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Nonhydride Mechanism of Metal-Catalyzed Hydrosilylation

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Supporting Information

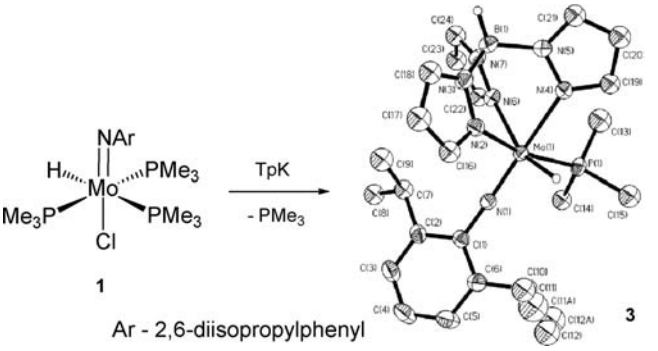
ABSTRACT: A 1:1:1 reaction between complex (Tp)(ArN═)Mo(H)(PMe_3) (**3**), silane $PhSiD_3$, and carbonyl substrate established that hydrosilylation catalyzed by **3** is not accompanied by deuterium incorporation into the hydride position of the catalyst, thus ruling out the conventional hydride mechanism based on carbonyl insertion into the M−H bond. An analogous result was observed for the catalysis by (O═)($PhMe_2SiO$)Re(PPh_3)$_2$(I)(H) and $(Ph_3PCuH)_6$.

Metal-catalyzed hydrosilylation of carbonyls has recently received renewed attention as a convenient reduction method.[1,2] Much current effort is aimed at replacing heavy late-transition-metal complexes for less expensive and more environmentally benign early metals, such as Ti,[3] Zr,[4] and Mo,[5,6] or first d series metals,[2d,7] particularly Fe[8] and Cu.[9] The mechanistic proposals offered for these metal catalysts share a common theme: the formation of a metal hydride intermediate upon the addition of silane followed by carbonyl insertion into the M−H bond to give an alkoxide (the *hydride mechanism*).[2e] Indeed, some metal hydride complexes have been obtained or observed under the hydrosilylation conditions and proved to turn over.[6,7b,10] But are they the actual catalysts, and what is the true role of the hydride ligand? Here we disclose a simple labeling experiment which allows one to probe the hydride mechanism. We apply this technique to several prominent recent examples of Mo, Re, and Cu catalysis and show that the reaction of metal hydrides with carbonyls is not necessarily part of the actual catalysis reaction.

Our previous mechanistic studies on Mo-catalyzed hydrosilylation suggested that complex (ArN═)(Me_3P)$_3$Mo(Cl)(H) (**1**) reacts by a phosphine dissociation mechanism, whereas the related complex Cp(ArN═)Mo(H)(PMe_3) (**2**) reacts by an unexpected associative mechanism.[6] Wishing to explore this mechanistic dichotomy further, we turned to the isolobal system Tp(ArN═)Mo(H)(PMe_3) (**3**; Tp = tris(pyrazolyl) borate). Complex **3** was prepared by reacting **1** with TpK and was studied by NMR and X-ray diffraction (Scheme 1). **3** was found to catalyze the hydrosilylation even more effectively than **2** (Table 1). Given the increased bulkiness and diminished donor ability of the Tp relative to the Cp ligand, the increased catalytic efficiency of **3** was surprising and prompted us to carry out a mechanistic study.

First, by EXSY NMR we found an exchange process in the Tp ligand of **3**. This exchange is dissociative [k(295.1 K) = 1.14 s^{-1},

Scheme 1. Preparation and Structure of (Tp)(ArN═)Mo(H)(PMe_3) (3)



$\Delta H^{‡}$ = 81.8 ± 2.1 kJ/mol, $\Delta S^{‡}$ = 32.4 ± 7.0 J/(mol·K)], suggesting dissociation of one of the pyrazolyl "legs". In contrast to complex **2**, which undergoes a slow but catalytically unimportant reaction with $PhSiH_3$, **3** is nonreactive toward silane. However, it slowly reacts with benzaldehyde to give the insertion product (Tp)(ArN)Mo(OCH_2Ph)(PMe_3) (**4**). Unlike the corresponding reaction of **2**, this insertion is dissociative [k(328.7 K) = (1.18 ± 0.02) × 10^{-1} $M^{-1}·s^{-1}$, $\Delta H^{‡}$ = 107.0 ± 7.0 kJ/mol, $\Delta S^{‡}$ = 61.2 ± 21.4 J/(mol·K)], but the reaction rate does not depend on the concentration of PMe_3,[11] suggesting that the rate-determining step is the dissociation of one of the pyrazolyl ligands. The next step, the reaction of **4** with phenylsilane to regenerate the starting hydride **3**, also shows a positive entropy of activation [k(295.1 K) = (2.35 ± 0.02) × 10^{-4} s^{-1}, $\Delta H^{‡}$ = 96.6 ± 1.8 kJ/mol, $\Delta S^{‡}$ = 12.5 ± 6.2 J/(mol·K)], indicating a significant dissociative (presumably of the Tp ligand) character of the rate-limiting step.

With these stoichiometric reactions in hand, a clear mechanistic picture emerged that the catalytic reaction proceeds via the silane heterolytic cleavage on the M−OR bond,[6] with all steps being activated by dissociation of the Tp. However, this hydride mechanism is not compatible with the very poor reactivity of **3** toward ketones. Their reactions were found to occur only upon heating at 50 °C for several days, whereas catalytic reactions are already fast at room temperature (Table 1, entries 2 and 3).

This controversy was eventually solved by the remarkable observation that a stoichiometric (1:1:1) reaction of PhCHO with $PhSiD_3$ and **3** results in immediate formation of $PhCHDOSiD_2Ph$ (>95% by NMR), keeping the complex **3** unchanged.

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Table 1. Catalytic Hydrosilylation Mediated by 3 (5 mol %, in C_6D_6)

entry	substrate	silane	conditions	conversion of substrate (%)	product (yield)
1	PhC(O)H	$PhSiH_3$	0.5 day, rt	100	$PhCH_2OSiH_2Ph$ (38%), $(PhCH_2O)_2SiHPh$ (62%)
2	PhC(O)Me	$PhSiH_3$	1.5 days, rt	100	$MePhHCOSiH_2Ph$ (85%), $(MePhHCO)_2SiHPh$ (15%)
3	cyclohexanone	$PhSiH_3$	53 min, rt	100	cyclohexyl-$OSiH_2Ph$ (85%), $(cyclohexyl\text{-}O)_2SiHPh$ (15%)
4	PhC(O)H	$PhMeSiH_2$	1.5 days, 50 °C	30	$PhCH_2OSiHMePh$ (30%)
5	PhC(O)Me	$PhMeSiH_2$	2.5 days, 50 °C	100	$MePhHCOSiHMePh$ (100%)
6	cyclohexanone	$PhMeSiH_2$	1 day, rt	100	cyclohexyl-$OSiHMePh$ (96%), $(cyclohexyl\text{-}O)_2SiMePh$ (4%)
7	cyclohexanone	$PhMe_2SiH$	1.5 days, 50 °C	11	cyclohexyl-$OSiMe_2Ph$ (11%)
8	PhCN	$PhSiH_3$	3 days, 50 °C	20	$PhCH{=}NSiH_2Ph$ (17%), $(PhCH{=}N)_2SiHPh$ (3%)

Close monitoring of catalytic reactions by ^1H and ^{31}P NMR revealed the presence of **3** in the reaction mixture. An analogous result was obtained for the stoichiometric reaction of cyclohexanone with $PhSiD_3$ and **3**, in which the Mo−H functionality remained unlabeled (>95%). Finally, we carried out the hydrosilylation of cyclohexanone by $PhSiD_3$ in the presence of 5 mol % **3** and observed the retention of the Mo−H group at the end of catalysis. These observations unequivocally establish that carbonyl insertion into the Mo−H bond of **3** is not a catalytically relevant event.

Kinetic studies of the latter reaction showed that reaction rates increase with increasing concentration of cyclohexanone but are insensitive to variation of the silane concentration.[11] Therefore, we conclude that the rate-determining step must be the activation of carbonyl. As **3** is nonreactive to both the silane and ketone, the only mechanistic alternative we are left with is that the metal center activates the carbonyl as a Lewis acid.

Lewis acid catalysis has been previously invoked for the hydrosilylation by $B(C_6F_5)_3$,[12] $AlCl_3$, $Ti(OPr^i)_4$, $TiCl_4$, $ZrCl_4$, and $HfCl_4$,[1e] but surprisingly it has not been considered for other metal complexes. To check the scope of this reactivity, we reinvestigated some recent prominent examples of catalytic hydrosilylation.

Toste et al. reported the hydrosilylation of carbonyls by $(O{=})_2Re(PPh_3)_2I$[10a] (**5**), and the related O_2MoCl_2-catalyzed reactions were disclosed by Royo et al.[13] The Toste group provided mechanistic evidence that the reaction occurs via Si−H addition across the Re=O bond to give the hydride $(O{=})(PhMe_2SiO)Re(PPh_3)_2(I)(H)$ (**6**), followed by carbonyl insertion into the Re−H bond.[14] We studied the 1:1:1 reaction of **6** with benzaldehyde and $DSiMe_2Ph$. At 50% conversion, no deuterium scrambling into the Re−H position was observed (integrates as 1H),[15] and the methylene part of the hydrosilylation product[16] integrates as 1H, which contradicts the conclusion by Toste et al. that silane addition to **5** is fast and that the rate-determining step is the aldehyde insertion into the Re−H bond of **6**. Another indication that the hydride mechanism is not the dominant reaction pathway comes from the observation that the 1:1:1 reaction of **6** with benzaldehyde and $DSiMe_2Ph$ takes about 1 h, whereas a 1:1 reaction of **6** with benzaldehyde was complete only overnight.

In a related catalysis by monooxo Re complexes, Abu-Omar et al. observed that $(O{=})Re(PPh_3)_2Cl_3$ reacts with $HSiEt_3$ to give the hydride derivative $(O{=})Re(PPh_3)_2(H)Cl_2$ (**7**).[10b] Although complex **7** is able to turn over, kinetic modeling of the potential hydride mechanism suggested that it is a minor process. We reacted **7** with PhHC=O and $DSiEt_3$ in the 1:1:1 ratio and initially observed formation of the insertion product $(O{=})Re(PPh_3)_2(OCH_2Ph)Cl_2$, which then slowly reacts with the silane to give $PhH_2C{-}OSiEt_3$ and $PhHDC{-}OSiEt_3$ in a 7:1 ratio, consistent with the occurrence of a minor hydride mechanism. We also checked whether the H/D scrambling in the products could come from a ReH/SiD exchange. To this end, complex **6** was reacted with $DSiEt_3$. No exchange was observed at room temperature, and only a minor exchange was observed after 1 day at 70 °C. However, we were surprised to notice that $(O{=})Re(PPh_3)_2Cl_3$ appears to be a poorer catalyst than hydride **7** (Table 1 in ref 10b), which is at odds with an ionic mechanism of hydrosilylation that avoids the formation of the latter. Given the fact that kinetic modeling of the hydride mechanism accounts for merely 20% of hydrosilylation,[10b] these observations suggest that **7** can be the true catalyst operating by a nonhydride mechanism.

Lipshutz et al. found that copper hydrides, such as the Stryker reagent $(Ph_3PCuH)_6$, catalyze hydrosilylation of carbonyls.[17] Several copper salts were found to mediate this reaction in the presence of alkoxide,[18] with the accepted mechanistic proposal being that an intermediate copper hydride is generated by the reaction of a copper alkoxide and silane followed by carbonyl insertion into the Cu−H bond.[17,18c,19,20] However, while aldehydes were indeed shown to insert into the Cu−H bond of $(Ph_3PCuH)_6$, ketones do not react with copper hydrides,[17b,18c] despite the efficiency of Cu-catalyzed hydrosilylation of ketones! To verify the mechanism, we first showed that $Ph_3PCuOBu^t$, prepared *in situ* from CuCl, Ph_3P, and $NaOBu^t$, does react with $HSiMe_2Ph$ to give $(Ph_3PCuH)_6$ in 46% isolated yield. However, when this hydride reacted[21] with stoichiometric amounts of benzaldehyde and $DSiMe_2Ph$, the exclusive formation of $PhHDC{-}OSiMe_2Ph$ was observed, without any deuterium incorporation into the hydride position, thus allowing us to rule out the hydride mechanism.

One limitation for the proposed labeling test comes from the possibility of fast H/D exchange.[19a] This is the case for our previously studied system $(ArN{=})(Me_3P)_3Mo(Cl)(H)$ (**1**), which was suggested to catalyze hydrosilylation of carbonyls by the hydride mechanism.[6a] **1** undergoes H/D exchange with silane at a rate comparable with the addition of benzaldehyde, so that the 1:1:1 reaction of **1** with PhHC=O and D_3SiPh results in deuterium scrambling in the hydride position and the product.[22]

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In conclusion, we have developed a simple stoichiometric labeling experiment allowing one to probe the hydride mechanism of hydrosilylation, which is important for the rational design of new catalysts. The true role of the hydride ligand in this catalysis remains unclear. One possibility is that it may provide enough space for carbonyl η^1-coordination to metal in the Lewis acid catalysis.

■ ASSOCIATED CONTENT

Supporting Information. Experimental procedures, spectral data, and details of kinetic studies; complete crystallographic data (CIF) for the complexes reported in this paper. This material is available free of charge via the Internet at http://pubs.acs.org

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(15) By the end of catalysis, about 15% decomposition of the catalyst is observed and about 20% of the remaining rhenium hydride is deuterated, presumably by the competing hydride mechanism. No silyl hydride signal of H−$SiMe_2$Ph was observed throughout the catalysis, suggesting that ReH/SiD exchange (ref 10a) is slower than hydrosilylation.

(16) A mixture of isotopomers $PhCH_2OSiMe_2Ph$ and $PhCHDOSiMe_2Ph$ is observed by ^{1}H NMR. ^{1}H−^{13}C HSQC, DEPT, and ^{1}H−^{29}Si HSQC experiments confirmed that isotopomers of the same hydrosilylation product were formed.

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(20) Carbonyl insertion is believed to be stereodefining in asymmetric versions (see ref 17b).

(21) No hydride signal is observed for the Lipshutz's catalyst (*R*-3,5-xyl-MeO-BIPHEP)CuH,[17b] making it a bad candidate for this experiment.

(22) The Re complex **6** does undergo H/D exchange with $PhMe_2SiD$,[10a] but slower than the 1:1:1 hydrosilylation, whereas complex **7** and $(Ph_3PCuH)_6$ do not show any H/D exchange with $PhSiD_3$ and $PhMe_2SiD$, respectively, during several days at room temperature.