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The Synthesis and Reactivity of a Molybdenum (IV) Stretched-Dihydrogen Complex

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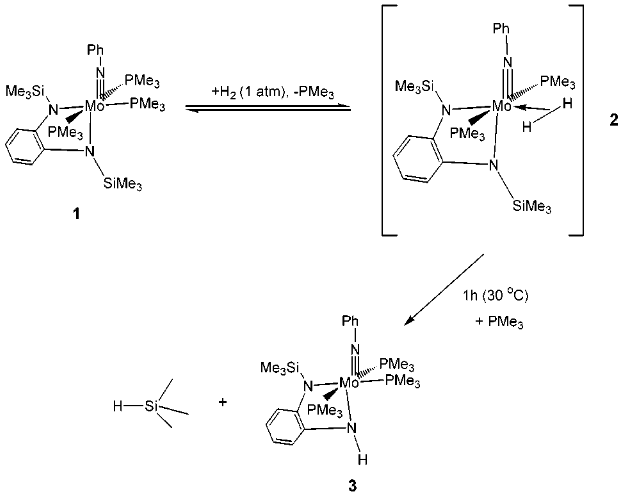
Since the original report of a molybdenum (0) dihydrogen complex by Kubas in 1984[1] there has been substantial interest in developing the synthesis and exploring the reactivity of these complexes. Metal-bound dihydrogen displays unique chemical and physical properties, can be electrophilic or superacidic, and exists in a stretched or unstretched mode.[2] Recently we have been interested in high-oxidation state molybdenum imido complexes supported by a chelating *o*-phenylenediamide ancillary ligand (o-$(Me_3SiN)_2C_6H_4$)[3] and have been exploring the possibility of generating related Mo(IV)-starting materials capable of oxidative addition reactions. Along these lines we have been able to synthesize a Mo(IV) tris-PMe_3 derivative of the above system that reacts with molecular hydrogen to afford a PMe_3-stabilized, stretched-dihydrogen complex. Of the various dihydrogen complexes known, none, to our knowledge, contain metal−ligand multiple bonds, and few contain amide functionalities.[4] Furthermore this is a rare example of a dihydrogen complex in a nominal d^2 configuration formed via the novel displacement of PMe_3 by molecular hydrogen. Our initial studies concerning the synthesis and characterization of this unique dihydrogen complex are reported herein.

Exposure of a cold (−10 °C), toluene-d_8 solution of $[Mo(NPh)(PMe_3)_3(o\text{-}(Me_3SiN)_2C_6H_4)]$[5] (**1**) to an atmosphere of molecular hydrogen (ca. 1 atm) results in a rapid color change from purple to green. The ^1H and ^{31}P NMR spectra of this solution indicate that **1** and the dihydrogen complex $[Mo(NPh)(PMe_3)_2(H_2)(o\text{-}(Me_3SiN)_2C_6H_4)]$ (**2**) are present in solution in a 1:3 ratio at −50 °C (Scheme 1). When allowed to warm to 30 °C, **2** undergoes an additional transformation to give a purple solution of $[Mo(NPh)(PMe_3)_3(o\text{-}(Me_3SiN)(NH)C_6H_4)]$ (**3**) over a 1 h period. Thus, the net reaction of **1** with H_2 is addition of H_2 across the Si−N bond of the diamide ligand.

Scheme 1



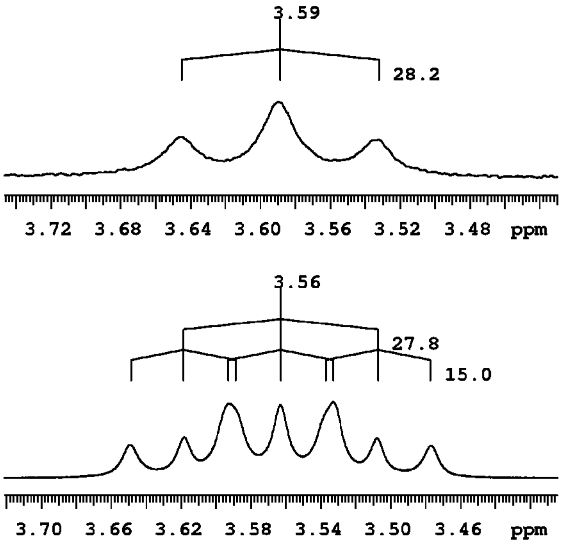


Figure 1. ^1H NMR spectra of the dihydrogen and deuterium hydride regions of **2** and **2a** respectively.

Dihydrogen complex **2** is stable for days under an atmosphere of molecular hydrogen (1 atm) at −20 °C but will convert to **3** at this temperature over a period of several weeks. Attempted isolation of **2** by concentration of toluene solutions *in vacuo* resulted in isolation of the starting material (**1**). Although efforts to scavenge PMe_3 with tris(pentafluorophenyl)borane[6] were successful, **2** remains reactive under these conditions and generates $HSiMe_3$ and unidentified metal-containing products. Presumably lack of phosphine in solution compromises the formation of **3**, and the bisphosphine analogue of **3** is not stable under these conditions. Complex **2** can be observed in degassed (H_2 free), phosphine-scavenged solutions by ^1H NMR spectroscopy, but it decomposes rapidly.

A characteristic resonance in the ^1H NMR spectrum of **2** is a broad triplet at 3.59 ppm ($^2J_{P-H} = 28$ Hz) (Figure 1). The dramatically different chemical shift of these protons relative to the hydride protons of the tungsten analogue, $[W(NPh)(PMe_3)_2H_2\text{-}(o\text{-}(Me_3SiN)_2C_6H_4)]$,[7] (9.26 ppm, br, t, $^2J_{P-H} = 40$ Hz, 18 °C, C_6D_6) prompted us to investigate the metal−hydrogen interaction in more detail.

Two methods that rely upon solution NMR spectroscopy can be used to differentiate between dihydrogen and dihydride complexes. The more reliable method uses an empirical relationship, developed by Morris, relating the $^1J_{H-D}$ coupling constant of the related deuterium hydride complex to the H−H distance (d_{HH}) in the dihydrogen complex (eq 1).[8a] The second is a relaxation-based method that relates T_1 min to d_{HH}.

$$d_{HH}\,(\text{Å}) = 1.42 - 0.0167\{J_{HD}\,(\text{Hz})\} \qquad (1)$$

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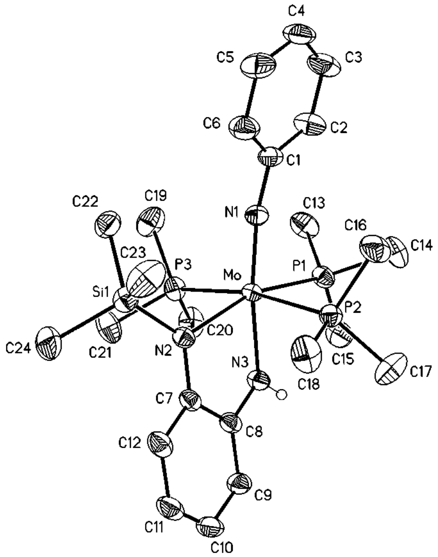


Figure 2. Thermal ellipsoid plot of **3** (thermal ellipsoids at 50% probability). Selected bond lengths (Å) and angles (deg): Mo−N(1) 1.7972(1), Mo−N(2) 2.2176(15), Mo−N(3) 2.0873(16), Mo−P(1) 2.5385(6), Mo−P(2) 2.4612(6), Mo−P(3) 2.5204(5).

The deuterium hydride isotopomer of **2** (**2a**) displays both coupling with phosphorus (t, 1:2:1, $^2J_{P-H} = 28$ Hz) and deuterium (t, 1:1:1, $^1J_{H-D} = 15$ Hz) (Figure 1). Using the $^1J_{H-D}$ of 15 Hz in eq 1 gives a value of 1.17 Å for d_{HH}, which is typical of a stretched-dihydrogen complex.[8(b)]

It is possible to correlate the distance between two nuclei to the relaxation rate due to homonuclear dipole−dipole interactions between the two nuclei as long as this is the only mechanism of relaxation. At T_1 min the equation for the dipole−dipole relaxation rate simplifies to that shown in eq 2, and the internuclear distance (r) can be found.[9]

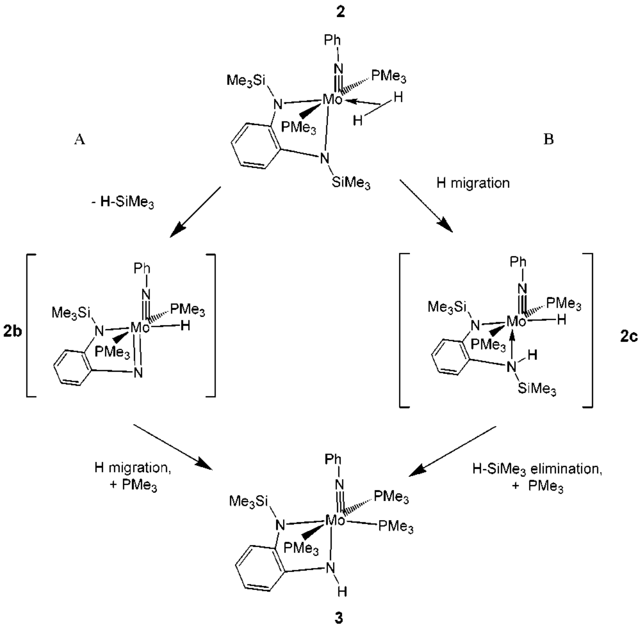
$$(T_1\ \text{min})^{-1} = 77.51\ \text{Å}^6\ \text{s}^{-1}/r^6 \qquad (2)$$

A plot of T_1 vs temperature for **2** yields a T_1 min of 36 ms, which is normal for a dihydrogen complex. Using eq 2, a value of 1.18 Å for d_{HH} (r in eq 2) is calculated and this distance is in excellent agreement with that value found through application of the measured $^1J_{H-D}$.

The tris-PMe$_3$ complex **3** is stable under inert atmosphere and can be isolated in high yields. An X-ray crystallographic study was carried out on single crystals of **3** grown from a cold toluene solution. Complex **3** crystallizes in a monoclinic unit cell, and the thermal ellipsoid plot of **3** is shown in Figure 2. The Mo−N(1) bond length of 1.7972(15) Å is typical for a Mo−N triple bond interaction.[3] The metal-amide bond lengths are also within the expected range.[3] The phosphines take up a meridianal bonding motif in **3**, and the Mo−P(1), P(2), and P(3) bond lengths of 2.5385(6), 2.4612(6), and 2.5204(5) Å, respectively, are as expected.

Some reasonable mechanisms for this transformation are shown in Scheme 2. Route A involves initial silane elimination, forming an intermediate, 18-electron, bent imido (**2b**), possibly by way of a four-centered transition state. This elimination is followed by hydride migration and coordination of PMe$_3$ to afford **3**. During this transformation the metal center is formally oxidized by two units. Mechanism B does not involve formal oxidation of the metal center. Initial H migration to an amide functionality gives the 18-electron hydrido-amine intermediate **2c**. A similar intermediate has been proposed in a mechanism involving H/D exchange with a rhenium triamide dihydrogen complex.[4] Subsequent silane elimination from **2c** and coordination of PMe$_3$ give **3**.[10]

Scheme 2



We are currently investigating the reactivity of **2** with unsaturated substrates in catalytic hydrogenation reactions.

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Supporting Information Available: Crystal data, structure refinement, atomic coordinates, bond lengths and angles for **1** and **3**, synthesis and characterization of **1**, **2**, and **3** (PDF). X-ray crystallographic file in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) PMe$_3$ does not deprotonate **2** at −20 °C in toluene; therefore, **2** is a weaker acid than [HPMe$_3$]$^+$ under these conditions; p$K\alpha^{\text{THF}}$ [HPMe$_3$]$^+$ = 8.7; Abdur-Rashid, K.; Fong, T. P.; Greaves, B.; Gusev, D. G.; Hinman, J. G.; Landau, S. E.; Lough, A. J.; Morris, R. H. *J. Am. Chem. Soc.* **2000**, *122*, 9155.

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