

O-Oximatosilanes: weak β -donor interactions as secondary bonds

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The oximatosilanes $\text{H}_3\text{SiON}=\text{CMe}_2$, $\text{ClH}_2\text{SiON}=\text{CMe}_2$ and $\text{H}_2\text{Si}(\text{ON}=\text{CMe}_2)_2$ were prepared from the reaction of lithiated acetone oxime with bromosilane and dichlorosilane respectively. They have been characterised by NMR (^1H , ^{13}C , ^{15}N , ^{17}O and ^{29}Si) and by gas-phase IR spectroscopy. The molecular structures of $\text{H}_3\text{SiON}=\text{CMe}_2$ and $\text{H}_2\text{Si}(\text{ON}=\text{CMe}_2)_2$ have been determined by low-temperature X-ray crystallography. Small Si–O–N angles have been detected in these structures, which are indicative of the formation of weak secondary interactions of the β -donor–acceptor type between silicon and nitrogen atoms. Important geometrical parameters: $\text{H}_3\text{SiON}=\text{CMe}_2$, Si–O 1.673(1), N–O 1.433(1) Å, Si–O–N 106.0(1)°, N=C 1.273(2) Å; $\text{H}_2\text{Si}(\text{ON}=\text{CMe}_2)_2$, Si–O 1.657(1), 1.650(1), N–O 1.466(2), 1.447(2), N=C 1.271(2), 1.266(2) Å, Si–O–N 102.5(1), 107.5(1)°. The geometries of $\text{H}_3\text{SiON}=\text{CMe}_2$, $\text{FH}_2\text{SiON}=\text{CMe}_2$ and $\text{ClH}_2\text{SiON}=\text{CMe}_2$ were calculated by optimisations at the MP2/6-311G** level of theory. The Si–O–N angles in $\text{FH}_2\text{SiON}=\text{CMe}_2$ and $\text{ClH}_2\text{SiON}=\text{CMe}_2$ are predicted to be smaller than that in $\text{H}_3\text{SiON}=\text{CMe}_2$. A natural bond orbital analysis describes the β -donor interaction as weak negative hyperconjugation $\text{lp}(\text{O})\rightarrow\sigma^*(\text{SiO})$ and $\text{lp}(\text{O})\rightarrow\sigma^*(\text{SiH})$. In general the β -donor bonds in oximatosilanes are found to be weaker than in the related hydroxyaminosilanes.

Recently, we have established β -donor interactions as a type of structure determining secondary bonding in hydroxyaminosilanes. The model systems we have characterised and structurally elucidated so far include the compounds $\text{H}_3\text{SiONMe}_2$, $\text{H}_3\text{SiONeEt}_2$ and $\text{H}_2\text{Si}(\text{ONMe}_2)_2$.¹ The latter has a small Si–O–N angle of only 95.2° and the donor contacts lead to (4 + 3) co-ordination in $\text{HSi}(\text{ONMe}_2)_3$ and (4 + 4) co-ordination in $\text{Si}(\text{ONMe}_2)_4$.³ The compound with the strongest β -donor bond found so far is $\text{ClH}_2\text{SiONMe}_2$, with its exceptionally small Si–O–N angle of only 79.7° in the crystal, corresponding to a Si···N distance of 2.028 Å which is similar to the sum of the covalent radii of silicon and nitrogen atoms (1.87 Å).⁴ This compound is present in the gas phase as two conformers, *anti* and *gauche*, distinguished by their torsion angles Cl–Si–O–N of 180.0 and 72.9°. Careful analysis of the gas-phase structure has shown the *anti* conformer to have a substantially stronger β -donor interaction (smaller Si–O–N angle 87.1°) than the *gauche* conformer (104.7°), which has led to the conclusion that the *anti*-positioned silicon substituent predominantly determines the strength of the β -donor interaction. This interpretation is consistent with the similar Si–O–N angles in $\text{H}_3\text{SiONMe}_2$ and the *gauche* conformer of $\text{ClH}_2\text{SiONMe}_2$, and is supported by a natural bond orbital (NBO) analysis, which describes β -donor interactions as negative hyperconjugation between the lone pair of electrons at nitrogen and antibonding orbitals at silicon. Theoretical studies have also shown that β -donor–acceptor interactions cannot be satisfactorily described in terms of pure electrostatic attraction.

We have now extended our investigations to *O*-oximatosilanes. Organosilicon derivatives of this class of compounds have been described,⁵ and the homoleptic compound $\text{Si}(\text{ON}=\text{CMe}_2)_4$ ⁶ is also known and its crystal structure has been determined. The compound $\text{Si}(\text{ON}=\text{CMe}_2)_4$ has a Si–O–N angle of 111.9° which is only slightly larger than that of $\text{Si}(\text{ONMe}_2)_4$ (109.1), and $\text{MeClSi}(\text{ON}=\text{CMe}_2)_2$ shows one of 109.3°.⁷ Compounds which are highly hydrogenated at silicon, *i.e.* the parent compounds of this class $\text{H}_3\text{SiON}=\text{CMe}_2$, have not yet been prepared and investigated in detail.

The interest in *O*-oximatosilanes arose from their use as cold curing catalysts in the silicone polymer industry, as is documented in a series of patents,⁸ and $\text{MeSi}(\text{ON}=\text{CMeEt})_3$ and $\text{H}_2\text{C}=\text{CHSi}(\text{ON}=\text{CMeEt})_3$ are commercially available neutral

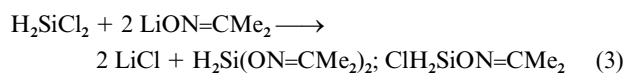
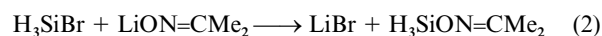
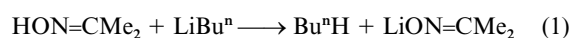
cross-linking agents for the condensation curing of silicones. Furthermore, hydroxylamines have been found to catalyse the alcoholysis of Si–H functions in polymers.⁹ However, the reasons for this reactivity are unknown. We have postulated that β -donor interactions play the key role, as they enlarge the co-ordination sphere of the silicon centres and in this way markedly increase their reactivity towards $\text{S}_{\text{N}}2$ reactions.

In this paper we report the synthesis of $\text{H}_3\text{SiON}=\text{CMe}_2$, $\text{H}_2\text{Si}(\text{ON}=\text{CMe}_2)_2$ and $\text{ClH}_2\text{SiON}=\text{CMe}_2$. The structures of $\text{H}_3\text{SiON}=\text{CMe}_2$ and $\text{H}_2\text{Si}(\text{ON}=\text{CMe}_2)_2$ have been determined by low-temperature crystallography and compared to the results of *ab initio* calculations.

Results and Discussion

Synthesis

The oximatosilanes have been prepared in analogy to the previously investigated *O*-hydroxyaminosilanes by reaction of *O*-lithiated acetone oxime with the corresponding halogenosilanes at low temperatures, equations (1)–(3). Reaction with



dichlorosilane resulted in the formation of $\text{H}_2\text{Si}(\text{ON}=\text{CMe}_2)_2$ as well as $\text{ClH}_2\text{SiON}=\text{CMe}_2$ which could be separated by fractionation at low temperatures. The overall yields achieved in this way are higher than 40%. All three compounds are air-sensitive, yet not pyrophoric, though $\text{ClH}_2\text{SiON}=\text{CMe}_2$ fumes enormously when exposed to moist air. The compounds can be stored at ambient temperature for at least a few days.

Spectroscopy

The identity of the compounds $\text{H}_3\text{SiON}=\text{CMe}_2$, $\text{H}_2\text{Si}(\text{ON}=\text{CMe}_2)_2$ and $\text{ClH}_2\text{SiON}=\text{CMe}_2$ was demonstrated by gas-phase IR spectroscopy and by NMR spectroscopy of the nuclei ^1H , ^{13}C , ^{15}N , ^{17}O and ^{29}Si . The two methyl groups of one oxime

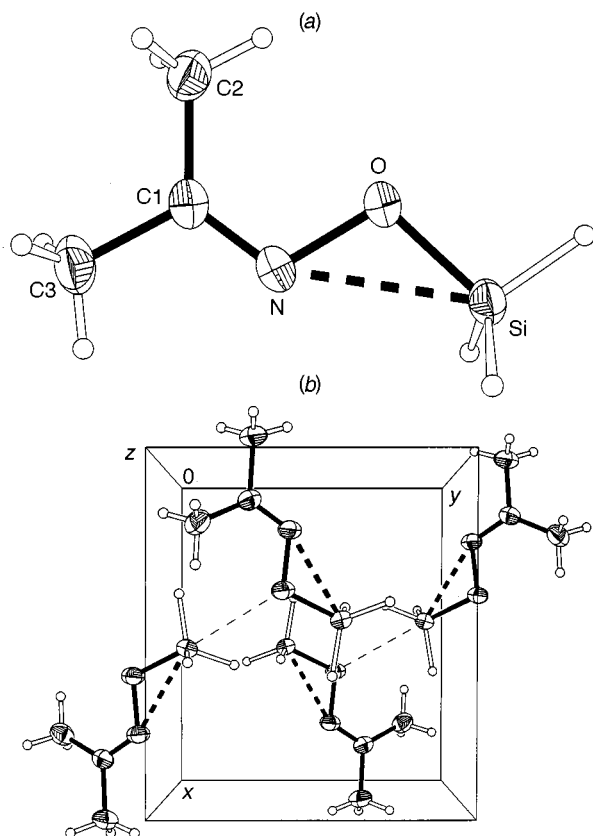


Fig. 1 (a) Molecular structure of $\text{H}_3\text{SiON}=\text{CMe}_2$ in the crystal as determined by low-temperature X-ray crystallography. (b) The unit cell showing the intermolecular $\text{Si}\cdots\text{O}$ contacts

substituent give rise to different singlets in the ^1H NMR spectrum due to their magnetic and chemical inequivalence. Singlet signals representing the silyl protons of $\text{H}_3\text{SiON}=\text{CMe}_2$, $\text{H}_2\text{Si}(\text{ON}=\text{CMe}_2)_2$ and $\text{ClH}_2\text{SiON}=\text{CMe}_2$ appear at the expected high chemical shifts of δ 4.78, 4.90 and 5.22 respectively. The ^{13}C NMR spectra show two quartets of quartets for the methyl groups and a septet for the nitrogen bound C atoms, all at usual chemical shifts for acetone oxime substituents. The ^{15}N NMR chemical shifts of $\text{H}_2\text{Si}(\text{ON}=\text{CMe}_2)_2$ and $\text{ClH}_2\text{SiON}=\text{CMe}_2$ are δ -30.8 and -32.6. The ^{15}N NMR signal of $\text{H}_3\text{SiON}=\text{CMe}_2$ is shifted to much lower frequencies at δ -52.7. This difference in chemical shift is also present in the ^{17}O NMR data, with signals at δ 177 for $\text{H}_2\text{Si}(\text{ON}=\text{CMe}_2)_2$ and $\text{ClH}_2\text{SiON}=\text{CMe}_2$ and at δ 149 for $\text{H}_3\text{SiON}=\text{CMe}_2$. The ^{29}Si NMR spectra of these compounds show signals at δ -29.8, -27.5 and -19.5, split into triplets [$\text{H}_2\text{Si}(\text{ON}=\text{CMe}_2)_2$ and $\text{ClH}_2\text{SiON}=\text{CMe}_2$] and quartets ($\text{H}_3\text{SiON}=\text{CMe}_2$) respectively.

Crystal structures of $\text{H}_3\text{SiON}=\text{CMe}_2$ and $\text{H}_2\text{Si}(\text{ON}=\text{CMe}_2)_2$

Single crystals of $\text{H}_3\text{SiON}=\text{CMe}_2$ and $\text{H}_2\text{Si}(\text{ON}=\text{CMe}_2)_2$ were grown by *in situ* methods in sealed capillaries on the diffractometer, but we were not successful in growing a suitable crystal of $\text{ClH}_2\text{SiON}=\text{CMe}_2$.

In the crystals of both compounds the molecules are present as monomers. The compound $\text{H}_3\text{SiON}=\text{CMe}_2$ is aggregated through $\text{Si}\cdots\text{O}$ contacts [2.493(1) Å] (Fig. 1), which are significantly shorter than the sum of the van der Waals radii of Si and O (3.40 Å). The $\text{O}\cdots\text{Si}-\text{O}$ units are almost linear (174.2°). Similar intermolecular contacts have also been found in the crystal structure of the related $\text{H}_3\text{SiONMe}_2$.¹ In the crystal of $\text{H}_2\text{Si}(\text{ON}=\text{CMe}_2)_2$ no intermolecular interactions could be detected which would normally be regarded as significant. This is paralleled by the crystal structure of the related silylhydroxylamine $\text{H}_2\text{Si}(\text{ONMe}_2)_2$.¹

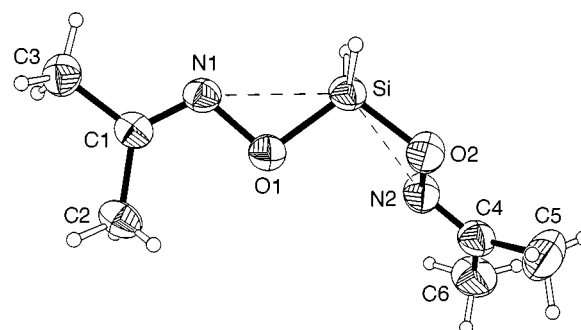


Fig. 2 Molecular structure of $\text{H}_2\text{Si}(\text{ON}=\text{CMe}_2)_2$ in the crystal as determined by low-temperature X-ray crystallography

In $\text{H}_3\text{SiON}=\text{CMe}_2$ the $\text{Si}-\text{O}-\text{N}$ angle is $106.0(1)^\circ$, *i.e.* markedly compressed as compared to related molecules not capable of β -donor-bond formation as isopropoxysilane $\text{H}_3\text{SiOCHMe}_2$ [$\text{Si}-\text{O}-\text{C}$ $118.4(1)^\circ$]² or methoxysilane H_3SiOMe [$\text{Si}-\text{O}-\text{C}$ $120.6(10)^\circ$].¹⁰ Hence, the $\text{Si}\cdots\text{N}$ distance of 2.493(2) Å is much smaller than the sum of the van der Waals radii of 3.54 Å. However, the β -donor-bond in the oximatosilane $\text{H}_3\text{SiON}=\text{CMe}_2$ is not as strong as in the related silylhydroxylamine $\text{H}_3\text{SiONMe}_2$, which shows a smaller $\text{Si}-\text{O}-\text{N}$ angle of $102.6(1)^\circ$.¹ This correlates with the basicity and donor ability, which is lower for an sp^2 -hybridised N atom in an oxime than for an sp^3 -hybridised N atom in a hydroxylamine, resulting in weaker donor-acceptor interactions. The $\text{Si}-\text{O}$ bond in $\text{H}_3\text{SiON}=\text{CMe}_2$ [1.673(1) Å] is elongated with respect to typical alkoxy silanes [*e.g.* $\text{Me}_2\text{HCOSiH}_3$ 1.649(1) Å],³ but similar to those in other oximatosilanes. The length of the $\text{N}-\text{O}$ bond in $\text{H}_3\text{SiON}=\text{CMe}_2$ [1.443(1) Å] is substantially longer than in acetone oxime (1.361 Å)¹¹ or other typical oximes (average value over 11 typical entries in the Cambridge Structure Database 1.399 Å), however other oximatosilanes also show relatively long $\text{N}-\text{O}$ bonds [average over seven values in the Cambridge Structure Database (Release 5.10) 1.424 Å].¹²

The $\text{N}=\text{C}$ double bond in $\text{H}_3\text{SiON}=\text{CMe}_2$ [1.273(2) Å] is slightly shorter than in acetone oxime (1.294 Å).¹¹ The methyl group in *cis* position relative to the oxygen atom in $\text{H}_3\text{SiON}=\text{CMe}_2$ is markedly bent away from the nitrogen atom as indicated by the angle $\text{N}=\text{C}-\text{C}$ of $126.4(1)^\circ$, whereas the second one is bent towards nitrogen by about the same amount [$\text{N}=\text{C}-\text{C}$ $115.5(1)^\circ$]. This distortion is less pronounced than in acetone oxime, where the corresponding angles are 130.6 and 113.3° .

No crystallographic symmetry is imposed on the molecular structure of $\text{H}_2\text{Si}(\text{ON}=\text{CMe}_2)_2$ shown in Fig. 2. There are two different $\text{Si}-\text{O}-\text{N}$ angles of $102.5(1)$ and $107.5(1)^\circ$. These are both substantially wider than in the corresponding silylhydroxylamine ($\text{Me}_2\text{NO})_2\text{SiH}_2$ [$94.2(1)$, $96.2(1)^\circ$], which again shows oximatosilanes to form weaker β -donor interactions as compared to hydroxyaminosilanes.

The molecular symmetry of $\text{H}_2\text{Si}(\text{ON}=\text{CMe}_2)_2$ in the crystal (C_1) is lower than in the related $\text{H}_2\text{Si}(\text{ONMe}_2)_2$ (pseudo- C_{2v}). The former has two oxime substituents, one with *anti* and one with *gauche* arrangement of the NOSiO unit. We have shown for $\text{ClH}_2\text{SiONMe}_2$ ⁴ that the strength of a β -donor bond is mainly dependent on the electronic nature of the silicon substituent in *anti* position relative to the nitrogen donor centre. The smaller $\text{Si}-\text{O}-\text{N}$ angle (102.5°) occurs in a SiON linkage which has an oxygen atom in *anti* position relative to its nitrogen centre, whereas the SiON linkage with the weaker β -donor interaction ($\text{Si}-\text{O}-\text{N}$ 107.5°) has a hydrogen atom as an *anti* substituent. The situation of the weaker β -donor interaction can thus be compared to that in $\text{H}_3\text{SiON}=\text{CMe}_2$ (SiON 106.0°). In the other case a stronger interaction has to be expected, as $\text{H}_2\text{Si}(\text{ONMe}_2)_2$ (*anti* substituent: O) has also a stronger β -donor interaction than in the simple $\text{Me}_2\text{NOSiH}_3$ (*anti* substituent:

Table 1 Selected bond lengths (Å) and angles (°) of H₃SiON=CMe₂ and H₂Si(ON=CMe₂)₂

	H ₃ SiON=CMe ₂		H ₂ Si(ON=CMe ₂) ₂ (XRD)		FH ₂ SiON=CMe ₂ MP2/6-311G**	ClH ₂ SiON=CMe ₂ MP2/6-311G**
	XRD	MP2/6-311G**	O(1) substituent	O(2) substituent		
Si–O	1.673(1)	1.686	1.657(1)	1.650(1)	1.677	1.678
Si–F/Cl					1.607	2.047
O–N	1.443(1)	1.416	1.446(2)	1.447(2)	1.421	1.426
C=N	1.273(2)		1.271(2)	1.266(2)	1.286	1.286
Si···N	2.493(2)	2.404	2.423(1)	2.501(1)	2.433	2.440
Si–O–N	106.0(1)	107.3	102.5(1)	107.5(1)	103.2	103.4
O–Si–O			106.6(1)			
F/Cl–Si–O					104.3	104.8
C=N–O	112.5(1)	112.8	112.1(1)	111.7(1)	113.0	112.7
O–Si–O–N			109.3(7)	67.6(1)		
N=C–C(<i>cis</i>)	126.4(1)	125.7	125.4(2)	126.2(2)	125.6	125.7
(<i>trans</i>)	115.5(1)	115.5	115.7(1)	115.5(2)	115.5	115.4

H). The distortion of the geometry of the N=CMe₂ group as found in H₃SiON=CMe₂ is also present in the two oxime groups in H₂Si(ON=CMe₂)₂.

Theoretical investigations

We have calculated the molecular geometry of H₃SiON=CMe₂ and two electronegatively substituted oximatosilanes FH₂SiON=CMe₂ and ClH₂SiON=CMe₂ at the MP2/6-311G** level of theory. In all cases the C_s symmetric structures represent the lowest energy minima on the potential hypersurface. Analogous calculations for H₂Si(ON=CMe₂)₂ are beyond our current computational resources. The results of these calculations are shown in Table 1.

The values for H₃SiONMe₂ show a reasonably good agreement between theory and crystal structure results, which adds support to the conclusion that major geometry distorting forces are absent in the crystal lattice. The agreement concerns the prediction of the Si–O–N angle as well as the distortion of the N=CMe₂ groups. The slightly smaller Si–O–N angle in the crystal can also be rationalised by the general tendency of partially bound systems to drive the partial bond towards completion upon crystallisation because of increase of the molecular dipole moment.¹³ This effect has also been shown to be operative in ClH₂SiONMe₂, where the Si–O–N angle in the solid state is more than 12° smaller than the calculated one.

We performed an NBO analysis to investigate negative hyperconjugation as a contribution to bonding in H₃SiON=CMe₂. Interactions of the type lp(N)→σ*(SiO) and lp(N)→σ*(SiH) could be used to describe the bonding in hydroxyaminosilanes.⁴ In the NBO picture these interactions are also operative in H₃SiON=CMe₂, however they are weaker than in comparable hydroxylamines as H₃SiONMe₂. As has also been found in the hydroxylamines, interactions of the type lp(O)→σ*(SiH) and lp(O)→σ*(N–C) seem to be important as well. The distortion of the geometry of the N=CMe₂ group can also be described in terms of negative hyperconjugation of the type lp(N)→σ*(C–C'), with C' being the methyl carbon enclosing the widened N=C–C angle.

We also calculated the structures of the oximatosilanes FH₂SiONCMe₂ and ClH₂SiONCMe₂ as the analogous hydroxyaminosilanes were shown to include the strongest β-donor bonds in p-block systems found so far. The calculated angles for the hydroxyaminosilanes were: H₃SiONMe₂, 102.5; FH₂SiONMe₂, 90.0; ClH₂SiONMe₂, 91.6°. The angle compression upon substitution of the silicon centre with fluorine or chlorine atoms in the oximatosilanes is much less pronounced: H₃SiON=CMe₂, 107.3; FH₂SiON=CMe₂, 103.2; ClH₂SiON=CMe₂, 103.4°. This confirms the observation that oximatosilanes form weaker secondary bonds of the β-donor–acceptor type than do hydroxyaminosilanes.

Conclusion

Oximatosilanes are another class of compounds which form secondary interactions between their silicon and nitrogen atoms as has previously been found for hydroxyaminosilanes and hydrazinosilanes. Although predictably weak, these β-donor interactions determine the structure of the Si–O–N units in this class of compounds. The β-donor interactions in oximatosilanes are much weaker than in the related hydroxyaminosilanes. The theoretical background established for the description of bonding in hydroxyaminosilanes is, however, fully applicable to oximatosilanes as well. Negative hyperconjugation, lp(N)→σ*(SiO) and lp(N)→σ*(SiH), can be used to describe the β-donor interaction in the NBO picture.

Experimental

General

The experiments were carried out using a standard Schlenk line or a vacuum line with greaseless stopcocks (Young taps), which is directly attached to the gas cell in an FTIR spectrometer (Midac Prospect FTIR). All NMR spectra were recorded at 21 °C on a JEOL JNM-LA400 spectrometer in sealed tubes with C₆D₆ as a solvent directly condensed onto the sample from K/Na alloy.

Preparations

(Acetone oximato)silane. *n*-Butyllithium (12.4 cm³, 1.6 M in hexane) was added dropwise to a solution of acetone oxime (1.46 g, 20 mmol) in diethyl ether (50 cm³). The mixture was stirred for 1 h at ambient temperature, and solvents removed *in vacuo*. The remaining salt was dissolved in diethyl ether (30 cm³) and then bromosilane (2.2 g, 20 mmol) was added at 196 °C by condensation. The mixture was slowly warmed to ambient temperature. All volatile products were condensed into a trap (–196 °C) and (acetone oximato)silane (0.83 g, 8 mmol, 40%) was isolated by repeated fractionation through a series of cooled traps (–10, –78, –196 °C) with the product retained in the –78 °C trap. The compound is a colourless liquid. ¹H NMR: δ 1.51 (s, 3 H, H₃C), 1.56 (s, 3 H, H₃C) and 4.78 (s, 3 H, H₃Si). ¹³C NMR: δ 15.1 (qq, ¹J_{CH} = 128.7, ³J_{CCCH} = 3.3, CH₃), 21.1 (qq, ¹J_{CH} = 128, ³J_{CCCH} = 3.0 Hz, CH₃) and 160.3 (spt, ²J_{CCH} = 6.5 Hz, C). ¹⁵N-{¹H} NMR: δ –52.7 (s). ¹⁷O-{¹H} NMR: δ 149.0 (s). ²⁹Si NMR: δ –29.8 (q, ¹J_{SiH} = 222.0 Hz, SiH₃). IR(gas): 2187 s cm^{–1} [ν(SiH)].

(Acetone oximato)chlorosilane and bis(acetone oximato)silane. *n*-Butyllithium (12.6 cm³, 20 mmol, 1.60 M in hexane) was added dropwise to a solution of acetone oxime (1.50 g, 20 mmol) in pentane (50 cm³) and then stirred for 1 h. The solvents were

removed *in vacuo* and dichlorosilane (3.0 g, 20 mmol) was condensed onto the salt at -196°C . The mixture was slowly warmed to ambient temperature and all volatile material was separated from the salt by condensation. An excess of dichlorosilane was removed by repeated condensation of the products in a -78°C trap (H_2SiCl_2 passes through). (Acetone oximato)chlorosilane and bis(acetone oximato)silane could be isolated as air sensitive, colourless liquids (m.p. = -40 and -15°C) by repeated condensation through a series of cooled traps (-10 , -20 , -196°C) with (acetone oximato)chlorosilane being retained in the -20°C trap and bis(acetone oximato)silane being stopped in the -10°C trap. Bis(acetone oximato)silane: ^1H NMR δ 1.62 (s, H, H_3C), 1.66 (s, 3 H, H_3C) and 4.90 (s, 2 H, H_2Si); ^{13}C NMR δ 15.1 (qq, $^1J_{\text{CH}} = 128.7$, $^3J_{\text{CCCH}} = 3.3$, CH_3), 21.1 (qq, $^1J_{\text{CH}} = 128$, $^3J_{\text{CCCH}} = 3.0$, CH_3) and 162.4 (spt, $^2J_{\text{CCH}} = 6.5$ Hz, C); ^{15}N - $\{^1\text{H}\}$ NMR δ -30.8 (s); ^{17}O - $\{^1\text{H}\}$ NMR δ 177.1 (s); ^{29}Si NMR δ -27.5 (t, $^1J_{\text{SiH}} = 256.0$ Hz, SiH_2); IR(gas) 2218s cm^{-1} [$\nu(\text{SiH})$]. (Acetone oximato)chlorosilane: ^1H NMR δ 1.52 (s, H, H_3C), 1.55 (s, 3 H, H_3C) and 5.22 (s, 2 H, H_2Si); ^{13}C NMR δ 15.1 (qq, $^1J_{\text{CH}} = 128.7$, $^3J_{\text{CCCH}} = 3.3$, CH_3), 21.1 (qq, $^1J_{\text{CH}} = 128$, $^3J_{\text{CCCH}} = 3.0$, CH_3) and 137.6 (spt, $^2J_{\text{CCH}} = 6.5$ Hz, C); ^{15}N - $\{^1\text{H}\}$ NMR δ -32.6 (s); ^{17}O - $\{^1\text{H}\}$ NMR δ 177.1 (s); ^{29}Si NMR δ -19.5 (t, $^1J_{\text{SiH}} = 274.6$ Hz, SiH_2); IR(gas) 2218s cm^{-1} [$\nu(\text{SiH})$].

Crystallography

Single crystals were grown *in situ* by slowly cooling the melt in sealed capillaries after generation of suitable seed crystals. Diffractometer: Enraf-Nonius CAD4, Mo- $K\alpha$ radiation ($\lambda = 0.71069 \text{ \AA}$), graphite monochromator, Solution: direct methods (SHELXTL).¹⁴ Refinement: SHELXL 93.¹⁵ No absorption correction applied. Non-H atoms were refined with anisotropic thermal displacement parameters; hydrogen atoms were located in Fourier-difference maps and refined isotropically.

Crystal data. (Acetone oximato)silane, $\text{C}_3\text{H}_9\text{NOSi}$, $M = 103.2$, monoclinic space group $P2_1/c$, $a = 8.393(1)$, $b = 7.50(1)$, $c = 9.706(1) \text{ \AA}$, $\beta = 91.45(1)$, $U = 612.4(1) \text{ \AA}^3$ at 151(2) K, cell from 88 reflections (θ 20–25°), $Z = 4$, $D_c = 1.119 \text{ g cm}^{-3}$, $2\theta_{\text{max}} = 53.94^\circ$, h -10 to 10 , k 0 – 9 , l -12 to 7 , ω scan, 2187 reflections collected, 1338 independent ($R_{\text{int}} = 0.0228$). Extinction correction (SHELXL 93) with extinction coefficient 0.011(5). 92 Parameters, $R = 0.0298$ [for 1178 reflections with $F_o > 4\sigma(F_o)$], $wR2 = 0.0951$ for all 1338 reflections. Residual electron density: minimum 0.32, maximum 0.29 e \AA^{-3} . $w = 1/[\sigma^2(F_o^2) + (0.0522P)^2 + 0.0755P]$ where $P = [\max(F_o^2, 0) + 2F_c^2]/3$.

Bis(acetone oximato)silane, $\text{C}_6\text{H}_{14}\text{N}_2\text{O}_2\text{Si}$, $M = 174.28$, triclinic, space group $P\bar{1}$, $a = 7.068(1)$, $b = 7.375(1)$, $c = 10.963(1) \text{ \AA}$, $\alpha = 87.16(1)$, $\beta = 79.61(1)$, $\gamma = 64.190(1)^\circ$, $U = 505.75(11) \text{ \AA}^3$ at 196(2) K, cell from 92 reflections (θ 19–24°), $Z = 2$, $D_c = 1.144 \text{ g cm}^{-3}$, $2\theta_{\text{max}} = 54.1^\circ$, h -7 to 9 , k 0 – 9 , l -13 to 13 , ω – θ scan, 2193 reflections collected, all independent. 144 Parameters, $R = 0.0441$ [for 1876 reflections with $F_o > 4\sigma(F_o)$], $wR2 = 0.0128$ for all 2191 reflections. Residual electron density: minimum 0.39, maximum 0.48 e \AA^{-3} . $w = 1/[\sigma^2(F_o^2) + (0.087P)^2 + 0.07P]$ where $P = [\max(F_o^2, 0) + 2F_c^2]/3$.

CCDC reference number 186/1027.

See <http://www.rsc.org/suppdata/dt/1998/2537/> for crystallographic files in .cif format.

Ab initio calculations

Ab initio molecular orbital calculations were carried out using the GAUSSIAN 94 program.¹⁶ Geometry optimisations and vibrational frequency calculations were performed from analytic first and second derivatives at the SCF and MP2 levels of

theory. Calculations were undertaken at the SCF level using the standard 3-21G*,^{17–19} 6-31G**^{20–22} and 6-311G**^{23,24} basis sets, while the larger two basis sets were used for calculations at the MP2 level of theory. The NBO analyses were performed using the programs built into GAUSSIAN 94.

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