring of the dppe ligand and the osmium-bound deuterium via an electrophilic substitution on the arene ring (the cationic dihydride serves as acid).

(24) Sabo-Etienne, S.; Chaudret, B. *Chem. Rev.* **1998**, *98*, 2077–2092.

(25) IR spectrum of *trans*-**1H**$^+$ (CH_2Cl_2) at 200 K features two ν_{OsH} bands at 2053 (ε/L mol^{-1} cm^{-1} = 25) and 2102 (ε = 41) cm^{-1}.

Scheme 3



trans-$[CpOs(P-P)(H)_2]^+$[5] and for *trans*-$[CpOs(LL')H_2]^+$ (LL′ = $(PR_3)_2$, $(CO)(PiPr_3)$).[26] The T_{1min} of *trans*-$[Cp^*Os(dppe)(H)_2]^+$ (530 ms at 500 MHz) may be compared with that measured for complex *trans*-$[CpOs(dppe)(H)_2]^+$ (610 ms at 300 MHz).[5] Cooling the sample again to 233 K does not result in any further change, showing that the *cis*−*trans* isomerization is irreversible. When the $HBF_4 \cdot Et_2O$ 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*-$\mathbf{1H}^+$ completely disappeared within 10 min.[27]

Thus, the protonation of compound **1** by $HBF_4 \cdot Et_2O$ occurs as shown in Scheme 3. Complex *cis*-$\mathbf{1H}^+$ is the kinetic product formed selectively at low temperatures (193 K) and isomerizes quantitatively to *trans*-$\mathbf{1H}^+$ at higher temperature. We cannot exclude that the minor amount of *trans*-$\mathbf{1H}^+$ 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 $[CpOs(dppm)H_2]^+$, 1:3 for $[CpOs(dppe)H_2]^+$, and 1:3 for $[CpOs(dppp)H_2]^+$ (changing to 10:1, 1:70, and 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 of CpOs(dppm)Br with $Na[BAr^F{}^*{}_4]$ under H_2, where $Ar^F* = 3,5\text{-}(CF_3)_2C_6H_3$),[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 $(\eta^2\text{-}H_2) \rightarrow (H)_2$ isomerization for the $Cp^*M(dppe)H_2^+$ (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.

For all the previously reported examples of $[CpOs(P-P)H_2]^+$ complexes, as well as for the $[Cp^*Os(dppe)H_2]^+$ 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 $M(\eta^2\text{-}H_2)$, 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.

Although formation of the *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 $(\eta^2\text{-}H_2)$-complexes' formation for the corresponding Fe and Ru complexes.[1d,2,3] The nonclassical $(\eta^2\text{-}H_2)$-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 $Cp^*Mo(dppe)H_3$ protonation, although a nonclassical intermediate could not be observed under any experimental conditions.[31] The former one was suggested for the $Cp^*W(dppe)H_3$ protonation, where the initial H-bonding interaction involves an important contribution from the metal atom.[32] 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 $HBF_4 \cdot Et_2O$ in CD_2Cl_2 was found to lead at low temperatures essentially exclusively to *cis*-$[Cp^*Os(dppe)(H)_2]^+BF_4^-$, which then quantitatively transforms into *trans*-$[Cp^*Os(dppe)(H)_2]^+BF_4^-$ above 230 K. 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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