The unexpected mechanism of carbonyl hydrosilylation catalyzed by (Cp)(ArN=)Mo(H)(PMe$_3$)†‡§

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Complex (Cp)(ArN=)Mo(H)(PMe$_3$) (2, Ar = 2,6-diisopropyl-phenyl) catalyzes the hydrosilylation of carbonyls by an unexpected associative mechanism. Complex 2 also reacts with PhSiH$_3$ by a σ-bond metathesis mechanism to give the silyl derivative (Cp)(ArN=)Mo(SiH$_2$Ph)(PMe$_3$).

Hydrosilylation of unsaturated organic molecules is second only to Direct Synthesis in the production of commodity organosilanes.[1] In the case of carbonyls, it also serves as a milder and greener alternative to reductions by metal hydrides, in that it produces protected alcohols in one step.[2] Most industrial applications of hydrosilylation are catalyzed by late transition metals,[1] which are expensive and toxic. These reactions are believed to proceed *via* the Ojima mechanism, involving a sequence of Si–H bond oxidative addition, migration, and C–H reductive elimination.[1d,3,4] Hydrosilylation by early metals is limited in scope and still poorly understood mechanistically.[5,6] For Group 6 and 7 high valent dioxo complexes, several groups concluded that the Si–H bond can add across the M=O unit to give a catalytically potent hydride.[7] Kinetic studies of some closely related monooxo systems suggest intermolecular heterolytic cleavage of an intermediate silane σ-complex as an alternative.[8,9]
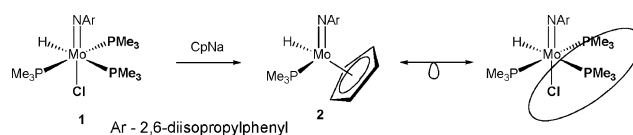
We have recently shown that the Mo(IV) complex (Me$_3$P)$_3$-(Cl)(ArN=)MoH (1) catalyzes hydrosilylation of carbonyls *via* a sequence of phosphine dissociation, carbonyl coordination, insertion into the M–H bond, followed by a reaction with silane.[6d] Noting that a *fac* ligand set (Cl$^-$, 2 Me$_3$P) is isolobal to the Cp$^-$ ligand, we chose to investigate the catalytic behaviour of the related complex (Cp)(ArN=)Mo(PMe$_3$)H (2). Kinetic and DFT studies revealed an unexpected associative mechanism, which unlike the previous schemes does not

involve Si–H addition either to the imido group or the metal. Finally, we report a rare case of a σ-bond metathesis on a d^n centre and the first example of a Mo(VI) silyl hydride.

Complex 2 was prepared by reacting compound 1 with CpNa in THF (Scheme 1) and characterised by NMR and IR spectroscopy. Compared to 1, complex 2 is a more sluggish catalyst of hydrosilylation (Table 1), which most likely reflects the fact that the PMe$_3$ ligand that dissociates from 1 to give a catalytically potent species is now "part of" the Cp ligand (see Scheme 1).

To underpin the mechanistic differences of these two hydrosilylation processes, stoichiometric reactions were tried. First of all we found (by EXSY) that coordinated PMe$_3$ in 2 is in a facile exchange with free phosphine, but unlike 1, this reaction is associative ($\Delta H^{\neq} = 24.7 \pm 0.4$ kJ mol^{-1}, $\Delta S^{\neq} = -101.0 \pm 1.0$ J/(mol*K)), ruling out PMe$_3$ dissociation as a first step in catalysis.[10] Although complex 2 is saturated,[11] it reacts slowly with benzaldehyde to give the alkoxy derivative Cp(ArN=)Mo(OCH$_2$Ph)(PMe$_3$) (3). This reaction is second order (k(26 °C) = $3.62 \pm 0.05*10^{-3}$ M^{-1}*s^{-1}) and also proceeds *via* an associative mechanism ($\Delta H^{\neq} = 59.4 \pm 2.3$ kJ mol^{-1}, $\Delta S^{\neq} = -93.0 \pm 7.2$ J/(mol*K)).[12] Complex 3 was characterized spectroscopically and by X-ray diffraction.[13] Interestingly, when 2 reacts with the amount of PhCH(=O) actually used in catalysis (1:20), the sole product is an η^2-aldehyde complex Cp(ArN=)Mo(OCH$_2$Ph)(η^2-PhCHO) (4) characterized by an upfield shifted CH signal at 5.58 ppm.[14] The same product forms when 3 reacts with excess PhCH(=O). The negative entropy of activation for this reaction ($\Delta H^{\neq} = 92.5 \pm 4.3$ kJ mol^{-1}, $\Delta S^{\neq} = -20 \pm 14$ J/(mol*K)) again points to an associative mechanism of substitution. Both 3 and 4 are active catalysts for hydrosilylation, with the activity of 3 being equal to that of 2 and the activity of 4 being about twice less.[13] With added PMe$_3$, complex 4 cleanly regenerates 3.

The alkoxy derivative 3 reacts with H$_3$SiPh in a second order reaction (k(26 °C) = $3.25 \pm 0.02*10^{-3}$ M^{-1}*s^{-1}) to regenerate the hydride 2. Kinetic measurements in the range 16–46 °C under pseudo-first order conditions revealed an associative mechanism ($\Delta H^{\neq} = 58.3 \pm 4.9$ kJ mol^{-1}, $\Delta S^{\neq} = -97 \pm 16$ J/(K*mol)). The kinetic isotope effect (k_H/k_D) is inverse at temperatures below +26 °C, and slightly

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Scheme 1 Preparation of 2 and its isolobal analogy with 1.

Table 1 Catalytic hydrosilylation by PhSiH$_3$ mediated by **2**

Entry	Substrate	Conversion of organic substrate	Product(s)	Conditions[a]	Yield (%)
1	PhC(O)H	100%	PhCH$_2$OSiH$_2$Ph, (PhCH$_2$O)$_2$SiHPh	0.5 day, RT	21, 79
2	PhC(O)Me	0%	—	5 days, 50 °C	0, 0
3	Cyclohexanone	54%	Cyclohexyl-OSiH$_2$Ph, (Cyclohexyl-O)$_2$SiHPh	5 days, 50 °C	36, 18
4	PhCN	10%	PhCH=NSiH$_2$Ph	3 days, 50 °C	100%

[a] Substrate : PhSiH$_3$: **2** = 1 : 1 : 0.05 in C$_6$D$_6$.
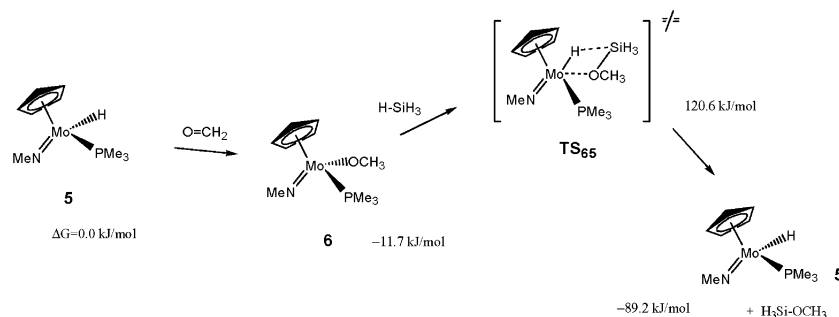
Scheme 2 Calculated mechanism of carbonyl hydrosilylation.

positive above +36 °C,[15] ruling out Si–H addition as a rate determining step.[16] This fact and the steric encumbrance of the putative Si–H addition product Cp(ArN=)Mo(η^2-H$_3$SiPh)-(OCH$_2$Ph)(PMe$_3$) allow us to disfavor the intermediacy of a silane σ-complex.[17,18] Of two basic sites available for silane attack, the imido[19] and the alkoxy groups, the latter is preferable on the grounds of sterics and charge concentration. Based on these arguments, the reaction pathway shown in Scheme 2 has been suggested.

DFT study[13] of a model system (SiH$_4$ for silane, MeN for imido, and H$_2$C=O for carbonyl) sheds further light on this process. H$_2$C=O addition across the Mo–H bond of **5** goes via the **TS$_{56}$** to give the alkoxy derivative **6**. SiH$_4$ adds easily across the Mo–O bond of **6** via a very late transition state **TS$_{65}$** to give the starting complex **5** and a silyl ether.[20] The calculated KIE (at 298 K) for this step is 1.0 (cf. KIE^{exp} = 0.80).

We have also explored the possibility that **2** may react with the silane to give a catalytically potent species. Reaction of **2** with PhSiD$_3$ leads to H/D exchange (3 h). Such a reversible hydride exchange is too slow to extract kinetic information by EXSY but DFT study reveals that the exchange preferably goes via PMe$_3$ dissociation/silane addition to give a dihydrides silyl species (ΔG_{298K} = 106.6 kJ mol^{-1}). Further evidence for such intermediates was found in the reaction of **2** with silane in the presence of BPh$_3$ which slowly gives the isomeric dihydrides Cp(ArN=)Mo(SiH$_2$Ph)H$_2$ (**7a**) and Cp(ArN=)Mo(H)(SiH$_2$Ph)H (**7b**) and, finally, a mixture of bis(silyl) Cp(ArN=)Mo(SiH$_2$Ph)$_2$H (**8**) and the monosilyl Cp(ArN=)Mo(SiH$_2$Ph)(PMe$_3$) (**9**) in the ratio 8 : 1. The absence of significant Si–H coupling (J < 10 Hz) in **7** and **8** rules out the possibility of a silane σ-complex,[18] thus making them the first examples of hydrido silyl derivatives of Mo(VI).[21]

2 reacts slowly (one week) and irreversibly with silane to give the silyl **9**. Kinetic studies revealed an associative mechanism ($\Delta H^{\neq}$ = 66.1 ± 2.3 kJ mol^{-1}, $\Delta S^{\neq}$ = −110.0 ± 7.2 J/(K*mol)) with a negligible isotope effect (1.10). These observations are consistent with a σ-bond metathesis process[8b,22] that avoids

the unfavorable Mo(VI) state. Such a σ-bond metathesis has some precedents in the late metal chemistry[23] but is only the second one observed for early metal d^n ($n \geq 2$) complexes such as **2**.[24] DFT study revealed a transition state of the H/Si exchange ($\Delta G^{\ddagger}$ = 141.7 kJ mol^{-1}) which bears all the typical features of a σ-bond metathesis: the SiH distance is 1.614 Å and the H–H distance in the incipient dihydrogen is 2.149 Å.[25] Unlike Hartwig's boryl/alkane metathesis,[24] there is no formation of an intermediate silane σ-complex, most likely because the LUMO of **2** is weakly π*(Mo–N) antibonding.[13] Complex **9** does not react with PhCH(=O) and does not catalyze its hydrosilylation with H$_3$SiPh.

In conclusion, we have shown that, unlike the parent hydride **1** and related oxo- and imido species, complex **2** catalyzes carbonyl hydrosilylation by an unexpected associative mechanism involving direct silane addition to the alkoxide ligand, which can be overall classified as an intermolecular heterolytic silane cleavage. This difference stems from the fact that in **1** there is a labile phosphine trans to the hydride easily freeing the reaction site, whereas in **2** PMe$_3$ dissociation is much less favourable. We also showed that, despite **2** being a d^2 complex, its reactions with PhSiH$_3$ proceed via an unexpected σ-bond metathesis that avoids the unfavorable Mo(VI) state. We, however, manage to observe the first Mo(VI) silyl hydrides in slow reactions of **2** with silane carried out in the presence of BPh$_3$.

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11 Complex **2** is formally an 18-electron compound if the imido ligand is considered as a 6e donor. However, the Mo–N π^* is low-lying and can be subject to an attack of a nucleophile. See Fig. SI40 in the Supporting information.§ The accessibility of this orbital may further increase upon bending of the imido ligand.

12 We also found that the $1/k_{eff}$ does not depend on phosphine concentration, which allows us to rule out the dissociation of PMe_3 in the first step.

13 See Supporting information for details§.

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