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An Unexpected Mechanism of Hydrosilylation by a Silyl Hydride Complex of Molybdenum

Andrey Y. Khalimon,[†] Stanislav K. Ignatov,[‡] Razvan Simionescu,[†] Lyudmila G. Kuzmina,[§] Judith A. K. Howard,[#] and Georgii I Nikonov*,[†]

[†]Chemistry Department, Brock University, 500 Glenridge Avenue, St. Catharines, Ontario L2S 3A1, Canada

[‡]Chemistry Department, N. I. Lobachevsky State University of Nizhnii Novgorod, Gagarin Avenue 23, 603950 Nizhny Novgorod, Russia

[§]N. S. Kurnakov Institute of General and Inorganic Chemistry, 31 Leninskii prospect, Moscow 119991, Russia

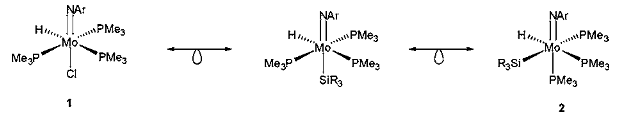
[#]Chemistry Department, University of Durham, South Road, Durham DH1 3LE, U.K.

Supporting Information

ABSTRACT: Carbonyl hydrosilylation catalyzed by (ArN)Mo(H)(SiH_2Ph)(PMe_3)$_3$ (**3**) is unusual in that it does not involve the expected Si−O elimination from intermediate (ArN)Mo(SiH_2Ph)(O^iPr)(PMe_3)$_2$ (**7**). Instead, **7** reversibly transfers β-CH hydrogen from the alkoxide ligand to metal.

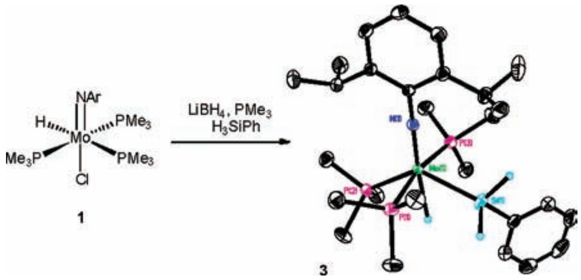
The need for inexpensive and less toxic catalysts has recently fueled significant interest in nonprecious metal catalysis.[1] In the field of carbonyl hydrosilylation,[2] titanium,[3] zirconium,[4] molybdenum,[5,6] tungsten,[7] rhenium,[8] iron,[9] and nickel[10] catalysts have been developed. Mechanistic studies revealed several reaction pathways based on Si−H oxidative addition:[6a,11] Si−H addition to M═O bonds,[8a] ionic hydrosilylation,[7,8b] and Si−H heterolytic splitting on M−O bonds.[6b,10] In particular, our group found that hydrosilylation of PhC(O)H by (ArN)Mo(H)(Cl)(PMe_3)$_3$ (**1**) proceeds via dissociation of PMe_3 trans to hydride and carbonyl coordination to give *trans*-(ArN)Mo(Cl)(H)(η^2-C(O)HPh)(PMe_3)$_2$ followed by the rate-determining rearrangement into (ArN)Mo(Cl)(OBn)(PMe_3)$_3$. In order to eliminate this rate-determining step, we sought to prepare an analogue of **1** having either the hydride or silyl (the required components of the Ojima mechanism[11]) in the cis position to the incoming carbonyl. We reckoned that the hypothetical complex **2** (Chart 1) would be an ideal target because it would place the PMe_3 ligands trans to each of the strongest trans-influence ligands (imido,[12] hydride, and silyl[13]). Attempts to prepare **2** resulted in its isomer (ArN)Mo(H)(SiH_2Ph)(PMe_3)$_3$ (**3**), which catalyzes hydrosilylation by an unusual mechanism.

Chart 1. Isolobal Relationship between 1 and 2



Complex **3** was prepared according to Scheme 1 and characterized by spectroscopic methods and X-ray diffraction analysis. Rewardingly, **3** turned out to be a much better catalyst than compound **1** (Table 1).[14] However, to our surprise, an X-ray study of **3** revealed a geometry very different from what was expected for compound **2**. First of all, the hydride ligand in **3** unexpectedly occupies the site trans to the imido group.[15] Second, the Mo−P distance to the PMe_3 trans to the silyl is very close to the Mo−P bond lengths to two mutually trans phosphines [2.4699(5) Å vs 2.4671(5) and 2.4861 (5) Å]. This decreased silyl trans influence is obviously a result of a decreased Si−Mo−P_{trans} bond angle of 131.78(2)°. Although in **3** the bulky PMe_3 and ArN groups are placed cis to each other, the electronic factor (trans influence) is clearly not at play, and thus the overall geometry should be dictated by sterics.[16]

Scheme 1. Preparation of Complex 3



To understand better the increased catalytic activity of **3**, stoichiometric reactions were carried out. ^1H EXSY NMR revealed fast exchange between the silicon-bound protons and free $PhSiH_3$, but no exchange with the molybdenum-bound hydride in the range 30−50 °C, ruling out Si−H elimination as the first step in silyl/silane exchange.[17]

We then looked at the possibility of PMe_3 dissociation from **3** and a σ-bond metathesis or oxidative addition/reductive elimination type of sequence for the silyl/silane exchange. To our surprise, a variable-temperature $^{31}P-^{31}P$ EXSY NMR study revealed a much more facile intramolecular phosphine exchange [$k_{295.1}^{intra}$ = (9.1 ± 0.1) × 10^{-2} s^{-1}][18] than the intermolecular exchange with the free PMe_3 [$k_{295.1}^{inter}$ = (1.80 ± 0.08) × 10^{-3} s^{-1}].[19]

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Table 1. Hydrosilylation of Organic Substrates at Room Temperature with 5 mol % Load of 3[a]

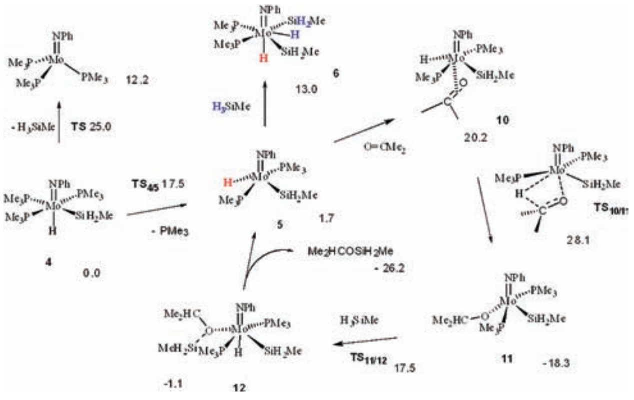
entry	substrate	silane	time	products	yield,[c] %
1	PhHC(O)	$PhSiH_3$	15 min	$PhH_2Si(OBn)/PhHSi(OBn)_2$	47/53
2	PhHC(O)	$PhMeSiH_2$	18 h	Ph(Me)HSi(OBn)	100
3	PhHC(O)	$(EtO)_3SiH$	18 h	$(EtO)_3Si(OBn)/(EtO)_2Si(OBn)_2/(EtO)Si(OBn)_3$	41/29/30
4	$Me_2C(O)$	$PhSiH_3$	3.4 h	$PhH_2Si(O^iPr)/PhHSi(O^iPr)_2$	73/17
5[b]	PhMeC(O)	$PhSiH_3$	24 h	$PhH_2Si[OCH(Me)Ph]/PhHSi[OCH(Me)Ph]_2/PhCH_2CH_3$	45/33/22
6	EtOH	$PhSiH_3$	20 min	$PhH_2Si(OEt)/PhHSi(OEt)_2$	67/33
7	PhCN	$PhSiH_3$	19.7 h	$(PhHC{=}N)SiH_2Ph$	20

[a] Conditions: 5.0 mol % **3**; solvent C_6D_6; the ratio of substrate/silane is 1:1; RT unless stated otherwise. [b] 1 mol % **3** was used; 50 °C. [c] Yields were determined according to ^1H NMR, using tetramethylsilane as the standard.

The positive entropy of activation ($\Delta S^{\ddagger}_{intra}$ = 14.6 ± 5.2 cal K^{-1} mol^{-1}) suggests a dissociatively activated mechanism, but its details remain unknown.[20] Fluxional octahedral complexes are rare and are typically observed for polyhydride compounds.[21] The fluxionality of **3** is particularly remarkable in comparison with the rigid structure of the closely related compound **1**. The large positive $\Delta S^{\ddagger}$ for the intermolecular PMe_3 exchange ($\Delta S^{\ddagger}_{inter}$ = 30.9 ± 10.6 cal K^{-1} mol^{-1}) suggests a dissociative mechanism that should lead to a coordinatively unsaturated species $(ArN)Mo(H)(SiH_2Ph)(PMe_3)_2$, which can be prone to interact with the free silane. To our further surprise, the rate of silyl/silane exchange [$k_{295.1}$ = (2.7 ± 0.1) × 10^{-3} s^{-1}] is slightly faster than that for the bound/free phosphine exchange, although the activation parameters ($\Delta S^{\ddagger}$ = 34.6 ± 5.6 cal K^{-1} mol^{-1} and $\Delta H^{\ddagger}$ = 31.0 ± 1.7 kcal mol^{-1}) suggested that the overall process is still dissociative.[22] This puzzle (the dissociative mechanism of silane exchange but slower PMe_3 dissociation and much slower $PhSiH_3$ dissociation) was solved by the remarkable observation that the bound/free PMe_3 exchange is facilitated by the addition of excess $PhSiH_3$ [$k^{inter}_{295.1}$ = (4.00 ± 0.05) × 10^{-3} s^{-1}].[23] To the best of our knowledge, this is the first observation of a dissociatively activated X/Y interchange[24] in which the incoming nucleophile Y (in this case, silane) lacks a lone pair of electrons.

Consistent with our experimental observations, the density functional theory (DFT) study[25] of gas-phase reactions of the model complex $(PhN)Mo(H)(SiH_2Me)(PMe_3)_3$ (**4**) suggested easier PMe_3 than silane dissociation (Scheme 2). The addition of $MeSiH_3$ to the 16-electron intermediate $(PhN)Mo(H)(SiH_2Me)(PMe_3)_2$ (**5**) goes via a barrier of 12.8 kcal mol^{-1} to give the Mo^{VI} d^0 product $(PhN)Mo(H)_2(SiH_2Me)_2(PMe_3)_2$ (**6**). This compound exhibits two types of hydrides: one trans to the imido, which is not involved in the exchange with silane, and another cis to the imido and two silyl groups. The latter hydride is formed upon Si–H addition and is involved in the exchange. We found experimental evidence for the feasibility of such an unusual molybdenum(VI) bis(silyl) intermediate.[26] The NMR reaction of complex *trans*-$(ArN)Mo(SiH_2Ph)(O^iPr)(PMe_3)_2$ (**7**) vide infra with excess $PhSiH_3$ at −45 °C showed the fast formation of $(ArN)Mo(H)_2(SiH_2Ph)_2(PMe_3)_2$ (**8**) in a mixture with the hydrosilylation products PhH_2SiO^iPr and $PhHSi(O^iPr)_2$.

Scheme 2. DFT-Calculated Mechanism of Hydrosilylation by 4 (Free Energies in kcal mol^{-1})



In a further attempt to understand the mechanism of carbonyl hydrosilylation, the reaction of **3** with acetone was studied. With 1 equiv of acetone, carbonyl insertion across the Mo–H bond takes place. The product **7** was observed in a mixture with the starting complex **3** and acetone, suggesting an equilibrium (Scheme 3).[27] The addition of excess PMe_3 to the mixture does not result in the expected Si–O elimination but merely shifts equilibrium toward **3**, suggesting *β*-CH activation in the O^iPr group. Reversible carbonyl insertion into an early transition metal–hydride bond is very rare[28] because alkoxide ligands to electropositive early metals usually defy CH activation. *β*-CH activation in the alkoxide ligand was further confirmed by the treatment of **7** with 1 equiv of benzonitrile, which resulted in fast transfer hydrogenation of the nitrile and quantitative formation of the benzylidenamide **9** formed as a mixture of two isomers.[29] Even more surprisingly, the addition of a different silane, *m*-$TolSiH_3$, to **7** results in quantitative regeneration of **3** with complete retention of the SiH_2Ph group. Therefore, the silyl ligand plays an unusual role of a spectator ligand, which is at odds with the classical Ojima mechanism of hydrosilylation.[11]

Scheme 3. Preparation and Reactivity of 7

The DFT study of a possible mechanism of hydrosilylation suggested that acetone coordination to **5** gives the high-energy adduct **10**. Carbonyl insertion into the Mo–H bond gives complex **11**, a model for **7** (Scheme 2). Complex **11** undergoes heterolytic splitting of silane on the Mo–O bond[6] via the rate-determining $\mathbf{TS_{11/12}}$ to give the silyl ether adduct **12**, which easily dissociates (barrier of 2.2 kcal mol^{-1}) the product $MeH_2Si(O^iPr)$ and regenerates the catalyst **5**.

In conclusion, we discovered unexpected features of the mechanism of hydrosilylation catalyzed by the silyl hydride complex **3**, such as the spectator role of the silyl ligand and a rare example of reversible C−H activation in the alkoxy intermediate.

ASSOCIATED CONTENT

Supporting Information

X-ray crystallographic data in CIF format and experimental and computational details. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: gnikonov@brocku.ca.

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(14) For example, hydrosilylation of PhC(O)H catalyzed by **1** requires 3 h at 50 °C (ref 6a) versus 15 min at room temperature in the **3**-catalyzed reaction.

(15) The hydride was located from Fourier difference synthesis and refined isotropically. Final R1 = 0.0320.

(16) The open N−Mo−Si bond angle of 108.24(5)° and the large N/Si separation (3.515 Å) rule out any Si−N interaction as a driving force for this unusual geometry. Similarly, the large silicon···hydride separation of 2.328 Å is not consistent with any Si−H interaction.

(17) A labeling experiment with D_3SiPh, however, proves the occurrence of a slow Mo−H/$PhSiD_2$-D exchange.

(18) $\Delta S^{\ddagger}_{\mathrm{intra}} = 14.6 \pm 5.2$ cal K^{-1} mol^{-1}, $\Delta H^{\ddagger}_{\mathrm{intra}} = 23.0 \pm 1.7$ kcal mol^{-1}, and $\Delta G^{\ddagger}_{295.1,\mathrm{intra}} = 18.7 \pm 3.2$ kcal mol^{-1}.

(19) $\Delta S^{\ddagger}_{\mathrm{inter}} = 30.9 \pm 10.6$ cal K^{-1} mol^{-1}, $\Delta H^{\ddagger}_{\mathrm{inter}} = 30.3 \pm 3.4$ kcal·mol^{-1}, and $\Delta G^{\ddagger}_{295.1,\mathrm{inter}} = 21.2 \pm 6.5$ kcal mol^{-1}

(20) The positive entropy of activation is not consistent with the conventional twist mechanism: (a) Bailar, J. C. Jr. *J. Inorg. Nucl. Chem.* **1958**, *8*, 165. (b) Bickley, D. G.; Serpone, N. *Inorg. Chem.* **1976**, *15*, 2577. (c) For fluxional octahedral complexes with negative entropies of activations, see: Ismail, A. A.; Sauriol, F.; Butler, I. S. *Inorg. Chem.* **1989**, *28*, 1007.

(21) For selected examples of fluxional octahedral nonhydride complexes, see ref 20c and references cited therein.

(22) Activation parameters were calculated using 1D ^{1}H EXSY NMR with the initial rate analysis: Naumann, C.; Patrick, B. O.; Sherman, J. C. *Tetrahedron* **2002**, *58*, 787.

(23) $\Delta S^{\ddagger}_{\mathrm{inter}} = 11.7 \pm 12.4$ cal K^{-1} mol^{-1}, $\Delta H^{\ddagger}_{\mathrm{inter}} = 23.9 \pm 4.0$ kcal mol^{-1}, and $\Delta G^{\ddagger}_{295.1,\mathrm{inter}} = 20.5 \pm 7.7$ kcal mol^{-1}

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(25) See the Supporting Information for details.

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