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Imido silyl complexes of molybdenum: synthesis, structure and unusual H₂/silane exchange

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Dedicated to Prof. Robert Morris, a true master of manipulating with hydrogen!

ABSTRACT: Reaction of complex $(\text{ArN})\text{Mo}(\text{H})(\text{Cl})(\text{PMe}_3)_3$ (**1**) with BPh_3 and silane H_3SiPh affords a new silyl complex $(\text{ArN})\text{Mo}(\text{SiH}_2\text{Ph})(\text{Cl})(\text{PMe}_3)_2$ (**3**) which catalyses facile H-H/Si-H exchange. EXSY experiments suggest that this exchange does not involve the classical pathways, such as oxidative addition of hydrogen or silane to the complex or σ -bond metathesis. It is suggested that the exchange may occur in an FLP cage comprised by the complex and the silane.

Keywords: hydrogen; silane; imido; molybdenum; EXSY

Draft

INTRODUCTION

Dihydrogen is the simplest and yet one of the most important molecules, being the integral part of industrial hydrogenation reactions.¹ Activation of its strong and nonpolar H-H bond of 432 kJ/mol² also presents a considerable challenge for chemists. Apart from poorly controlled radical reactions, cleavage of the H-H bond requires reaction center(s) featuring both nucleophilic and electrophilic properties. Indeed, the biggest breakthroughs in the activation of dihydrogen have been the discovery by Kubas of dihydrogen complexes of transition metals³ and Stephan's discovery of the Frustrated Lewis Pairs (FLP) chemistry,⁴ using ambiphilic transition metal complexes⁵ or a combination of main-group electrophiles and nucleophiles, respectively. The H-H bond can be also cleaved heterolytically in σ -bond metathesis reactions⁶ and upon addition to antiaromatically destabilized compounds, such as boroles.⁷ We have previously reported a serendipitous H-H/Si-H exchange between dihydrogen and silane catalyzed by the molybdenum complex $(\text{ArN}=\text{Mo}(\text{PMe}_3)_3(\text{H})(\text{SiH}_2\text{Ph}))$ ($\text{Ar} = 2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3$) that involves neither the oxidative addition of H-H or Si-H to metal, nor a σ -bond metathesis pathway.⁸ Although the precise nature of this reaction remains unknown, kinetic studies suggested that the exchange involves initial activation of silane by the metal complex.

Here we report the preparation of novel silyl imido complexes that mediate a similar H-H/Si-H exchange.

RESULTS AND DISCUSSION.

We have previously reported that a reaction of the imido hydride $(\text{ArN})\text{Mo}(\text{H})(\text{Cl})(\text{PMe}_3)_3$ (**1**) with the labelled silane PhSiD_3 results in exchange between the Mo-bound hydride and the

deuterium of silane, while the exchange of Mo-H for silyl does not happen.⁹ Given the results of mechanistic studies on **1**-catalyzed hydrosilylation, one could postulate that the Mo-H/Si-D metathesis proceeds via phosphine dissociation, silane oxidative addition/reductive elimination (Scheme 1, path A). Elimination of dihydrogen, leading to the formation of the silyl product **2** was not observed (Scheme 1, path B). However, we later found that if the reaction between **1** and PhSiH₃ is carried out in the presence of borane BPh₃, the sole product of the reaction is the silyl complex (ArN)Mo(SiH₂Ph)(Cl)(PMe₃)₂ (**3**). This unexpected observation suggests that the H/D exchange proceeds by some unknown non-dissociative pathway avoiding formation of the dihydride silyl complex **4**,¹⁰ e.g. by addition of Si-H across the Mo-imide multiple bond.^{11,12}

The silyl complex **3** was characterized by NMR spectroscopy. The Si-bound hydrogens give rise to a triplet at 5.93 ppm due to the coupling to two equivalent phosphines (³J_{H-P} = 3.3 Hz). The observation of satellites with ¹J_{H-Si} = 158 Hz and correlation in the ¹H-²⁹Si HSQC NMR with the ²⁹Si signal at 6.3 ppm support the assignment to the SiH₂Ph group. The phosphines contribute 18H to the overlapping signals at 1.21-1.25 ppm (m, 30H, 4CH₃ of NAr and 2PMe₃) and give rise to one singlet in ³¹P NMR at 0.30 ppm.

Scheme 1. Reactions of 1 with H_3SiPh .

Addition of PMe_3 to a solution of **3** in benzene results in clean generation of the silyl complex **2**. Alternatively, **2** can be generated by a reaction of the alkoxide complex $(\text{ArN})\text{Mo}(\text{OCy})(\text{Cl})(\text{PMe}_3)_3$ (**5**) with excess PhSiH_3 . When only an equimolar amount of PhSiH_3 is used, the reaction produces a mixture of **2** and the parent compound $(\text{ArN})\text{Mo}(\text{H})(\text{Cl})(\text{PMe}_3)_3$.¹³ In the ^1H NMR spectrum, the SiH_2Ph group of **2** is evinced by a phosphorus-coupled triplet at 5.78 ($^3J_{\text{H-P}} = 3.4$ Hz, $^1J_{\text{H-Si}} = 154$ Hz) integrated as 2H. The phosphine ligands give rise to a broad doublet at 1.16 ppm ($J_{\text{H-P}} = 4.6$ Hz, 9H) and a virtual triplet at 1.25 (vt, $J_{\text{H-P}} = 3.2$ Hz, 18H). The connectivity **2** was further confirmed by X-ray diffraction study.

The molecular structure of **2** is presented in Figure 1. The geometry can be characterised as distorted octahedral. The linear Mo1-N1-C1 bond angle ($177.6(6)^\circ$) and short Mo-N bond of $1.755(7)$ Å indicate the presence of a triple Mo-imido bond, provided by donation of the imido lone pair to molybdenum.¹⁴ The Mo1-Si1 bond of $2.558(3)$ Å is longer than in the related imido silyl complex (ArN)Mo(H)(SiH₂Ph)(PMe₃)₃ (**5**), $2.501(1)$ Å.¹⁵ This difference can be attributed to the proximity of a bulky chloride ligand and to increased *trans*-influence due to the more open Si1-Mo1-P3 bond angle than in **5**, $142.71(9)$ vs $131.78(2)^\circ$, respectively. The significant decrease of the Si1-Mo1-P3 bond angle in comparison with the almost linear P1-Mo1-P2 angle of $175.44(9)^\circ$ illustrates avoided *trans*-influence between the stronger *trans*-influencing silyl and the *trans* PMe₃.

As previously stated, the 16e silyl complex **3** can be generated *in situ* by reacting the hydride **1** with PhSiH₃ in the presence of BPh₃. When this reaction is carried out in benzene in a closed flask the evolved hydrogen can be observed as a resonance at 4.54 ppm in ¹H NMR. We were intrigued by the observation of a noticeable broadness of this peak accompanied by the broadness of the free silane signal at 4.23 ppm. An exchange spectroscopy (EXSY) study at room temperature showed that the H₂ resonance and the free silane resonance are in exchange. Even more remarkably, we did not observe any exchange of the Mo-SiH₂Ph group with either hydrogen or silane.

Figure 1. Molecular structure of complex **2**. Selected bond lengths (Å) and angles (°): Mo1-N1 1.755(7), Mo1-Si1 2.558(3), Mo1-Cl1 2.572(2), Mo1-P1 2.490(2), Mo1-P2 2.506(2), Mo1-P3 2.576(3), N1-Mo1-Cl1 173.8(2), Si1-Mo1-Cl1 70.94(8), P3-Mo1-Cl1 72.38(8), Si1-Mo1-P3 142.71(9), P1-Mo1-P2 175.44(9).

Carrying out the EXSY experiments in the temperature range 10–41°C allowed for determination of the activation parameters from kinetic measurements: $\Delta H^\ddagger = 54(12)$ J/mol, $\Delta S^\ddagger = -87(39)$ J/(K·mol). The negative entropy of activation indicates that the exchange proceeds via an associative mechanism. A very similar H-H/Si-H exchange has been previously observed for the related hydrido silyl complex **5**.⁸ In that case, like for complex **2**, there was no exchange between either of the components and the metal complex but the presence of the molybdenum complex was required to catalyse this process. The direct involvement of phosphine in the exchange can be ruled out because adding PMe_3 to a mixture of phenylsilane and hydrogen does not bring about any observable EXSY phenomenon.

Although, the detailed mechanistic picture is still unclear, we can surely rule out the possibility of hydrogenation of the Mo-Si bond or the Mo-Si/Si-H exchange by σ -bond metathesis, because

these reactions would lead to the appearance of the MoSiH_2Ph signal in the EXSY spectrum, which was not observed. We tentatively postulate that the exchange occurs by an FLP-type mechanism (FLP=Frustrated Lewis Pairs⁴), i.e. by encapsulation of hydrogen into a cage comprised by **3** (acting as the acid component) and silane acting as the base (Chart 1), before the latter undergoes oxidative addition to molybdenum. However, this idea requires thorough verification by computational chemists.

Chart 1. A possible FLP mechanism for the **3-catalysed $\text{H}_2/\text{PhSiH}_3$ exchange.**

In conclusion, we prepared a silyl imido complex of molybdenum that catalyses hydrogen/silane exchange without invoking the usual oxidative addition/reductive elimination or σ -bond metathesis pathways. The exact nature of this usual process, however, remains unknown.

EXPERIMENTAL SECTION

All manipulations were carried out using conventional inert atmosphere glove-box and Schlenk techniques. Dry diethyl ether, toluene, hexanes, and acetonitrile were obtained using Innovative Technology solvent purification columns and other solvents were dried by distillation over appropriate drying agents. C_6D_6 and PhMe-d_8 were dried by distillation over K/Na alloy. NMR spectra were obtained with Bruker DPX-300 and Bruker DPX-600 instruments (^1H : 300 and 600 MHz; ^2D : 92.1 MHz; ^{13}C : 75.5 and 151 MHz; ^{29}Si : 59.6 and 119.2 MHz; ^{31}P : 121.5 and 243 MHz; ^{11}B : 96.3 and 192.6 MHz). IR spectra were measured on an ATI Mattson FTIR spectrometer.

Elemental analyses were performed by the “ANALEST” laboratory (University of Toronto). PhSiH_3 was prepared by the reaction of PhSiCl_3 with LiAlH_4 . Compounds $(\text{ArN}=\text{MoCl(H)(PMe}_3)_3$ (**1**) and $(\text{ArN})\text{Mo(OCy)(Cl)(PMe}_3)_3$ (**4**) were prepared according to literature procedures.⁹ All catalytic and NMR scale reactions were done under nitrogen atmosphere using NMR tubes equipped with Teflon valves. NMR analysis was performed at room temperature unless stated otherwise.

NMR scale preparation of $(\text{ArN})\text{Mo(SiH}_2\text{Ph)(Cl)(PMe}_3)_2$ (3**).** BPh_3 (9.4 mg, 0.040 mmol) was added to a solution of **1** (21.0 mg, 0.04 mmol) and PhSiH_3 (4.8 μl , 0.04 mmol) in C_6D_6 (0.60 ml) in a vial. Immediate formation of the precipitate of $\text{Me}_3\text{B}\cdot\text{PMe}_3$ was observed. The solution was filtered and transferred into an NMR tube. NMR analysis showed quantitative formation of $(\text{ArN})\text{Mo(SiH}_2\text{Ph)(Cl)(PMe}_3)_2$. ^1H NMR (300 MHz, C_6D_6 ; 297 K, δ , ppm): 1.21-1.25 (m, 30H, 4 CH_3 of NAr and 2 PMe_3), 3.77 (sept, $^3J_{\text{H-H}} = 6.9$ Hz, 2H, 2CH, NAr), 5.93 (t+sat, $^3J_{\text{H-P}} = 3.3$ Hz, $^1J_{\text{H-Si}} = 158.2$ Hz, 2H, SiH_2Ph), 6.87-7.31 (m, 6H, *m*-H and *p*-H of SiH_2Ph and NAr), 7.88 (d, $^3J_{\text{H-H}} = 7.5$ Hz, 2H, *o*-H, SiH_2Ph). ^{31}P NMR (121.5 MHz; C_6D_6 ; 297 K, δ , ppm): 0.3 (s, PMe_3). ^1H - ^{13}C HSQC NMR (300 MHz; 75.5 MHz; $J = 145.0$ Hz; C_6D_6 ; 297 K, δ , ppm): 15.8 (PMe_3), 23.7 (CH_3 , NAr), 29.2 (CH, NAr), 123.0 (*m*-C and *p*-C of NAr and SiH_2Ph), 125.9, 126.5, 127.5, 136.5 (*o*-C, SiH_2Ph). ^1H - ^{29}Si HSQC NMR (300 MHz; 59.6 MHz; $J = 200.0$ Hz; C_6D_6 ; 297 K, δ , ppm): 6.3 (SiH_2Ph).

Synthesis of $(\text{ArN})\text{Mo(SiH}_2\text{Ph)(Cl)(PMe}_3)_3$ (2**).** Phenylsilane (50.0 μl , 0.527 mmol) was added to a solution of **5** (20.0 mg, 0.032 mmol) in toluene. The quick release of hydrogen was observed. The solution was stored at -30 °C. The product $(\text{ArN})\text{Mo(SiH}_2\text{Ph)(Cl)(PMe}_3)_3$ crystallized as tetragonal crystals. Yield: 40%. ^1H NMR (300 MHz, C_6D_6 ; 297 K, δ , ppm): 1.16 (bd, $J = 4.6$ Hz, 9H, 1 PMe_3), 1.22 (d, $J = 6.7$ Hz, 12H, 4 CH_3 , 2 Pr^i), 1.25 (vt, $J = 3.2$ Hz, 18H, 2 PMe_3), 4.00 (sept,

$J = 6.7$ Hz, 2H, 2Prⁱ), 5.78 (t+sat, $^3J_{\text{H-P}} = 3.4$ Hz, $^1J_{\text{H-Si}} = 153.8$ Hz, 2H, SiH₂Ph), 6.86-6.93 (m, 2H, *m*-H, Ar), 6.95-7.02 (m, 1H, *p*-H, Ar), 7.21-7.26 (m, 1H, *p*-H, Ph), 7.28-7.33 (m, 2H, *m*-H, Ph), 8.31-8.49 (m, 2H, *o*-H, Ph). ^{31}P NMR (121.5 MHz; C₆D₆; 297 K, δ , ppm): -4.7 (bs, PMe₃). ^{13}C -NMR (75.5 MHz; C₆D₆; 298 K; δ , ppm): 19.4 (bs, 2PMe₃), 19.9 (bs, 1PMe₃), 25.3 (s, 4CH₃, 2Prⁱ), 27.6 (bs, 2C-H, 2Prⁱ), 124.4 (2 *m*-C-H, Ar), 126.3 (*p*-C-H, Ar), 127.6 (2*m*-C-H, Ph), 127.8 (*p*-C-H, Ph), 137.9 (2 *o*-C-H, Ph), 145.6 (*ipso*-C-C, Ar), 152.1 (*ipso*-C-N, Ar). Elem. Anal. (%): calc. for C₂₇H₅₁ClMoNP₃Si (642.100): C 50.50, H 8.01, N 2.18; found: C 49.95, H 7.52, N 2.35.

X-ray diffraction study. Single crystal was coated with polyperfluoro oil and mounted on the Bruker SMART-6K diffractometer with a CCD area detector at 123(2) K.¹⁶ The Bruker SAINT program¹⁷ was used for data reduction. An absorption correction based on measurements of equivalent reflections was applied (SADABS).¹⁸ The structure was solved by direct methods and refined by full-matrix least squares procedures, using $\omega(|F_o|^2 - |F_c|^2|)^2$ as the refined function.¹⁹ All non-hydrogen atoms were found from the electron density map and refined with anisotropic thermal parameters, whereas all hydrogen atoms were calculated geometrically and refined using the “riding” model. The accuracy of this X-ray study reflects the poor quality of available single crystals and their high absorption factor but is nevertheless sufficient to establish and discuss the molecular geometric parameters.

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to either the imine or chloride ligands. Whereas coordination to the imine moiety is less likely because of the steric encumbrance imposed by the bulky Dipp substituent, the latter possibility cannot be ruled out.

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Captions:

Scheme 1. Reactions of **1** with H₃SiPh.

Figure 1. Molecular structure of complex **2**. Selected bond lengths (Å) and angles (°): Mo1-N1 1.755(7), Mo1-Si1 2.558(3), Mo1-Cl1 2.572(2), Mo1-P1 2.490(2), Mo1-P2 2.506(2), Mo1-P3 2.576(3), N1-Mo1-Cl1 173.8(2), Si1-Mo1-Cl1 70.94(8), P3-Mo1-Cl1 72.38(8), Si1-Mo1-P3 142.71(9), P1-Mo1-P2 175.44(9).

Chart 1. A possible FLP mechanism for the **3**-catalysed H₂/PhSiH₃ exchange.

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