Synthesis, Structure, and Properties of the Stable and Highly Acidic Dihydrogen Complex *trans*-[Os(η^2-H$_2$)(CH$_3$CN)(dppe)$_2$](BF$_4$)$_2$. Perspectives on the Influence of the *trans* Ligand on the Chemistry of the Dihydrogen Ligand

Marcel Schlaf, Alan J. Lough, Patricia A. Maltby, and Robert H. Morris*

Department of Chemistry, University of Toronto, Toronto, Ontario M5S 1A1, Canada

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The complex *trans*-[Os(H)(CH$_3$CN)(dppe)$_2$]BF$_4$ **(2)** is prepared from the known complex *trans*-[Os(η^2-H$_2$)(H)(dppe)$_2$]BF$_4$ **(1)**, dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$, by substitution of the η^2-H$_2$ ligand with CH$_3$CN. **2** was identified as a potential precursor for a highly acidic and stable η^2-H$_2$ complex on the basis of its electrochemical potential $E_{1/2}$(Os^{III}/Os^{II}). The stable complex *trans*-[Os(η^2-H$_2$)(CH$_3$CN)(dppe)$_2$](BF$_4$)$_2$ **(3)** is formed when **2** is protonated with excess HBF$_4$·Et$_2$O in anhydrous CH$_2$Cl$_2$. The pK_a of **3** is estimated to be −2 because it is partially deprotonated by Et$_2$O. This makes it the most acidic, stable dihydrogen complex to be fully characterized. Its properties are compared to the known complex *trans*-[Os(η^2-H$_2$)(CH$_3$CN)(en)$_2$](CF$_3$SO$_3$)$_2$ **(5)**, en = H$_2$NCH$_2$CH$_2$NH$_2$, to illustrate the influence of the chelating ligand (π-acidic dppe versus σ-basic en), and to the complexes *trans*-[Os(η^2-H$_2$)(X)(dppe)$_2$]PF$_6$, X = H **(1)**, Cl **(4)**, and Br **(6)**, to illustrate the influence of the *trans* ligand on the characteristic properties of the η^2-H$_2$ ligand. The ligand field strength of X is an important factor. The structures of **2** and **3a,b** (**3** crystallizes in 2 forms) were determined by X-ray diffraction. In **3a** the hydrogen atoms of the η^2-H$_2$ ligand were isotropically refined, resulting in an H−H distance of 0.9(1) Å. In **3b** there is residual electron density associated with the η^2-H$_2$ ligand, but the hydrogen atoms were not located. There is a close dihydrogen−fluorine contact of approximately 2.4 Å in **3a**.

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Introduction

The heterolytic activation of dihydrogen, i.e. the splitting into a proton and a hydride by side-on coordination to a transition metal in η^2-H$_2$ complexes, is one of the most interesting features of this class of compounds.[1,2] It opens the possibility of unique reactivity patterns of these complexes including catalysis and selective proton transfer to an ancillary ligand.[3,4] Several enzyme systems found in nature such as hydrogenases and nitrogenases are believed to involve the heterolytic activation of dihydrogen at a metal center during sequential proton−electron transfer steps.[5−7]

Several examples of highly acidic η^2-H$_2$ dihydrogen complexes have been reported in the literature. Chinn et al. estimated the pK_a value of their thermally unstable complex [(η^5-C$_5$Me$_5$)Re(CO)(NO)(η^2-H$_2$)]BF$_4$ to be −2, based on its deprotonation by Et$_2$O.[8] The complex [(η^5-C$_5$Me$_5$)Re(CO)(NO)(η^2-H$_2$)]BF$_4$ has however only been observed at low temperature as it quantitatively loses the η^2-H$_2$ ligand above 243 K.

Keady et al.[9] postulated that a highly acidic dihydrogen [(C$_5$H$_5$)Ru(dfepe)(η^2-H$_2$)]$^+$ or dihydride [(C$_5$H$_5$)Ru(dfepe)(H)$_2$]$^+$ (dfepe = (C$_2$F$_5$)$_2$PCH$_2$CH$_2$P(C$_2$F$_5$)$_2$) complex is the intermediate in the reaction of the very electron deficient ruthenium complex (C$_5$H$_5$)Ru(dfepe)Cl with AgBF$_4$ under hydrogen gas to give (C$_5$H$_5$)Ru(dfepe)(H). Attempts to isolate the protonated form of the complex by precipitation with Et$_2$O from the reaction mixture yielded the monohydride species suggesting that the protonated form has a pK_a < −2. Recently Smith et al.[10] have described the preparation of the complexes [(P^{i}Pr$_3$)$_2$Os(NCCH$_3$)$_2$H$_4$]$^{2+}$ (believed to contain at least one η^2-H$_2$ ligand) and [(P^{i}Pr$_3$)$_2$Os(NCCH$_3$)$_3$(η^2-H$_2$)]$^{2+}$ by electrochemical oxidation of (P^{i}Pr$_3$)$_2$OsH$_6$ in CH$_3$CN in the presence of HBF$_4$. An upper limit of pK_a 18.9 in CH$_3$CN (approximately 12 on the aqueous scale) for these complexes was indicated by the fact that they were deprotonated by piperidine. However dicationic dihydrogen complexes are not necessarily strong acids; the complex [Os(H$_2$)(NH$_3$)$_5$]$^{2+}$ is a very weak acid.[11,12]

Our group has investigated systems of the type [Os(η^2-H$_2$)(CO)(L)(PPh$_3$)$_2$]$^+$ (L = pyridine-2-thiolate, quino-

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[⊗] Abstract published in *Advance ACS Abstracts,* April 1, 1996.

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line-8-thiolate). The complex with L = pyS forms a stable, isolable dihydrogen complex with a pK_a value of -1.[4,13] This complex was targeted for synthesis on the basis of an empirical ligand-additivity method for predicting the properties of a complex.[12]

In the first systematic studies of the influence of the ligands on dihydrogen acidity, the pK_a's of the series of complexes [Ru(C_5H_5)(H_2)($PR_2CH_2CH_2PR_2$)]$^+$ [14] and *trans*-[M(η^2-H_2)(H)($PR_2CH_2CH_2PR_2$)$_2$]$^+$, M = Fe, Ru, and Os,[15] were measured as a function of the substituent R on the chelating phosphine ligand. The pK_a values decreased by 4 units in the first series and by 7 units in the second series (M = Ru) when R was changed from 4-$C_6H_4OCH_3$ to 4-$C_6H_4CF_3$. On the basis of hydrogen atom abstraction energies ΔH_{BDE}, which were calculated by use of eq 1,[15-17] it was proposed that the complexes with the most electron-withdrawing substituents (4-$C_6H_4CF_3$) had the most residual H−H bonding, which made them less acidic than expected.[15]

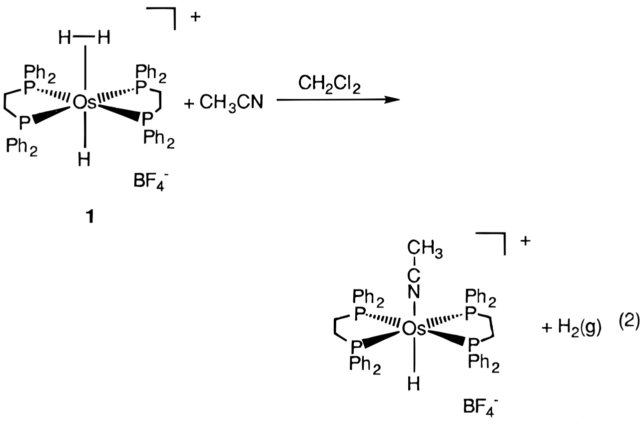
$$\Delta H_{\mathrm{BDE}}\{\mathrm{MH_2}^+\} = 1.37\ \mathrm{p}K_\mathrm{a}\{\mathrm{MH_2}^+\} + 23.1E°\{\mathrm{MH^+/MH}\} + 66 \quad (1)$$

Support for this proposal was provided by the discovery that the trihydride complex [Ru(H)$_3$(L-L)$_2$]$^+$, L-L = 1,1′-bis(diphenylphosphino)ferrocene, which has electron-donating chelating ligands and no H−H bonding, is more acidic (pK_a = 4) than the complex [Ru(η^2-H_2)H($PR_2CH_2CH_2PR_2$)$_2$]$^+$, R = 4-$C_6H_4CF_3$ (pK_a = 10), which has significant H−H bonding with *d*(HH) = 0.90 Å.[15]

In an extension of our group's focus on the influence of the trans ligand, X, on the chemistry of the dihydrogen ligand in the complexes of the general type *trans*-[M(η^2-H_2)(X)(L-L)$_2$][Y] (M = Fe, Ru, Os; L-L = diphosphine ligand; X = H^-, Cl^-, Br^-; Y = BF_4^-, BPh_4^-, PF_6^-),[15,18-22] we present here the synthesis, structure, and properties of the complex *trans*-[Os(η^2-H_2)(CH_3CN)(dppe)$_2$](BF_4)$_2$ and the parent monohydride compound *trans*-[Os(H)(CH_3CN)(dppe)$_2$]BF_4.

Results and Discussion

Preparation and Properties of the Monohydride Complex. The complex *trans*-[Os(H)(CH_3CN)(dppe)$_2$]BF_4 **(2)** is prepared by substituting the dihydrogen ligand in the complex *trans*-[Os(η^2-H_2)(H)(dppe)$_2$]BF_4 **(1)** with CH_3CN (eq 2).[21]



1

2

(2)

The reaction proceeds quantitatively at room temperature by stirring a solution of the starting material in neat CH_3CN or in CH_2Cl_2 in the presence of excess CH_3CN and is irreversible under ambient conditions. The complex **2** is isolated as a pure white, microcrystalline solid in quantitative yield. It is air-stable in solution and as a solid. As the dihydrogen complex **1** can be prepared directly from the starting material *cis*-$OsBr_2$(dppe)$_2$, this synthesis is simpler and more effective than an alternative route which involves the reaction of *trans*-OsHBr(dppe)$_2$ with $NaPF_6$ in THF in the presence of excess CH_3CN.[23,24]

The $^{31}P\{^1H\}$ NMR spectrum of **2** in CH_2Cl_2 consists of a singlet at +33.30 ppm with ^{187}Os satellites ($J(^{31}P,^{187}Os)$ = 195.0 Hz) as the only peaks indicating the equivalence of all 4 phosphorus nuclei in solution. In the ^1H NMR spectrum, the hydride ligand appears as a binomial quintet at −16.63 ppm with a coupling *J*(H,P) of 16.2 Hz. The methyl group of the CH_3CN ligand appears as a singlet at +1.81 ppm. There are two weak absorptions in the infrared spectrum at 2267 cm^{-1} for ν(CN) and at 2066 cm^{-1} for ν(Os−H). The CN stretching wavenumber is slightly changed from the 2255[25] to 2270 cm^{-1} [26] value for free CH_3CN. This suggests that a σ-interaction dominates in Os−N bonding where the strongly Lewis acidic, 5-coordinate fragment [Os(H)(dppe)$_2$]$^+$ attracts the nonbonding electrons on the nitrogen. If π-back-donation into the π^* orbital of the C−N bond were present, a lowering of the C−N stretching frequency, ν(CN), would be expected.[25] The rod-shaped CH_3CN ligand fits well into the sterically encumbered [Os(H)(dppe)$_2$]$^+$ cavity, and this may also constitute an important factor in the formation and stability of complex **2**.

The electrochemical properties of the complexes [Os(H)(L^z)(dppe)$_2$]$^{(z+1)+}$ (L = variety of anionic and neutral ligands) have recently been investigated in detail by our group.[24] The oxidation of **2** is reversible with an $E_{1/2}$(Os^{III}/Os^{II}) of 0.58 V vs Fc$^+$/Fc in 0.2 M $^nBu_4NPF_6$ in CH_2Cl_2.

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(16) Equation 1 relates the pK_a of an η^2-H_2 complex to the electrochemical potential $E_{1/2}$\{MH$^+$/MH\} (vs the (Fc$^+$/Fc) couple) for the oxidation of the parent hydride complex and the bond dissociation energy ΔH_{BDE} (in kcal/mol) needed to remove a hydrogen atom from the M(η^2-H_2) unit in solution.

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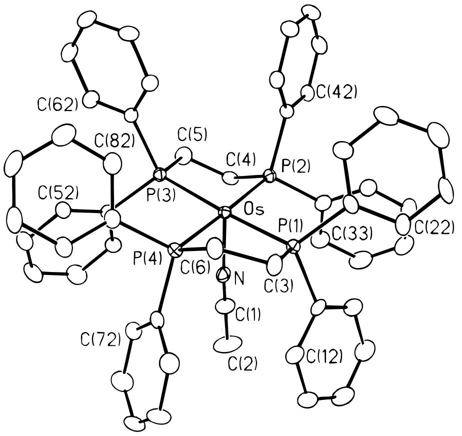
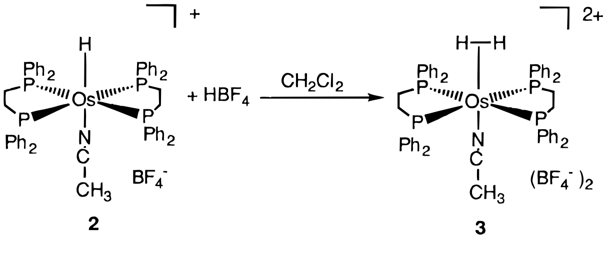


Figure 1. Structure of the cation of **2** with thermal ellipsoids plotted at the 50% probability level.

Structure of *trans*-[Os(H)(CH$_3$CN)(dppe)$_2$]BF$_4$ (2) in the Solid State. The structure of the cation is shown in Figure 1. It consists of a distorted pseudo-square-based pyramid defined by the four phosphorus atoms and the CH$_3$CN ligand. A discrete regular BF$_4^-$ counterion is not shown. The hydride ligand that complements the octahedral coordination of the d^6 osmium center was not located, but its presence was confirmed by a ^{1}H NMR spectrum of the crystal sample used. The closest contact between the cation and anion occurs at 2.239 Å between one of the fluorine atoms and a hydrogen atom of the CH$_3$CN ligand. The four phosphorus atoms define a plane with a small mean deviation of 0.037 Å. The osmium atom is minimally displaced from this plane by 0.066 Å toward the nitrogen atom. Table 1 lists and compares bond lengths and angles of **2** with data from the two structures obtained for the two forms of the dihydrogen complex **3** (vide infra). In structure **2** the osmium−phosphorus bond distances vary between 2.314(2) and 2.347(2) Å. The osmium−nitrogen distance is 2.109(4) Å, close to the reported average value of 2.098 Å [27] and the 2.081(8)−2.096(8) distances in [Os(NCMe)$_3$(PMe$_2$Ph)$_3$](PF$_6$)$_2$.[28] The osmium−nitrogen vector is not perfectly perpendicular to the plane defined by the four phosphorus atoms but is tilted toward P(2) with the angle N−Os−P(2) = 85.26(13)° and the CH$_3$CN ligand deviating slightly from linear geometry with an angle N−C(1)−C(2) of 178.5(7)°. The carbon−nitrogen and carbon−carbon distances in the CH$_3$CN ligand are 1.127(7) and 1.461(9) Å. Those appear to be unchanged within the 3σ level from the average values of 1.136 and 1.470 Å reported for uncoordinated nitriles.[29]

Preparation of the Dihydrogen Complex. The dihydrogen complex *trans*-[Os(η^2-H$_2$)(CH$_3$CN)(dppe)$_2$](BF$_4$)$_2$ **(3)** is generated by reaction of **2** in CH$_2$Cl$_2$ with excess HBF$_4$·Et$_2$O under 1 atm of argon or hydrogen gas (eq 3).



(3)

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 2 and 3a,b[a]

	2	3a	3b
Os−N	2.109(4)	2.079(6)	2.066(5)
N−C(1)	1.127(7)	1.117(9)	1.126(8)
C(1)−C(2)	1.461(9)	1.472(11)	1.473(9)
Os−P(1)	2.328(2)	2.385(2)	2.405(2)
Os−P(2)	2.347(2)	2.392(2)	2.387(2)
Os−P(3)	2.3422(14)	2.386(2)	2.401(2)
Os−P(4)	2.314(2)	2.396(2)	2.394(2)
P(1)−C(3)	1.865(5)	1.826(7)	1.836(7)
P(1)−C(11)	1.831(5)	1.821(7)	1.818(6)
P(1)−C(21)	1.831(5)	1.818(8)	1.819(7)
P(2)−C(4)	1.838(6)	1.844(8)	1.836(6)
P(2)−C(31)	1.828(5)	1.820(8)	1.821(6)
P(2)−C(41)	1.840(5)	1.832(7)	1.831(6)
P(3)−C(5)	1.854(6)	1.832(7)	1.839(6)
P(3)−C(51)	1.827(5)	1.815(7)	1.821(6)
P(3)−C(61)	1.831(6)	1.829(7)	1.832(6)
P(4)−C(6)	1.837(5)	1.843(8)	1.877(12)
P(4)−C(6*)			1.82(2)
P(4)−C(71)	1.832(5)	1.843(7)	1.683(13)
P(4)−C(71*)		1.828(8)	2.02(2)
P(4)−C(81)	1.833(5)	1.815(8)	1.801(7)
C(3)−C(6)	1.533(7)	1.541(11)	1.509(14)
C(3)−C(6*)			1.43(2)
C(4)−C(5)	1.525(7)	1.520(10)	1.519(9)
N−Os−P(1)	92.54(12)	95.6(2)	87.2(2)
N−Os−P(2)	85.26(13)	88.7(2)	86.4(2)
N−Os−P(3)	92.54(12)	83.6(2)	88.9(2)
N−Os−P(4)	96.21(13)	88.3(2)	95.5(2)
Os−N−C(1)	176.5(5)	177.7(7)	177.6(5)
N−C(1)−C(2)	178.5(7)	178.5(8)	179.3(8)
P(2)−Os−P(3)	82.07(5)	81.92(7)	82.57(6)
P(1)−Os−P(4)	82.50(5)	81.51(7)	80.71(6)
P(1)−C(3)−C(6)	112.2(4)	108.6(5)	114.8(6)
P(1)−C(3)−C(6*)			114.8(9)
P(2)−C(4)−C(5)	107.6(4)	112.7(5)	109.3(4)
P(3)−C(5)−C(4)	112.9(4)	107.6(5)	111.9(4)
P(4)−C(6)−C(3)	112.0(4)	110.5(5)	110.5(7)
P(4)−C(6*)−C(3)			117.8(13)
Os−P(1)−C(3)	110.5(2)	104.0(2)	107.8(2)
Os−P(1)−C(11)	115.3(2)	117.0(3)	114.5(2)
Os−P(1)−C(21)	119.8(2)	118.8(3)	119.9(2)
Os−P(2)−C(4)	105.2(2)	108.2(2)	106.3(2)
Os−P(2)−C(31)	121.0(2)	113.1(2)	118.5(2)
Os−P(2)−C(41)	121.6(2)	122.9(2)	120.4(2)
Os−P(3)−C(5)	108.9(2)	105.7(3)	108.3(2)
Os−P(3)−C(51)	117.4(2)	120.3(2)	115.0(2)
Os−P(3)−C(61)	104.4(3)	119.1(2)	122.5(2)
Os−P(4)−C(6)	107.2(2)	109.2(3)	102.0(4)
Os−P(4)−C(6*)			109.9(6)
Os−P(4)−C(71)	117.0(2)	116.7(3)	121.7(4)
Os−P(4)−C(71*)		111.9(4)	113.2(5)
Os−P(4)−C(81)	121.7(2)	120.0(2)	121.1(2)
C(3)−P(1)−C(11)	103.2(2)	104.6(4)	106.2(4)
C(3)−P(1)−C(21)	99.9(3)	104.7(3)	102.0(3)
C(4)−P(2)−C(31)	103.4(3)	105.5(4)	103.6(3)
C(4)−P(2)−C(41)	101.8(2)	100.0(3)	102.2(3)
C(5)−P(3)−C(51)	104.4(3)	103.9(3)	105.5(3)
C(5)−P(3)−C(61)	98.4(2)	101.5(3)	100.9(3)
C(6)−P(4)−C(71)	105.8(3)	108.1(4)	107.4(6)
C(6)−P(4)−C(71*)		99.3(5)	
C(6*)−P(4)−C(71*)			97.4(9)
C(6)−P(4)−C(81)	99.9(2)	101.6(3)	97.0(4)
C(6*)−P(4)−C(81)			109.6(8)

[a] Only *ipso* carbons of phenyls.

With the rigorous exclusion of air and moisture, a colorless solution of **3** in CH$_2$Cl$_2$ is stable for several days. From a CH$_2$Cl$_2$ solution, **3** forms air- and moisture-

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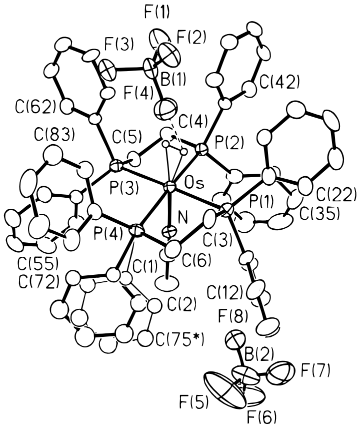

Figure 2. Structure of complex **3a** with the BF$_4^-$ anions in position.

sensitive clear colorless crystals in high yields. Depending on crystallization conditions and cosolvent, two different crystal morphologies and compositions were isolated and structurally analyzed. With pentane as the cosolvent and a slight excess of HBF$_4$ type **3a**, whose structure is shown in Figure 2, was obtained. **3a** crystallizes with 1 equiv of CH$_2$Cl$_2$ in the asymmetric unit. Crystals of the type **3b** were isolated with Et$_2$O as the cosolvent in the presence of a 10-fold excess of HBF$_4$. **3b** crystallizes with an additional 1 equiv of HBF$_4$ and with 1 equiv of CH$_2$Cl$_2$ in the asymmetric unit.

Structure of *trans*-[Os(η^2-H$_2$)(CH$_3$CN)(dppe)$_2$](BF$_4$)$_2$ (3) in the Solid State. Since the structures of both the parent monohydride **2** and two forms of the η^2-H$_2$ complex **3a,b** have been determined, there is the unique opportunity to assess the effect of protonation of the hydride ligand on the fragment [Os(CH$_3$CN)(dppe)$_2$]$^{2+}$. Table 1 lists selected bond lengths and angles of **3** in comparison with the structure of the parent monohydride **2**. The numbering scheme chosen is an attempt to optimize an overlay of the structures **2a**, **3a**, and **3b** with respect to the conformation of the phenyl rings.

In **3a** the η^2-H$_2$ ligand was located and isotropically refined. For **3b** the positions for the hydrogen atoms of the η^2-H$_2$ ligand could not be refined but electron density in the expected position at a distance of 1.7 Å from the osmium center was detected in the Fourier difference map. ^{1}H NMR spectra of the crystal samples in both cases confirmed the presence of the η^2-H$_2$ ligand. In both structures **3** as in **2** the four phosphorus atoms define a plane from which the osmium center is minimally displaced by 0.04 Å **(3a)** and 0.02 Å **(3b)**, respectively. In **3a,b** the displacement is toward the η^2-H$_2$ ligand while in **2** the displacement is away from the hydride ligand. The osmium nitrogen bonds in **3a,b** are 2.079(6) and 2.066(5) Å, respectively. Both are shorter compared to structure **2**, because of the weaker *trans* influence of the η^2-H$_2$ vs the hydride ligand. This allows a closer σ-type interaction between the *trans*-nitrogen ligand and the metal. In contrast the osmium phosphorus bonds are consistently longer than in **2** with the shortest bond being 2.385(2) Å in **3a** and 2.387(2) Å in **3b**. This lengthening also exists in solution; the ^1J(P,Os) value of 195.0 Hz for **2** is greater than the value of 161.6 Hz for **3** (see below). This observation may be rationalized as a consequence of the strong π-acceptor ability of the η^2-H$_2$ ligand withdrawing electron density from the metal center.[30] There could then be reduced π-back-bonding from the metal to the phosphine ligands, and this would result in a lengthening of the osmium−phosphorus bonds. There is recent experimental and theoretical evidence that phosphines, including triarylphosphines, are π-acceptor ligands.[31−33]

Table 2. Bond Lengths (Å) and Angles (deg) Describing the Coordination Geometry of the η^2-H$_2$ Ligand in 3a

H(1Os)−H(2Os)	0.9(1)	Os−H(1Os)	1.82(10)
Os−H(2Os)	1.63(7)		
H(2Os)−Os−H(1Os)	29(4)	P(2)−Os−H(2Os)	82(3)
N−Os−H(1Os)	164(4)	P(3)−Os−H(1Os)	112(4)
N−Os−H(2Os)	166(3)	P(3)−Os−H(2Os)	84(3)
P(1)−Os−H(1Os)	69(4)	P(4)−Os−H(1Os)	92(3)
P(1)−Os−H(2Os)	97(3)	P(4)−Os−H(2Os)	101(3)
P(2)−Os−H(1Os)	91(3)		

The nitrogen−carbon bond distances as well as the phosphorus ligand bite angles P(2)−Os−P(3) and P(1)−Os−P(4) do not show a consistent trend when comparing structures **2** and **3**. As in structure **2**, the CH$_3$CN ligand in **3a,b** is not perfectly perpendicular to the plane defined by the four phosphorus atoms but bends toward P(3) in structure **3a** and away from P(4) toward P(2) in **3b**. In all three structures this bending appears to minimize steric repulsion between the CH$_3$CN ligand and the *syn*-oriented phenyl rings of the phosphines.

Table 2 lists bond lengths and angles describing the coordination geometry of the η^2-H$_2$ ligand in **3a**. The positional parameters of the η^2-H$_2$ ligand are associated with high esd values that allow only a qualitative interpretation of the structural data, but do provide information about the relative orientation of the η^2-H$_2$ ligand in the solid state. The approximate H−H distance is 0.9(1) Å. The η^2-H$_2$ ligand is almost eclipsed with the P(1)−Os−P(3) vector. This eclipsed conformation has previously been noted in *trans*-[Fe(η^2-H$_2$)(H)(dppe)$_2$]BPh$_4$,[34] *trans*-Mo(η^2-H$_2$)(CO)(dppe-d$_{20}$)$_2$,[35] and *trans,mer*-W(η^2-H$_2$)(CO)$_3$(P^{i}Pr$_3$)$_2$[35] and is possibly favored because of optimized π-bonding between the filled d$_{yz}$ and d$_{xz}$ orbitals of the d^6 metal center and the σ^* orbital of the η^2-H$_2$ ligand. In a theoretical study of the complex [Fe(η^2-H$_2$)(H)(PH$_3$)$_4$]$^+$, Maseras et al.[36] pointed out that the eclipsed conformation is related to a distortion of the octahedral geometry, in which the phosphine atoms that lie in the plane defined by the metal and η^2-H$_2$ ligand bend away from the hydrogen atoms. This leads to a hybridization of the metal orbitals that maximizes the π-back-bonding. The slight displacement of the osmium atom toward the η^2-H$_2$ in both structures **3** is consistent with this argument. In contrast the complexes [Os(η^2-H$_2$)(X)(dppe)$_2$]$^+$, X = Cl

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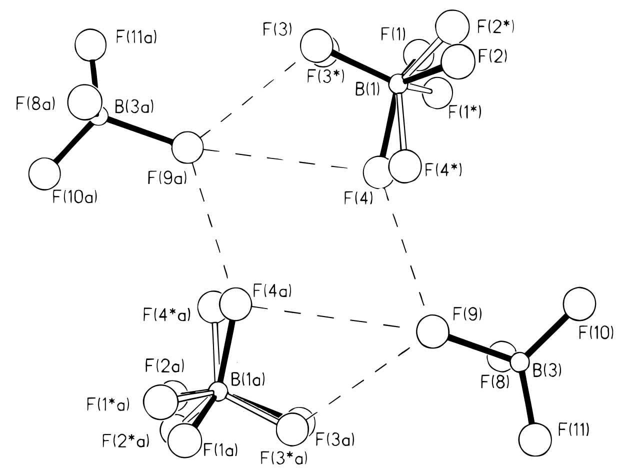

Figure 3. Structure of the protonated BF_4^- cluster in **3b**.

(4) and Br **(6)**,[22] show a staggered conformation. This may be because the distortion becomes energetically unfavorable with the larger *trans* ligands Cl and Br and their filled, nonbonding p orbitals.

The closest contacts between the two BF_4^- counterions and the cation in **3a** occur between F(4) and H(1Os) and F(5) and a phenyl ring hydrogen on C(32) with distances of 2.365 and 2.325 Å, respectively. The orientation of the BF_4^- ion in Figure 2 suggests that there is a weak electrostatic interaction between F(4) and H(1Os) as indicated by the dotted line. The $Os(\eta^2\text{-}H_2)$ unit appears to be poised to transfer a proton to the very weak base BF_4^-, but this process, which occurs readily in solution with weak bases (vide infra), is arrested in the solid state. In an X-ray and neutron diffraction study of the complex *trans*-$[Os(\eta^2\text{-}H_2)(Cl)(dppe)_2]PF_6$ **(4)**,[22] we recently observed a similar phenomenon between the η^2-H_2 ligand and the PF_6^- counterion. In structure **3b** the closest contact occurs between F(2) and a hydrogen atom on C(6) in the ligand backbone with a distance of 2.053 Å. The similarity of the structures of the cations **3a,b** suggests that the proton of the additional 1 equiv of HBF_4 in **3b** is not associated with the cation but is located between the fluorines of the counterions containing B(1) and B(3) and two other anions related to these by the center of symmetry. These four anions make a ring with 6 close F−F distances of between 2.530 and 2.619 Å (see Figure 3). Assuming symmetrical bonding, this would result in possible proton fluorine distances of approximately 1.3 Å. By comparison to the hydrogen-bonding distance in solid HF, which has been determined to be 1.57 Å,[37] or the hydrogen fluorine bond distance of 1.145 Å in KHF_2,[38] this distance does indeed suggest the presence of a proton between the two fluorine atoms. Large crystals of **3** will be needed to obtain more accurate data on the location of the η^2-H_2 and the proton of the addition 1 equiv of HBF_4 in a future neutron diffraction study.

Spectroscopic Properties of 3. The $^{31}P\{^1H\}$ NMR spectra of **3a,b** in CH_2Cl_2 are identical and show a singlet at +27.7 ppm, shifted 5.6 ppm downfield from the parent monohydride signal. The ^1H NMR in CD_2Cl_2 displays a singlet at +1.71 ppm for the methyl group of the CH_3CN ligand and a typical broad dihydrogen resonance at −9.85 ppm. The extra acid associated with **3b** appears as a broad peak between 2 and 4 ppm; traces of water, protonated by the compound, are probably responsible for this peak.

Table 3. Observed and Calculated T_1 Values of the Dihydrogen Ligand in *trans*-$[Os(\eta^2\text{-}H_2)(CH_3CN)(dppe)_2](BF_4)_2$ (2) in CD_2Cl_2 at 400 MHz

T, K	T_1(obs), ms	T_1(calc), ms[a]	*T*, K	T_1(obs), ms	T_1(calc), ms[a]
294	34.6	35	229	29.7	29
272	30.1	30	208	36.9	37
251	28.2	28	186	52.0	56

[a] Calculated by use of a computer program fitting the T_1 data to the temperature-dependent T_1 equation with a temperature-dependent correlation time $\tau = \tau_0 e^{E_a/RT}$; E_a = 2.2 kcal/mol and τ_0 = 2.7 ps.

The classification of **3** as a dihydrogen complex is based on variable-temperature $T_1(^1H)$ measurements and the coupling constant $^1J(H,D)$ of the η^2-HD isotopomer. Table 3 lists the measured and calculated T_1 times as a function of temperature. The T_1 minimum (400 MHz) of 28 ms occurs at 253 K. This was determined by direct observation as well as by fitting the equations that describe the dominant dipolar relaxation mechanism to the variable-temperature T_1 data as previously reported.[39] In order to calculate the H−H distance, the T_1 minimum value must be corrected for the relaxation contribution from the four phosphorus nuclei and the ortho-hydrogen atoms of the dppe ligands.[40] The H−H distance is then calculated to be 0.94 ± 0.01 Å if the dihydrogen ligand is in the fast-spinning regime (rotational frequency of the η^2-H_2 ligand $\gg$ 400 MHz) or 1.19 ± 0.01 Å in the slow-spinning one (rotational frequency of the η^2-H_2 ligand $\ll$ 400 MHz). Recent work suggests that H−H distances between these values might be possible if the motion of the η^2-H_2 ligand is described as hopping between possible orientations rather than free spinning.[41]

The η^2-HD isotopomer of **3** is obtained by partial exchange with D_2 gas in a saturated CD_2Cl_2 solution; several days are required for a partial exchange. In a CD_2Cl_2 solution under hydrogen gas no isotope exchange into the η^2-H_2 ligand is found. This establishes the deuterium gas as the source of the deuterium in the η^2-HD complex. The ^1H NMR resonance of the η^2-HD ligand can be observed by nulling out the residual signal of the η^2-H_2 isotopomer by an inversion recovery pulse sequence using the relationship $T_1 = \tau_{null}/\ln 2$ and the known T_1 of **3** at room temperature. The ^1H NMR spectrum of the η^2-HD compound has an overlapping 1:1:1 triplet of binomial quintets with $J(H,D)$ = 21.4 Hz and $J(H,P)$ = 5 Hz. We believe that the most likely mechanism for the incorporation of deuterium into the η^2-H_2 ligand involves slow exchange of H_2 with D_2 via a dissociative pathway with subsequent proton exchange with free HBF_4 in solution.

Acidity of the Dihydrogen Complex. Complex **3** can only be observed in dry CH_2Cl_2. The addition of water to a solution of complex **3** in CD_2Cl_2 leads to

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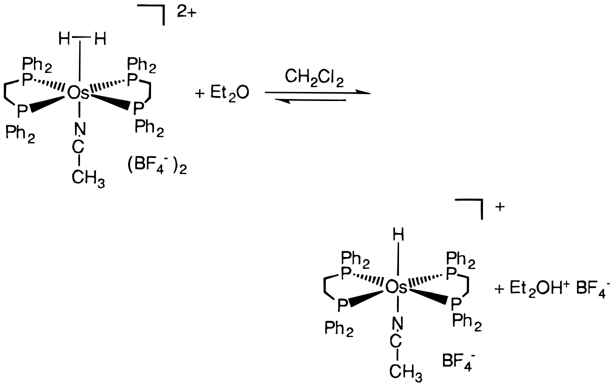
complete deprotonation of the dihydrogen ligand to give the monohydride complex **2**. Subsequent addition of a large excess of $HBF_4 \cdot Et_2O$ quantitatively regenerates the dihydrogen complex. The ^1H NMR spectrum of crystalline **3** washed with freshly distilled Et_2O under anhydrous conditions shows a mixture of the complexes **2** and **3**. This indicates that partial deprotonation of the dihydrogen complex occurred. The addition of excess dry Et_2O to a solution of **3** in CH_2Cl_2 leads to complete deprotonation quantitatively generating **2** as indicated by the ^{31}P NMR spectrum (eq 4).



(4)

We therefore conclude that the pK_a of the complex falls between the two extreme values −1.74 (formal pK_a H_3O^+)[42] and −2.4 (pK_a Et_2OH^+).[43] For the purpose of calculations (vide infra) the value is assumed to be −2 ± 1 on an aqueous scale. To our knowledge this is the most acidic stable η^2-H_2 complex known to date.

3 was targeted as a potentially stable and acidic η^2-H_2 complex on the basis of our application[12] of Lever's ligand additivity model,[44] which predicts that an η^2-H_2 complex will be stable against loss of H_2 if the oxidation of its corresponding N_2 complex occurs between 0.5 and 2.0 V (versus NHE). The closer the value is to the upper limit of this range the more acidic the η^2-H_2 complex will be. The calculated electrochemical potential of the corresponding hypothetical dinitrogen complex *trans*-[Os(N_2)(CH_3CN)(dppe)$_2$](BF_4)$_2$ is 2.08 V, which puts complex **3** on the borderline of stability against loss of η^2-H_2 and correctly predicts its high acidity.

The high acidity of **3** with its approximate pK_a value of −2 sharply contrasts with the reactivity of the similar complex *trans*-[Os(η^2-H_2)(CH_3CN)(en)$_2$](CF_3SO_3)$_2$ **(5)** recently described by Taube and co-workers[45,46] which is not deprotonated by water. This puts a lower limit of about +2 on the pK_a of **5**. The pK_a of **5** is actually estimated by us to be about 18 on the basis of a calculated pK_a difference between **5** and **3** of 20.[44,47] The explanation for this difference lies with the more electron-donating ethylenediamine ligands in **5**. These σ-donors make the osmium center more reducing compared with π-acidic dppe ligands. In agreement with a more electron-rich osmium center the *J*(H,D) coupling value of 17.7 Hz for **5** compared to 21.4 Hz for **3** also indicates that **5** has a longer H−H distance and is closer to a dihydride form than **3**, i.e., further along on a hypothetical reaction coordinate from Os^{II}(η^2-H_2) toward the oxidation product $Os^{IV}(H)_2$. The *J*(H,D) coupling values can also be used to estimate the H−H distances (vide infra) in **5** and **3** to be 1.12 and 1.06 Å, respectively.[48] The T_1(min, 400 MHz) of **5** is reported by Li and Taube to be 32 ms. This translates into an H−H distance of 1.21 Å for a slow-spinning η^2-H_2 ligand and 0.96 Å for a fast-spinning one compared to 1.18 and 0.94 Å, respectively, for **3**.

Depending on the ancillary ligands in the η^2-H_2 complex the contributions from the $\sigma(H_2) \rightarrow \sigma(Os)$ donation and $\pi(Os) \rightarrow \sigma^*(H_2)$ back-bonding modes in the M(η^2-H_2) unit will vary. In complex **3** we believe the σ-type interaction to be dominant, as the doubly positive charge and lack of π-donating ligands in the ligand set lowers the energy of the filled d orbitals and prevents effective back-donation into the σ* orbital of the η^2-H_2 ligand. Complex **5** is predicted to be more reducing and have more π-back-donation into the σ* orbital of the η^2-H_2 ligand than **3**. There must however still be a limited degree of π-back-bonding present in complex **3** as suggested by its stability against loss of H_2 gas and the observation that so far no stable η^2-H_2 complexes of main group based Lewis acids are known,[49] which by definition cannot act as π-donors toward coordinated H_2.

Influence of the *Trans* Ligand. It is instructive to compare the properties of **3** to the isoelectronic η^2-H_2 compounds [Os(η^2-H_2)(X)(dppe)$_2$](Y) [X = H, Y = BF_4 **(1)**;[21] X = Cl, Y = PF_6 **(4)**;[22] X = Br, Y = BF_4 **(6)**[22]] to illustrate the sensitivity of the pK_a, H−H distance, T_1(min), and *J*(H,D) of the η^2-H_2 ligand to the nature of the *trans* ligand. Table 4 lists the characteristic properties of **1**, **4**, and **6** in comparison to **3**. The columns in Table 4 are arranged in order of increasing H−H distances as determined from single crystal diffraction studies and the observed *J*(H,D) coupling values. Complexes **4** and **6** are classified as having an elongated dihydrogen ligand as indicated by the dotted lines between the two hydrogen atoms.[1] In this series, complex **3** is unique as it possesses only neutral ligands and consequently bears a double positive charge, a fact which is closely related to its high acidity.

Table 4 includes H−H distances calculated from *J*(H,D) by use of an empirical equation derived from a data base of *J*(H,D) and H−H distances for dihydrogen complexes.[22,48] These calculated H−H distances which presumably apply to the complex in solution are in agreement with the distance from X-ray and neutron diffraction studies. The distances calculated from *J*(H,D) coupling values fall in the range of those calculated from T_1(min) data by use of spectral density functions for fast or slow H_2 spinning.[22,39] It appears that a new spectral density function which describes a motion other than spinning is required to bring the d_{HH} values calculated from *J*(H,D) and T_1(min) into agreement.

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(47) The difference in pK_a of complexes **3** and **5** is traced to their electrochemical potentials. The additive electrochemical contribution of each nitrogen of the en ligands in **5** is 0.06 V whereas that of the dppe ligands in **3** is 0.36 V.[44] Therefore the conjugate base monohydride complex of **5**, [OsH(en)$_2$(CH_3CN)]$^+$, is predicted to be 1.2 ± 0.3 V more reducing than that of **3**. Use of eq 1 with $\Delta E_{1/2} = 1.2$ V and with the assumption of $\Delta H_{BDE} \approx 0$ gives $\Delta pK_a \approx 20$.

(48) Reference 22 describes how the following equation relates the dihydrogen H−H distance and the *J*(H,D) from solution ^1H NMR: $d_{HH} = -0.0167J(H,D) + 1.42$.

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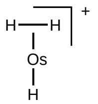
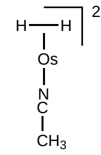
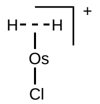
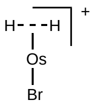
Table 4. Comparison of Properties of the Complexes $[Os(\eta^2\text{-}H_2)(L^z)(dppe)_2]^{(z+2)+}$ ($L^z = H^-$, CH_3CN, Cl^-, Br^-)

	 **1**	 **3**	 **4**	 **6**
d(H−H) (Å) by neutron diff	0.97(2)[a]		1.22(3)[a]	
d(H−H) (Å) by X-ray diff		0.9(1)	1.11(6)	1.13(8)
d(H−H) (Å) from T_1(min,400 MHz) slow/fast spinning	1.00/1.25	0.94/1.19	1.04/1.31	1.08/1.36
d(H−H) (Å) from J(H,D)	0.99	1.06	1.19	1.19
J(H,D) (Hz)	25.5	21.4	13.9	13.7
spectrochem param $f^*(L^z)$	1.6[b,c]	1.22	0.98[c]	0.92[c]
pK_a (exptl)	13.6 ± 0.3	−2 ± 1	7.4 ± 0.3	5.4 ± 0.3
$E_{1/2}\{MH^+/MH\}$ (mV) (vs Fc/Fc$^+$)	−0.20 ± 0.05	+0.58 ± 0.05	−0.13 ± 0.05	−0.11 ± 0.05
$\Delta H_{BDE}\{M(\eta^2\text{-}H_2)\}$ (kcal/mol)	80 ± 2	77 ± 3	73 ± 1	71 ± 2

[a] Value corrected for a significant librational motion of the H_2. [b] Estimated value based on literature data.[57−59] [c] Effective ligand field parameter $f^*(L^z) = f(L^z) + \delta$ with $\delta = 0.20$ to account for the influence of negative charge on the ligand.[51]

The elongation of the H−H bond in **4** and **6** may be a result of the π-effect of the *trans* Cl^- or Br^- ligand.[22] The influence of the *trans* ligand and its π-donor abilities on the properties of the η^2-H_2 ligand in the series of compounds $[Os(\eta^2\text{-}H_2)(L^z)(NH_3)_4]^{(z+2)+}$ [50] has recently been investigated by Craw et al.[51] They presented a qualitative model in which a linear correlation between the observed J(H,D) coupling values and an effective spectrochemical parameter $f^*(L^z)$[52,53] was established. A large ligand field parameter $f^*(L^z)$ implies a large splitting $\Delta(L^z)$ of the osmium $t_{2g}(\pi)$ and $e_g^*(\sigma)$ levels in an idealized octahedral geometry. The low energy of the t_{2g} orbitals then results in a reduced π-donor ability of the metal and less back-bonding into the σ^* orbital of the η^2-H_2 ligand. This leads to a shorter H−H bond associated with a larger J(H,D) coupling value. Consequently a larger J(H,D) value is expected for stronger field ligands $L^z = H^-$, CH_3CN vs the weaker ligands $L^z = Cl^-$, Br^-. The observed trend in the J(H,D) coupling values in the complexes $[Os(\eta^2\text{-}H_2)(L^z)(dppe)_2]^{(z+2)+}$ closely mirrors that of the analogous ammine complexes $[Os(\eta^2\text{-}H_2)(L^z)(NH_3)_4]^{(z+2)+}$: 13.9 vs 10.2 Hz for $L^z = Cl^-$ and 21.4 vs 20.3 Hz for $L^z = CH_3CN$ for the dppe and NH_3 complexes, respectively.

A Mulliken population analysis of the Os−H and H−H bonds in the Os(η^2-H_2) unit given in the paper by Craw et al. also shows that the J(H,D) coupling value in the series $L^z = H^-$, CH_3CN, and Cl^- decreases with decreasing H−H bond population and increasing Os−H bond population. Of interest would be whether this again finds its equivalent in the analogous phosphine complexes. Possibly the calculated bond populations could be correlated with calculated ΔH_{BDE}.

A consistent correlation between the H−H distances and the bond dissociation energies ΔH_{BDE} emerges from the data of Table 4. ΔH_{BDE} decreases with increasing H−H distance. This indicates that the ΔH_{BDE} values calculated from eq 1 reflect the amount of residual H−H bonding in the η^2-H_2 ligand. If the bond dissociation energy term ΔH_{BDE} does not change among complexes, then eq 1 indicates that a plot of pK_a versus $E_{1/2}\{MH^+/MH\}$ values should give a slope of −16.9. The upper dotted line in Figure 4 has this slope with an intercept calculated on the basis of $\Delta H_{BDE} = 80$ kcal mol^{-1}, while the lower one refers to one with 71 kcal mol^{-1}. No one line describes the properties of all the complexes. The strong field hydride and acetonitrile ligands are near to the upper line. Strong field ligands cause a large splitting of the osmium $t_{2g}(\pi)$ and $e_g^*(\sigma)$ levels, which results in less back-bonding into the σ^* orbital of the η^2-H_2 ligand. The consequence is a strong H−H interaction in the η^2-H_2 ligand as expressed by the high ΔH_{BDE}. The complexes of these ligands have pK_a values greater than expected on the basis of $E_{1/2}$ because of the high ΔH_{BDE} value.

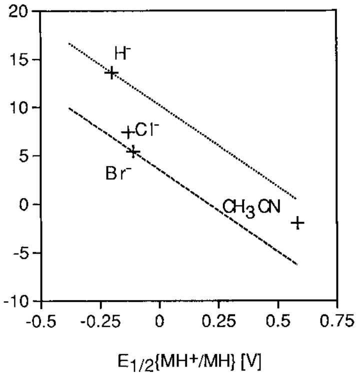


Figure 4. Plot of pK_a vs $E_{1/2}\{MH^+/MH\}$ for complexes $[Os(\eta^2\text{-}H_2)(L^z)(dppe)_2]^{(z+2)+}$ ($L^z = H^-$, Cl^-, Br^-, CH_3CN). The upper and lower dotted lines are calculated by use of eq 1 with $\Delta H_{BDE} = 80$ and 71 kcal/mol, respectively.

Within the series of the three monocationic compounds $[Os(\eta^2\text{-}H_2)(X)(dppe)_2]^+$ [X = H^- **(1)**, Cl^- **(4)**, Br^- **(6)**] the observed pK_a is inversely correlated to the $E_{1/2}\{MH^+/MH\}$ values and decreases with increasing H−H distance and decreasing J(H,D). The dicationic complex **3** however falls out of this trend. A similar linear correlation between enthalpies of protonation and $E_{1/2}$ values for a series of cationic metal hydride complexes has recently been noted by Angelici et al.[54] Within the same series ΔH_{BDE} must change linearly with $E_{1/2}\{MH^+/MH\}$ to produce such a regular correlation.

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Conclusions

The very acidic but stable η^2-H_2 complex *trans*-[Os(η^2-H_2)(CH_3CN)(dppe)$_2$](BF_4)$_2$ has been synthesized and fully characterized. Its stability and acidity (estimated $pK_a = -2$) were correctly predicted by the application of a ligand additivity model. In a comparison of the series of complexes [Os(η^2-H_2)(L^z)(dppe)$_2$]$^{(z+2)+}$ (L^z = H, CH_3CN, Cl, Br), several trends in the influence of the *trans* ligand on the characteristic properties of the η^2-H_2 ligand are observed. The H−H distances, as determined or estimated by neutron, X-ray, or NMR methods, increase in the order $H^- < CH_3CN < Cl^- < Br^-$. In the same order there is a decrease in the observed J(H,D) coupling values and the calculated ΔH_{BDE}, where ΔH_{BDE} is the amount of energy required to remove a hydrogen atom from the M(η^2-H_2) unit. The H−H distances, J(H,D), and ΔH_{BDE} can qualitatively be correlated with an effective spectrochemical parameter $f^*(L^z)$ of the *trans* ligand that accounts for the influence of the charge of the ligand.

While the pK_a values of the complexes do increase as the $E_{1/2}$ values of the corresponding monohydride complexes decrease, the relationship is not linear. In order to explain the observed trend, the influence of the *trans* ligand on the amount of H−H bonding as reflected by ΔH_{BDE} must be taken into account. A correlation between ΔH_{BDE} and the parameter $f^*(L^z)$ might be useful in this regard.

Experimental Section

Oxygen and water were excluded at all times by the use of a glovebox supplied with purified nitrogen or vacuum lines supplied with purified N_2 or Ar; N_2 was used unless otherwise stated. Et_2O and pentane were dried over and distilled from sodium−benzophenone ketyl. For the acidity studies this was done immediately before use. CH_2Cl_2 and CH_3CN were distilled from calcium hydride. Deuterated solvents were dried over Linde type 4 Å molecular sieves and degassed prior to use. The phosphine ligands were used as purchased from Aldrich, Strem Chemicals, or Digital Speciality Chemicals Ltd. The complex *trans*-[Os(η^2-H_2)(H)(dppe)$_2$]BF_4 was prepared as reported previously.[21]

NMR spectra were recorded on a Varian Unity 400 (400 MHz for ^{1}H, 162 MHz for ^{31}P), Varian Gemini 200 (200 MHz for ^{1}H), and Varian Gemini 300 (300 MHz for ^{1}H, 120.5 MHz for ^{31}P) spectrometers. All ^{31}P NMR were proton decoupled, unless stated otherwise. ^{31}P NMR chemical shifts were measured relative to ~1% P(OMe)$_3$ in C_6D_6 sealed in coaxial capillaries and are reported relative to H_3PO_4 by use of δ(P(OMe)$_3$) = 140.4 ppm. ^{1}H chemical shifts were measured relative to partially deuterated solvent peaks but are reported relative to tetramethylsilane. In all cases, high-frequency shifts are reported as positive. Variable-temperature T_1 measurements were made at 400 MHz, using the inversion recovery method with calibration of the 90°/180° pulse at each temperature. The temperature of the probes were calibrated with the temperature dependence of the chemical shifts of MeOH.

***trans*-[Os(H)(CH_3CN)(dppe)$_2$]BF_4 (2).** [Os(η^2-H_2)(H)(dppe)$_2$]BF_4 (0.250 g, 0.232 mmol) was dissolved in 10 mL of CH_3CN and stirred for 12 h, after which time quantitative conversion to the product as monitored by ^{31}P NMR of the reaction mixture had occurred. The volume of the CH_3CN solution was reduced in vacuo to begin precipitation. Addition of 20 mL of Et_2O caused complete precipitation of a white powder. Isolated yield: 0.240 g (0.215 mmol), >90%. Anal. Calcd for $C_{54}H_{52}BF_4NOsP_4$: C, 58.12; H, 4.70; N, 1.26. Found: C, 57.77; H, 4.69; N, 1.56. FAB MS (m/z): calcd for $C_{54}H_{52}N^{192}OsP_4$, 1030; obsd 1030 (weak, M^+), 989 ($M^+ - CH_3CN$), 987 ($M^+ - CH_3CN$, 2H). $E_{1/2}$\{MH^+/MH\} vs Fc^+/Fc [0.2 M ^{n}Bu$_4$NPF$_6$ in CH_2Cl_2; scan rate 250 mV/s] = 584 mV. ^{1}H NMR (CD_2Cl_2, 400 MHz): −16.63 (qnt, 1H, J(H,P) = 16.2 Hz, OsH), 1.81 (s, 3H, CH_3CN), 2.06 (m, 4H, CH_2), 2.54 (m, 4H, CH_2), 6.7 (br s), 7.1−7.4 (m), (40 H, Ph). ^{31}P\{^{1}H\} NMR (CH_2Cl_2): 33.3 (s), 33.3 (d, J(P,Os) = 195.0 Hz). IR: ν(Os−H) 2066 cm^{-1}, ν(CN) 2267 cm^{-1} (w, br, Nujol mull).

***trans*-[Os(η^2-H_2)(CH_3CN)(dppe)$_2$](BF_4)$_2$ (3).** [Os(H)(CH_3CN)(dppe)$_2$]BF_4 (0.200 g, 0.179 mmol) was dissolved in 5 mL of CH_2Cl_2 to give a clear colorless solution. $HBF_4 \cdot Et_2O$ (85% in Et_2O) (50 μL, 0.239 mmol) was added causing the transient appearance of a red color. Addition of 15 mL of Et_2O to the clear, light pink to colorless solution resulted in the formation of a white precipitate. Isolated yield: 0.175 g, 0.142 mmol, 80% (washing even with small amounts of dry Et_2O leads to partial deprotonation of the product). ^{1}H NMR (CD_2Cl_2, 400 MHz): −9.85 (br, 2H, Os(η^2-H_2)), +1.7 (s, 3H, CH_3CN), 2.4 (m, 4H, CH_2), 3.0 (m, 4H, CH_2), 6.5 (m, br), 7.1−7.8 (m) (40 H, Ph). T_1(min) (400 MHz, CD_2Cl_2): 28 ms at 253 K. ^{31}P\{^{1}H\} NMR (CH_2Cl_2): 27.68 (s), 27.68 (d, J(P,Os) = 161.6 Hz). The IR spectrum of **3** could not be obtained due to its limited solubility in suitable solvents and extreme sensitivity to moisture.

Observation of *trans*-[Os(η^2-HD)(CH_3CN)(dppe)$_2$](BF_4)$_2$. D_2 gas was bubbled into a solution of *trans*-[Os(η^2-H_2)(CH_3CN)(dppe)$_2$](BF_4)$_2$ and excess $HBF_4 \cdot Et_2O$ in CD_2Cl_2. The solution was transferred into an NMR tube fitted with a Teflon screw top, and the tube was sealed under an atmosphere of D_2(g). After 72 h partial incorporation of deuterium into the dihydrogen ligand had occurred. The η^2-HD complex was observed by nulling out the signal of the η^2-H_2 complex with an inversion recovery pulse sequence using its known T_1 value at room temperature. J(H,D) = 21.4 Hz, and J(H,P) = 5 Hz.

X-ray Crystal Structure Determinations of *trans*-[Os(H)(CH_3CN)(dppe)$_2$]BF_4 (2), *trans*-[Os(η^2-H_2)(CH_3CN)(dppe)$_2$](BF_4)$_2 \cdot CH_2Cl_2$ (3a), and *trans*-[Os(η^2-H_2)(CH_3CN)(dppe)$_2$](BF_4)$_2 \cdot HBF_4 \cdot CH_2Cl_2$ (3b). Crystals of **2** were prepared by slow diffusion of Et_2O into a saturated solution of the complex in CH_2Cl_2. Crystals of **3** were obtained by slow diffusion of pentane into a saturated solution of **3** in CH_2Cl_2 **(3a)** or by slow diffusion of Et_2O into a solution of **2** (0.160 g, 0.143 mmol) in 3 mL of CH_2Cl_2 and 200 μL of $HBF_4 \cdot Et_2O$ (1.15 mmol, 10-fold excess) **(3b).** The complex crystallizes as **3b** with an additional 1 equiv of HBF_4 in the asymmetric unit. In all three cases NMR spectra of the crystals redissolved in CD_2Cl_2 confirmed the identity of the compounds and the presence of the hydride or dihydrogen ligand, respectively.

Intensity data were collected on a Siemens P4 diffractometer using graphite monochromated Mo Kα radiation (λ = 0.710 73 Å). The ω scan technique was applied with variable scan speeds. General data collection parameters are listed in Table 5. In each case the intensities of 3 standard reflections measured every 97 reflections showed no decay. Data for the compounds were corrected for Lorentz and polarization effects and for absorption.[55] For all structures the Os atom position was solved by the Patterson method and other non-hydrogen atoms were located by successive difference Fourier syntheses. The structures were refined by full-matrix least squares on F^2. The weighting scheme was $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$. Hydrogen atoms except for those on the CH_3 group on the CH_3CN ligand and the hydride/dihydrogen ligands were positioned on geometric grounds (C−H 0.96 Å, U_{iso} = 0.031(3) Å^2 for **2**; C−H 0.96 Å, U_{iso} = 0.042(4) Å^2 for **3a**; C−H 0.96 Å, U_{iso} = 0.039(3) Å^2 for **3b**). In **3a** the hydrogen atoms bonded to Os were located from a difference Fourier and refined with isotropic thermal parameters (H(1Os), U_{iso} = 0.062(33) Å^2; H(2Os), U_{iso} = 0.017(19) Å)^2). The hydrogen atoms bonded to Os in **2** and **3b** were not located. In structure **3a** the phenyl ring defined by P(4)−C(71) shows conformational disorder. For **3b** the disorder extends

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(55) Sheldrick, G. M. University of Göttingen, Germany.

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Table 5. Summary of Crystal Data, Details of Intensity Collection, and Least-Squares Refinement Parameters

	2	**3a**	**3b**
empirical formula	$C_{54}H_{52}NOsP_4BF_4$	$C_{54}H_{53}NOsP_4(BF_4)_2{\cdot}0.7CH_2Cl_2$	$C_{54}H_{52}NOsP_4(BF_4)_3{\cdot}CH_2Cl_2$
fw	1115.86	1263.12	1374.40
cryst size, mm	0.48, 0.28, 0.32	0.34, 0.63, 0.25	0.25, 0.21, 0.35
cryst system	monoclinic	hexagonal	triclinic
space group	$P2_1/n$	$R\bar{3}$	$P\bar{1}$
a, Å	13.426(4)	47.951(8)	12.091(2)
b, Å	16.471(8)	47.951(8)	12.201(1)
c, Å	21.643(7)	12.369(3)	20.244(4)
α, deg	90	90	99.99
β, deg	91.18(2)	90	104.33
γ, deg	90	120	93.16
V, Å^3	4785(3)	24630(8)	2834.6(8)
Z	4	18	2
D(calc), g cm^{-3}	1.549	1.533	1.610
abs coeff, cm^{-1}	28.53	25.80	25.34
temp, K	173	173	173
min, max 2θ, deg	6.0, 54.0	6.0, 52.0	6.0, 54.0
refls measd	10 683	10 779	12 276
indepdt refls	10 253	10 149	11 683
obsd refls [$F > 4.0\sigma(F)$]	7860	7629	9442
min, max transm coeff	0.4112, 0.8100	0.2797, 0.8262	0.4795, 0.8301
R_{int}	0.060	0.025	0.0389
no. of params	599	650	748
weighting^{a,b}	0.0668, 1.365	0.0829, 184.3	0.0493, 9.490
$R_1{}^a$	0.0436	0.0546	0.0496
w$R_2{}^a$	0.1125	0.1518	0.1224
min, max peak in ΔF map, e Å^{-3}	−1.68, 1.95	−1.172, 1.567	−1.338, 1.598

[a] Definition of R indices: $R_1 = \Sigma(F_o - F_o)/\Sigma(F_o)$; w$R_2 = [\Sigma[w(F_o{}^2 - F_c{}^2)^2]/\Sigma[w(F_o{}^2)^2]]^{1/2}$.

to C(6) in the backbone of the phosphine ligand. The occupancies of the disordered atoms were refined to 46:54* in **3a** and 59:41* in **3b**. (The asterisks here and in Table 1 refer to the occupancies in the respective disordered sites.) Crystal data, data collection, and least-squares parameters are listed in Table 5. All calculations were performed and diagrams created using SHELXTL-PC[56] on a 486-66 personal computer.

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Supporting Information Available: X-ray crystal and structure information for complexes **2**, **3a**, and **3b**, including tables of data collection parameters, complete atomic coordinates, intramolecular bond lengths and angles, and thermal parameters, and a plot of the structure of **3b** (27 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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