$[Os(\eta^2\text{-}H_2)(CO)(pyS)(PPh_3)_2]BF_4$—A Stable but Highly Acidic Dihydrogen Complex

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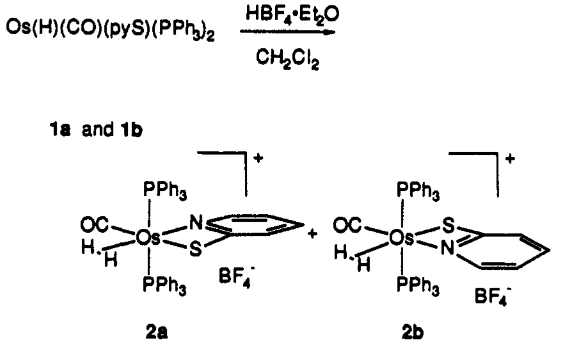
Summary: The dihydrogen complex $[Os(\eta^2\text{-}H_2)(CO)(pyS)(PPh_3)_2]BF_4$*, 2, has a* pK_a *of about –1 but is stable to* H_2 *loss. These properties were predicted before the synthesis of this complex by use of a ligand additivity method. The X-ray crystal structure determination reveals a distorted square pyramidal arrangement of the heavy donor atoms; the* H_2 *ligand was not located.* ^1H *NMR studies indicate that 2 has an elongated* H_2 *ligand with an H–H distance of 1.08 Å.*

One of us recently described a method which allows one to make some predictions about the stability and properties of dihydrogen complexes.[1] It is based on estimated electrochemical potentials that are calculated by use of Lever's ligand additivity model.[2] An important reaction of dihydrogen complexes is the heterolytic cleavage of the H–H bond to give a proton and a hydride complex.[3] One prediction of our work is that the most acidic dihydrogen complexes $M(H_2)L_5$[4] which are stable with respect to loss of dihydrogen at 20 °C will have corresponding dinitrogen complexes[5] with $E_{1/2}(M(N_2)L_n{}^+/M(N_2)L_n)$ near 2 V vs NHE;[6] complexes with $E_{1/2}(MN_2)$ greater than 2 V are likely to lose H_2 at 20 °C. Clearly, stable dihydrogen complexes must have weakly coordinating counterions such as BF_4^- or PF_6^- and must be dissolved in weakly coordinating solvents. To data only two examples of highly acidic dihydrogen complexes have been reported.[7] The complex $[Re(\eta^2\text{-}H_2)(C_5Me_5)(CO)(NO)]^+$ is deprotonated by diethyl ether[8] and has an estimated pK_a of –2. However it decomposes above 235 K with the loss of dihydrogen. The unstable complex $[Ru(\eta^2\text{-}H_2)(C_5Me_5)(CO)_2]^+$ has similar properties. The hypothetical dinitrogen complexes of both of these complexes have $E_{1/2}(RuN_2)$ greater than 2 V. As a test of the prediction we sought a known hydride complex that, when protonated, would give a dihydrogen complex which is both stable and very acidic. Certain complexes $MH(CO)(X)(L)(PR_3)_2$, M = Os, were expected to yield, upon protonation, dihydrogen complexes $[Os(H_2)(CO)X(L)(PR_3)_2]^+$ with the desired properties, while the corresponding Ru complexes were expected to be unstable ($E_{1/2}(RuN_2)$ > 2 V). One unstable complex of this type, $[Ru(H_2)H(CO)(triphos)]^+$, has been reported, but its pK_a was not determined.[9]

According to our method, a promising candidate to form a stable acidic dihydrogen complex is the compound $OsH(CO)(pyS)(PPh_3)_2$ (1, pySH = 2-pyridinethiol).[10] The mixture of isomers of $[Os(\eta^2\text{-}H_2)(CO)(pyS)(PPh_3)_2]BF_4$ (**2a**/**2b** in ratio 5/1)[1,12] was prepared by reaction of 1 in CH_2Cl_2 with $HBF_4{\cdot}Et_2O$ under Ar according to eq 1. The isomeric ratio reflects the one found in the parent monohydride complex 1.[10] Both isomers are stable in solution under Ar at 20 °C for at least 24 h and are very acidic (vide infra), as expected on the basis the $E_{1/2}$ of 1.8 V for the hypothetical complex $[Os(\eta^2\text{-}N_2)(CO)(pyS)(PPh_3)_2]^+$.[13] Only **2a** has been successfully crystallized, and only in the presence of 1 equiv of protonated thiopyridine. The free thiopyridine was a contaminant of starting complex 1.[11]



(1)

The ^1H NMR spectrum of the mixture of isomers ($CDCl_3$) has typically broad dihydrogen signals at –5.70 ppm (major isomer, **2a**) and –6.84 ppm (**2b**). A variable temperature 400-MHz T_1 study of the H_2 peak of **2a** in CD_2Cl_2 gives a T_1(min) of 16 ± 1 ms at 241 K. The T_1(min) of the minor isomer is also approximately 16 ms. The T_1(min) value corresponds to an H–H distance of 0.86 Å (fast spinning) or 1.08 Å (slow spinning).[14,15] The

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(1) Morris, R. H. *Inorg. Chem.* **1992**, *31*, 1471–1478.

(2) Lever, A. B. P. *Inorg. Chem.* **1990**, *29*, 1271–1285.

(3) Jessop, P. G.; Morris, R. H. *Coord. Chem. Rev.* **1992**, *121*, 155–284.

(4) All L not necessarily the same.

(5) Often the dinitrogen complex is hypothetical, but its properties can still be predicted (see ref 1).

(6) All $E_{1/2}$ values are reported vs NHE with $Fe(C_5H_5)_2{}^+/Fe(C_5H_5)_2$ at 0.6 V.

(7) Chinn, M. S.; Heinekey, D. M.; Payne, N. G.; Sofield, C. D. *Organometallics* **1989**, *8*, 1824–1826.

(8) The pK_a of protonated diethyl ether is reported to be –2.6 in aqueous sulfuric acid. Perdoncin, G.; Scorrano, G. *J. Am. Chem. Soc.* **1977**, *99*, 6983.

(9) Michos, D.; Luo, X. L.; Crabtree, R. H. *Inorg. Chem.* **1992**, *31*, 4245–4250.

(10) (a) Mura, P.; Olby, B. G.; Robinson, S. D. *J. Chem. Soc., Dalton Trans.* **1985**, 2101. (b) ^{31}P NMR ($CDCl_3$): δ 21.5 (s, **1a**, hydride trans to N), 22.6 (s, **1b**, H trans to S); **1a**/**1b** = 5/1. This is the opposite assignment to that proposed by Mura et al.

(11) **2a**·($pySH_2BF_4$) was isolated in >90% yield by reaction of 1 (contaminated with some free thiopyridine) with $HBF_4{\cdot}Et_2O$ in toluene and then recrystallization from CH_2Cl_2 by addition of hexane to give colorless crystals suitable for an X-ray study. $\delta(^{31}P)$ (300 MHz, CH_2Cl_2): 9.1 (s). $\delta(^1H)$ (400 MHz, $CDCl_3$): –5.70 (br, 2 H, $Os(H_2)$), 2.00 (br, 2 H, $pySH_2{}^+$), 5.85, 6.29, 6.72, 7.16 (br, 4 H, 2-pyridinethiol ligand protons), 7.20–8.00 (30 H, phenyl region). ν(CO) 1993 cm^{-1} (CH_2Cl_2 solvent).

(12) **2b**: $\delta(^{31}P)$ (300 MHz, CH_2Cl_2): 11.8 (s). $\delta(^1H)$ (400 MHz, $CDCl_3$): –6.84 (br, $Os(H_2)$), other peaks are obscured by resonances of **2a**.

(13) The mercaptopyridine ligand is not listed in Lever's paper. The E_L value of –0.28 V for the anionic chelate is estimated from an average of the E_L values of the thiophenolate and pyridine ligands.

(14) Earl, K. A.; Jia, G.; Maltby, P. A.; Morris, R. H. *J. Am. Chem. Soc.* **1991**, *113*, 3027–3039.

(15) Desrosiers, P. J.; Cai, L. H.; Lin, Z. R.; Richards, R.; Halpern, J. *J. Am. Chem. Soc.* **1991**, *113*, 4173–4184.

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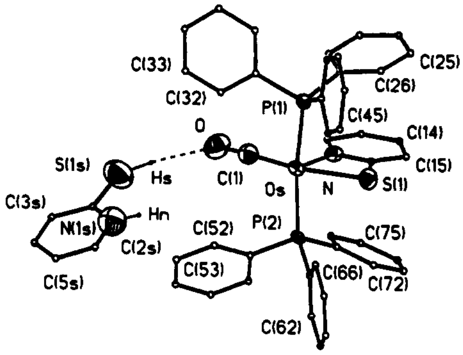

Figure 1. ORTEP diagram of **2a**·[$pySH_2BF_4$]·CH_2Cl_2. The BF_4^- counterions and one molecule of CH_2Cl_2 are not shown. The dotted line between O and S emphasizes the positioning of the two groups in the lattice; it does not indicate a hydrogen bond. Some bond lengths: Os–P(1) 2.402(3), Os–P(2) 2.404(3), Os–S(1) 2.450(3), Os–N 2.070(3), Os–C(1) 1.848(15) Å. Some bond angles: P(1)–Os–P(2) 172.7(1), P(1)–Os–S(1) 87.6(1), P(2)–Os–S(1) 85.2(1), P(1)–Os–N 90.2(3), P(2)–Os–N 88.2(3), S(1)–Os–N 67.3(3), P(1)–Os–C(1) 91.0(4), P(2)–Os–C(1) 96.3(4), S(1)–Os–C(1) 162.8(4), N–Os–C(1) 95.6(5)°.

reaction of **1** with $DBF_4{\cdot}Et_2O$ in $CDCl_3$ produces [Os(η^2-HD)(CO)(pyS)(PPh_3)$_2$]BF_4, **2**-d_1; only the 1:1:1 triplet of the major isomer, **2a**-d_1, was detectable by ^1H NMR. The HD coupling constant, J_{HD}, of 21 Hz is indicative of an elongated H–D bond; therefore the 1.08 Å H–H distance is the more likely one.[3] The elongation is surprising considering that electron-poor **2a** might be expected to be a poor π-base to H_2. A reviewer suggests that **2a** might be acting as a strong σ acceptor to achieve this elongation. The ν(CO) of **2a** in CH_2Cl_2 is 1993 cm^{-1}, shifted from 1888 cm^{-1} for the parent complex **1**.

The structure of **2a** along with co-crystallized [$pySH_2$]$^+$ is shown in Figure 1; two BF_4^- counterions and a solvating CH_2Cl_2 are not shown.[16] The dihydrogen ligand was not located but must be approximately trans to nitrogen. The other ligands form a distorted square pyramid with the PPh_3 groups mutually trans (POsP = 172.7(1)°) and the Os–N and Os–C(1) bonds approximately perpendicular to the P–Os–P axis and at 95.6(5)° to each other. The small bite angle of the pyS ligand (67.3(3)°) positions the sulfur off the square plane toward the N. The structure is equally consistent with a distorted pentagonal bipyramidal dihydride formulation [Os(H)$_2$(pyS)(CO)(PPh_3)$_2$]$^+$ but the NMR data do not support this. There is not a hydrogen bond between the sulfur atom of [$pySH_2$]$^+$ and the oxygen atom of the carbonyl group because the distance is greater than 4.0 Å. The structure of **2a** is somewhat related to that of [Os(H_2)(O_2CMe)(PPh_3)$_3$]$^+$ which is a much less acidic complex.[17]

We estimate the pK_a of **2** to be ca. −1 on the basis of the following observations. Stirring a sample of **2a** in $CDCl_3$ with excess dry Et_2O gives no reaction, as indicated by ^{31}P NMR. If D_2O is added to the same sample, only the peak for the monodeuteride complex **1a**-d_1 at 20.9 ppm is observed in the ^{31}P NMR. This places the pK_a of **2** between −2.6 (for Et_2OH^+) and 0 for H_3O^+. Complex **1** is not protonated by [$HPPh_3$]BF_4 (pK_a = 2.7).[18] An attempt to exchange the counterion BF_4^- with BPh_4^- by use of a methanol solution of $NaBPh_4$ quantitatively gave back the monohydride complex **1**.

Hydrogen gas is evolved from colorless **2a**·[$pySH_2BF_4$] in the solid state by heating to 100 °C under vacuum for 60 min. The bright orange compound produced[19] does not react in CH_2Cl_2 with H_2 to give back **2**. Instead, an insoluble precipitate forms.

Complexes related to **2** including those of Fe and Ru are being examined to see if acidic, stable complexes can be prepared directly from H_2 gas.

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Supplementary Material Available: A table of crystal data and data collection and refinement details and complete tables of atomic coordinates, bond lengths and angles, and general temperature factor expressions for **2a** (8 pages). Ordering information is given on any current masthead page.

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(16) Crystals of **2a**·[$pySH_2BF_4$]·CH_2Cl_2 at 213 K are triclinic, of space group $P\bar{1}$, with a = 12.750(8) Å, b = 14.025(4) Å, c = 14.646(3) Å, α = 78.89(2)°, β = 82.56(4)°, γ = 77.43(4)°, and V = 2498(1) Å^3 for Z = 2; R = 0.049. The positions of H_s and H_n as observed in the electron difference map were included in the calculations but were not refined.

(17) Siedle, A. R.; Newmark, R. A.; Korba, G. A.; Pignolet, L. H.; Boyle, P. D. *Inorg. Chem.* **1988**, *27*, 1593–1598.

(18) Streuli, C. A. *Anal. Chem.* **1960**, *32*, 985.

(19) $\delta(^{31}P)$ (CH_2Cl_2, 300 MHz): 4.4 (d, $^2J_{PP}$ = 13.3 Hz), 3.6 (s), −2.6 (d, $^2J_{PP}$ = 13.6 Hz).