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Dihydrogen Activation by a Diruthenium Analogue of the Fe-Only Hydrogenase Active Site

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Hydrogenases, enzymes that have been recognized since the 1930s, have come into sharp focus because the unusual nature of their active sites imply mechanistically unusual pathways.[1,2] The blossoming molecular biology of the hydrogenases coincides with intense research on dihydrogen ligands[3] augmented by the topicality of the "hydrogen economy".[4] The Fe−only hydrogenases have received particular recent attention because their active site structure[5,6] (Figure 1), which resembles the iconic $Fe_2(SR)_2(CO)_6$, is amenable to synthetic modeling. A particular challenge to modeling is the distal iron, where proton reduction is proposed to occur via a *terminal* hydrido intermediate.

The diiron site has been studied extensively by synthetic modeling and theoretical experiments.[1] Models with *bridging* hydride ligands can been prepared via the protonation of the Fe^I-Fe^I bond in $[Fe_2(SR)_2(CO)_4L_2]^z$ (L_2 = $(PMe_3)_2$, z = 0; L_2 = $(PMe_3)(CN)$, z = 1-).[7,8] Although the resulting hydrides $[Fe_2(SR)_2(\mu\text{-H})(CO)_4L_2]^{(z+1)+}$ appear not to adopt biologically relevant stereochemistry, they efficiently catalyze the reduction of protons to dihydrogen.[7,9] Interaction between diiron dithiolates and H_2 is further implicated in the photochemical H_2/D_2O exchange catalyzed by $[Fe_2(S_2C_3H_6)(\mu\text{-X})(CO)_4(PMe_3)_2]^+$ (X = H, SMe).[8,10] Despite these advances, *no models with terminal hydride or dihydrogen ligands have been produced*. We have begun to investigate this and related challenges through studies on diruthenium systems of the type $Ru_2(S_2C_3H_6)(CO)_4(PR_3)_2$.[11,12] Experiments described below demonstrate that such diruthenium dithiolates oxidatively add H_2 and that the resulting dihydrido species can be protonated to form a dihydrogen complex. Binuclear dihydrogen complexes are rare.[3,13]

We chose to examine the photohydrogenation of $Ru_2(S_2C_3H_6)(CO)_4(PCy_3)_2$ (**1**, Cy = C_6H_{11}). As in previous studies on related diiron dithiolates, phosphine ligands were deployed to simulate the electronic role of the cyanide donor ligands found in the enzyme. ^{31}P NMR studies show that **1** is dynamic in solution at room temperature apparently resulting from the rapid interconversion of two rotamers, although this detail is the topic of continuing studies. UV-photolysis of toluene solutions of **1** under a flowing atmosphere of H_2 gave the dihydride $Ru_2(S_2C_3H_6)(\mu\text{-H})(H)(CO)_3(PCy_3)_2$ (**2**), Scheme 1. The ^1H NMR spectrum of **2** exhibits well-resolved signals for the bridging and the terminal hydride ligands, coupled to two and one ^{31}P centers, respectively. The ^{31}P NMR spectrum shows that the phosphine ligands are nonequivalent. Crystallographic characterization supports the NMR data, revealing that the phosphine ligands have moved from diaxial positions in **1** to mutually trans basal positions in dihydride **2** (Figure 2). The isomerization is perhaps driven by steric interactions between the dithiolate backbone and the axial ligand sites; such interactions would be aggravated by opening of the RuSRu angles, which accompanies the oxidative addition. Spectroscopic measurements indicate that the ethanedithiolate $Ru_2(S_2C_2H_4)(CO)_4(PCy_3)_2$ also adds H_2 similarly. The mutually trans stereochemistry of the hydride

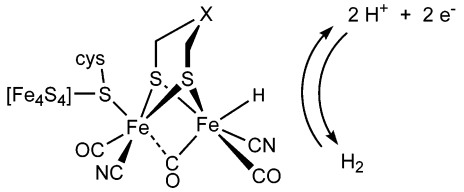
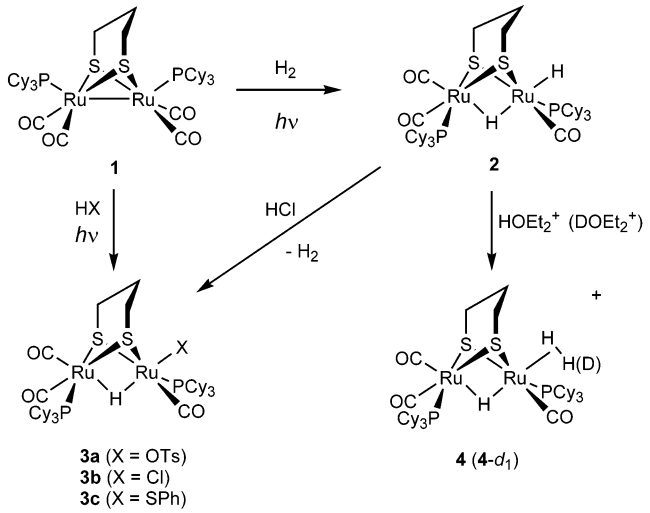


Figure 1. Proposed active site (H_{red} state) of the Fe-only hydrogenase enzyme based on crystallographic analyses.[1] X is assumed to be NH_n but could also be CH_2 or O.[6]

Scheme 1



ligands is proposed to arise intramolecularly from an initially formed cis-dihydride via a pathway akin to the isomerization of $[(C_5H_5)Ru(PR_3)_2(H_2)]^+$ into *trans*-$[(C_5H_5)Ru(PR_3)_2(H)_2]^+$.[14] In solution, **2** does not exchange with D_2O or D_2. The Ru−Ru distance increases by a substantial 0.2 Å from 2.6875(8) to 2.8970(9), whereas protonation of the $Fe_2(SR)_2(CO)_4L_2$ systems elongates the Fe−Fe distance by only 0.05 Å.[7]

The photoaddition of H_2 is representative of a potentially general reaction whereby substrates oxidatively add to the diruthenium species with loss of CO. Photolysis of a toluene solution of **1** and HOTs ($HOSO_2C_6H_4Me$) gave a single isomer of hydride $Ru_2(S_2C_3H_6)(\mu\text{-H})(OTs)(CO)_3(PCy_3)_2$ (**3a**) as assigned by ^1H and ^{31}P NMR measurements. Similar reactivity was observed for HCl and HSPh to give the corresponding chloro and thiophenolato complexes **3b** and **3c**. In the case of the HOTs reaction, IR and NMR measurements indicate that the conversion commences with (non-photochemical) protonation of the Ru−Ru bond to give $[Ru_2(S_2C_3H_6)(\mu\text{-H})(CO)_4(PCy_3)_2]OTs$. Photodissociation of CO from this cation permits coordination of the counteranion. Spectroscopic measurements indicate that the coordination geometries of **3a**−**3c**

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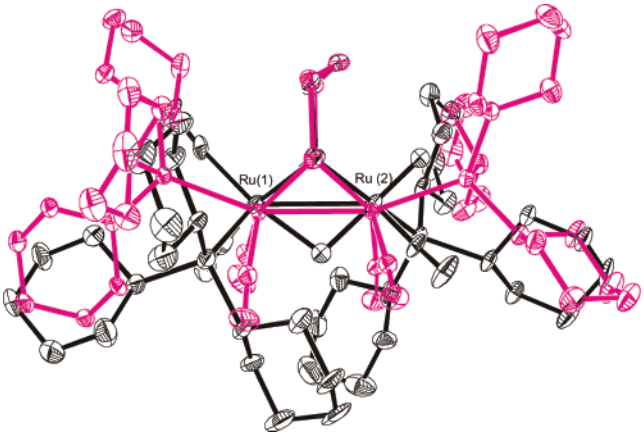

Figure 2. Molecular structures of $Ru_2(S_2C_3H_6)(CO)_4(PCy_3)_2$ (**1**) (magenta) and $Ru_2(S_2C_3H_6)(\mu\text{-}H)(H)(CO)_3(PCy_3)_2$ (**2**) (black) with thermal ellipsoids set at the 35% probability level. Solvate and H atoms were excluded for clarity; Ru−H positions were refined. Selected distances (Å) and angles (deg) for **2** are as follows: Ru(1)−Ru(2), 2.8970(9); Ru(1)−H(1), 2.01(3); Ru(2)−H(1), 1.77(3); Ru(2)−H(2), 1.57(3); Ru(1)−S(1), 2.419(2); Ru(1)−S(2), 2.415(2); Ru(2)−S(1), 2.4198(19); Ru(2)−S(2), 2.4193(18); Ru(1)−P(1), 2.389(2); Ru(2)−P(2), 2.316(2); Ru(1)−C(40), 1.913(7); Ru(1)−C(41), 1.845(9); Ru(2)−C(42), 1.854(7); Ru(1)−S(1)−Ru(2), 73.55(6); Ru(1)−S(2)−Ru(2), 73.64(5); Ru(2)−Ru(1)−H(1), 36.9(10); Ru(1)−Ru(2)−H(1), 43.0(11); Ru(1)−Ru(2)−H(2), 135.7(17); H(1)−Ru(2)−H(2), 178(2).

are analogous to that for **2**. The structure of chloride **3b** was confirmed crystallographically. Addition of HCl to **2** afforded **3b** and H_2.

Interesting results come from protonation experiments that probe the formation of the corresponding dihydrogen complex. Treatment of **2** with $[H(OEt_2)]BAr^F{}_4$ (Ar^F = C_6H_3-3,5-$(CF_3)_2$) in acetone-d_6 solution (25 °C) resulted in the formation of free H_2 and HD, detected by ^{1}H NMR spectroscopy. Acetone is proposed to displace an incipiently formed H_2 ligand, and the HD arises similarly but after the H/D exchange between $[H(OEt_2)]BAr^F{}_4$ and acetone-d_6. NMR data of the product are consistent with $[Ru_2(S_2C_3H_6)(\mu\text{-}H)(CO)_3(PCy_3)_2(OCMe_2\text{-}d_6)]^+$. ^{1}H NMR analysis for the protonation of **2** in CD_2Cl_2 solution indicates formation of $[Ru_2(S_2C_3H_6)(\mu\text{-}H)(CO)_3(PCy_3)_2(H_2)]^+$ (**4**, Scheme 1). In particular, we observe a ^{31}P-coupled triplet at δ −13.2 and a broad singlet of intensity 2H at δ −5.9 (T_1 at 25 °C = 30 ms, 11.7 T). ^{1}H NMR data for **4**-d_1, derived from the reaction of **2** with $[D(OEt_2)]BAr^F$ gave a triplet at δ −6.1 with $^1J_{H-D}$ of 31 Hz, indicative of a H−D distance of 0.90 Å.[3] We observed no deuterium incorporation into the μ-H ligand, even after several days at room temperature. Solutions of $[Ru_2(S_2C_3H_6)(\mu\text{-}H)(H_2)(CO)_3(PCy_3)_2]^+$, which are stable for several days at room temperature, catalyze the exchange between D_2 and H_2, a characteristic reaction of hydrogenases.[1,2]

In summary, we report the following advances in hydrogenase modeling: (i) the first example of H_2 addition to a hydrogenase model, (ii) demonstration that the terminal hydride is more hydridic than the bridging hydride, and (iii) first dihydrogen complex of a hydrogenase active site model. The $Ru_2(SR)_2(CO)_{6-x}L_x$ complexes are sufficiently diverse and manipulable[11,15] that it should be possible to prepare a range of hydride derivatives and probe their reactivity. We anticipate that these developments will guide the preparation of the corresponding diiron model systems and a fuller understanding of the underlying enzymology.

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Supporting Information Available: Preparative details, spectroscopic data, and crystallographic analyses. This material is available free of charge via the Internet at http://pubs.acs.org.

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