Hydrosilylation

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Agostic NSi–H···Mo Complexes: From Curiosity to Catalysis**

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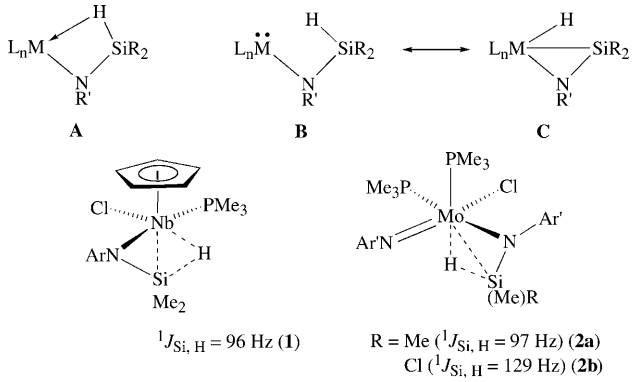
Dedicated to Professor Robert West on the occasion of his 80th birthday

Although agostic silylamido complexes **A** have been known since 1992 (Scheme 1),[1,2] their reactivity has been virtually unstudied, so they largely remain a laboratory curiosity.[3] We recently discovered a silane–imide coupling reaction,[4] allowing for the preparation of agostic silylamido complexes **1** and



Scheme 1. Agostic silylamido complexes (Ar = 2,6-diisopropylphenyl, Ar′ = 2,6-dimethylphenyl).

2a,**b** with a d^2 configuration (Scheme 1).[2] Bonding in these species can be represented by two canonical forms (**B** and **C**; Scheme 1), one of which has a silanimine character (**C**). This fact suggests that **1** and **2a**,**b** could serve as intermediates for silanimine complexes, which, although very scarce,[5] are known to exhibit a wealth of reactivity.[5a,b,6] Herein, we describe the preparation, structure, and reactivity of a new agostic silylamido complex, **3**. For the first time, we report the catalytic and stoichiometric reactions of such a complex and provide evidence for the intermediacy of a silanimine complex.

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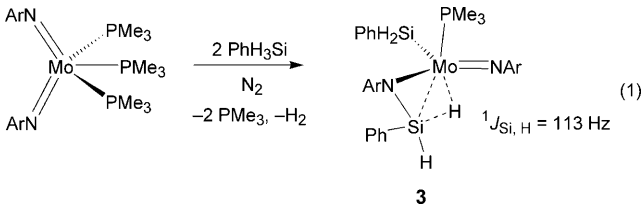
The reaction of bis(imido) compound $(ArN)_2Mo(PMe_3)_3$ (Ar = 2,6-diisopropylphenyl) with two equivalents of $PhSiH_3$ leads to a product of double silane addition, the β-agostic NSi–H···Mo complex **3** [Eq. (1)]. The structure of **3** is fluxional at room temperature, but at 223 K the ^1H NMR spectrum shows an up-field signal characteristic of the proton of an agostic Si–H_a moiety[3] at $\delta = 4.35$ ppm (br m), which is coupled to a signal assigned to the terminal Si–H proton at $\delta = 6.03$ ppm (d, $^2J_{H,H} = 5.4$ Hz). The diastereotopic protons



(1)

of the PhH_2Si group give rise to signals at $\delta = 5.68$ and 5.97 ppm. The agostic Si–H_a bond is also clearly seen from the red-shifted band at 1694 cm^{-1} in the IR spectrum of **3**, whereas three classical Si–H stretches are detected at 2014, 2041, and 2165 cm^{-1}. The ^{29}Si NMR spectrum of **3** contains two signals. The classical SiH_2Ph group gives rise to a triplet at $\delta = 1.2$ ppm ($^1J_{Si,H} = 153.5$ Hz), whereas the silyl group participating in the β-agostic interaction gives rise to an up-field-shifted signal at $\delta = -72.9$ ppm (dd, $^1J_{Si,H_a} = 113.0$, 245.3 Hz). The $^1J_{Si,H_a}$ coupling constant for the agostic Si–H_a bond (113.0 Hz) is slightly increased in comparison with the values observed for **1** (96 Hz) and **2a** (97 Hz), which may indicate a lower extent of Si–H activation, owing to a greater electron deficiency of the 16-electron Mo^{IV} center in **3**.[7]

The molecular structure of **3** can be described as a distorted molybdenum-centered trigonal bipyramid having the PMe_3 group and the agostic hydride ligand in the apical positions (Figure 1). The Mo1–Si1 bond involving the agostic silyl group (2.634(1) Å) is significantly longer than the Mo1–Si2 bond involving the terminal silyl group (2.495(1) Å), but is comparable with the Mo–Si bonds involving the agostic silyl groups in the related complexes **1** (2.646(1) Å) and **2a** (2.668(1) Å). The agostic hydride ligand is at a long Mo1–H1b distance of 1.92(5) Å, whereas the Si1–H1b bond of 1.49(5) Å is normal.

Complex **3** was found to catalyze a surprising variety of hydrosilylation processes.[8] Thus, the reaction of benzaldehyde with $PhSiH_3$ in the presence of 0.5 mol% of **3** gives a 100% conversion of benzaldehyde after 16 h (Table 1, entry 1). Hydrosilylation of ketones (acetophenone and

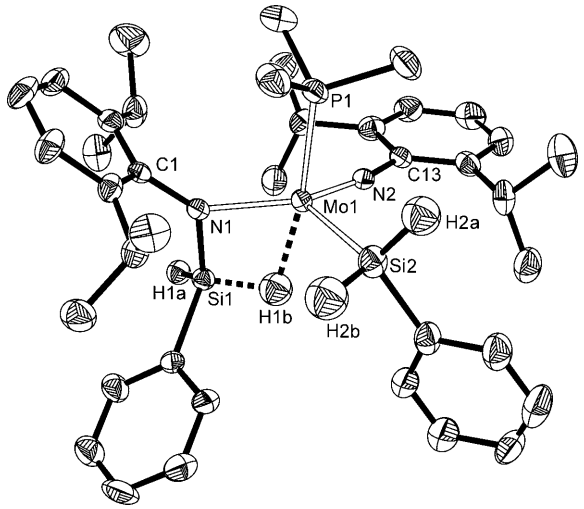


Figure 1. Molecular structure of **3**. Selected distances [Å] and angles [°]: Mo1–Si1 2.634(1), Mo1–Si2 2.495(1), Mo1–N1 2.062(4), Si1–N1 1.694(4), Mo1–N2 1.754(4), Mo1–H1b 1.92(5), Si1–H1a 1.43(4), Si1–H1b 1.49(5), Si2–H2a 1.44(6), Si2–H2b 1.54(6); Mo1-N1-Si1 88.50(16), Mo1-Si1-N1 51.49(12), Mo1-N1-C1 140.0(3), Mo1-N2-C13 169.5(3). Hydrogen atoms not bonded to silicon are omitted for clarity.

Table 1: Hydrosilylation of organic substrates by $PhSiH_3$ (1:1) at room temperature.

Entry	Substrate	*c*(**3**) [mol%]	*t*	Products	Yield [%][a]
1	PhHC=O	0.5	16 h	$PhSiH_2(OCH_2Ph)$	43
				$PhSiH(OCH_2Ph)_2$	57
2	PhMeC=O	1.0	20 days	$PhSiH_2OCHMePh$	44
				$PhSiH(OCHMePh)_2$	29
				$PhSiH(OCHMePh)_3$	21
				$PhCH_2CH_3$	6
3	Me_2C=O	1.0	5 days	$PhH_2Si(OiPr)$	34
				$PhHSi(OiPr)_2$	42
4	PhC≡CH	2.7	17 h	polyphenylacetylene	100
5	EtOH	5.0	5 min	$PhH_2Si(OEt)$	33
				$PhHSi(OEt)_2$	67
6	*i*PrOH	5.0	5 min	$PhH_2Si(OiPr)$	18
				$PhHSi(OiPr)_2$	82
7	PhCN	5.0	6 days	$PhHC{=}NSiH_2Ph$	20

[a] Yields were determined with ^{1}H NMR spectroscopy, using tetramethylsilane as a standard.

acetone) by $PhSiH_3$ at room temperature is more sluggish (Table 1, entries 2 and 3). An increase of reaction time and temperature leads to silane redistribution[9] and to partial carbonyl reduction to alkanes.[10]

In contrast, **3** turned out to be inactive in the hydrosilylation of alkenes and alkynes. Thus, reactions of $PhSiH_3$ with 1-hexene, cyclohexene, and styrene result only in partial reduction to the corresponding alkanes.[11] However, **3** catalyzes the isomerization of 1-hexene into 2-hexene[12] and polymerizes phenylacetylene (turnover number (TON) = 34, turnover frequency (TOF) = 2; Table 1, entry 4).[13]

Catalytic alcoholysis of $PhSiH_3$ by ethanol or isopropyl alcohol is fast and gives a 100% conversion in only 5 min (TON = 20, TOF = 245; Table 1, entries 5 and 6).[14] Hydrosilylation of benzonitrile by $PhSiH_3$ selectively gives $PhHC{=}NSiH_2Ph$ with a 20% conversion after 6 days (Table 1, entry 7). To our knowledge, such a selective monoaddition is unprecedented in the catalytic hydrosilylation of nitriles.[15]

To shed more light on these catalytic processes, stoichiometric reactions were attempted. Addition of excess $PhSiH_3$ to **3** results in a slow silane coupling and redistribution to yield PhH_2SiSiH_2Ph, SiH_4, and Ph_2SiH_2.[9,16] An ^{1}H-^{1}H EXSY NMR experiment indicated an exchange between free $PhSiH_3$ and the classical PhH_2Si ligand, but not the PhH_2Si group of the agostic ligand. However, an NMR experiment with the labeled silane $PhSiD_3$ showed, after 5 min at room temperature, a nearly statistical distribution of deuterium at all the silicon centers in [D_4]-**3**, suggesting a fast exchange between both silyl groups and the free silane (Scheme 2). When **3** is treated with (*m*-Tol)SiH_3, after 10 min at room temperature, the tolylsilyl group replaces only the classical PhH_2Si ligand (43% conversion), whereas the PhH_2Si group of the agostic ligand remains unchanged in $\mathbf{3}_{tol}$ (as indicated by ^{1}H-^{13}C HMBC-GP NMR spectroscopy (HMBC-GP: heteronuclear multiple bond correlation gradient pulse); Scheme 2). In all stoichiometric reactions of **3** with unsaturated organic substrates, one equivalent of free $PhSiH_3$ is released. These observations suggest the intermediate formation of a silanimine complex **D** (Scheme 2).[5]

Treatment of **3** with olefins leads to products of Si–C coupling, containing only one classical Si–H group. Thus, reaction of **3** with ethylene cleanly gives the ethyl vinylsilyl derivative **4** (Scheme 3), which was characterized by spectroscopic methods and by X-ray diffraction (Figure 2). Similarly, reaction of **3** with styrene gives the hydrido vinylsilyl complex **5** (Scheme 3), which probably emerges from styrene coupling with the silanimine intermediate **D** (Scheme 2), followed by C–H activation in the CH_2CHPh fragment. Similar alkene insertion into a Zr–Si bond has been observed previously by

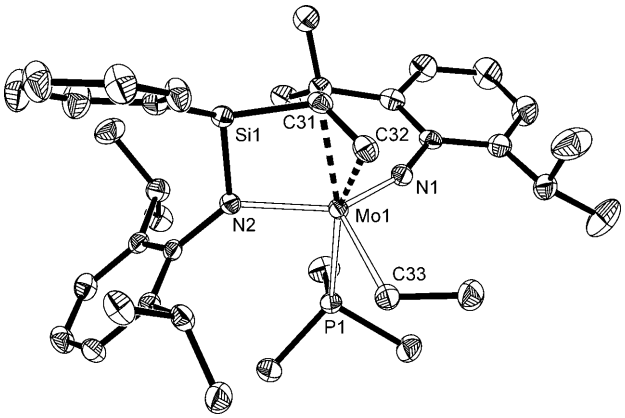
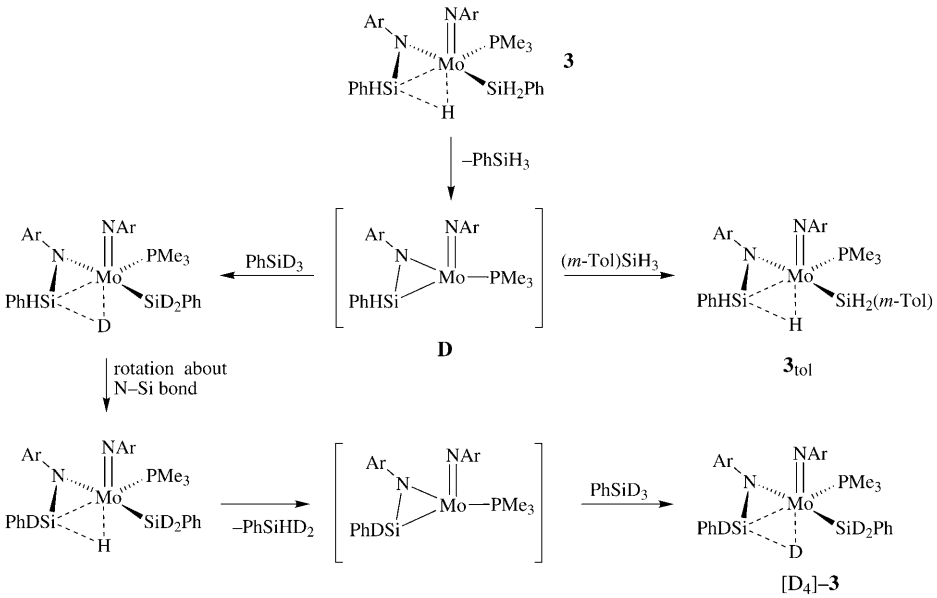
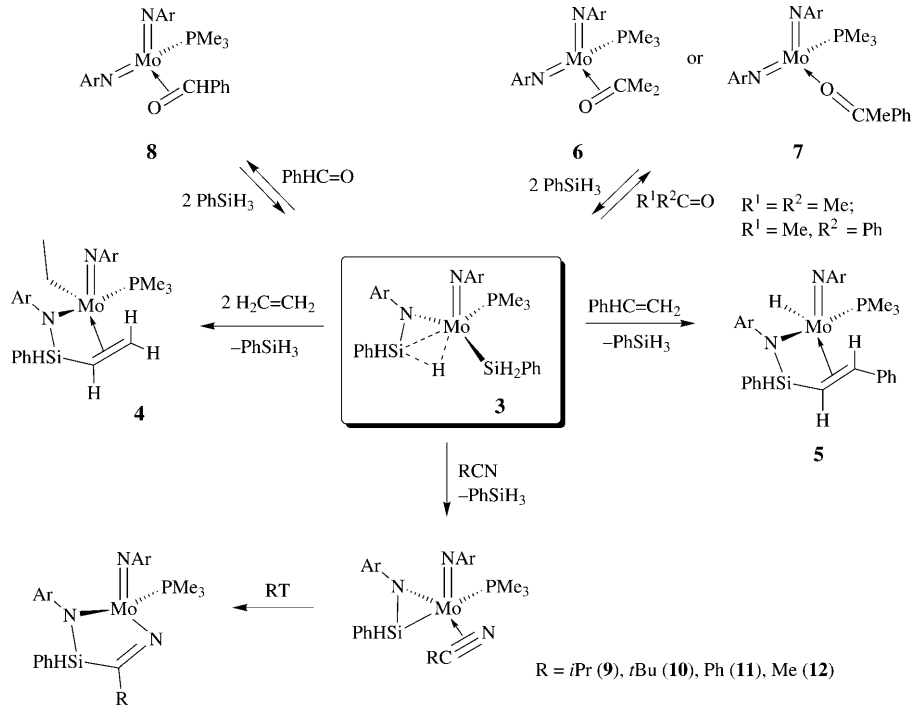


Figure 2. Molecular structure of **4** (one of two independent molecules is shown). Selected distances [Å] and angles [°]: Mo1–Si1 2.9036(8), Mo1–N1 1.769(2), Si1–N2 1.740(2), Mo1–C31 2.283(3), Mo1–C32 2.238(3), Mo1–C33 2.216(3), Mo1–P1 2.5757(8); Mo1-N2-Si1 99.02(10), N2-Si1-C31 95.92(11), N1-Mo1-N2 139.72(10), N1-Mo1-C33 108.77(11), N2-Mo1-C33 111.01(10), N1-Mo1-P1 84.79(8), N2-Mo1-P1 94.23(6), C33-Mo1-P1 82.52(8). Hydrogen atoms are omitted for clarity.



Scheme 2. Silane/silyl exchange in **3** via the silanimine intermediate **D**.



Scheme 3. Stoichiometric reactions of **3** with organic molecules.

Berry et al. for the silanimine complex $Cp_2Zr(\eta^2\text{-}NtBu{=}SiMe_2)(PMe_3)$.[5a]

Surprisingly, NMR experiments indicated that reactions of **3** with acetone and acetophenone lead to the selective formation of the ketone complexes **6**[17] and **7**,[18] respectively, accompanied by the evolution of one equivalent of $PhSiH_3$ and the formation of a difficult-to-characterize mixture of volatile silicon-containing compounds (Scheme 3). All attempts to trace the fate of the extruded silylene fragment :SiHPh were unsuccessful. The same ketone adducts can be easily prepared by the reaction of $(ArN)_2Mo(PMe_3)_3$ with the corresponding ketone. The treatment of **6** or **7** with two equivalents of $PhSiH_3$ results in elimination of the ketone and selective regeneration of **3**. Catalytic hydrosilylation of acetophenone with $PhSiH_3$ mediated by complex **6** (1.0 mol%) is much slower than that catalyzed by **3**, affording after 20 days only 35% conversion.

The analogous reaction of **3** with benzaldehyde gives a highly fluxional product, unstable even at low temperature, which in its ^1H NMR spectrum exhibits a doublet at $\delta = 13.28$ ppm ($J_{P,H} = 7.2$ Hz) assigned to the O=CH proton, which couples to the phosphorous nucleus. This fact, and the observation of a down-field Si–H signal at $\delta = 6.83$ ppm (1H), suggest the formation of a complex with a η^1-coordinated benzaldehyde, that is, (ArN)-$(PMe_3)Mo(\eta^1\text{-}O{=}CHPh)(\eta^2\text{-}NAr{=}SiHPh)$.[18] As for ketones, the reaction of $(ArN)_2Mo(PMe_3)_3$ with benzaldehyde gives an η^2 complex (**8**), characterized by an up-field C–H signal at $\delta =$ 5.69 ppm in its ^1H NMR spectrum.[17] These observations suggest that in the hydrosylation of carbonyl compounds the active catalyst is probably formed from **3** after silane elimination, but before silylene extrusion from **D**.

As in the reaction with acetone, treatment of **3** with nitriles (CH_3CN, PhCN, *i*PrCN, and *t*BuCN) gives initially the η^2-adducts (**9**–**12**; Scheme 3), evidenced by the diagnostic ^{13}C NMR signal at $\delta = 192$–204 ppm for the carbon nucleus of the nitrile group.[19] The rate of reaction depends on the steric demands of the R group and varies from 10 min for R = Me to a couple of hours for R = *t*Bu. The initial adducts **9**–**12** are unstable in solution and undergo a slow rearrangement through the insertion of the C≡N moiety into the Mo–Si bond of the silanimine fragment to give **13**–**16** (Scheme 3). The rate of rearrangement is also highly dependent on the bulkiness of the nitrile substituent (as expected, the slowest

reaction was observed for the R = *t*Bu complex **10**). Surprisingly, NMR studies suggest the formation of a [PhHSi–C(R)=N] fragment, rather than N-addition to silicon.[15g,h,20] In particular, a long-range ^{1}H-^{13}C HMBC NMR study of **13** shows the coupling of SiH, CH, and CH_3 protons to the imine carbon nucleus, thus, indicating the presence of direct bonding between the silicon atom and the imine carbon atom.

In summary, we discovered stoichiometric and catalytic reactivity of an agostic silylamido complex of molybdenum, including the unprecedented selective hydrosilylation of benzonitrile. Labeling experiments indicated the formation of a silanimine intermediate.

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