

Isostructural η^2 -Dihydrogen Complexes $[\text{Os}(\text{NH}_3)_5(\text{H}_2)]^{n+}$ ($n = 2, 3$) and the Hydrogenation of Acetone

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Abstract: The reduction of $\text{Os}(\text{NH}_3)_5(\text{CF}_3\text{SO}_3)_3$ in methanol or aqueous solution affords the dihydrogen complex $[\text{Os}(\text{NH}_3)_5(\text{H}_2)]^{2+}$, $[\mathbf{1}]^{2+}$. The one-electron oxidation of this species generates a trivalent dihydrogen complex $[\mathbf{1}]^{3+}$ which, unlike its precursor, is capable of hydrogenating acetone to isopropyl alcohol. The use of methanol as a solvent offers important advantages for the preparation of a number of Os(II) complexes over other nonaqueous solvents previously used.

The remarkable affinity of the $(\text{NH}_3)_5\text{Ru}^{\text{II}}$ and $(\text{NH}_3)_5\text{Os}^{\text{II}}$ fragments for π -acid ligands has prompted a considerable amount of research activity in the last two decades.¹ The instability of some pentaammineosmium(II) complexes in the presence of protic solvents was first documented over 25 years ago by Gulens and Page;² in aqueous solution, the complexes $[\text{Os}(\text{NH}_3)_5\text{X}]^{2+}$ (where $\text{X} = \text{NH}_3, \text{H}_2\text{O}, \text{Cl}^-, \text{I}^-$) were reported to decompose readily to osmium(III) and molecular hydrogen. Consequently, our group, until recently, has taken great care to avoid protic solvents or impurities in our preparation of various pentaammineosmium(II) complexes with unsaturated organic ligands.³ Thus, it came as a surprise to learn that Shepherd et al. have synthesized several such complexes with olefins in aqueous solution.⁴ Their report prompted us to reevaluate our own synthetic methodologies and investigate the reduction of the precursor $\text{Os}(\text{NH}_3)_5(\text{OTf})_3$ ($\text{OTf} = \text{CF}_3\text{SO}_3$) in water as well as methanol, a solvent which can readily solvate both ionic salts and nonpolar ligands. We find that in the absence of π -acids, this reduction results in moderate yields of the dihydrogen complex $[\text{Os}(\text{NH}_3)_5(\text{H}_2)]^{2+}$ ($[\mathbf{1}]^{2+}$), in both solvents. Its characterization is the major focus of the present paper, but the utility of methanol as reaction medium for the preparation also of other complexes of $[\text{Os}(\text{NH}_3)_5]^{2+}$ is touched on as well.

Results

When $\text{Os}(\text{NH}_3)_5(\text{OTf})_3$ is reduced in CH_3OH with granular Zn^0/Hg^0 , small bubbles are detected, and the solution develops a yellow color. Judging from cyclic voltammetric data, we conclude that the isolated solid contains several electroactive species. ^1H NMR spectra of this mixture reveal that one of these components, $[\mathbf{1}]^{2+}$, is a pentaammineosmium(II) complex (quadrupole-broadened ammine resonances at 4.10 (3 H) and 3.42 (12 H) ppm) with two hydridic protons (-8.473 ppm). By repeating this reaction with the addition of HOTf, a crystalline salt of $[\mathbf{1}]^{2+}$ can be synthesized in moderate yield (50%). A similar product results by reducing $\text{Os}(\text{NH}_3)_5(\text{OTf})_3$ in an acidified aqueous solution.⁵ Neither the rate nor yield were altered when the reduction of $\text{Os}(\text{NH}_3)_5(\text{OTf})_3$ in methanol was repeated under 1 atm of H_2 .

A sample of crystalline $[\mathbf{1}](\text{OTf})_2$ (18 mg) was dissolved in CD_3OD (1 mL) along with trace amounts of NaOCH_3 (1 mg).

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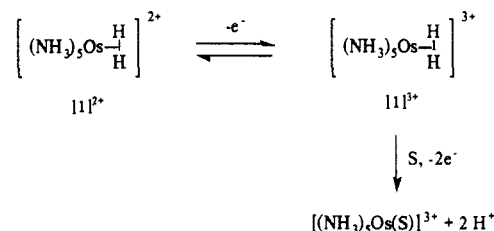
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(5) The aqueous solution is 1 M in CF_3COOH ; addition of NaBPh_4 results in the salt $[\mathbf{1}](\text{BPh}_4)_2$.

Scheme I. Electrochemical Oxidations Arising from the Complex $[\text{Os}(\text{NH}_3)_5(\text{H}_2)]^{2+}$, $[\mathbf{1}]^{2+}$ ($\text{S} = \text{CH}_3\text{CN}$ or H_2O)



After 10 min a ^1H NMR spectrum of the sample shows a significant loss of intensity for both the ammine and the hydridic resonances, in contrast to that observed in neutral solution.⁶ Replacing the high field singlet with a triplet (1:1:1) with a coupling constant of 15.2 Hz. When the same experiment is repeated under acidic conditions (100 mg HOTf added), no exchange of the amines is detected; however, the hydridic resonance significantly decreases yielding to the triplet observed in base. The osmium complex was then precipitated with ether, dissolved in acidic CH_3OH , and reprecipitated. An NMR spectrum of this material shows complete recovery of the hydride singlet. Finally, a sample of $[\mathbf{1}](\text{OTf})_2$ was dissolved in CH_3OH with 1 equiv of NaOMe . After 20 h the product was isolated and shown by NMR to be unaltered. Taken together, these observations confirm that $[\mathbf{1}]^{2+}$ is an η^2 -dihydrogen complex, stable to both acid and base. The 1:1:1 triplet, with a secondary isotopic shift of +0.031 ppm,⁷ is a manifestation of deuterium-hydrogen coupling of a magnitude which could result only from an H-D bond.⁸ In acetone, the dihydrogen protons show a moderately long relaxation lifetime with $T_1 = 345 \pm 3$ ms (20 °C; 400 MHz).⁹ Collman et al.¹⁰ have characterized $\text{Os}(\text{OEP})\text{H}_2$ and find 115 ± 21 ms as the minimum value of T_1 for their complex (-20 °C, in THF; $^1J_{\text{HD}} = 12$ Hz). An infrared spectrum of $[\mathbf{1}](\text{OTf})_2$ recorded for a precipitate on a NaCl salt plate reveals a very weak, broad absorption at 2231 cm^{-1} which we assign to $\nu(\text{MH}_2)$.¹¹ When the spectrum is taken

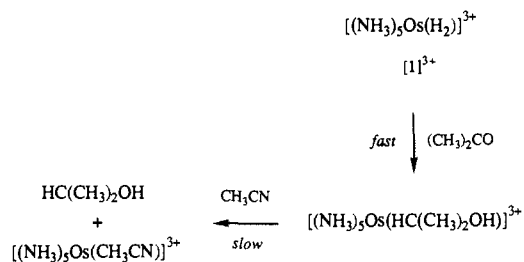
(6) H/D exchange on $[\mathbf{1}]^{2+}$ is not observed in a neutral methanol solution after 15 min for either ammine or hydride protons.

(7) As measured in acetone- d_6 . This value ($\delta_{\text{HH}} - \delta_{\text{HD}}$) is in good agreement to free H_2/HD (+0.036 ppm). Evans, D. F. *Chem. Ind.* **1961**, 1960.

(8) Typical H-D couplings for bis-hydrides are less than 2 Hz, whereas for dihydrogen complexes, values from 13 to 36 Hz have been reported. See: Bautista, M. T.; Earl, K. A.; Morris, R. H. *Inorg. Chem.* **1988**, *27*, 1124. Bautista, M. T.; Earl, K. A.; Maltby, P. A.; Morris, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 4056. Bautista, M. T.; Earl, K. A.; Maltby, P. A.; Morris, R. H.; Schweitzer, C. T.; Sella, A. *J. Am. Chem. Soc.* **1988**, *110*, 7036. Siedle, A. R.; Newmark, R. A.; Korba, G. A.; Pignolet, L. H.; Boyle, P. D. *Inorg. Chem.* **1988**, *27*, 1593. Antoniutti, S.; Albertin, G.; Amendola, P.; Bordignon, E. *J. Chem. Soc., Chem. Commun.* **1989**, 229. Esteruelas, M. A.; Sola, E.; Oro, L. A.; Meyer, O.; Werner, H. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1563. Also see ref 17.

(9) Typical T_1 values for dihydrogen complexes range from 4 to 125 ms. In view of the relatively small moment of inertia for this complex, T_1 is expected to reach its minimum value at lower temperature. See ref 18.

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Scheme II. Reduction of Acetone by $[\text{Os}(\text{NH}_3)_5\text{H}_2]^{3+}$ 

on an acetone solution a similar band appears at 2190 cm^{-1} . A cyclic voltammogram of $[\mathbf{1}]^{2+}$ in dry acetonitrile solution¹² (electrolyte: Bu_4NPF_6 ; scan rate, 100 mV/S) approaches that of a reversible couple with $E_{1/2} = 0.58\text{ V}$ (NHE) provided that a switching potential of less than 0.8 V is maintained. When the solution is subjected to more positive potentials, a second anodic wave is observed at about $E_{p,a} = 1.3\text{ V}$ (Figure 1) which is irreversible and integrates for twice the number of electrons of the reversible couple; subsequent scanning reveals that a significant amount of the complex $[\text{Os}(\text{NH}_3)_5(\text{CH}_3\text{CN})]^{3+}$ has been formed. These data suggest that the moiety $[\text{Os}(\text{NH}_3)_5\text{H}_2]^{3+}$ undergoes further oxidation to yield Os(III) and two protons as shown in Scheme I.

The addition of small amounts of acetone to the acetonitrile solution (ca. 1 mM) dramatically affects the electrochemistry of $[\mathbf{1}]^{2+}$: the first oxidation becomes chemically irreversible, even at moderate scan rates ($<10\text{ V s}^{-1}$), and the second oxidation wave vanishes altogether. A subsequent cathodic scan produces a single wave at $E_{p,c} = -0.56\text{ V}$, consistent with the reduction of the isopropyl alcohol complex $[\text{Os}(\text{NH}_3)_5(\text{CH}_3)_2\text{CHOH}]^{3+}$. In contrast to the behavior observed for $[\mathbf{1}]^{2+}$, the more positive $[\mathbf{1}]^{3+}$ acts as an efficient reducing agent for acetone.

A solution of $[\mathbf{1}]^{2+}$ was prepared ($45.7\text{ mg}/2.0\text{ mL}$) in CD_3CN containing ca. 135 mg of acetone. Treatment with 1 equiv (13 mg) of the mild oxidant $\text{Fe}(\text{Cp})_2\text{PF}_6$ resulted in a rapid color change from blue to yellow; since the reduction potential of the blue species $\text{Fe}(\text{Cp})_2^{2+}$ (0.55 V) is slightly negative to that of $[\mathbf{1}]^{2+}$, the absence of blue indicated that an irreversible reaction of $[\mathbf{1}]^{3+}$ had occurred. NMR spectra of the solution recorded over the following 2 days revealed the slow formation of free isopropyl alcohol- d_1 in solution.¹³ Small colorless crystals appeared in the sample tube over this same period which, when isolated, were shown by cyclic voltammetry to be $[\text{Os}(\text{NH}_3)_5(\text{CD}_3\text{CN})](\text{OTf})_3$. By repeating this experiment with an integration standard (anisole), it was established that isopropyl alcohol- d_1 was being produced in $>80\%$ yield (Scheme II). The addition of methanol- d_1 (0.63 M) to the solution prior to oxidation acted to facilitate solvolysis of the paramagnetic complex $[\text{Os}(\text{NH}_3)_5((\text{CH}_3)_2\text{CHOH})]^{3+}$ ¹⁴ but did not affect the overall yield of free isopropyl alcohol.

A methanol solution of $[\mathbf{1}](\text{OTf})_2$ ($50\text{ mg}/1\text{ mL}$) was treated with $200\text{ }\mu\text{L}$ of 2-butyne and allowed to stand. An identical experiment was performed with the addition of 1 equiv of NaOMe . After 24 h, the products were isolated, and their NMR spectra showed that no reaction had occurred. In separate experiments $[\mathbf{1}]^{2+}$ also failed to react with pyridine, PPh_3 , water, or acetonitrile after several hours. Only upon dissolving $\mathbf{1}$ in 6 M $\text{HOTf}(\text{aq})$ at $50\text{ }^\circ\text{C}$ were there signs of decomposition.¹⁵

The electrochemical behavior of $[\mathbf{1}]^{2+}$ was also investigated in water. Under neutral conditions cyclic voltammograms (Na OTf ; $50\text{--}1000\text{ mV/s}$) reveal two chemically irreversible waves at 0.43 and 0.88 V , the latter of which is both broader and larger than

the first. The first oxidation appears to modify the glassy carbon electrode surface as subsequent "first scans" failed to reproduce these values unless the electrode surface was freshly polished. The addition of high concentrations ($1\text{--}6\text{ M}$) of triflic acid (HOTf), however, acted to inhibit both the fouling of the electrode and decomposition of $[\text{Os}(\text{NH}_3)_5(\text{H}_2)]^{3+}$; at low pH ($\ll 1$) the oxidation of $[\mathbf{1}]^{2+}$ in water was found to be reversible ($E_{1/2} = 0.41\text{ V}$). A rotating-disk-electrode voltammogram shows that the second oxidation involves twice the current of the first and supports the electrochemical scheme shown in Figure 1. Similar results were obtained with a sample of $[\mathbf{1}](\text{OTf})_2$ in strongly acidic methanol.

Discussion

Since the first communication by Kubas in 1980,¹⁶ a variety of dihydrogen complexes have been characterized.¹⁷ In particular, solution ^1H NMR has proven invaluable for the confirmation of an H-H bond and the determination of this bond length.¹⁸ The observation of a strong H-D coupling ($J_{\text{HD}} = 15.2\text{ Hz}$) for the complex $[\text{Os}(\text{NH}_3)_5(\text{HD})](\text{OTf})_2$ ($[\mathbf{1}-d_1]^{2+}$) clearly indicates a significant dihydrogen bond for $[\mathbf{1}]^{2+}$, yet this value is considerably smaller than seen for free HD (43.2 Hz)¹⁹ or most dihydrogen complexes thus far reported.^{17,18} Parallel to this finding, the relaxation time (T_1) for $[\mathbf{1}]^{2+}$ (345 ms , 400 MHz) at $20\text{ }^\circ\text{C}$ is considerably longer than for other dihydrogen complexes, which typically show values of $4\text{--}125\text{ ms}$.^{18,20} Taken together with the low-frequency (MH_2) stretch, these observations suggest a significant lengthening of the H-H bond as a result of metal backbonding. J_{HD} values as low as 13 Hz have been reported for dihydrogen complexes,²¹ but for these examples it remains unclear whether such low values are indicative of an elongated H-H bond or a rapid equilibrium with the bis-hydride;¹⁷ such an equilibrium for $[\mathbf{1}]^{2+}$, at this point, also cannot be ruled out.

Morris²² et al. have found a correlation between the stability of a dihydrogen complex and the $\text{N}\equiv\text{N}$ stretching frequency for the analogous dinitrogen species, on the basis of which metal complexes featuring dinitrogen stretches from 2060 to 2160 cm^{-1} are predicted to form stable dihydrogen complexes. When this value lies higher or lower, H_2 dissociation or oxidative addition outside is anticipated, respectively. The species $[\text{Os}(\text{NH}_3)_5(\text{N}_2)]^{2+}$ displays a dinitrogen stretch at 2010 cm^{-1} , well below the stability limits of the Morris criteria. Of the other dihydrogen complexes reported,¹⁸ octahedral d^6 Group VIII metals are the most prevalent, but a stable dihydrogen complex as a di- or trivalent cation is unprecedented for any transition metal. We attribute the stability of $[\mathbf{1}]^{2+}$ and $[\mathbf{2}]^{3+}$ to the combination of high coordination number, which disfavors oxidative addition, and significant backbonding which stabilizes dihydrogen coordination. It is worth noting that the tetraammine analogue to $[\mathbf{1}]^{2+}$, $[\text{Os}(\text{en})_2(\text{H})_2]^{2+}$, exists as a classical bis-hydride.²³

With the exception of polyhydrides, $[\mathbf{1}]^{2+}$ constitutes the first example of a dihydrogen complex void of other π -acids which are capable of competing for π -electron density. As a result this species is remarkably stable to strong acid (HOTf), moderate base (NaOMe), and dissociation or substitution of dihydrogen even in π -acidic solvents.²⁴ The resistance of $[\mathbf{1}]^{2+}$ toward deprotonation or dihydrogen transfer can be understood in terms of the stability gained from the π -accepting ability of the σ^* orbital of dihydrogen; to date the only example of a stable pent-

(11) $\nu(\text{MH}_2)$ values have been reported as low as 2300 cm^{-1} for dihydrogen complexes. See refs 17 and 18.

(12) % $\text{H}_2\text{O} < 0.002$ as determined by the manufacturer.

(13) ^1H NMR of isopropyl alcohol- d_1 in acetone: 3.88 (M, 1 H), 1.08 (d, 6 H).

(14) Solvolysis of $[\text{Os}(\text{NH}_3)_5((\text{CH}_3)_2\text{CHOH})]^{3+}$ was complete in 2 h.

(15) Over extended periods of time (30 min) a solution of $[\mathbf{1}](\text{OTf})_2$ in 6 M HOTf evolves a gas thought to be hydrogen.

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(20) These T_1 values are often recorded at subsambient temperatures.

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(24) The complex $[\mathbf{1}]^{2+}$ is stable for at least several hours in acetone, acetonitrile, pyridine, DMF, and water.

ammineosmium(II) complex containing only saturated ligands is $[\text{Os}(\text{NH}_3)_6]^{2+}$.²⁵ Yet hydride H/D exchange does occur on $[\mathbf{1}]^{2+}$ in the presence of base; the isoelectronic species $[\text{CpRu}(\text{dmpe})(\text{H}_2)]^+$ has been estimated to have a $\text{p}K_a$ of about 18 in acetonitrile.²⁶

The reversibility of the $[\mathbf{1}]^{3+/2+}$ couple in dry CH_3CN on the cyclic voltammetric time scale has provided an opportunity to compare the reactivity as reducing agents of dihydrogen complexes which differ by one in electron count. In the form $[\mathbf{1}]^{2+}$, the complex appears to be unreactive to acetone and other substrates over a period of many hours. The complete disappearance of both the second (1.3 V) anodic wave and the first cathodic wave ($E_{1/2} = 0.58$ V) in the presence of acetone, when account is taken of experimental conditions (scan rate = 50–500 mV/s; $[\text{Os}] \cong [\text{acetone}] \cong 1$ mM), shows that the specific rate for the reaction of $[\mathbf{1}]^{3+}$ with the ketone exceeds $10^3 \text{ M}^{-1} \text{ s}^{-1}$. Cyclic voltammetric data in the more basic solvent H_2O shows that $[\mathbf{1}]^{3+}$ can undergo reversible proton dissociation.²⁷ The oxidation of $[\mathbf{1}]^{2+}$, which occurs at a potential similar to that recorded in CH_3CN , is reversible only at very low pH, which suggests that the $\text{p}K_a$ for $[\mathbf{1}]^{3+}$ is quite low. As the pH is raised toward neutral, cyclic voltammograms of $[\mathbf{1}](\text{OTf})_2$ at moderate scan rates (50–500 mV/s) become chemically irreversible. These observations are consistent with a scheme in which deprotonation of $[\mathbf{1}]^{3+}$ is accompanied by a significant reorganization of the metal center so that reprotonation is slow relative to the scan rate. Oxidation of $[\mathbf{1}]^{2+}$ yields a product which can undergo a further $2e^-$ oxidation, just as in the case of acetonitrile but at considerably lower potential. We ascribe this process to $[\text{Os}(\text{NH}_3)_5\text{H}]^{2+} + \text{H}_2\text{O} = [\text{Os}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+} + \text{H}^+ + 2e^-$. Considering that Os(II) has a greater reducing potential than Os(III), the tendency of dihydrogen to polarize to "H⁺" and "H⁻" on the latter is most likely responsible for the reactivity of $[\mathbf{1}]^{3+}$ with acetone; the reduction in question can be regarded as involving transfer of the elements H⁻ and H⁺ to the substrate. The difference in the electrochemical behavior of $[\mathbf{1}]^{2+}$ in neutral water and acetonitrile suggests that $\text{p}K_a$ is higher in the latter solvent, a not unexpected outcome in view of the weaker proton basicity of the latter (CH_3CN is not significantly protonated in 1 M aqueous acid). It should be noted that when the acetonitrile is not completely dry, the first oxidation wave in this solvent also is no longer reversible.

The established general synthetic route³ to (π -acid)pentaammineosmium(II) complexes utilizes $\text{Os}(\text{NH}_3)_5(\text{OTf})_3$ as the direct precursor; this material is reduced, usually by Mg^0 , in a saturated ether (1,2-dimethoxyethane) with an excess of the desired π -acid kept in situ. The main drawback to this method is the incompatibility of the reducing metal, Mg, with protic ligands such as phenols, amides, and carboxylic acids. (In DME, Zn/Hg amalgam is ineffective as a reducing agent for $\text{Os}(\text{NH}_3)_5(\text{OTf})_3$.) Here is where we find utility of the MeOH/Hg/Zn system: provided that the entering π -acid ligand is

maintained in high concentrations (e.g., 1 M), the reduction of $\text{Os}(\text{NH}_3)_5(\text{OTf})_3$ in methanol with Zn/Hg amalgam typically results in >80% yield of the desired salt $[\text{Os}(\text{NH}_3)_5(\pi\text{-acid})](\text{OTf})_2$.³⁰ Under these conditions, the formation of $[\mathbf{1}]^{2+}$ has not been detected.

Conclusions

The isostructural complexes $[\mathbf{1}]^{2+}$ and $[\mathbf{1}]^{3+}$ extend the range of known dihydrogen complexes to include species which carry a high charge and which are devoid of auxiliary π -acids. A high reactivity of the dihydrogen coordinated to Os(III) has also been demonstrated.

Experimental Section

¹H NMR spectra and T_1 measurement were obtained on a Varian XL-400 spectrometer. Electrochemical experiments were performed under argon using a PAR Model 173 potentiostat driven by a PAR Model 175 universal programmer. Cyclic voltammograms were recorded with a Pt⁰ working electrode (1 mm²), a Pt⁰ counter electrode, and a reference which was calibrated with the ferrocene/ferricenium couple ($E^\circ = 0.55$ V; NHE) in situ. All potentials are reported vs the normal hydrogen electrode.

Reagents. $\text{Os}(\text{NH}_3)_5(\text{OTf})_3$ was synthesized as described by Lay et al.³¹ Acetone was purified by vacuum distillation over B_2O_3 ,³² Et_2O by distillation over NaK alloy, and MeOH by distillation over $\text{Mg}(\text{OMe})_2$ prepared in situ from Mg^0 and I_2 under argon.³³ Granular Zn/Hg amalgam was prepared from 30 mesh granular Zn⁰ which was washed with 3 M HCl (aqueous) and then treated with a saturated HgCl_2 (aqueous) solution for 20 min. All other reagents were used as supplied. Solvents were deoxygenated by purging with argon, and reactions were carried out under argon atmosphere in a Vacuum Atmospheres Corp. glovebox.

Synthesis of $[\mathbf{1}](\text{OTf})_2$: A suspension of $\text{Os}(\text{NH}_3)_5(\text{OTf})_3$ (1.02 g), MeOH (10 mL), and HOTf (5.0 mL) was stirred with granular Zn/Hg amalgam until the salt has completely dissolved. After an additional 5 min, the reaction mixture was filtered. The filtrate was slowly treated with ether until white crystals began to form (ca. 50 mL). The crystals were collected, washed with ether, and reprecipitated from acetone with ether (yield: 50%). The compound $[\mathbf{1}-d_1](\text{OTf})_2$ was precipitated from acidic $\text{CH}_3\text{OH}/\text{CD}_3\text{OD}$ with ether. **Characterization of $[\mathbf{1}](\text{OTf})_2$:** ¹H NMR (acetone-*d*₆; ppm (Δ TMS)) 4.10 (b, 3 H), 3.42 (b, 12 H), -8.47 (s, 2 H). For $[\mathbf{1}-d_1](\text{OTf})_2$ -8.50 (t, 1:1:1), $J_{\text{HD}} = 15.2$ Hz; IR (ppt from acetone) ν (MHz) = 2231 cm^{-1} , (in acetone solution) 2190 cm^{-1} ; CV (100 mV s⁻¹; Bu₄NPF₆; CH₃CN) $E_{1/2} = 0.58$ V, NHE. Anal. Calcd for C₂H₁₇OsS₂F₆O₆N₅: C, 4.17; H, 2.98; N, 12.17; S, 11.14. Found: C, 4.48; H, 2.93; N, 12.05; S, 10.67.

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(27) Deprotonation of dihydrogen coordinated to Ni(III) has been prepared in various bacterial dehydrogenases²⁸ and is thought to play a role in the reduction of olefins.²⁹