Diversity of Catalysis by an Imido-Hydrido Complex of Molybdenum. Mechanism of Carbonyl Hydrosilylation and Silane Alcoholysis

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Stoichiometric reductions of multiple bonds by early transition metal hydrides are well established,[1] but little is known about their catalytic versions such as hydrosilylation of carbonyls.[2,3] It is generally believed that hydrosilylation on late metals proceeds via a Chalk−Harrod type sequence of Si−H activation, silyl migration, and C−H elimination.[4,5] But very little mechanistic data are available, and in no case were all these key steps observed on a single metal center.[5] For unsaturated carbonyls, an alternative mechanism was suggested, in which carbonyl coordinates to the silicon atom of the silyl ligand, followed by hydride shift.[6]
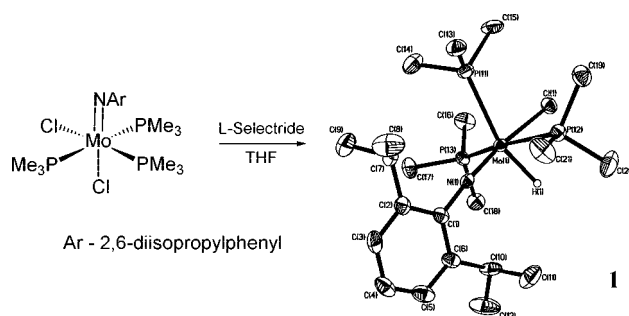
In the case of titanocene catalyst, Buchwald suggested a Ti−O/H-Si σ-bond metathesis as the final step.[3c] Toste et al. provided compelling evidence that hydrosilylation by a Re(V) dioxo complex includes Si−H addition to the Re=O bond in the silane activation step.[7] Related catalysis by oxo-complexes of Mo appears to follow a similar mechanism.[8] However, kinetic studies by Abu-Omar suggest that this pathway may not be generally applicable even for other Re(V) oxo-complexes.[9] Here, we report the catalytic behavior of a new imido/hydride complex of Mo and a mechanistic investigation of its catalysis of hydrosilylation.

The reaction of $(ArN)MoCl_2(PMe_3)_3$ with L-selectride allows for selective production of a monosubstituted product $(ArN)Mo(Cl)(H)(PMe_3)_3$ (**1**), characterized by NMR, IR, and X-ray diffraction analysis (Scheme 1). The complex has an octahedral structure, with the chloride lying trans to the imido group. The PMe_3 trans to the hydride forms a longer Mo−P bond than the *cis*-phosphines (2.572(1) Å vs 2.485(1) and 2.469(1) Å). The ^{1}H NMR spectrum shows a downfield hydride signal at δ 5.31 (dt, $^2J_{H−P} = 28.5$ Hz, $^2J_{H−P} = 51.9$ Hz) coupled to the two equivalent *cis*-phosphines and the unique *trans*-PMe_3. The presence of a hydride is also evident from the observation of an IR stretch at 1714 $cm^{−1}$.

Complex **1** has been found to catalyze a diversity of silane reactions (Table 1), including a rare example of selective catalytic hydrosilylation of nitrile to imine,[10,11] and is only the second example of an imido catalyst for hydrosilylation.[9c] Carbonyls are converted to protected alcohols, whereas 1-hexene is mainly reduced to hexane. Only a sluggish reaction is observed with 1-octyne. **1** also catalyzes alcoholysis and hydrolysis of $PhSiH_3$ (1−3 h) to give H_2 and silyl ether and polysiloxane, respectively.

The mechanism of hydrosilylation of benzaldehyde was scrutinized by studying the individual steps under stoichiometric conditions. Complex **1** does not react with silane, which is in contrast to $HSiR_3$ addition to the Re=O bond documented by Toste et al.[7a] and H/Cl exchange observed by Abu-Omar.[9c] However, it undergoes a slow H/D exchange (78% after 3 days) when reacted with D_3SiPh.

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Scheme 1. Preparation of Complex **1**

In contrast, **1** easily reacts with PhC(O)H affording the benzoxy derivative $(ArN)Mo(Cl)(OCH_2Ph)(PMe_3)_3$ (**2**), as the major product. An intermediate *trans*-$(ArN)Mo(Cl)(H)(\eta^2$-PhC(O)H)(PMe_3)_2$ (**3**, Scheme 2), with the aldehyde ligand trans to the hydride, was observed by ^{1}H NMR. At −5 °C, **3** is the sole reaction product. The η^2-coordination of PhC(O)H in **3** results in an upfield shift of the OCH proton (5.77 ppm) and a significant reduction of its C=O IR stretch (1595 $cm^{−1}$).[12] The nonequivalent trans phosphine groups give rise to a pair of coupled doublets ($^2J_{P−P} = 109.3$ Hz) at 1.4 and −5.6 ppm in the ^{31}P NMR. At large aldehyde concentration, the reaction obeys pseudo-first-order kinetics (k_1(268 K) = 7.6 × $10^{−4}$ $s^{−1}$),[13] consistent with a rate-limiting PMe_3 elimination, followed by the fast addition of aldehyde. PMe_3 elimination is reversible, as addition of excess phosphine to **3** cleanly regenerates complex **1** and free PhC(O)H.

In the absence of PMe_3, **3** decomposes to an intractable mixture of products (2 h). But with an equivalent of PMe_3 added, it slowly (5 h) rearranges at room temperature into **2**. The reaction is first order in **3** and most likely proceeds via phosphine elimination and readdition to give an isomer of **2** where the hydride ligand is cis to the aldehyde. Fast hydride migration to the cis-coordinated aldehyde furnishes the benzoxy ligand. Analogous hydride migration has been observed previously for a hydride complex of Re.[9c] The lower value of k_1 (2.1 × $10^{−4}$ $s^{−1}$ at 295 K) for this process compared to that of the previous step is consistent with the difference in the trans influence of phosphine and hydride ligands.

A fast reaction of **3** with H_3SiPh regenerates the hydride **1** and closes the cycle. Kinetic measurements in the presence of a large excess of phosphine revealed a first-order dependence on the complex and the silane. The $1/k_{eff}$ is proportional to phosphine concentration, which suggests the reaction mechanism depicted in Scheme 2. Whether silane activation proceeds via Si−H addition to give a Mo(VI) complex or via σ-bond metathesis[3c] is not clear at this point, although we favor the latter possibility.

***Table 1.*** Catalytic Hydrosilylation and Alcoholysis Mediated by **1**

entry	substrate	silane	conversion of org. substrate	product(s)	conditions	yield, %[a]
1	PhC(O)H	PhSiH₃	100%	PhSiH₂(OCH₂Ph)/PhSiH(OCH₂Ph)₂	3 h/50 °C	32/68
2	PhC(O)H	PhMeSiH₂	68%	MePhHSi(OCH₂Ph)	1 day/22 °C	68
3	PhC(O)H	(EtO)₃SiH	95%	(EtO)₃Si(OCH₂Ph)/(EtO)₂Si(OCH₂Ph)₂/(EtO)Si(OCH₂Ph)₃	1 day/50 °C	13/39/42
4	PhC(O)Me	PhSiH₃	100%	PhSiH₂(OCHMePh)/PhSiH(OCHMePh)₂/PhSi(OCHMePh)₃/PhCH₂CH₃	1 day/50 °C	39/33/5/23
5	1-hexene	PhSiH₃	89%	C₆H₁₃SiH₂Ph/2-hexene/Hexane	1 day/60 °C	3/6/80
6	1-octyne	PhSiH₃	35%	PhSiH₂(CH=CH)Hex(α)/PhSiH₂(CH=CH)Hex(β)/ PhSiH(CH=CH)Hex₂(α₂)/PhSiH(CH=CH)Hex₂(β₂)	15 days/22 °C	1/2/4/4
7	ethanol	PhSiH₃	100%	PhSiH₂(OEt)/PhSiH(OEt)₂	1 h/22 °C	26/74
8	PhCN	PhSiH₃	100%	PhH₂Si(N=CHPh)/PhHSi(N=CHPh)₂	13 days/50 °C	76/24

[a] All reactions were performed using 5 mol % of **1**. Yields were determined by NMR using TMS as an internal standard.

Scheme 2. Mechanism of Aldehyde Hydrosilylation by **1**
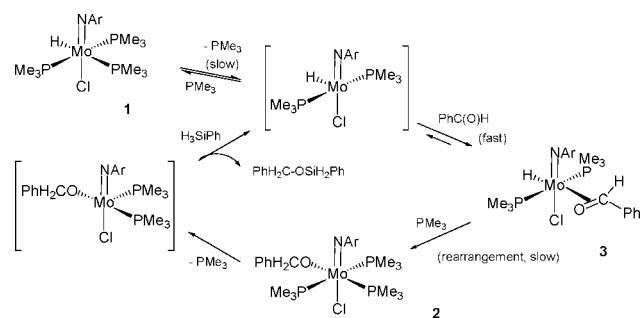
Scheme 3. Mechanism of Silane Alcoholysis by **1**
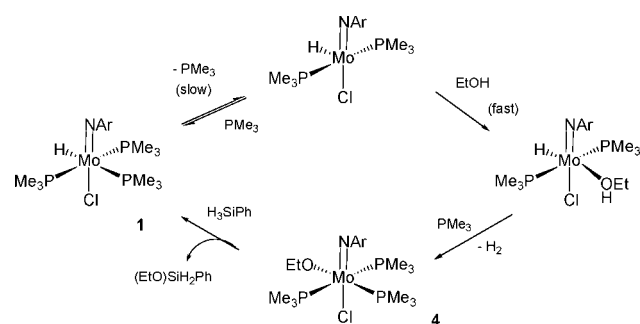
The hydrosilylation of aldehydes mediated by **1** is different from the previously established schemes in that it (i) does not involve initial Si—H bond addition to the metal as in the Chalk—Harrod mechanism,[4] (ii) does not proceed via Si—H addition to the M=X bond as in Toste hydrosilylation,[7] and (iii) does not include an attack of an external carbonyl on coordinated silyl or silane as suggested by Chan et al.[6] and Abu-Omar et al.[9c]

The study of the reaction between **1** and EtOH revealed first-order kinetics in **1** and saturation behavior upon increase of alcohol concentration. At a 20-fold excess of EtOH, $1/k_{eff}$ is proportional to phosphine concentration, which suggests that the reaction starts with a reversible dissociation of PMe₃, followed by the addition of alcohol to Mo (Scheme 3).[13] Such addition probably acidifies the OH bond enough to allow for proton transfer to the hydride to generate dihydrogen. Elimination of H₂ and phosphine readdition furnish the product (ArN)Mo(Cl)(OEt)(PMe₃)₃ (**4**),[13] which like **2** can react with silanes to give the hydrosilylation product R₃SiOEt and **1**. In contrast, earlier suggested mechanisms of silane alcoholysis implied silane activation by an electrophilic metal center, making it amenable to an attack by an external nucleophile.[14] Also, the above kinetics are not consistent with a direct proton transfer from EtOH to **1**, which is observed in systems with "dihydrogen bonding".[15] The difference likely comes from the lower acidity of EtOH in comparison with perfluoro alcohols, normally used for dihydrogen bonding.

In conclusion, complex **1** catalyzes a variety of silylation reactions, including a rare example of selective catalytic hydrosilylation of nitriles to imines. The mechanism of aldehyde hydrosilylation and silane alcoholysis mediated by **1** includes the substrate activation to give an alkoxy complex which then reacts with silane to furnish the alkoxy silane.

Supporting Information Available: Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA8085388