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Mechanistic Aspects of Hydrosilylation Catalyzed by (ArN=)Mo(H)(Cl)(PMe_3)$_3$

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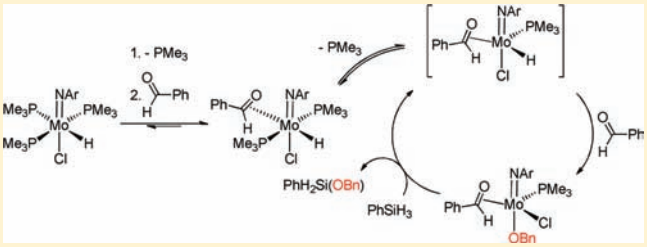
Supporting Information

ABSTRACT: The reaction of (ArN=)$MoCl_2(PMe_3)_3$ (Ar = 2,6-diisopropylphenyl) with L-Selectride gives the hydrido-chloride complex (ArN=)Mo(H)(Cl)(PMe_3)$_3$ (**2**). Complex **2** was found to catalyze the hydrosilylation of carbonyls and nitriles as well as the dehydrogenative silylation of alcohols and water. Compound **2** does not show any productive reaction with $PhSiH_3$; however, a slow H/D exchange and formation of (ArN=)Mo(D)(Cl)(PMe_3)$_3$ (**2**$_D$) was observed upon addition of $PhSiD_3$. Reactivity of **2** toward organic substrates was studied. Stoichiometric reactions of **2** with benzaldehyde and cyclohexanone start with dissociation of the *trans*-to-hydride PMe_3 ligand followed by coordination and insertion of carbonyls into the Mo−H bond to form alkoxy derivatives (ArN=)Mo(Cl)(OR)(PMe_2)L_2 (**3**: R = OCH_2Ph, L_2 = 2 PMe_3; **5**: R = OCH_2Ph, L_2 = η^2-PhC(O)H; **6**: R = OCy, L_2 = 2 PMe_3). The latter species reacts with $PhSiH_3$ to furnish the corresponding silyl ethers and to recover the hydride **2**. An analogous mechanism was suggested for the dehydrogenative ethanolysis with $PhSiH_3$, with the key intermediate being the ethoxy complex (ArN=)Mo(Cl)(OEt)(PMe_3)$_3$ (**7**). In the case of hydrosilylation of acetophenone, a D-labeling experiment, i.e., a reaction of **2** with acetophenone and $PhSiD_3$ in the 1:1:1 ratio, suggests an alternative mechanism that does not involve the intermediacy of an alkoxy complex. In this particular case, the reaction presumably proceeds via Lewis acid catalysis. Similar to the case of benzaldehyde, treatment of **2** with styrene gives *trans*-(ArN=)Mo(H)(η^2-CH_2=CHPh)(PMe_3)$_2$ (**8**). Complex **8** slowly decomposes via the release of ethylbenzene, indicating only a slow insertion of styrene ligand into the Mo−H bond of **8**.



INTRODUCTION

The development of efficient synthetic methodologies for selective and efficient reduction of multiple carbon−carbon or carbon-heteroatom bonds is a fundamental problem of organic and organometallic chemistry.[1] In this respect, the ability of transition metal compounds to induce catalytic reactions of this kind has been recognized and used extensively for many years.[1,2] The hydrosilylation methodology stands aside from other catalytic reduction methods due to the availability, stability and cost of silanes, as well as the safety, low toxicity, and simplicity of experimental procedures.[3] To date, however, most practical protocols of hydrosilylation involve the application of late transition metal catalyst which are very efficient but suffer from the high cost and recognized toxicity.[2] To circumvent these problems, the development of iron catalysis[4] and the use of early transition metal systems[3,5] has recently received significant attention. In this regard, catalysis based on molybdenum is quite promising[6,7] because of the low cost and environmentally benign nature of this metal.[8]

Until very recently, the main mechanistic proposal for metal catalyzed hydrosilylation had been based on the variations of Chalk−Harrod mechanism[9] (for alkenes and alkynes) and Ojima mechanism (for carbonyls),[10] which starts with oxidative addition of silane to metal, substrate coordination, and migration of the silyl (or the hydride ligand) followed by either reductive C−H elimination (or Si−C for alkenes and O−Si elimination for carbonyls). Heterolytic splitting of silanes on the polar M−O bonds (or σ-bond metathesis) was suggested for early metal systems.[5a] Recently, several groups provided evidence for alternative mechanisms involving the addition of carbonyls to an intermediate silylene complex (Gade−Hoffmann mechanism),[11] addition of a silane across the M=O double bond (Toste mechanism),[6c,12] ionic hydrosilylation (e.g., Dioumaev-Bullock,[13] Abu-Omar et al.,[14] Brookhart et al.,[15] and our group[16]).

Here we report a detailed study of catalytic hydrosylilation of organic substrates mediated by an imido/hydride complex of Mo(IV), as well as insights into the possible mechanism(s) of these reactions. A preliminary communication has been published.[17]

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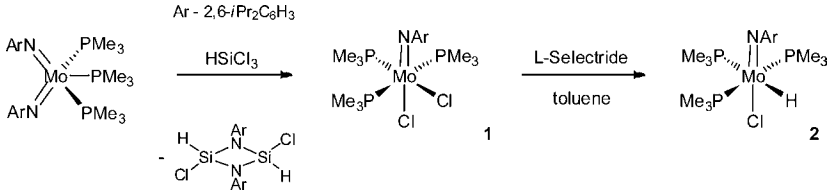
Scheme 1. Reaction of $(ArN=)Mo(PMe_3)_3$ with $HSiCl_3$ and Preparation of the Hydride Complex 2



RESULTS AND DISCUSSION

Preparation of Hydrido-chloride Complex $(ArN=)Mo(H)(Cl)(PMe_3)_3$ (2). We have previously found that the bis(imido) complex $(ArN=)_2Mo(PMe_3)_3$ reacts with $HSiCl_3$ to give the mono(imido) derivative $(ArN=)MoCl_2(PMe_3)_3$ (**1**) and a silanimine dimer $(ArN=SiHCl)_2$ (Scheme 1).[18] Spectroscopic characterization of complex **1** has been reported earlier and is now confirmed by the X-ray structure determination. The complex adopts an octahedral geometry, with one of the chloride substituents lying *trans* to the imido group (Figure 1) and the second chloride occupies an equatorial position (cis- to ArN^{2-}) and coplanar with all three PMe_3 ligands. The imido moiety in **1** is almost linear (the Mo1−N1−C1 angle is 172.7(3)°; Table 1), which indicates that the ArN^{2-} ligand acts as a 6e donor stabilizing the 18e valence shell of Mo.[19] Similar structural features were reported for the analogous complex $(^tBuN=)MoCl_2(PMe_3)_3$.[20]

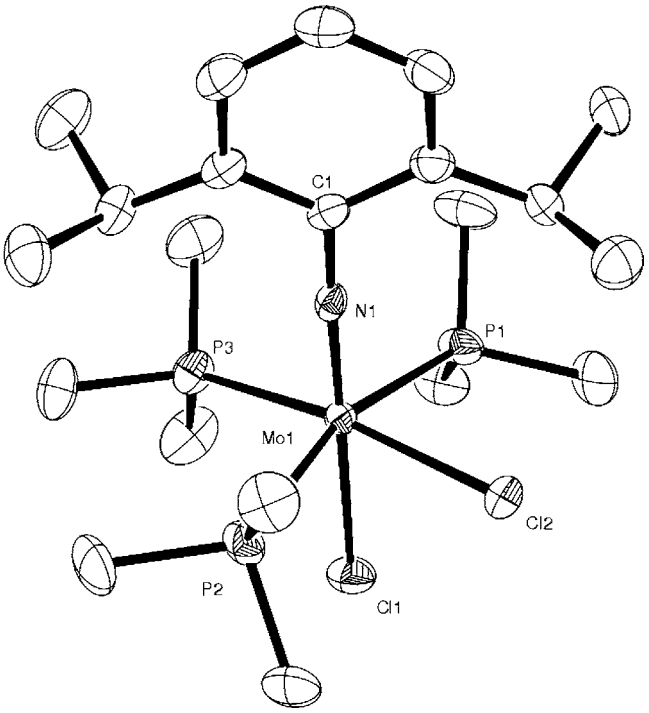


Figure 1. ORTEP plot of the molecular structure of complex **1** (hydrogen atoms are omitted for clarity).

Complex **1** was found to be quite robust and, surprisingly, did not show any reactivity with excess of $NaBH_4$ as well as $MeLi/H_2$, $Na(Hg)/H_2$, and KC_8/H_2. On the other hand, addition of L-Selectride (1 equiv.) to **1** affords cleanly the hydrido-chloride derivative $(ArN=)Mo(H)(Cl)(PMe_3)_3$ (**2**; Scheme 1). Compound **2** was fully characterized by multinuclear NMR, IR and X-ray diffraction analysis.[17] The ^{31}P NMR spectrum of **2** exhibits two sets of signals: a doublet at δ −1.1 ppm ($^2J_{P-P}$ = 13.4 Hz) corresponding to two equivalent phosphines and a triplet at δ −17.8 ppm ($^2J_{P-P}$ = 13.4 Hz) for the unique PMe_3 group lying *trans* to the hydride. The ^1H NMR spectrum of **2** shows a downfield hydride signal at δ 5.31 (dt) coupled to two equivalent *cis*-PMe_3 ($^2J_{H-P}$ = 28.5 Hz) and the unique *trans*-PMe_3 ($^2J_{H-P}$ = 51.9 Hz). The presence of the hydride is also evident from the observation of a characteristic Mo−H stretch at 1714 cm^{-1} in the IR spectrum. X-ray diffraction analysis revealed an octahedral geometry, with the chloride lying *trans* to the imido group and the hydride occupying a site cis to the imido group. For the subsequent discussion it is important to point out that the phosphine *trans* to the hydride forms a significantly longer Mo−P bond than the mutually *cis*-phosphines (2.572(1) Å vs 2.485(1) and 2.469(1) Å, respectively).[17]

Table 1. Selected Bond Distances (Å) and Angles (deg) for Complex 1

distances (Å)		angles (deg)	
Mo1−N1	1.753(4)	Mo1−N1−C1	172.7(3)
Mo1−Cl1	2.5079(14)	N1−Mo1−Cl1	179.28(13)
Mo1−Cl2	2.5206(13)	Cl1−Mo1−Cl2	85.31(5)
Mo1−P1	2.5080(15)	N1−Mo1−Cl2	94.95(13)
Mo1−P2	2.5158(14)	P1−Mo1−P2	163.84(5)
Mo1−P3	2.4987(15)	P1−Mo1−P3	90.45(5)
N1−C1	1.405(6)	P2−Mo1−P3	99.51(5)

Catalytic Reactivity of Complex 2. Complex **2** has been found to catalyze a variety of hydrosilylation reactions (Tables 2 and 3). Thus, the room temperature treatment of benzaldehyde with $PhSiH_3$ in the presence of 5.0 mol % of **2** results in the quantitative conversion of the substrate after one day, affording a mixture of $PhH_2Si(OBn)$ and $PhHSi(OBn)_2$[21,22] in 37 and 63% yield, respectively (Table 2, entry 1). An increase in temperature up to 50 °C leads to a faster reaction, so that the full conversion of PhC(O)H was observed after only 3 h (Table 2, entry 2). The use of $PhMeSiH_2$[22c,23] or poly(methylhydrosiloxane) (PMHS) instead of $PhSiH_3$ results in more sluggish reactions, with the conversion of benzaldehyde being in the range 50−68% (Table 2, entries 3 and 4).

With acetophenone as the substrate, the activity of hydrosilylation by $PhSiH_3$ is much reduced,[23] with the complete conversion of the carbonyl being achieved only after 11 days at room temperature (Table 2, entry 5). On the other hand, the hydrosilylation of acetophenone with PMHS[25] catalyzed by **2** requires heating (50 °C) and gives full conversion after 48 h (Table 2, entry 6). Much faster reactions with both $PhSiH_3$ and PMHS were observed for the cyclohexanone which was fully converted to the corresponding silyl ethers within one hour (Table 2, entries 7−9).[25,26] Low catalytic activity of **2** was also found in the hydrosilylation of 1-octyne (Table 3, entry 1), which leads to only 35% conversion of the alkyne to form a mixture of $PhH_2SiCH{=}CH(Hex)$,

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Table 2. Catalytic Hydrosilylation of Ketones and Aldehydes Mediated by Complex 2[a]

entry	substrate	silane	T (°C)/time	products[d]	substr. conv.[e] (%)	yield[e] (%)
1	PhC(O)H	$PhSiH_3$	RT/24 h	$PhH_2Si(OBn)$	100	37
				$PhHSi(OBn)_2$		63
2[b]			50/3 h	$PhH_2Si(OBn)$	100	32
				$PhHSi(OBn)_2$		68
3		$PhMeSiH_2$	RT/24 h	PhMeHSi(OBn)	68	68
4[c]		PMHS	50/48 h	$(BnO)_xPMS$	50	50
5	PhC(O)Me	$PhSiH_3$	RT/11 days	$PhH_2Si[OCH(Me)Ph]$	100	54
				$PhHSi[OCH(Me)Ph]_2$		23
				$PhSi[OCH(Me)Ph]_3$		12
				$PhCH_2CH_3$		11
6[c]		PMHS	50/48 h	$[Ph(Me)CHO]_xPMS$	100	100
7	cyclohexanone	$PhSiH_3$	RT/35 min	$PhH_2Si(OCy)$	100	79
				$PhHSi(OCy)_2$		21
8[c]		PMHS	RT/20 min	$(CyO)_xPMS$	50	50
9[c]			50/1 h	$(CyO)_xPMS$	100	100

[a]Conditions: 5 mol % **2**, C_6D_6, substrate/silane = 1/1, C_{subst} = 2.0 M. [b]3 mol % **2**. [c]6 mol % **2**. [d]Reactions with $PhSiH_3$ give Ph_2SiH_2 and SiH_4 byproduct.[24] [e]Detected by ^1H NMR using tetramethylsilane as a standard.

Table 3. Catalytic Hydrosilylation of Alkenes and Alkynes and Alcoholysis/Hydrolysis of $PhSiH_3$ by 2.[a]

entry	substrate	T (°C)/time	products[c]	substr. conv.[e] (%)	yield[e] (%)
1	1-octyne	RT/15 days	$PhH_2SiC(Hex)=CH_2$	35	4
			$PhH_2SiCH=CH(Hex)$		7
			$PhHSi[CH=CH(Hex)][C(Hex)=CH_2]$		12%
			$PhHSi[CH=CH(Hex)]_2$		12
2	1-hexene	RT/72 h and 60/24 h	$PhH_2Si(Hex)$	89	3
			2-hexene		6
			hexane		80
3	EtOH	RT/1 h	$PhH_2Si(OEt)$	100	26
			$PhHSi(OEt)_2$		74
4	H_2O[b]	RT/3 h	polysiloxane	100[d]	
5	MeCN	50/6 days	$EtN(SiH_2Ph)_2$	45	45
6	PhCN	RT/18 h and 50/12 days	$PhH_2Si(N=CHPh)$	5	5
7			$PhH_2Si(N=CHPh)$	100	76
			$PhHSi(N=CHPh)_2$		24

[a]Conditions: 5 mol % of **2**; silane: $PhSiH_3$; C_6D_6; substrate/silane = 1/1; C_{subst} = 2.0 M. [b]$H_2O/PhSiH_3$ = 5/1. [c]Ph_2SiH_2 and SiH_4 were also observed.[24] [d]Conversion of $PhSiH_3$. [e]Detected by ^1H NMR using TMS as a standard.

$PhH_2SiC(Hex)=CH_2$, $PhHSi[CH=CH(Hex)][C(Hex)=CH_2]$, and $PhHSi[CH=CH(Hex)]_2$.[27]

Complex **2** turned out to be inactive in the hydrosilylation of alkenes. Despite the fact that addition of $PhSiH_3$ to 1-hexene in the presence of 5.0 mol % **2** gives 86% conversion of the alkene, the reaction affords mostly hexane,[28] as well as a small amount of isomerization product, 2-hexene (6%), was observed (Table 3, entry 2).[29]

Ethanolysis of $PhSiH_3$ in the presence of 5.0 mol % **2** is fast (Table 3, entry 3). After 1 h at room temperature, the reaction is complete, affording a mixture of silyl ethers PhH_2SiOEt (26%) and $PhHSi(OEt)_2$ (74%).[22b,30] Interestingly, a similar reaction of phenylsilane with excess water[31] (ca. 5 equivs) is more sluggish and leads to the formation of polysiloxane with the 100% conversion of $PhSiH_3$ after 3 h at room temperature (Table 3, entry 4).

The last but not the least, the hydride complex **2** was found to catalyze the addition of phenylsilane to nitriles, including a rare example of a selective catalytic hydrosilylation of benzonitrile to the corresponding silyl imine.[7,16b,32,33] Thus, the room temperature reaction of PhCN with one equivalent of $PhSiH_3$ and 5.0 mol % **2** leads to only stoichiometric (5%) formation of $PhH_2Si(N=CHPh)$ (Table 3, entry 6). An increase of the reaction time (up to 13 days) and temperature (up to 50 °C) results in full conversion of benzonitrile, producing of a mixture of $PhH_2Si(N=CHPh)$ and $PhHSi(N=CHPh)_2$ in 76 and 24%, respectively (Table 3, entry 7). In contrast, the hydrosilylation of acetonitrile with $PhSiH_3$ affords, after 6 days at 50 °C, $EtN(SiH_2Ph)_2$[33d,34] (45%, Table 3, entry 5). No monoaddition products $PhH_2Si(N=CHMe)$ and $PhHSi(N=CHMe)_2$ were seen by NMR at any step of the reaction.

Stoichiometric Reactivity of Complex 2: Mechanistic Aspects of Hydrosylilation. To shed light on the mechanism of catalysis, stoichiometric reactions between complex **2** and unsaturated organic molecules were studied. In our preliminary communication, we suggested a possible mechanism of the hydrosilylation of benzaldehyde (Scheme 2) on the basis of studying individual steps under stoichiometric conditions.[17] It is important to mention that the hydrido-chloride complex **2** shows no visible reaction with $PhSiH_3$ (1−2 equivs) over a period of several days. No addition of silane to either the molybdenum center or across the Mo=N bond[18] in **2** was observed. Such a behavior is in contrast with the previously observed addition of R_3SiH to the Re=O bond in $Re(O)_2I(PPh_3)_2$[12] and the H/Cl exchange observed for $Re(O)Cl_3(PCy_3)_2$ and $Re(NMes)Cl_2(PPh_3)_2$ by Abu-Omar et al.[14a] However, **2** undergoes a slow H/D exchange (78% after 3 days) when reacted with 1 equiv. of $PhSiD_3$. In the presence of excess $PhSiD_3$ (ca. 4.2 equivs), ∼ 93% of hydride in **2** is substituted by deuteride after 1 day at room temperature (Table 4).

In contrast, we have found that **2** reacts easily with carbonyl compounds (aldehydes and ketones) and alcohols. Thus, the treatment of **2** with benzaldehyde affords the benzoxy derivative $(ArN=)Mo(Cl)(OCH_2Ph)(PMe_3)_3$ (**3**; Scheme 2).

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Scheme 2. Mechanism for the Hydrosilylation of PhC(O)H with $PhSiH_3$ Catalyzed by Complex 2

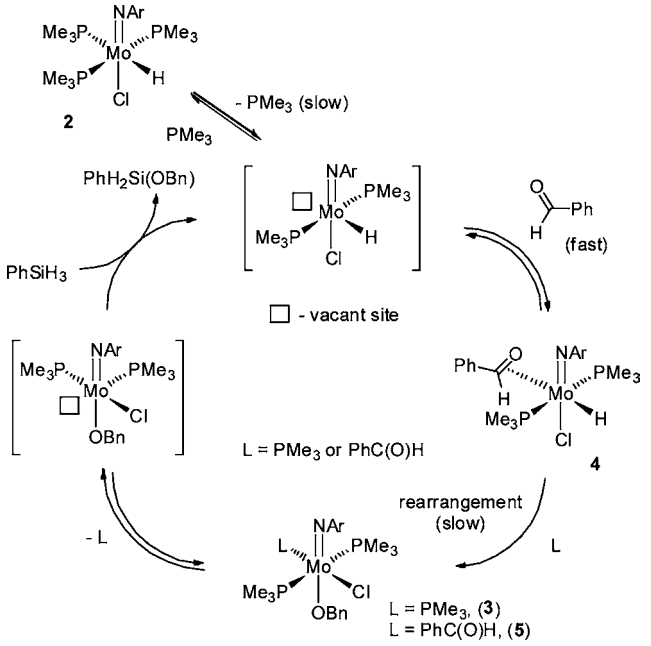

Table 4. Change in the Integral Intensity of the Mo-*H* Signal in the ^1H NMR Spectrum of 2 upon Addition of $PhSiD_3$ (4.2 equivs.)

time	Mo-*H* (%)
10 min	91
6 h	45
26 h	7

Monitoring the reaction by NMR revealed the initial formation of intermediate *trans*-(ArN=)Mo(H)(Cl)(η^2-O=CHPh)-$(PMe_3)_2$ (**4**, mixture of two isomers;[35] Scheme 2). At −5 °C, complex **4** is the sole reaction product. The η^2-coordination of benzaldehyde in **4** results in a significant upfield shift of the OC*H* resonance to δ 5.77 ppm in the ^1H NMR spectrum and reduction of its C=O stretch (1595 cm^{-1}) in the IR spectrum.[36] Also, the η^2-coordination of PhC(O)H results in the nonequivalence of the mutually *trans* phosphine groups. The latter give rise to a pair of coupled doublets at δ 1.43 and −5.59 ppm ($^2J_{P-P}$ = 109.3 Hz) in the $^{31}P\{^1H\}$ NMR spectrum. At large aldehyde concentration, the reaction obeys the pseudo first order kinetics (k_1(−5 °C) = (7.6 ± 0.2) × 10^{-4} s^{-1}; Figure 2),[37] consistent with the rate-limiting dissociation of the *trans*-to-hydride PMe_3 ligand, followed by fast addition of aldehyde. Such an exclusive dissociation of the unique *trans*-PMe_3 is in accordance with the longest Mo−P_{trans} distance (see above) and is further supported by the observation of exchange of the *trans* PMe_3 with an external phosphine in the room temperature $^{31}P-^{31}P$ EXSY NMR experiment (Figure 3). Dissociation of PMe_3 from **2** in the reaction with benzaldehyde is reversible, as addition of excess phosphine (ca. 10 equivs) to **4** regenerates complex **2** and free benzaldehyde.

In the absence of PMe_3, the benzaldehyde adduct **4** decomposes within two hours to an intractable mixture of products. However, in the presence of one equiv. of PMe_3 it slowly (within 5 h) rearranges at room temperature into the benzoxy derivative **3**. The reaction is first order on **4** (Figure 4) and proceeds, most likely, via dissociation of the coordinated

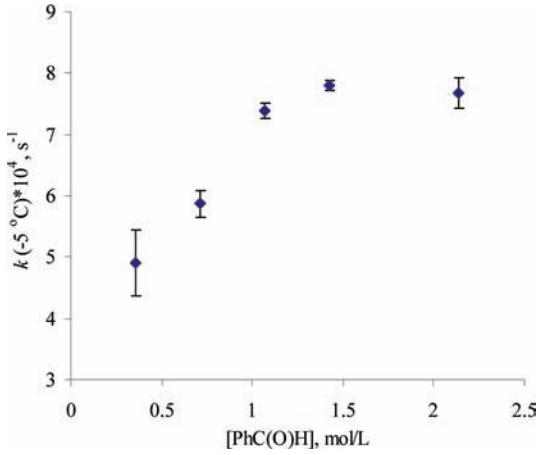

Figure 2. Dependence of the *k* of the reaction of **2** with PhC(O)H (−5 °C) on the concentration of PhC(O)H. The plateau region corresponds to the pseudo first order regime.

benzaldehyde and readdition to give an isomer where the Mo-bound hydride is cis to the aldehyde ligand.[38] This suggestion is supported by a series of $^1H-^1H$ EXSY NMR experiments which show a fast intermolecular exchange of **4** with benzaldehyde and a slow intramolecular exchange of the PMe_3 ligands. No exchange of **4** with an external phosphine was observed by $^1H-^1H$ EXSY NMR.[37] Further fast migration of the hydride to the cis-coordinated aldehyde would produce the benzoxy ligand. Analogous hydride migration has been shown previously by Abu-Omar et al. for the rhenium hydride complex Re(O)(H)$Cl_2(PPh_3)_2$.[14a] The smaller k(22 °C) = (2.1 ± 0.1) × 10^{-4} s^{-1} of the formation of **3** from **4** than the rate constant of aldehyde addition to **2** (k_1(−5 °C) = (7.6 ± 0.2) × 10^{-4} s^{-1}) agrees well qualitatively with the difference in the *trans*-influence of phosphine and hydride ligands. However, we cannot exclude the possibility that the rearrangement of **4** to **3** occurs via dissociation of phosphine at a rate too slow to be determined by the EXSY experiment. The readdition of PMe_3 on the aldehyde-phosphine or hydride-phosphine edge of the complex would bring the hydride and η^2-aldehyde into cis position, suitable for hydride migration. This latter reaction sequence is in accord with the slower rate of rearrangement of **4** into **3** in the presence of PMe_3 than decomposition of **4** in the absence of free phosphine.

Another insertion of coordinated benzaldehyde into the Mo−H bond is observed when **4** reacts with excess benzaldehyde. In this case the sole product is the benzoxy aldehyde complex (ArN=)Mo(Cl)(OCH_2Ph)(η^2-PhC(O)H)-$(PMe_3)_2$ (**5**, Scheme 3). Alternatively, compound **5** could be obtained by the reaction of **3** with excess PhC(O)H. The latter reaction is reversible as the addition of a large excess of PMe_3 (ca. 10 equivs) to **5** cleanly regenerates complex **3**. The ^1H NMR spectrum of **5** shows two mutually coupled diastereotopic OCH_2Ph signals at δ 4.62 ppm and 5.14 ppm ($^2J_{H-H}$ = 12.2 Hz) and an upfield benzaldehyde proton at δ 5.37 ppm (d, $^2J_{H-P}$ = 3.9 Hz), diagnostic for the η^2-coordination of aldehyde.[36] The ^{13}C NMR spectrum of **5** displays a significant upfield shift of the carbonyl signal (δ 90.7 ppm) additionally suggesting the η^2-coordination of PhC(O)H.

At large benzaldehyde concentrations (ca. 5−15 equiv.), the formation of **5** obeys the first order kinetics in **4** with k_{eff}(22 °C) = (3.1 ± 0.1) × 10^{-4} s^{-1}. The reaction constant does not depend on the concentration of benzaldehyde, suggesting the

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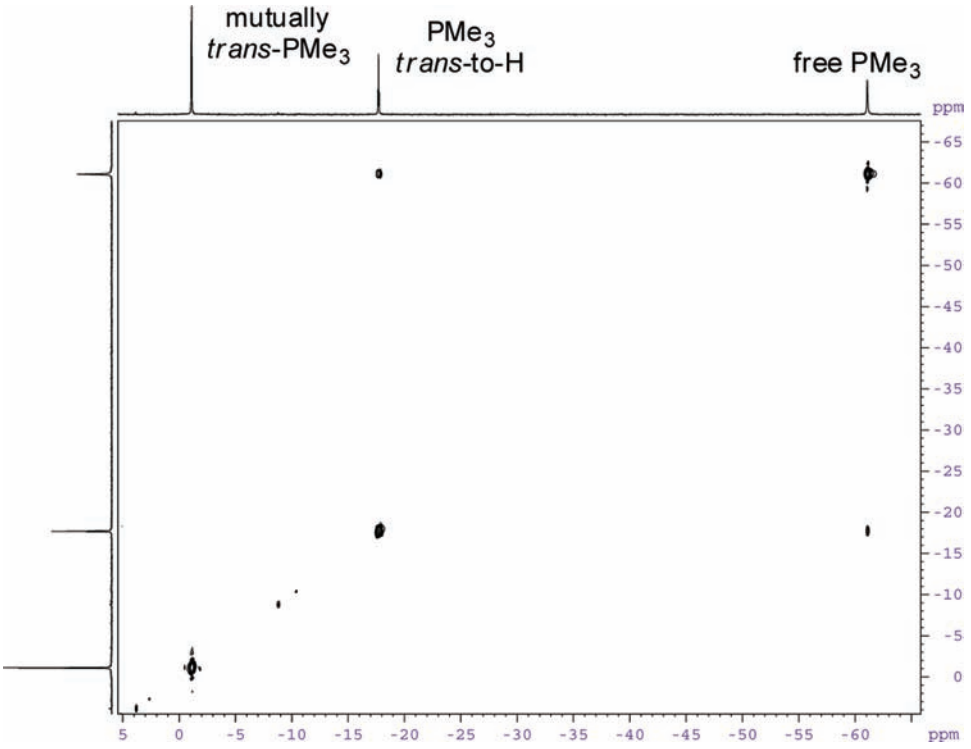


Figure 3. $^{31}P-^{31}P$ EXSY NMR spectrum (22 °C) for the mixture of **2** with PMe_3.

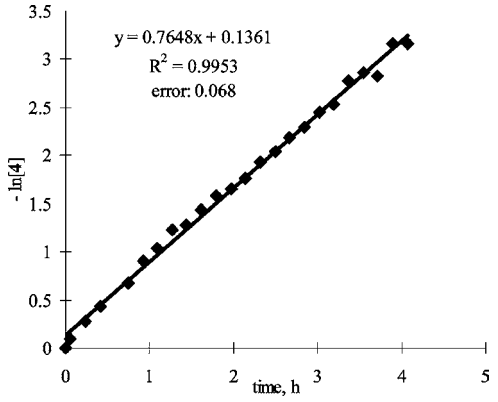


Figure 4. Kinetic profile for the rearrangement of **4** into **3** at 22 °C (standard error: 0.068).

rate-limiting PMe_3 dissociation (dissociation of benzaldehyde in this case is suppressed), followed by coordination of PhC(O)H. Such a dissociative mechanism for the reaction of **4** with excess benzaldehyde is also consistent with the kinetic VT NMR studies which reveal a large positive value of the entropy of activation, $\Delta S^{\ddagger} = 29.8 \pm 9.2$ cal K^{-1} mol^{-1} ($\Delta H^{\ddagger} = 30.8 \pm 2.7$ kcal·mol^{-1}, $\Delta G^{\ddagger}_{295.1} = 22.0 \pm 5.4$ kcal·mol^{-1}).[37] Analogously to complex **4**, the exchange between the phosphine ligand in **5** and free PMe_3 was too slow to be observed by EXSY NMR. However, EXSY experiments revealed a fast exchange of the coordinated benzaldehyde with free PhC(O)H.[37] Interestingly, we also observed an exchange between the diastereotopic protons of the benzoxy ligand in **5**. This exchange occurs with a large positive activation entropy $\Delta S^{\ddagger} = 47.8 \pm 6.4$ cal K^{-1} mol^{-1} ($\Delta H^{\ddagger} = 31.3 \pm 1.9$ kcal mol^{-1}) (Figure 5), suggesting a dissociatively activated process, most likely triggered by the

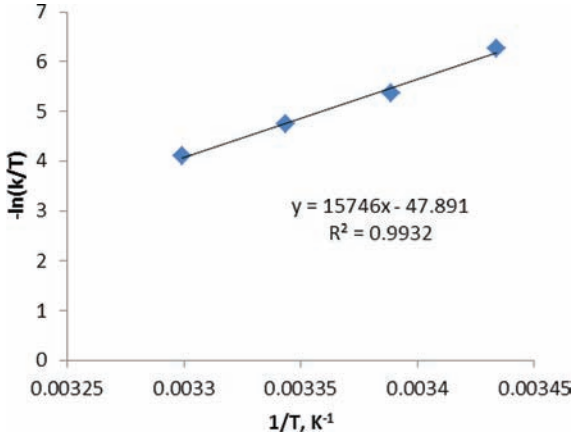
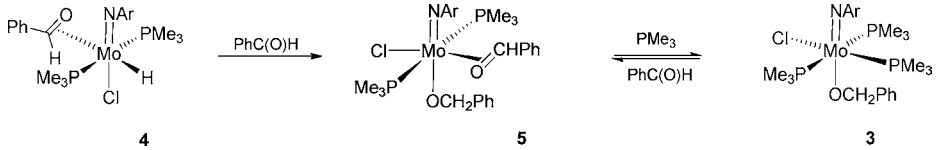


Figure 5. Eyring plot for the exchange of two enantiomers of **5**.

Scheme 3. Preparation of Complex 5



4 **5** **3**

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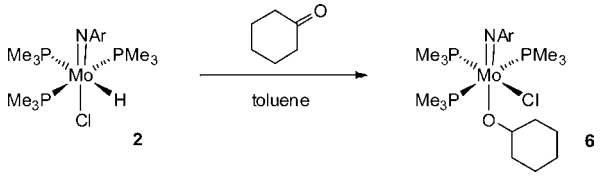
dissociation of the coordinated benzaldehyde. This process generates the C_s symmetrical fragment (ArN=)Mo(Cl)-(OCH^{a}H^{b}Ph)(PMe$_3$)$_2$, in which both methylene protons become equal, thus accounting for the H^a/H^b exchange.

Similar to the case of benzaldehyde, reaction of hydride **2** with one equivalent of cyclohexanone eventually gives the cyclohexoxy derivative (ArN=)Mo(Cl)(OCy)(PMe$_3$)$_3$ (**6**; Scheme 4). However, no η^2-cyclohexanone intermediate, analogous to **4**, was observed upon monitoring the reaction

Scheme 4. Preparation of Complex 6



by NMR, suggesting that the rearrangement of such an η^2-adduct into **6** is much faster than the transformation of **4** into **3**. Furthermore, complex **6** showed no further reaction with cyclohexanone: the adduct (ArN=)Mo(OCy)(Cl)(η^2-O=C$_6$H$_{10}$)(PMe$_3$)$_2$ similar to **5** was not observed by NMR, presumably because of steric constraint. Attempts to force the ketone coordination by addition of an equivalent of BPh$_3$ to **6** led to decomposition to a mixture of **1** and unidentified products.

Complex **6** was characterized by NMR spectroscopy and X-ray diffraction analysis (Figure 6). **6** has an octahedral geometry with the cyclohexoxy ligand laying *trans* to the imido group

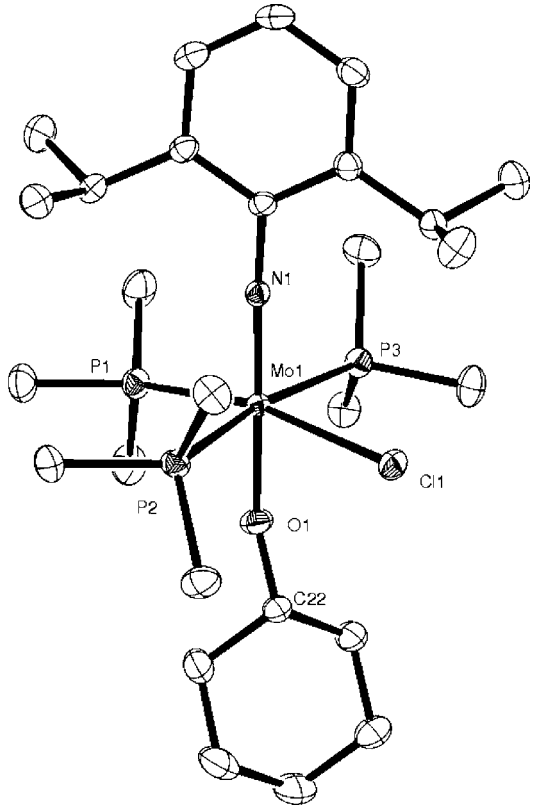


Figure 6. ORTEP plot of the molecular structure of **6** (hydrogen atoms are omitted for clarity).

(the O1−Mo1−N1 angle is 175.99(11)°, Table 5), consistent with the strong *trans*-influence of the ArN^{2-} ligand[39] and

Table 5. Selected Bond Distances and Angles for Complex 6

distances (Å)		angles (deg)	
Mo1−N1	1.786(3)	Mo1−N1−C1	176.4(2)
Mo1−O1	1.984(2)	N1−Mo1−O1	175.99(11)
Mo1−Cl1	2.5462(8)	P1−Mo1−Cl1	166.80(3)
Mo1−P1	2.4762(9)	P2−Mo1−P3	168.64(3)
Mo1−P2	2.5524(9)	N1−Mo1−Cl1	98.02(8)
Mo1−P3	2.5072(9)	N1−Mo1−P2	90.88(8)

reduced steric repulsion in the molecule when the phosphines are arranged in the meridian fashion. The chloride ligand is occupying an equatorial position and is coplanar with all three PMe$_3$ ligands. The C1−N1−Mo1 angle in **6** is almost linear (176.4(2)°), suggesting that the imido ligand donates six electrons, stabilizing the formal 18e valence shell. [19]

Complex **6** undergoes phosphine dissociation at room temperature which was observed directly by ^{1}H and ^{31}P NMR spectroscopy. Exchange of the PMe$_3$ ligands in **6** with free phosphine was also observed in the 2D ^{31}P−^{31}P and 1D ^{1}H EXSY NMR experiments.[35] Judging by the peak intensities in the ^{31}P−^{31}P EXSY NMR spectrum, the cis-to-chloride phosphines dissociate easier than the *trans*-PMe$_3$ ligand (Figure 7), consistent with the stronger phosphine *trans*-influence compared with the chloride *trans*-influence. The intramolecular PMe$_3$ exchange was also observed by 1D ^{1}H EXSY NMR and most likely proceeds via dissociation of one of the cis-to-chloride PMe$_3$ ligands.

Both complexes **3** and **6** undergo fast reactions with PhSiH$_3$ to furnish the corresponding hydrosylilation products and regenerate the hydride-chloride **2**, thus closing the possible catalytic cycle. An NMR experiment between the benzoxy complex **3** and the labeled silane PhSiD$_3$ resulted in the exclusive formation of (ArN=)Mo(D)(Cl)(PMe$_3$)$_3$ (**2$_D$**). The reactions between complex **3** and excess PhSiH$_3$ in the presence of large excess PMe$_3$ is first order in the complex. The linear dependence of k_{eff} on the PhSiH$_3$ concentration (Figure 8A) shows that the reaction has the first order in silane too, i.e., the second order overall reaction. The $1/k_{eff}$ is proportional to phosphine concentration (Figure 8B), which indicates the PMe$_3$ dissociation from **3** prior to the addition of silane (Scheme 2).

Although these stoichiometric reactions establish that **2** is a potent catalyst operating through the commonly accepted hydride mechanism,[40] the actual catalytic process can be more complicated. Our recent studies on carbonyl hydrosilylation by complex Tp(ArN=)Mo(PMe$_3$)(H) suggested the possibility of a nonhydride mechanism of reduction, when the metal-bound hydride is not transferred to the substrate.[7c] Namely, we found that a 1:1:1 reaction of Tp(ArN=)Mo(PMe$_3$)(H), ketone and the D-labeled silane PhSiD$_3$ results in the complete retention of the hydride on molybdenum and exclusive delivery of deuterium to the substrate, which is at odds with the key assumptions of the hydride mechanism. Our preliminary investigation of other catalytic systems showed that the nonhydride mechanism is not pertinent to molybdenum only and is operative both for early and late metal systems.[7c] Guan et al. has recently observed a similar result for an iron catalyst.[4m] As to the **2**-catalyzed hydrosilylation, attempted reaction of benzaldehyde with PhSiD$_3$ in the presence of a stoichiometric

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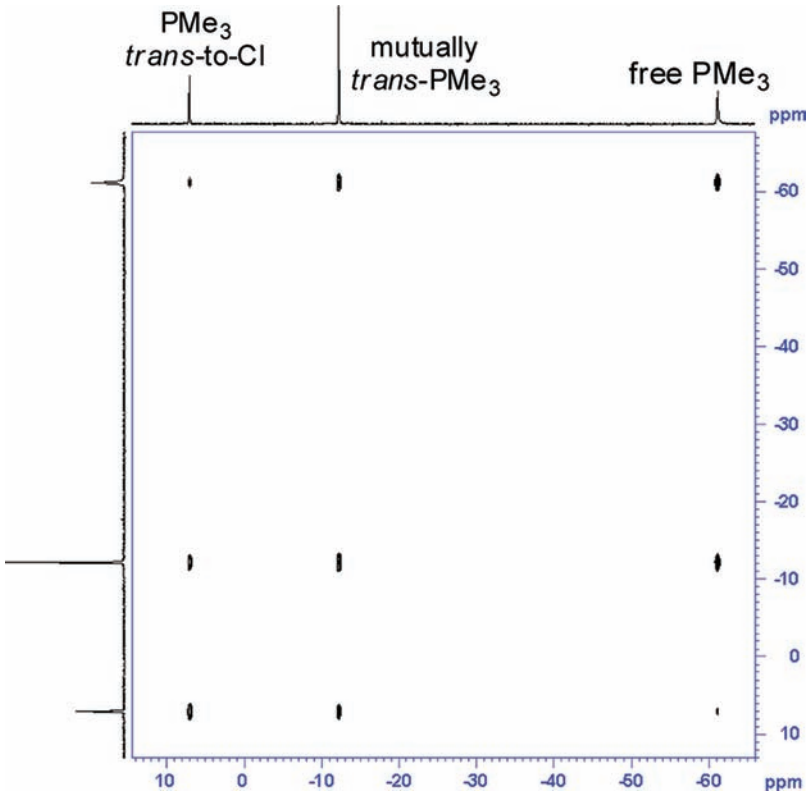


Figure 7. $^{31}P-^{31}P$ EXSY NMR spectrum (22 °C, t_m = 0.5 s) of the mixture of **6** and PMe_3.

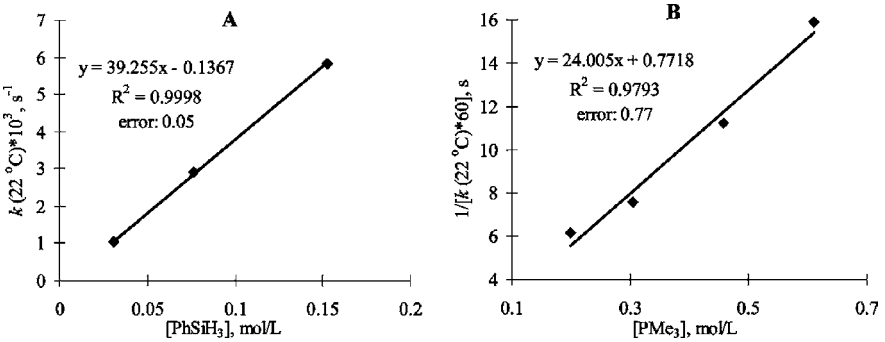
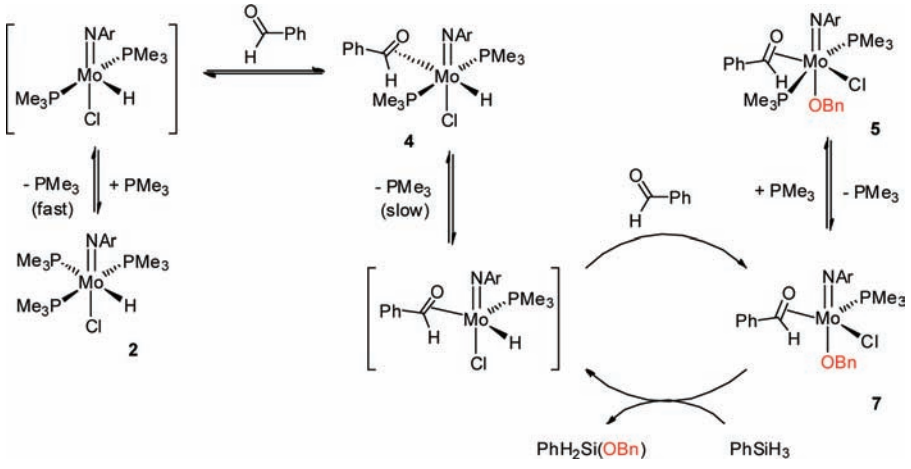


Figure 8. Dependence of the k of the reaction of **3** with $PhSiH_3$ at 22 °C on the concentration of (A) $PhSiH_3$ (standard error 0.05) and (B) PMe_3 (standard error 0.77).

Scheme 5. Alternative Mechanism for the Hydrosilylation of PhC(O)H with $PhSiH_3$ Mediated by 2



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amount of **2** gives primarily $\mathbf{2_D}$ as the major product along with a small amount of **2** and **1**. This observation suggests that the nonhydride mechanism is not the predominant reaction pathway in the case of aldehydes, so that the mechanistic proposal of Scheme 2 stands experimental verification.

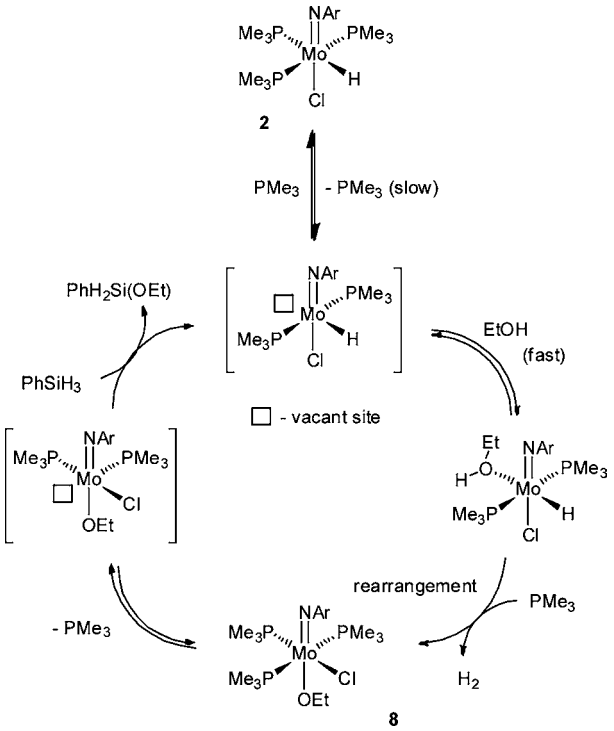
Another challenge for the mechanism outlined in Scheme 2 comes from the fact that under the catalytic conditions of hydrosilylation the aldehyde is present in large excess (relative to the catalyst), and therefore, the actual catalysis may involve the intermediacy of complex **5** instead of **3** (Scheme 2). In this case, the last step of the cycle, the reaction of **5** with $PhSiH_3$, could occur via either η^2-PhC(O)H or PMe_3 dissociation (see above). Further addition of $PhSiH_3$ would result in the formation of the hydrosilylation product and the unsaturated intermediate (ArN=)Mo(H)(Cl)$(PMe_3)_2$, which is instantaneously intercepted by the aldehyde to give **4** and then the benzoxy derivative **5** (Scheme 5). Whichever of the benzoxy complex **3** or **5** is the real intermediate, the final step of this process should include a reaction of silane with the benzoxy group. Our experiments suggest that this is a second-order reaction, but we do not have firm data to speculate whether it goes via the oxidative addition of the Si−H bond to metal to give a Mo(VI) silyl hydride, via the Si−H coordination and formation of a Mo(IV) silane σ-complex,[41] or via an intermolecular σ-bond metathesis or heterolytic silane splitting on the Mo−O bond.[5g,7b] We have recently observed the first Mo(VI) silyl hydride derivatives, as well as established the heterolytic Si−H activation on the Mo-OR bond for the related Cp(ArN=)Mo(OBn)(PMe_3) system, thus confirming the possibility of oxidative addition and heterolytic splitting pathways, respectively.[7b] The small kinetic isotope effect for the reaction of **3** with $PhSiH_3$, $k_H/k_D = 0.96 \pm 0.01$ at 10 °C, appears to favor the σ-bond metathesis or heterolytic silane splitting over the silane oxidative addition pathway. However, one can expect a small KIE for all three mechanisms of silane addition if the preceding phosphine dissociation is the rate limiting step. In the latter case, our experimental data do not allow us to differentiate between the three possible pathways.

How general is this mechanistic proposal? It appears that it applies to aldehydes only. The first observation is that qualitatively the hydrosilylation of cyclohexanone is faster than the hydrosilylation of benzaldehyde, although usually aldehydes react faster than ketones. Second, no η^2-coordinated species has been observed in the case of ketones (cyclohexanone and acetophenone). And third, our test for a nonhydride mechanism (vide supra) suggests that this is the prevailing pathway in the case of **2**-catalyzed hydrosilylation of acetophenone. Indeed, a 1:1:1 reaction of **2** with PhC(O)Me and $PhSiD_3$ at room temperature results overnight in the formation of a mixture of **2** (80%) and deuteride complex $\mathbf{2_D}$ (20%). The predominant incorporation of deuterium into the hydrosilylation product $PhCD(CH_3)OSiD_2Ph$ was also observed by NMR. This result clearly indicates that insertion of PhC(O)Me into the Mo−H bond of **2** (the hydride mechanism[40]) is not the main pathway in this hydrosilylation. Our tentative explanation of the nonhydride mechanism is that it may proceed via a Lewis acid activation of the substrate.[7c] The formation of the minor amount of $\mathbf{2_D}$ (20%) in the labeling experiment with acetophenone can be accounted for by the competing (minor) hydride pathway or a slow H/D exchange between **2** and $PhSiD_3$.

In the case of analogous reaction **2** with cyclohexanone and $PhSiD_3$ (in the 1:1:1 ratio), at 50% conversion a 3:2 mixture of **2** and $\mathbf{2_D}$ is formed, which changes to the 2:3 ratio upon the completion of the reaction. This result indicates that both the hydride and nonhydride mechanisms can operate in this system, most likely because of the reduced steric bulk of cyclohexanone in comparison with acetophenone.

Mechanistic Aspects of Silane Alcoholysis Catalyzed by 2. Analogously to the **2**-catalyzed hydrosilylation of benzaldehyde, the mechanism of ethanolysis of $PhSiH_3$ mediated by **2** also likely involves the intermediacy of the alkoxy complex (ArN=)Mo(Cl)(OEt)$(PMe_3)_3$ (**8**; Scheme 6). The reaction between **2** and ethanol obeys the first order kinetics in **2**, with the k_{eff} being proportional to the ethanol

Scheme 6. Mechanism for the Ethanolysis of $PhSiH_3$ Mediated by Complex 2



concentration (Figure 9, A).[37] With excess ethanol (ca. 20 eqiuvs), the $1/k_{eff}$ is proportional to phosphine concentration (Figure 9, B). This fact suggests that the reaction starts with a reversible dissociation of phosphine, most likely that one positioned *trans* to the hydride (confirmed by $^{31}P-^{31}P$ EXSY NMR; see Figure 3), followed by addition of alcohol to molybdenum (Scheme 6). Such a coordination of EtOH to the metal probably acidifies the O−H bond sufficiently to allow for proton transfer to the hydride to generate dihydrogen. Dissociation of H_2 and phosphine readdition furnishes the ethoxy complex **8**. Similar to the benzoxy derivative **3**,[42] complex **8** can react with silanes to give the alkoxysilane product and regenerate the starting hydrido-chloride **2**. In contrast, previous mechanisms of silane alcoholysis implied the activation of silane by an electrophilic metal center, making it amenable for an attack by an external nucleophile (alcohol),[43] similarly to the key step of the ionic hydrosilylation mechanisms.[13] Another conceivable mechanism of silane alcoholysis by **2** could involve a direct proton transfer from the alcohol to **2** to give a cationic dihydrogen complex as observed in systems with "dihydrogen bonding".[44] However,

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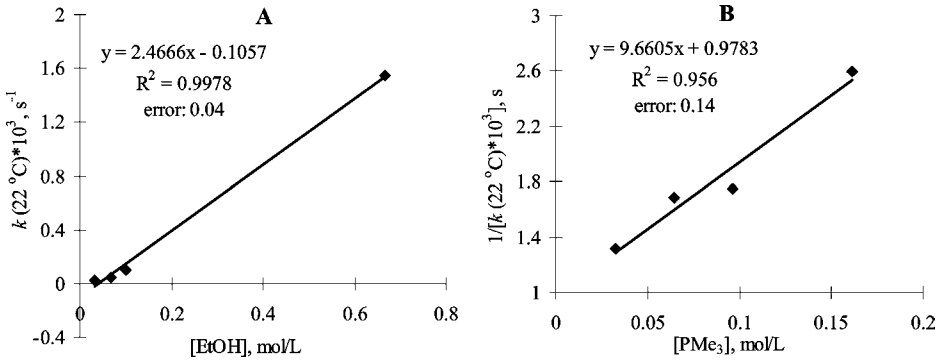
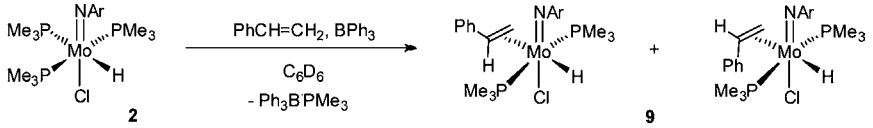


Figure 9. Dependence of the k of the reaction of **2** with EtOH at 22 °C on the concentration of (A) EtOH (standard error 0.04) and (B) PMe_3 (standard error 0.14).

Scheme 7. Reaction of Complex 2 with Styrene



Scheme 7.

the above kinetics (Figure 9) are not consistent with this possibility. The difference between our system and the typical system for dihydrogen bonding and protonolysis most likely comes from the lower acidity of ethanol in comparison with perfluoro alcohols, normally used for studying the dihydrogen bonding.

Mechanistic Aspects of 2-Catalyzed Reactions of Silanes and Alkenes. In contrast to reactions with benzaldehyde and cyclohexanone, the addition of styrene to **2** does not lead to the expected insertion of $PhCH{=}CH_2$ into the Mo−H bond. Rather, the adduct *trans*-(ArN=)Mo(H)(Cl)(η^2-$CH_2{=}CHPh$)$(PMe_3)_2$ (**9**) is formed in a mixture with the starting material. With an equivalent of BPh_3 added, the reaction proceeds to completion (by NMR) to give complex **9** and $Ph_3B{\cdot}PMe_3$ (Scheme 7). No further transformation of **9** into the putative insertion product (ArN=)Mo(Cl)$(CH_2CH_2Ph)(PMe_3)_3$ was observed by NMR upon the readdition of PMe_3. The latter reaction resulted only in the substitution of the η^2-$CH_2{=}CHPh$ ligand and the recovery of the hydride complex **2**.

Compound **9** was characterized by IR and NMR spectroscopy, which reveals the presence of two isomers (7:1, according to $^{31}P\{^1H\}$ NMR). In the ^1H NMR spectrum of **9**, the hydride ligand of the major isomer gives rise to a downfield signal at δ 6.84 ppm (multiplet), coupled in the $^1H{-}^{31}P$ HSQC spectrum (at −18 °C) to two nonequivalent, mutually coupled ^{31}P NMR resonances at δ 0.4 ppm (d, $^2J_{P-P}$ = 111.0 Hz) and δ 1.0 ppm (d, $^2J_{P-P}$ = 111.0 Hz). For the minor isomer of **9**, the Mo*H* signal shows up as a doublet of doublets at δ 5.97 ppm ($^2J_{H-P}$ = 51.3 Hz, $^2J_{H-P}$ = 31.8 Hz). At −18 °C, the ^{31}P NMR spectrum of the minor isomer also contains two mutually coupled signals at δ −2.2 ppm (d, $^2J_{P-P}$ = 103.7 Hz) and δ 0.8 ppm (d, $^2J_{P-P}$ = 103.7 Hz). The large value of the $^2J_{P-P}$ for both isomers indicates the *trans*-arrangement of the PMe_3 ligands, consistent with the structure depicted in Scheme 7. The presence of hydride ligand is also evident from the observation of a Mo−H stretch at 1757 cm^{-1} in the IR spectrum. In the ^1H NMR spectrum, the η^2-coordination[45] of styrene results in the observation of three nonequivalent upfield shifted C*H* signals at δ 4.08, 3.50, and 2.63 ppm (δ 3.82, 3.33, and 3.18 ppm for the minor isomer), coupled in the $^1H{-}^{13}C$ HSQC to the ^{13}C NMR resonances at δ 60.5 and 49.6 ppm (δ 72.2 and 51.7 ppm for the minor isomer). Complex **9** is thermally unstable in solution and slowly (1 week) decomposes to give $PhCH_2CH_3$ and a difficult-to-characterize mixture of unidentified compounds. The formation of ethylbenzene indicates that insertion of the coordinated styrene ligand into the Mo−H bond is, indeed, possible but is extremely slow.

CONCLUSIONS

The compound **2** has been found to catalyze a variety of hydrosilylation reactions, including a rare example of the hydrosilylation of nitriles. Possible catalytic cycles for the hydrosilylation were proposed on the basis of studying conceivable steps under stoichiometric conditions. Low temperature VT NMR studies, as well as kinetic measurements for the reactions of **2** with benzaldehyde and ethanol, indicate that the hydrosilylation of carbonyls and silane alcoholysis proceed via the initial substrate activation, but not silane addition. The catalytic cycle of hydrosilylation of benzaldehyde includes the intermediacy of the Mo(IV) benzoxy complex **5**, formed by the insertion of PhC(O)H into the Mo−H bond of **2**. **5** reacts with $PhSiH_3$ to afford the silyl ether and to recover the hydride **2**. On the other hand, a 1:1:1 D-labeling experiment demonstrated that **2**-catalyzed hydrosilylation of more sterically demanding substrates, such as acetophenone, proceeds via a nonhydride mechanism, which we tentatively consider as a Lewis acid activation of the substrate. Analogously to carbonyls, complex **2** reacts with styrene to form the η^2-styrene adduct **9**, which slowly decomposes (presumably via insertion of the coordinated styrene $CH_2{=}CHPh$ into the Mo−H bond) to form ethylbenzene. Intuitively, such products of insertion of organic substrates into the Mo−H bond of **2** could serve as intermediates not only in hydrosilylation but also in other catalytic processes, such as hydrogenation and/or hydroboration reactions.[46] These reactions are currently under investigation in our laboratories and will be reported in due course.

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EXPERIMENTAL SECTION

All manipulations were carried out using conventional inert atmosphere glovebox and Schlenk techniques. Dry diethyl ether, toluene, hexanes, and acetonitrile were obtained, using Innovative Technology solvent purification columns, other solvents were dried by distillation over appropriate drying agents. C_6D_6 and PhMe-d_8 were dried by distillation over the K/Na alloy. NMR spectra were obtained with a Bruker DPX-300 and Bruker DPX-600 instruments (^{1}H: 300 and 600 MHz; ^{2}D: 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). $PhSiCl_3$, $(EtO)_3SiH$, $SiMe_4$, $PhMeSiCl_2$, PMHS, PMe_3, and BPh_3 were purchased from Aldrich. $PhSiH_3$ and $PhSiD_3$ were prepared by the reaction of $PhSiCl_3$ with $LiAlH_4$ and $LiAlD_4$, respectively. Organic substrates (benzaldehyde, acetophenone, acetone, 1-hexene, styrene, benzonitrile, acetonitrile, 1-octyne, ethanol, and propanol-2) were purchased from Sigma-Aldrich and used without further purification. Preparation of $(ArN{=})MoCl_2(PMe_3)_3$ (**1**)[18] was reported previously. All catalytic and NMR scale reactions, as well as kinetic experiments were done under nitrogen atmosphere using NMR tubes equipped with Teflon valves. The structures and yields of all hydrosilylated products were determined by NMR analysis using tetramethylsilane as an internal standard. NMR analysis was performed at room temperature unless stated otherwise.

Preparation of $(ArN)Mo(H)(Cl)(PMe_3)_3$ (2). A solution of L-Selectride in THF (1.9 mL, 1.9 mmol, 1.0 M) was added at −30 °C to a solution of **1** (1.05 g, 1.9 mmol) in 50 mL of toluene. The mixture was stirred at −30 °C for 15 min, then allowed to reach ambient temperature and stirred for additional two hours. Once the reaction reached room temperature the color of the mixture changed from pale green to brown and formation of precipitate was observed. The mixture was filtered and the residue was extracted with 50 mL of toluene. All volatiles were removed in vacuum to give a fine brown solid of complex **2**. Yield: 0.55 g, 65%. ^{1}H NMR (300 MHz; C_6D_6; 25 °C; δ, ppm): 1.19 (d, $^3J_{H-H}$ = 6.6 Hz, 4 *CH*$_3$, N*Ar*); 1.35 (d, $^2J_{H-P}$ = 5.7 Hz, 9H, P*Me*$_3$); 1.45 (vt, $^2J_{H-P}$ = 3 Hz, 18H, 2 P*Me*$_3$); 4.37 (sept, $^3J_{H-H}$ = 6.9 Hz, 2H, 2 *CH*, N*Ar*); 5.31 (dt, $^1J_{H-P}$ = 28.5 Hz, $^1J_{H-P}$ = 51.9 Hz, 1H, Mo-*H*); 6.86 (m, 3H, N*Ar*). ^{31}P{^{1}H} NMR (121.5 MHz; C_6D_6; 25 °C; δ, ppm): −17.75 (t, $^2J_{P-P}$ = 13.4 Hz, 1P, *P*Me$_3$); −1.10 (d, $^2J_{P-P}$ = 13.4 Hz, 2P, 2 *P*Me$_3$). ^{13}C{^{1}H} NMR (75.5 MHz; C_6D_6; 25 °C; δ, ppm): 21.1 (vt, $^1J_{C-P}$ = 11.3 Hz, P*Me*$_3$); 21.2 (d, $^1J_{C-P}$ = 15.9 Hz, P*Me*$_3$); 24.2 (s, *CH*$_3$, N*Ar*); 26.6 (s, *CH*, N*Ar*); 123.2, 124.9, 144.3 (all singlets, N*Ar* aromatic carbons). IR (nujol, selected bands): 1714 cm^{-1} (s, Mo−H). Elem. Anal. (%) Calcd for $C_{21}H_{45}ClMoNP_3$ (535.903): C, 47.07; H, 8.46; N, 2.61. Found: C, 46.47; H, 8.14; N, 2.77.

A. NMR Scale Reaction of 2 with Benzaldehyde. *Low-Temperature VT Reaction.* PhC(O)H (5.2 μL, 0.051 mmol) was added at −80 °C to a solution of **2** (24.1 mg, 0.043 mmol) in 0.6 mL of toluene-d_8 in an NMR tube. The mixture was immediately frozen in liquid N_2 and the sample was placed into the NMR machine precooled to −30 °C. The temperature was dropped down to −50 °C and the reaction was monitored by VT NMR spectroscopy. NMR analysis showed the selective formation of *trans*-$(ArN)Mo(H)(Cl)(\eta^2\text{-}PhC(O)H)(PMe_3)_2$ (**4**) at −5 °C. All attempts to isolate **4** were unsuccessful and led to mixtures of **4**, $(ArN)MoCl_2(PMe_3)_3$ (**1**), $(ArN)Mo(Cl)(OCH_2Ph)(PMe_3)_3$ (**3**; see the NMR scale generation and characterization below), and unidentified decomposition products.

4. In solution, this complex exists as a mixture of two isomers, depending on the orientation of coordinated benzaldehyde (5:1 ratio, according to the ^{31}P{^{1}H} NMR spectrum).

Major Isomer of ***4***. ^{1}H NMR (600 MHz; toluene-d_8; 0 °C; δ, ppm): 7.71 (d, $^3J_{H-H}$ = 6.6 Hz, 2H, *o*-H, η^2-O=CH*Ph*); 7.32 (dd, $^2J_{H-P}$ = 35.0 Hz, 1H, Mo*H*); 7.29 (t, $^3J_{H-H}$ = 6.6 Hz, 2H, *m*-H, η^2-O=CH*Ph*); 6.99 (m, 1H, *p*-H, η^2-O=CH*Ph*); 7.08 (m, 2H, *m*-H of N*Ar*, overlapping with signals of minor); 6.85 (m, 1H, *p*-H of N*Ar*, overlapping with signals of minor isomer); 5.77 (s, 1H, η^2-O=C*H*Ph); 4.37 (bs, 1H, *i*-Pr, N*Ar*); 4.12 (sept, $^3J_{H-H}$ = 6.9 Hz, 1H, *i*-Pr, N*Ar*); 1.49 (d, $^2J_{H-P}$ = 9.6 Hz, 9H, P*Me*$_3$, overlapping with signals of minor isomer); 1.43 (bs, 6H, *i*-Pr, N*Ar*, overlapping with signals of minor isomer); 1.28 (d, $^3J_{H-H}$ = 6.9 Hz, 3H, *i*-Pr, N*Ar*); 1.21 (m, 3H, *i*-Pr, N*Ar*); 1.16 (d, $^2J_{H-P}$ = 9.6 Hz, 9H, P*Me*$_3$). ^{31}P{^{1}H} NMR (243 MHz; toluene-d_8; −17 °C; δ, ppm): 1.43 (d, $^2J_{P-P}$ = 109.3 Hz, 1P, *P*Me$_3$); −5.59 (d, $^2J_{P-P}$ = 109.3 Hz, 1P, *P*Me$_3$).

Minor Isomer of ***4***. ^{1}H NMR (600 MHz; toluene-d_8; 0 °C; δ, ppm): *o*-H, *m*-H, and *p*-H signals of η^2-O=CH*Ph* are obscured by the corresponding signals of major isomer; 7.08 (m, 2H, *m*-H of N*Ar*, overlapping with signals of major isomer); 6.85 (m, 1H, *p*-H of N*Ar*, overlapping with signals of major isomer); 6.59 (dd, $^2J_{H-P}$ = 41 and 49 Hz, 1H, Mo*H*); 5.17 (s, 1H, η^2-O=C*H*Ph); 4.31 (bs, 1H, *i*-Pr, N*Ar*); 3.46 (bs, 1H, *i*-Pr, N*Ar*); 1.49 (m, 9H, P*Me*$_3$, overlapping with signal of major isomer); 1.43 (bs, 6H, *i*-Pr, N*Ar*, overlapping with signal of major isomer); 1.26 (m, 3H, *i*-Pr, N*Ar*); 1.20 (d, $^2J_{H-P}$ = 7.8 Hz, 9H, P*Me*$_3$); 1.03 (d, $^3J_{H-H}$ = 6.9 Hz, 3H, *i*-Pr, N*Ar*). ^{31}P{^{1}H} NMR (243 MHz; toluene-d_8; −17 °C; δ, ppm): 0.77 (d, $^2J_{P-P}$ = 114.2 Hz, 1P, *P*Me$_3$); −5.56 (d, $^2J_{P-P}$ = 114.2 Hz, 1P, *P*Me$_3$).

^{13}C{^{1}H} NMR (151 MHz; toluene-d_8; −17 °C; both isomers; δ, ppm): 150.5, 149.5, 148.2, 147.3, 146.8, 146.7, 144.7, 143.7 (*o*-C and *i*-C of N*Ar* and *i*-C of η^2-O=CH*Ph* for both isomers); 129.5 (s, η^2-O=CH*Ph*, *o*-C, minor isomer); 128.6 (s, η^2-O=CH*Ph*, *p*-C, major isomer); *m*-C and *p*-C signals of η^2-O=CH*Ph* of minor isomer are overlapping with PhMe-d_8 signals and corresponding signals of major isomer; 128.0 (s, η^2-O=CH*Ph*, *o*-C, major isomer); 126.7 (s, η^2-O=CH*Ph*, *m*-C, major isomer); 125.5 (s, *m*-C, N*Ar*, overlapping signals for both isomers); 123.1 and 123.0 (s, *p*-C, N*Ar* for two isomers); 86.8 (bs, η^2-O=C*H*Ph, major isomer); 76.9 (s, η^2-O=C*H*Ph, minor isomer); 27.0 (s, *i*-Pr, N*Ar*, both isomers); 26.9 (s, *i*-Pr, N*Ar*, major isomer); 25.9 (s, *i*-Pr, N*Ar*, both isomers); 23.4 (s, *i*-Pr, N*Ar*, minor isomer); 23.2 (s, *i*-Pr, N*Ar*, major isomer); 17.2 (d, $^1J_{C-P}$ = 27.5 Hz, P*Me*$_3$, major isomer); 16.9 (d, $^1J_{C-P}$ = 24.9 Hz, P*Me*$_3$, minor isomer); 16.8 (s, *i*-Pr, N*Ar*, minor isomer); 13.7 (d, $^1J_{C-P}$ = 24.9 Hz, P*Me*$_3$, minor isomer); 13.5 (d, $^1J_{C-P}$ = 27.5 Hz, P*Me*$_3$, major isomer). IR (nujol, selected bands): 1771 cm^{-1} (s, Mo−H); 1595 cm^{-1} (s, C=O).

B. RT Reaction. Benzaldehyde (5.2 μL, 0.051 mmol) was added at room temperature to a solution of **2** (24.1 mg, 0.043 mmol) in 0.6 mL of C_6D_6 in an NMR tube. NMR analysis after 10 min at room temperature showed the selective formation of $(ArN)Mo(H)(Cl)(\eta^2\text{-}PhC(O)H)(PMe_3)_2$ (**4**). The reaction mixture was left at room temperature for 5 h and was monitored by NMR spectroscopy, which during this time revealed the rearrangement of **4** into **3**.

An analogous room temperature reaction of **2** (27.9 mg, 0.049 mmol) with excess PhC(O)H (50.1 μL, 0.49 mmol) leads to the formation of $(ArN)Mo(Cl)(OCH_2Ph)(\eta^2\text{-}PhC(O)H)(PMe_3)_2$ (**5**). All attempts to isolate either **3** or **5** in the analytically pure form were unsuccessful.

Addition of excess $PhSiH_3$ (ca. 10 equiv. to **2**) at room temperature to both **3** and **5** affords after 5 min $PhH_2Si(OBn)$ and $PhHSi(OBn)_2$ and regenerates the complex **2**.

3. ^{1}H NMR (300 MHz; C_6D_6; δ, ppm): 7.40 (d, $^3J_{H-H}$ = 7.5 Hz, 2H, *o*-H, OCH_2Ph); 6.86−7.26 (m, 6H, *m*-H and *p*-H of N*Ar* and OCH_2Ph); 5.13 (s, 2H, OCH_2Ph); 4.32 (bm, 2H, 2 *CH*, N*Ar*); 1.58 (m, 6H, 2 *CH*$_3$, N*Ar*); 1.47 (d, $^3J_{H-H}$ = 6.3 Hz, *CH*$_3$, N*Ar*); 1.35 (bm, 27H, P*Me*$_3$); 1.26 (d, $^3J_{H-H}$ = 6.3 Hz, *CH*$_3$, N*Ar*). ^{31}P{^{1}H} NMR (121.5 MHz; toluene-d_8; δ, ppm): 8.29 (t, $^2J_{P-P}$ = 15.8 Hz, 1P, *P*Me$_3$); 9.50 (d, $^2J_{P-P}$ = 15.8 Hz, 2P, 2 *P*Me$_3$). ^{13}C{^{1}H} NMR (75.5 MHz; C_6D_6; δ, ppm): 151.4 (s, *i*-C, N*Ar*); 147.5 (s, *i*-C, OCH_2Ph); 144.7 (s, *o*-C, N*Ar*); 126.5, 125.3, 123.9 (*m*-C and *p*-C of N*Ar* and *p*-C of OCH_2Ph); *o*-C and *m*-C signals of OCH_2Ph are overlapping with signal of C_6D_6; 71.5 (s, OCH_2Ph); 27.2 (s, *i*-Pr, N*Ar*); 22.8 (s, *i*-Pr, N*Ar*); 21.9 (vt, $^1J_{C-P}$ = 21.2 Hz, P*Me*$_3$); 21.2 (s, *i*-Pr, N*Ar*); 20.9 (s, *i*-Pr, N*Ar*); 20.8 (s, *i*-Pr, N*Ar*); 16.6 (d, $^1J_{C-P}$ = 20.4 Hz, P*Me*$_3$).

5. ^{1}H NMR (300 MHz; C_6D_6; δ, ppm): 1.02 (d, $^2J_{H-P}$ = 7.2 Hz, 9H, P*Me*$_3$); 1.15 (m, 3H, *CH*$_3$, N*Ar*); 1.19 (m, 3H, *CH*$_3$, N*Ar*); 1.28 (m, 3H, *CH*$_3$, N*Ar*); 1.30 (d, $^2J_{H-P}$ = 7.9 Hz, 9H, P*Me*$_3$); 1.41 (m, 3H, *CH*$_3$, N*Ar*); 3.43 (sept, $^3J_{H-H}$ = 6.5 Hz, 1H, *CH*, N*Ar*); 4.60 (d, $^2J_{H-H}$ = 12.3 Hz, 1H, OCH_2Ph); 4.83 (sept, $^3J_{H-H}$ = 6.5 Hz, 1H, *CH*, N*Ar*);

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5.13 (d, $^2J_{H-H}$ = 12.3 Hz, 1H, OC*H*$_2$Ph); 5.37 (d, $^3J_{H-P}$ = 3.9 Hz, 1H, η^2-PhC(O)*H*); 6.82−7.60 (m, 13 H, aromatic protons of N*Ar* and 2 C*Ph*).). ^{31}P{^{1}H} NMR (121.5 MHz; C_6D_6; δ, ppm): −5.3 (d, $^2J_{P-P}$ = 290.3, 1P, PMe_3); −6.9 (d, $^2J_{P-P}$ = 290.3, 1P, PMe_3). ^{13}C{^{1}H} NMR (75.5 MHz; C_6D_6; selected resonances; δ, ppm): 11.3 (dd, $^1J_{C-P}$ = 17.8 Hz, J_{C-P} = 4.4 Hz, P*Me*$_3$); 13.3 (dd, $^1J_{C-P}$ = 18.7 Hz, J_{C-P} = 5.0 Hz, P*Me*$_3$); 25.5 (s, *CH*, N*Ar*); 26.6 (s, *CH*, N*Ar*); 71.5 (s, O*CH*$_2$Ph); 90.7 (s, η^2-Ph*C*(O)H).

Preparation of (ArN)Mo(Cl)(OCy)(PMe$_3$)$_3$ (6). Cyclohexanone (64.0 mg, 0.650 mmol) was added to a toluene solution of **2** (350.0 mg, 0.650 mmol). The reaction mixture was left at room temperature for 24 h, after which time the mixture was placed into freezer. The product was crystallized at −78 °C, filtered off and dried in vacuum, affording a light-green crystalline solid of **8**. Yield: 120 mg, 51%. ^{1}H NMR (300 MHz; C_6D_6; δ, ppm): 0.72−1.53 (m, 8H, O*Cy* and 12H, 4 *CH*$_3$, N*Ar*); 1.25 (d, $^2J_{H-P}$ = 7.3 Hz, 9H, P*Me*$_3$); 1.29 (vt, $^2J_{H-P}$ = 2.9 Hz, 18H, 2 P*Me*$_3$); 1.53−1.64 (m, 1H, O*Cy*); 1.67−1.80 (m, 2H, O*Cy*); 1.92−2.04 (m, 2H, O*Cy*); 3.1−4.3 (bm, 1H, *CH*, N*Ar*); 4.07 (m, 1H, *CH*-O, O*Cy*); 4.3−5.4 (bm, 1H, *CH*, N*Ar*); 6.85−7.08 (m, 3H, N*Ar*). ^{31}P{^{1}H} NMR (121.5 MHz; C_6D_6; δ, ppm): −12.2 (d, $^2J_{P-P}$ = 14.8 Hz, 2P, 2 P*Me*$_3$); 7.0 (t, $^2J_{P-P}$ = 14.8 Hz, 1P, P*Me*$_3$). ^{13}C{^{1}H} NMR (75.5 MHz; C_6D_6; δ, ppm): 17.3 (vt, $^1J_{C-P}$ = 9.4 Hz, P*Me*$_3$); 22.7 (d, $^1J_{C-P}$ = 20.7 Hz, P*Me*$_3$); 26.3 (s, *Cy*); 27.2 (s, *Cy*); 39.8 (s, *Cy*); 76.1 (s, *C*-O, *Cy*); 124.3 (s, N*Ar*); 128.7 (s, N*Ar*); 151.4 (s, *i*-C, N*Ar*). ^{1}H NMR (600 MHz; CD_2Cl_2; 258 K; δ, ppm): 0.84 (m, 4H, O*Cy* (γ)); 1.10 (d, $^2J_{H-H}$ = 6.9 Hz, 12H, N*Ar*); 1.34 (vt, $^2J_{H-P}$ = 2.6 Hz, 18H, 2 P*Me*$_3$); 1.47 (d, $^2J_{H-P}$ = 7.7 Hz, 9H, P*Me*$_3$); 1.55 (bm, 2H, O*Cy*(δ)); 1.66 (bd, $^2J_{H-H}$ = 10.7 Hz, 2H, O*Cy*(β)); 3.60 (bt, $^2J_{H-H}$ = 9.3 Hz, 1H, *CH*-O); 3.71 (b, 1H, *CH*); 4.55 (b, 1H, *CH*); 6.88 (b, 1H, *p*-*Ar*), 6.93 (m, 2H, *m*-*Ar*).

^{13}C NMR (150.9 MHz; CD_2Cl_2; 258 K; δ, ppm): 149.4 (s, *i*-*Ar*), 143.1 (s, *o*-*Ar*), 123.8 (s, *m*-*Ar*), 122.7 (s, *p*-*Ar*), 75.4 (s, HC-O), 38.7 (s, β-Cy and γ-Cy), 26.6 (s, CH (Ar)), 25.9 (s, CH (Ar)), 25.6 (s, Me (Ar)), 25.5 (s, δ-Cy), 25.1 (s, Me (Ar)), 22.1 (d, $^1J_{C-P}$ = 22.6 Hz, PMe_3), 16.7 (vt, J_{C-P} = 9.3 Hz, PMe_3)

X-ray. Single crystals for X-ray analysis formed in an NMR tube contained the solution of **8** in C_6D_6. Elem. Anal. (%) Calcd. for $C_{27}H_{55}ClMoNOP_3$ (634.05): C, 51.15; H, 8.74; N, 2.21. Found: C, 50.89; H, 9.01; N, 2.06.

NMR Scale Reaction of 2 with Ethanol. EtOH (1.2 μL, 0.02 mmol) was added in one portion at room temperature to a solution of **2** (10.1 mg, 0.019 mmol) in 0.6 mL of C_6D_6 in an NMR tube. Release of the gas was observed almost immediately and the color of the mixture slowly turned from brown to light green. The reaction mixture was monitored by NMR spectroscopy for 16 h at room temperature until all starting material was consumed. All volatiles were pumped off, the oily residue was dried under vacuum, redissolved in fresh C_6D_6 and checked with NMR analysis that showed the presence of only one product (ArN)Mo(Cl)(OEt)(PMe$_3$)$_3$ (**8**). Complex **8** is stable in solution at room temperature at least for a week. All attempts to isolate **8** in an analytically pure form gave a difficult-to-separate mixture of **8** and (ArN=)MoCl$_2$(PMe$_3$)$_3$ (**1**). Addition of excess $PhSiH_3$ to a solution of **7** in C_6D_6 at room temperature gives, after 5 min, the formation of PhH$_2$Si(OEt) and recovers **2**.

8. ^{1}H NMR (300 MHz, C_6D_6 δ, ppm): 7.00 (m, 3H, *m*-H and *p*-H of N*Ar*); 4.31 (bs, 2H, 2*CH*, N*Ar*); 4.11 (q, $^3J_{H-H}$ = 6.9 Hz, 2H, O*CH*$_2$); 1.26 (m, 27H, 3P*Me*$_3$); 1.19 (d, $^3J_{H-H}$ = 6.9 Hz, 6H, 2*CH*$_3$, N*Ar*); 1.17 (d, $^3J_{H-H}$ = 6.9 Hz, 6H, 2*CH*$_3$, N*Ar*); 1.10 (t, $^3J_{H-H}$ = 6.9 Hz, 3H, OCH$_2$*CH*$_3$). ^{31}P{^{1}H} NMR (121.5 MHz; C_6D_6; δ, ppm): 8.19 (t, $^2J_{P-P}$ = 15.8 Hz, PMe_3); −9.19 (d, $^2J_{P-P}$ = 15.8 Hz, 2PMe_3). ^{13}C{^{1}H} NMR (75.5 Hz; C_6D_6; δ, ppm): 123.3 (s, N*Ar*); 123.2 (s, NAr); 64.4 (s, O*CH*$_2$); 26.1 (s, *CH*, N*Ar*); 25.6 (s, *CH*$_3$, N*Ar*); 25.1 (s, *CH*$_3$, N*Ar*); 21.4 (d, $^1J_{C-P}$ = 23.1 Hz, P*Me*$_3$); 20.7 (s, OCH$_2$*CH*$_3$); 16.8 (vt, $^1J_{C-P}$ = 11.6 Hz, P*Me*$_3$).

NMR Scale Reaction of 2 with PhCH$_2$OH. PhCH$_2$OH (8.5 μL, 0.08 mmol) was added in one portion at room temperature to a solution of **2** (8.6 mg, 0.016 mmol) in 0.6 mL of C_6D_6 in an NMR tube. Immediate gas release and changing of color from brown to light green was observed. The mixture was left at room temperature for 5 h. NMR analysis showed full conversion of the starting material and formation of a difficult-to-separate mixture of **3** and (ArN)-MoCl$_2$(PMe$_3$)$_3$ (**1**) (3:1, respectively, according to ^{31}P{^{1}H} NMR analysis). Lowering the temperature of the experiment does not improve selectivity of the reaction.

NMR Scale Reaction of 2 with Styrene. Styrene (5.3 μL, 0.046 mmol) was added in one portion at room temperature to a solution of **2** (26.2 mg, 0.046 mmol) in 0.6 mL of C_6D_6 in an NMR tube. No visual changes were observed. The mixture was left at room temperature for 5 min and then the reaction was monitored by NMR analysis for 24 h. Release of phosphine and formation of styrene adduct (ArN)Mo(H)(Cl)(η^2-CH$_2$=CHPh)(PMe$_3$)$_2$ (**9**) in a mixture with the starting material was detected by NMR spectroscopy (**2**/**9** = 1.3 by ^{31}P NMR). No further conversion of **2** into **9** was observed after additional 24 h. BPh_3 (11.2 mg, 0.046 mmol) was added to the mixture at room temperature. Immediate formation of the white precipitate of Ph$_3$B•PMe$_3$ was observed. NMR analysis after 5 min at room temperature showed full conversion of **2** and quantitative formation of **9** as a mixture of two isomers (7:1 ratio). The mixture was filtered, all volatiles were pumped off, and the residue was extracted with 1 mL of hexane to give a brown oil. Yield: 13.2 mg, 51%. The product is not stable in solution at room temperature and slowly (1 week) decomposes to give PhCH$_2$CH$_3$ and a difficult-to-characterize mixture of unidentified compounds.

IR (nujol, selected bands): 1757 cm^{-1} (s, Mo−H)

Major Isomer of ***9***. ^{1}H NMR (300 MHz; C_6D_6; δ, ppm): 7.61 (bd, $^3J_{H-H}$ = 6.9 Hz, 1H, *o*-H, CH$_2$=C*H*Ph); 7.43 (bd, $^3J_{H-H}$ = 6.9 Hz, 1H, *o*-H, CH$_2$=CH*Ph*); 7.27 (bm, 4H N*Ar* and *m*-H of CH$_2$=CH*Ph*); 7.02 (bm, 1H, *p*-H, CH$_2$=CH*Ph*); 6.84 (bm, 2H, N*Ar* and Mo-*H*, found by ^{1}H−^{31}P HSQC NMR); 4.08 (bm, 1H, CH$_2$=CHPh); 3.50 (bm, 1H, CH$_2$=CHPh); 3.33 (bm, 2H, 2 *CH*, N*Ar*); 2.63 (broad dd, J_{H-H} = 12.9 Hz, 1H, CH$_2$=CHPh); 1.40 (bm, 9H, P*Me*$_3$, overlapping with signal for minor isomer); 1.20 (bd, $^3J_{H-H}$ = 6.6 Hz, 6H, 2 *CH*$_3$, N*Ar*); 1.12 (bm, 15H, 2 *CH*$_3$ of N*Ar* and P*Me*$_3$). ^{1}H{^{31}P} NMR (300 MHz; C_6D_6; δ, ppm): 7.61 (d, $^3J_{H-H}$ = 6.9 Hz, 1H, *o*-H, CH$_2$=C*H*Ph); 7.43 (d, $^3J_{H-H}$ = 6.9 Hz, 1H, *o*-H, CH$_2$=CH*Ph*); 7.29 (m, 4H, N*Ar* and *m*-H of CH$_2$=CH*Ph*); 7.04 (m, 1H, *p*-H, CH$_2$=CH*Ph*); 6.84 (m, 2H, N*Ar* and Mo-*H*, found by ^{1}H−^{31}P HSQC NMR); 4.08 (dd, J_{H-H} = 13.7 and 11.0 Hz, 1H, CH$_2$=CHPh); 3.50 (dd, J_{H-H} = 11.0 and 3.9 Hz, 1H, CH$_2$=CHPh); 3.33 (sept, $^3J_{H-H}$ = 6.9 Hz, 2H, 2 *CH*, N*Ar*); 2.63 (dd, J_{H-H} = 13.7 and 3.9 Hz, 1H, CH$_2$=CHPh); 1.40 (s, 9H, P*Me*$_3$); 1.20 (d, $^3J_{H-H}$ = 6.9 Hz, 6H, 2 *CH*$_3$, N*Ar*); 1.15 (d, $^3J_{H-H}$ = 6.9 Hz, 6H, 2 *CH*$_3$, N*Ar*); 1.11 (s, 9H, P*Me*$_3$). ^{31}P NMR (121.5 MHz; C_6D_6; selectively decoupled from methyl groups; δ, ppm): −0.05 (d, $^2J_{P-H}$ = 39.2 Hz, 2 PMe_3). ^{31}P{^{1}H} NMR (243 MHz; toluene-d$_8$; −18 °C; δ, ppm): 0.4 (d, $^2J_{P-P}$ = 111.0 Hz, PMe_3); 1.0 (d, $^2J_{P-P}$ = 111.0 Hz, PMe_3, major isomer). ^{13}C{^{1}H} NMR (75.5 MHz; C_6D_6; δ, ppm): 149.0, 147.3, 146.6, 143.2 (s, quaternary C of N*Ar* and CH$_2$=CH*Ph*); 135.7 (s, *o*-C, CH$_2$=CH*Ph*); 128.4, 126.8, 125.7, 124.2, 123.4 (s, *m*-C and *p*-C of N*Ar* and CH$_2$=CH*Ph*); 60.5 (s, CH$_2$=*CH*Ph); 49.6 (bs, *CH*$_2$=C=CHPh); 28.4 (s, *CH*, N*Ar*); 24.9 (s, *CH*$_3$, N*Ar*); 23.9 (s, *CH*$_3$, N*Ar*); 17.9 (d, $^1J_{C-P}$ = 12.8 Hz, P*Me*$_3$); 17.5 (d, $^1J_{C-P}$ = 12.1 Hz, P*Me*$_3$).

Minor Isomer of ***9***. Because of the low abundance of minor isomer, we present only selected data. ^{1}H NMR (300 MHz; C_6D_6; δ, ppm): 5.97 (dd, $^2J_{H-P}$ = 51.3 Hz, $^2J_{H-P}$ = 31.8 Hz, 1H, Mo-*H*); 3.82 (m, 1H, CH$_2$=CHPh, minor isomer); 3.18 (m, 2H, CH$_2$=CHPh, minor isomer); 1.40 (bm, 9H, P*Me*$_3$, overlapping with the signal for major isomer). ^{1}H{^{31}P} NMR (300 MHz; C_6D_6; δ, ppm): 5.97 (s, 1H, Mo-*H*); 3.82 (dd, J_{H-H} = 12.9 Hz, 1H, CH$_2$=CHPh); 3.20 (m, 1H, CH$_2$=CHPh); 3.13 (dd, J_{H-H} = 12.9 and 3.6 Hz, 1H, CH$_2$=CHPh); 1.37 (s, 9H, P*Me*$_3$). ^{31}P{^{1}H} NMR (243 MHz; toluene-d$_8$; δ, ppm): −2.7 (d, $^2J_{P-P}$ = 104.0, PMe_3); 0.6 (d, $^2J_{P-P}$ = 104.0, PMe_3). ^{31}P{^{1}H} NMR (243 MHz; toluene-d$_8$; −18 °C; δ, ppm): −2.2 (d, $^2J_{P-P}$ = 103.7 Hz, PMe_3); 0.8 (d, $^2J_{P-P}$ = 103.7 Hz, PMe_3). ^{1}H−^{13}C HSQC NMR (f1: 300 MHz; f2: 75.5 MHz; J = 145.0 Hz; C_6D_6; δ, ppm, selected resonances): 72.2 (PhCH=CH$_2$); 51.7 (PhCH=CH$_2$).

General Procedure for Hydrosilylation Reactions Using 2. A solution of organic substrate and silane (1:1 ratio), and tetramethylsilane (5 mol %) in 0.6 mL of C_6D_6 was added in one portion at room

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temperature to complex **2** (5−6 mol %). The mixture was immediately transferred to an NMR tube. Depending on the substrate, the reaction mixture was monitored by NMR analysis either at room temperature or at 50 °C. Structures of all products were determined by NMR spectroscopy. Conversion of organic substrates and yields of products were calculated by NMR analysis using tetramethylsilane as the internal standard.

General Procedure for Kinetic NMR Studies with 2. Reagents were added at −50 °C to a solution of **2** (16.5 mg, 0.031 mmol) and 5.0 mol % P(*o*-Tol)$_3$ in 0.6 mL of toluene-d$_8$ in an NMR tube. After addition the mixture was immediately frozen in liquid nitrogen and the NMR tube was placed into precooled (−30 °C) NMR machine. For benzaldehyde, depending on the experiment, the sample was slowly warmed up to a desired temperature (−5 °C for the reaction of **2** with PhC(O)H to produce **4**, room temperature for the rearrangement of **4** into **3**) and the reaction of **3** with PhSiH$_3$ and PMe$_3$ to form **2**) and monitored by ^{31}P{^{1}H} NMR analysis. The rate constants were obtained from the integration of the ^{31}P NMR signals of PMe$_3$ ligands (integrals were normalized to the integral of the standard, P(*o*-Tol)$_3$), resulting in the linear −ln[C]/time plots. An analogous procedure was used for kinetic NMR studies in the case of ethanol.[37]

Experimental Details of EXSY NMR Studies. The EXSY NMR spectra were acquired on a Bruker Avance AV600 spectrometer equipped with a BBO-Z grad probe and VT accessory. ^{31}P and ^{1}H 2D EXSY NMR spectra were recorded with a pulse sequence "noesygpph" (2D homonuclear correlation via dipolar coupling, dipolar coupling may be due to NOE or chemical exchange, phase sensitive, with gradient pulses in mixing time)[47] from Bruker pulse program library. A total of 2 scans per FID for ^{1}H and 4 scans for ^{31}P of 2K data points were used per time increment. A total of 256 time increments were collected for both ^{1}H and ^{31}P. The FIDs were Fourier transformed to generate and 1024 × 1024 data matrix. Two EXSY spectra were recorded, one EXSY spectrum with a mixing time (t_m) of between 100 and 500 ms, which contains the exchange cross peaks and a reference EXSY spectrum with a mixing time 0 ms, which shows no exchange cross peaks. All spectra were processed and analyzed using Bruker Topspin 2.1 Pl4 software running on Windows XP. The series of ^{1}H 1D EXSY NMR spectra were recorded using the "selnogp" (1D NOESY using selective refocusing with a shaped pulse, dipolar coupling may be due to NOE or chemical exchange)[48] pulse sequence from the Bruker library. Each spectrum was acquired using 16 scans and 32 K data points with a spectral width of 20 kHz. The offset frequency was always adjusted on resonance with the analyzed signal. The acquired FIDs were processed using a line broadening of 0.3 Hz and zero filled to 65 K points. A series of 5 to 8 1D EXSY spectra were recorded with a mixing time ranging from 25 to 2000 ms optimized for each exchange rate and a ^{1}H 1D spectrum used as a reference. T1 relaxation times were measured by inversion recovery method using Bruker "t1ir" pulse program.

X-ray Diffraction Study. Single crystals were coated with polyperfluoro oil and mounted on the Bruker Smart APEX three-circle diffractometer with CCD area detector at 150−153 K.[49] The crystallographic data and characteristics of the structure solution and refinement are given in Table 6. The Bruker SAINT program[50] was used for data reduction. An absorption correction based on measurements of equivalent reflections was applied (SADABS).[51] The structures were solved by direct methods[52] and refined by full-matrix least-squares procedures, using $\omega(|F_o^2| - |F_c^2|)^2$ as the refined function. All non-hydrogen atoms were found from the electron density map and refined with anisotropic thermal parameters, whereas all hydrogen atoms were calculate geometrically and refined using the "riding" model. Relatively high residual density in the structure of **6** may be attributted to a partial twinning of the crystal, which we failed to model completely.

■ ASSOCIATED CONTENT

Supporting Information

X-ray crystallographic data in CIF format for the structure determinations for complexes **1** and **6**, kinetic plots, and selected NMR data. This material is available free of charge via the Internet at http://pubs.acs.org.

Table 6. Data Collection and Refinement Data for 1 and 6

compd	1	6
formula	$C_{21}H_{44}Cl_2MoNP_3$	$C_{27}H_{55}ClMoNOP_3$
FW	570.32	634.02
color, habit	green, plate	dark-green, plate
cryst size (mm^3)	0.40 × 0.25 × 0.06	0.30 × 0.28 × 0.04
cryst syst	monoclinic	monoclinic
space group	*P*2(1)/*c*	*P*21/*c*
a (Å)	17.819(2)	12.6249(11)
b (Å)	9.5317(11)	19.6456(17)
c (Å)	16.9762(19)	13.7219(12)
$\alpha/\beta/\gamma$ (deg)	90.00/97.754(2)/90.00	90.00/102.5750(10)/90.00
V (Å^3)	2857.0(6)	3321.7(5)
Z	4	4
T (°C)	150(2)	153(2)
ρ_{calcd}, g/cm^3	1.326	1.268
F(000)	1192	1344
radiation	graphite monochromatized MoKα (0.71073)	graphite monochromatized MoKα (0.71073)
μ (cm^{-1})	0.822	0.639
transmission factors	0.7344 and 0.9523	0.8315 and 0.9749
θ_{max} (deg)	28.000	28.500
total no. of reflns	27785	34861
no. of unique reflns	6892 [*R*(int) = 0.0723]	8402 [*R*(int) = 0.0337]
no. with $I \geq n\theta(I)$	5066	7286
no. of variables	253	307
R_1	0.0666	0.0433
wR_2	0.1259	0.1262
GOF	1.169	1.170
residual density, max/min	0.737/−1.479	2.572/−0.436

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Notes

The authors declare no competing financial interest.

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