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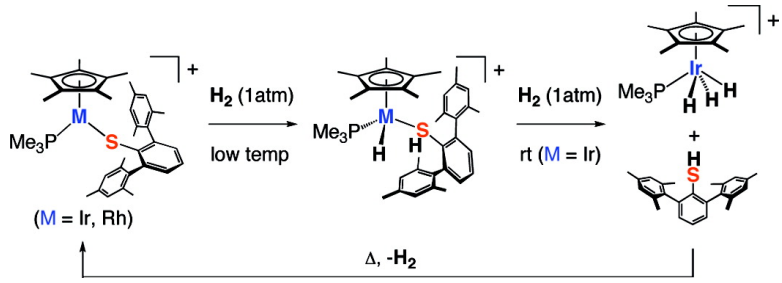

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Reversible Heterolysis of H_2 Mediated by an M−S(Thiolate) Bond (M = Ir, Rh): A Mechanistic Implication for [NiFe] Hydrogenase

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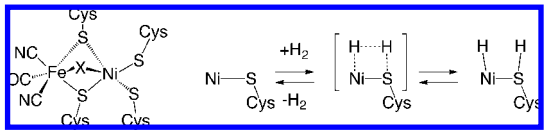
Heterolytic cleavage of dihydrogen is a key step in the function of hydrogenases, which catalyze hydrogen evolution and uptake under mild conditions.[1] The recent crystallographic and theoretical studies on [NiFe] hydrogenases have demonstrated that the cysteine-rich nickel center is a plausible binding site of H_2[2] and that a cysteine sulfur on nickel may accept a proton generated from the H_2 heterolysis (Scheme 1).[3] Various transition metal complexes have been shown to promote heterolysis of H_2.[4] However, such reactions occurring at thiolate complexes remain scarce,[5] most of which require rigorous conditions e.g., high-pressure of H_2 and/or the presence of external protons. Thus it is desirable to synthesize new thiolate complexes, which are capable of splitting H_2 under mild conditions, to gain insight into the mechanism of [NiFe] hydrogenases.

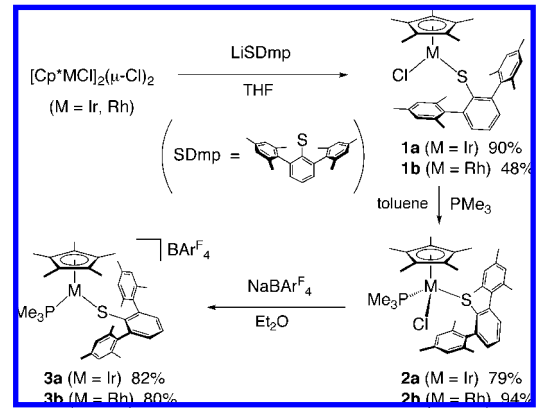
Scheme 1. Active Site of [NiFe] Hydrogenase (Oxidized Form, X = OH or O) and a Possible H_2 Heterolysis at the Ni−S(cys) Site



In the course of our study on transition metal thiolate complexes,[6] we found that the sterically encumbering 2,6-dimesitylphenyl thiolate (SDmp)[7] stabilizes coordinatively unsaturated metal centers.[6h−k] We herein report that the SDmp complex of iridium, [Cp*Ir(PMe_3)(SDmp)](BAr^F_4) (**3a**), promotes facile H_2 heterolysis generating [Cp*Ir(PMe_3)H_3](BAr^F_4) (**4**) and H-SDmp. This reaction was found to be reversible, and formation of an intermediate [Cp*Ir(PMe_3)(H)(HSDmp)](BAr^F_4) (**5a**) was detected. A similar heterolysis of H_2 was found to occur with the rhodium congener [Cp*Rh(PMe_3)(SDmp)](BAr^F_4) (**3b**), via [Cp*Rh(PMe_3)(H)(HSDmp)](BAr^F_4) (**5b**), while characterization of hydride complexes relevant to **4** was not possible.

Complexes **3a** and **3b** were prepared from the sequential reactions of [Cp*MCl]$_2$(μ-Cl)$_2$ (M = Ir, Rh)[8] with LiSDmp, PMe_3, and $NaBAr^F_4$ (Ar^F = 3,5-$(CF_3)_2C_6H_3$),[9] as shown in Scheme 2. Addition of LiSDmp to a THF suspension of [Cp*MCl]$_2$(μ-Cl)$_2$ led to a dark green solution (Ir) or a bluish green solution (Rh), from which the corresponding thiolate−chloride complex, Cp*IrCl(SDmp) (**1a**) or Cp*RhCl(SDmp) (**1b**), was isolated. Treatment of **1a** and **1b** with PMe_3 gave Cp*M(PMe_3)Cl(SDmp) (**2a**; M = Ir, **2b**; M = Rh), and the subsequent removal of chloride was attained by the reactions with $NaBAr^F_4$. The resulting cationic 16e complexes, **3a** and **3b**, were obtained as dark green and dark purple crystals, respectively. The molecular structures of **1a**,**b**, **2a**, and **3a**,**b** were determined by X-ray analysis. Coordinative unsaturation of **1a**,**b** and **3a**,**b** is evident in their X-ray structures, where the M−S distances of 2.2617(7) (**1a**), 2.2694(7) (**1b**), 2.2095(10) (**3a**), and 2.2149(11) Å (**3b**) are notably shorter than those of **2a** (2.4194(18) Å) and other electronically saturated thiolate complexes of iridium and rhodium (2.32−2.38 Å).[10]

Scheme 2



Exposure of a dark green CD_2Cl_2 solution of **3a** to 1 atm of H_2 at room temperature resulted in decolorization of the solution, from which [Cp*Ir(PMe_3)H_3](BAr^F_4) (**4**)[11] was isolated in 64% yield as colorless crystals (Scheme 3). The reaction was monitored by the ^{1}H NMR spectrum in CD_2Cl_2, to find that **4** and H-SDmp were formed quantitatively. Interestingly, when a mixture of complex **4** and H-SDmp in toluene was heated at 100 °C under Ar, **3a** and H_2 were regenerated, and **3a** was isolated in 81% yield as crystals. The reversible conversion between **3a**+H_2 and **4**+HSDmp provides us with an intriguing functional model of [NiFe] hydrogenase, implying that H_2 activation at a Ni−S(Cys) bond may be a good possibility. In the reaction of **3a**, H_2 may first approach the coordinatively unsaturated Ir, and the splitting of H_2 would occur at the Ir−S bond. This mechanism was corroborated by the formation of [Cp*Ir(PMe_3)(H)(HSDmp)](BAr^F_4) (**5a**) in the reaction of **3a** with H_2. When the reaction was carried out in CD_2Cl_2 for 5 h at −20 °C, **5a** was detected by ^{1}H NMR as the major product (80%), in which the proton signals for Ir-*H* and *H*-SDmp appeared at δ −15.27 as a doublet with J_{PH} = 35.6 Hz and at δ 5.26 as a broad singlet, respectively. The ^{1}H NMR spectrum also showed signals of unreacted **3a** (12%) along with those of **4** (7%) and H-SDmp (6%).

The analogous thiol−hydride complex of rhodium, [Cp*Rh(PMe_3)(H)(HSDmp)](BAr^F_4) (**5b**), was formed in the reaction of [Cp*Rh(PMe_3)(SDmp)](BAr^F_4) (**3b**) with 1 atm of H_2 in CD_2Cl_2 at −40 °C. Because **5b** degrades to an uncharacterizable Rh-hydride(s)[12] and H-SDmp more rapidly than the reaction of the Ir congener, it was necessary to monitor the reaction at a lower temperature and at a shorter reaction time (1.5 h). According to the ^{1}H NMR measurement, the products consist of **5b** (89%), **3b** (10%), H-SDmp (2%), and others (1%), and the proton signals for Rh-*H* and *H*-SDmp of **5b** were observed at δ −11.41 (dd, J_{RhH} = 14.4 Hz, J_{PH} = 35.6 Hz) and 4.56 (bs).

The green block crystals of **5a** were separated manually from the crystalline products, which were subject to the elemental analysis and

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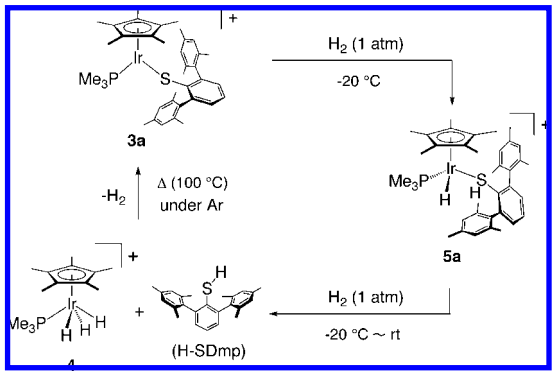
Scheme 3



structural characterization. The X-ray derived structure of **5a** is shown in Figure 1. A hydride was located at one of the three legs of the piano-stool geometry of **5a**. The Ir−S(thiol) distance of 2.3238(17) Å is longer than the Ir−S(thiolate) bonds of **1a** (2.2617(7) Å) and **3a** (2.2095(10) Å), but it is notably shorter than that of **2a** (2.4194(18) Å), which is electronically analogous to **5a**. It might be that the sulfur atom of **5a** has a sulfonium ion character. A similar M−S bond shortening upon protonation of the thiolate sulfurs of complexes $CpFe(CO)_2SPh$ and $[Cr(S^tBu)(CO)_5]^-$ has been reported.[13]

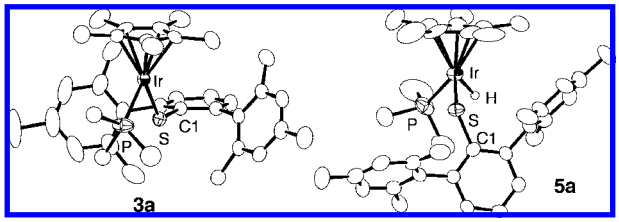


Figure 1. ORTEP drawings of the cationic parts of **3a** (left) and **5a** (right). Selected bond distances (Å) and angles (deg): **3a**: Ir−S 2.2095(10), Ir−P 2.3096(13), S−C1 1.791(3), P−Ir−S 82.80(4), Ir−S−C1 121.63(13). **5a**: Ir−S 2.3238(17), Ir−P 2.254(2), Ir−H 1.50(6), S−C1 1.791(7), P−Ir−S 94.51(8), Ir−S−C1 123.0(2).

The deuterated compounds, $[Cp^*Ir(PMe_3)D_3](BAr^F{}_4)$ (**4**-d_3) and D-SDmp, were generated from the reaction of **3a** with D_2, and their deuterium atoms were readily replaced by hydrogen atoms under 1 atm of H_2 at room temperature. Thus a facile proton exchange between H-SDmp and **4** is occurring. A kinetic study of the reactions of **3a** with 1 atm of H_2 and D_2 in CD_2Cl_2 was conducted by ^1H NMR at −20 °C. By monitoring the decrease in the signals of **3a**, the reactions were shown to obey a pseudo-first-order kinetics, expressed as $-d[\mathbf{3a}]/dt = k_{H(D)}[\mathbf{3a}]$. The rate constants were determined to be $k_H = 9.56(20) \times 10^{-5}$ s^{-1} and $k_D = 4.11(8) \times 10^{-5}$ s^{-1}. The observed kinetic isotope effect (KIE) of 2.3 (k_H/k_D) indicates that a H−H cleaving process is involved in the rate-determining step. This KIE value may be compared with the one ($k_H/k_D = 1.55$ (10 °C)) estimated for the H_2 activation by the [NiFe] hydrogenase from *Allochromatium vinosum*, in which the rate-determining step was attributed to an H−H cleaving process.[14]

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Supporting Information Available: Experimental details and spectral data for **1**−**5** and information on X-ray analyses, and a CIF file of the X-ray crystallographic data for **1a**,**b**, **2a**, **3a**,**b**, **4**, and **5a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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