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Poly(methimazolyl)silanes: Syntheses and Molecular Structures†

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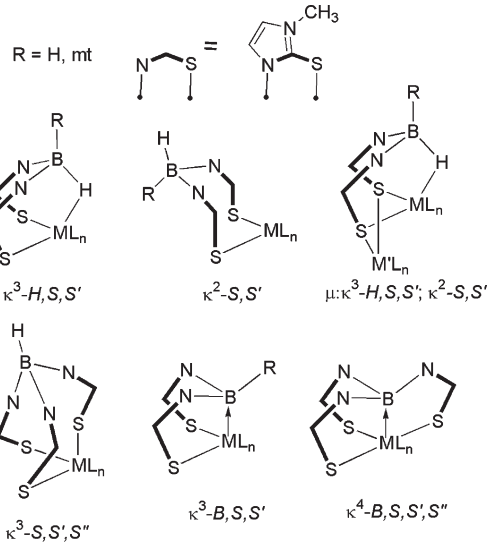
A new class of multidentate "scorpionate" ligands is readily obtained from the reactions of methimazole with a range of organochlorosilanes. A recurrent structural feature to emerge is the intramolecular S-capping of the tetrahedral inner Si coordination spheres, the nature of which is responsive to the substitution pattern at silicon.

Within the past decade methimazole (H−mt) and related 2-mercaptoimidazoles have attracted considerable interest, as they are the essential building block in 2-mercapto-1,3-diazol-3-yl borates (Scheme 1), a class of multidentate ligands that exhibits surprising features in transition metal complex chemistry.

Since the first reports on methimazolylborates by Reglinski et al.,[1] the coordination chemistry of this class of ligands has been widely investigated[2] and a range of coordination modes have been identified (Scheme 1) that reveal striking differences between methimazolylborate and pyrazolylborate coordination chemistries. Among these was the discovery of the first metallaboratranes (Scheme 1, κ^3-*B,S,S′* and κ^4-*B,S,S′,S″* coordination modes), which included transannular metal−boron dative bonding.[3]

Despite these extensive investigations of methimazolylborates and related compounds, silicon analogues (i.e., methimazolyl-substituted silanes) have not been reported until recently, when we published selected mt-substituted silanes that can undergo a variety of reactions with transition metal complexes: $PhCl_2Si(mt)$ was shown to react with $(Ph_3P)_2Pt(C_2H_4)$ under insertion of Pt(0) into the mt-ligand's C═S bond and formation of an imidazol-2-yl-Pt(II)-complex-stabilized silanethione.[4] Metallasilatranes (comprising formal Pd→Si and Pt→Si dative bonds) became accessible from $ClSi(mt)_3$ (or $Si(mt)_4$) in reactions with $MCl_2(PPh_3)_2$ (M = Pd, Pt),[5] and the reaction of Ru(COD)(COT) [(COD) = 1,5-cyclooctadiene, (COT) = 1,3,5-cyclooctatriene] with $Ph(H)Si(mt)_2$ proved the Si−H bond to be a third reactive site for attaching methimazolylsilanes to transition metals[6] (Scheme 2).

Scheme 1



For further investigations of methimazolylsilanes, with particular focus on the intramolecular coordination properties of their S-donor functions, we have now extended the library of structurally characterized mt-substituted silanes and report herein full details of their synthesis and characterization.

Results and Discussion

In general, the reactions between organochlorosilanes and methimazole in the presence of triethylamine as sacrificial base provided easy access to a variety of methimazolylsilanes (Scheme 3), thus serving as a general approach for their synthesis.

According to Scheme 3, a range of mono-, bis-, and tris-(methimazolyl)silanes as well as tetrakis(methimazolyl)silane

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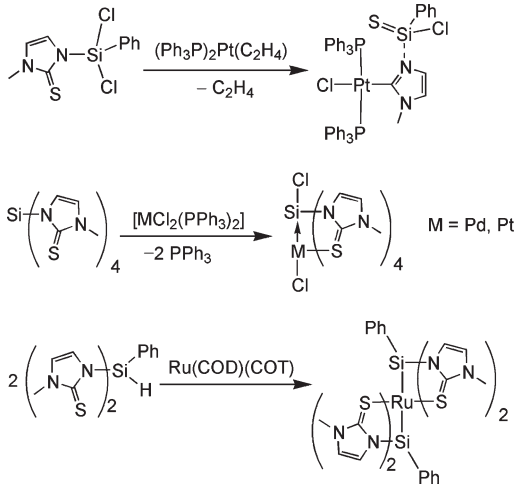
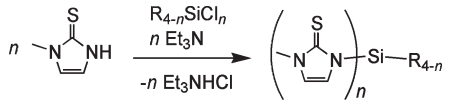
Scheme 2



Scheme 3



were prepared and their molecular structures were determined by single-crystal X-ray diffraction analysis (Figures 1 and 2, Table 1). A common feature of these methimazolylsilane molecules (and the previously reported examples, see Supporting Information) is the *n*-fold S-capped tetrahedral environment of the silicon atom (*n* = number of methimazolyl moieties per silane molecule). The S−Si separations range from 3.17 to 3.50 Å; thus, they are shorter than the sum of the van der Waals radii (3.9 Å),[7] and effects on the bonding properties within the methimazolylsilane molecules should result therefrom. In the molecules of compounds $Me_2Si(mt)_2$, $Me(H)Si(mt)_2$, $PhMeSi(mt)_2$, $Ph(H)Si(mt)_2$, and $PhSi(mt)_3$ both S−Si-capping *trans* to N−Si and *trans* to C−Si bonds are encountered. Comparison of the S−Si separations reveals that those *trans* to an N−Si bond are generally shorter than those *trans* to a C−Si bond (Table 1). Similar behavior is observed for compound $PhClSi(mt)_2$, which exhibits shorter S−Si capping *trans* to a Cl−Si bond versus longer S−Si separation *trans* to C−Si. As to the origin of the Si−S separations observed, electrostatic attraction between Si and S atoms is in general reasoned by their electropositive and electronegative nature, respectively. Orbital interactions (electron donation into σ^* MOs) might also contribute to the overall electronic situation, as indicated by the results of X-ray crystallography. The S−Si interaction appears to influence the *trans*-disposed N−Si bonds. In Table 1 the N−Si bond lengths are listed and a general trend of N−Si bond lengthening is observed (in compounds $Me_2Si(mt)_2$, $Me(H)Si(mt)_2$, $PhMeSi(mt)_2$, $Ph(H)Si(mt)_2$, $PhSi(mt)_3$, and $ClSi(mt)_3$) for those connections bearing a *trans*-Si−S cap. Natural bond orbital (NBO) analysis of $PhHSi(mt)_2$ as a representative example, however, proved S-localized lone pairs to comprise only up to 3% Si-contribution. Furthermore, an atoms in molecules (AIM) analysis did not reveal a bond critical point between Si and S atoms (for details see the Supporting Information).

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In sharp contrast with 2-mercapto-azolinyl-substituted stannanes (e.g., 2-mercaptobenzothiazolinylstannanes), which clearly exhibit hypercoordinate Sn atoms due to four-membered Sn(N−C−S) chelates,[8] the combination of the thermodynamically disadvantaged S−Si bond and the rather rigid Si-bound methimazol-3-yl moiety offers only limited geometric freedom for the variability of the S−Si distances. Although all of these Si−S separations are shorter than the sum of the van der Waals radii, one can discern rather attractive versus rather repulsive contacts by analysis of the Si−N−C(S) and Si−N−C(C) angles (Table 1, Scheme 4). In case of S−Si separations of about 3.41···3.43 Å (e.g., in compounds $PhMeSi(mt)_2$, $EtSi(mt)_3$, $PhSi(mt)_3$, and $PhClSi(mt)_2$) the Si−N−C angles at the methimazol-3-yl moiety are similar. Significantly shorter S−Si separations cause significant bond angle deformations by means of smaller Si−N−C(S) versus wider Si−N−C(C) angles, thus hinting at S−Si attraction. This phenomenon is found for S−Si caps *trans* to N−Si and Cl−Si bonds. For the S−Si caps *trans* to C−Si bonds a widening of the Si−N−C(S) angle is observed in many cases, thus indicating rather repulsive forces. In the hydride-bearing compounds $Me(H)Si(mt)_2$ and $Ph(H)Si(mt)_2$, however, both the S−Si interactions *trans* to N−Si and *trans* to C−Si bonds seem rather attractive, and these compounds exhibit the shortest S−Si separations of both the *trans*-C−Si and *trans*-N−Si class.

This leads to the conclusion that both the S−Si capping *trans* to N−Si/Cl−Si and *trans* to C−Si are electronically attractive. Repulsive interactions due to the steric bulk of further substituents at the Si atom, however, may cause a net repulsion for the weaker S−Si capping *trans* to C−Si bonds in compounds $Me_2Si(mt)_2$ and $Ph_2Si(mt)_2$ or rather balanced situations in compounds $PhMeSi(mt)_2$, $PhSi(mt)_3$, and $PhClSi(mt)_2$.

The general choice of the tetrahedral faces to be S-capped may be driven by a combination of sterically favorable arrangements of the Si-bound substituents, attractions of S−Si caps, and intramolecular C-H−π contacts. Figure 2 illustrates this intramolecular "S−Si capping + C-H−π-contact" feature, which appears in the above molecular structures.

The hydrogen atom in 4-position of each of the methimazol-3-yl moieties (i.e., H4, H8, and H12 in Figure 2) points to π-electron-rich atoms of a neighboring substituent, thus forcing the S atom of its own methimazol-3-yl moiety (S1, S2, and S3, respectively) to cap the tetrahedral face opposite this hydrogen contact acceptor. This model explains why none of the 2-fold methimazolyl-substituted silanes exhibit two S−Si contacts *trans* to N−Si (which might be electronically favorable as regards N−Si−S electrostatic interactions): The S-capping of one tetrahedral face *trans* to the second methimazolyl moiety results in the setting up of a hydrogen contact to this methimazolyl group and allows

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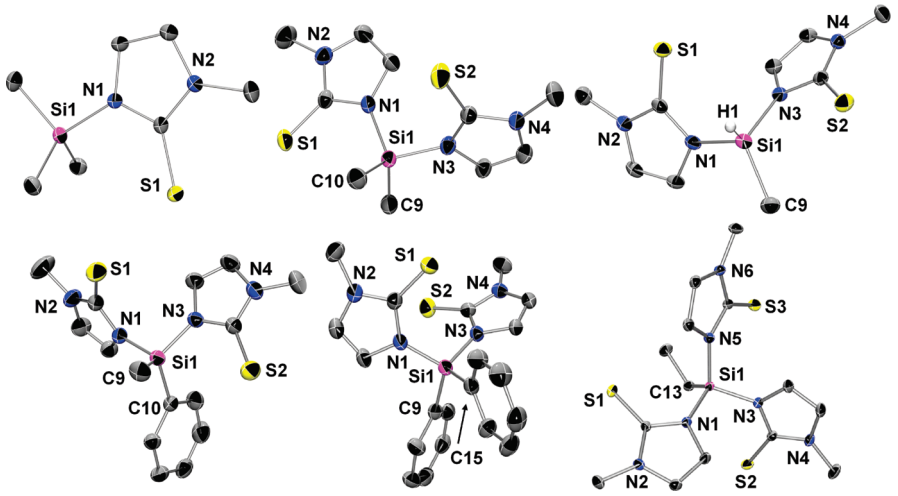

Figure 1. Molecular structures of $Me_3Si(mt)$ (one of the two crystallographically independent molecules), $Me_2Si(mt)_2$, $Me(H)Si(mt)_2$, $PhMeSi(mt)_2$ in $PhMeSi(mt)_2 \cdot 0.5$ toluene, $Ph_2Si(mt)_2$ in $Ph_2Si(mt)_2 \cdot 0.5$toluene, and $EtSi(mt)_3$ in $EtSi(mt)_3 \cdot CH_2Cl_2$ (ORTEP diagrams with 50% probability ellipsoids, C-bound hydrogen atoms and solvent molecules, if applicable, omitted for clarity).

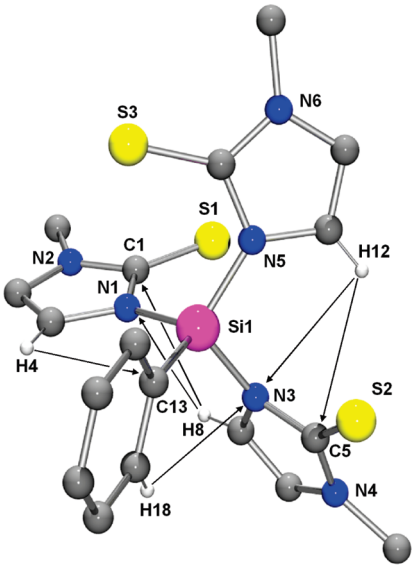

Figure 2. Molecular structure of $PhSi(mt)_3$ in $PhSi(mt)_3 \cdot$ toluene (ball-and-stick diagram, atomic spheres of arbitrary size, most hydrogen atoms and toluene molecule omitted for clarity). Selected C−H···π(X) (X = C, N) hydrogen contacts* (indicated by thin arrows). H···X distances [Å] and C−H···X angles [deg]: C4−H4···C13 2.84, 102.6; C8−H8···N1 2.82, 99.6; C−H8···C1 2.89, 117.5; C12−H12···N3 2.88, 99.0; C12−H12···C5 2.91, 119.0; C18−H18···N3 2.74, 107.4. (*The hydrogen atoms in this structure have been refined in idealized positions, i.e., with $C(sp^2)$−H bond lengths restrained to 0.950 Å.)

only for generating the second S−Si cap *trans* to one of the other substituents. The complete absence of S−Si capping *trans* to N−Si in compounds $Ph_2Si(mt)_2$ and $PhClSi(mt)_2$ may be a result of further hydrogen contacts within the system of methimazolyl and phenyl substituents. As the intramolecular C−H···π(X) distances and the capping S−Si separations indicate rather weak interactions, intermolecular packing effects in the crystal may contribute to the favorable molecular conformation.

Regarding the Si−N−C(C) and Si−N−C(S) bond angle deformation and S−Si separations, which have been discussed as a result of net repulsive or net attractive Si−S capping, these hydrogen contacts may play a secondary role only. Comparison between the structural features of $Me_2Si(mt)_2$ and $PhMeSi(mt)_2$ (Table 1) supports this conclusion: Both the structures of $Me_2Si(mt)_2$ and $PhMeSi(mt)_2$ bear one S−Si cap *trans* to C−Si and one *trans* to Si−N each. The increased Lewis acidity of the Si atom in $PhMeSi(mt)_2$ (as a result of replacing an sp^3 C atom by a more electronegative sp^2 C atom in the coordination sphere) causes a shortening of both S−Si separations (by 0.074 Å *trans* to C−Si, 0.067 Å *trans* to N−Si). The difference in the S−Si distances is 0.133 Å for compound $Me_2Si(mt)_2$. Unlike $Me_2Si(mt)_2$, compound $PhMeSi(mt)_2$ bears a phenyl group and exhibits hydrogen contacts between this π-electron system and one methimazolyl group, the analogue of which could not establish such contacts in $Me_2Si(mt)_2$. The difference in S−Si separations within this molecule, however, is similar (0.126 Å).

With respect to the question whether S−Si interactions in these methimazolylsilanes can be regarded as Si-hypercoordination, differing opinions can be found in the literature. S−Si capping with similar S−Si separations (i.e., ca. 3.05−3.48 Å) has also been reported for ligands of higher flexibility, the S−Si separations of which cannot be regarded as a sole result of steric constraints. In the dithiocarboxylate-bearing silanes reported by Kano et al., these S−Si distances are discussed in terms of Si-hypercoordination.[9] Similar S−Si separations were also found for a series of O-silylated thiobenzoates $PhC(=S)O\text{-}SiR_3$ (R = Ph, O-C_6H_3-2,6-Me_2, O-*t*Bu), but the authors interpret this result as a lack of intramolecular interaction.[10] Our experimental (single-crystal XRD) observations, i.e., the systematic trends in the slight dependence of the S−Si separation on the substitution pattern about the Si atom, provide support for the presence of weak intramolecular donor−acceptor interactions. Si-hypercoordination (i.e., more than four donor atoms in the first coordination sphere) is usually indicated by a notable shift of the ^{29}Si

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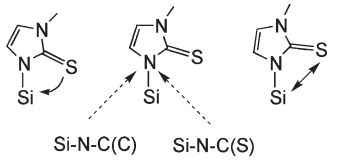
Table 1. Selected Si−S Separations and Si−N Bond Lengths [Å] and Angles [deg] of Compounds $Me_3Si(mt)$, $Me_2Si(mt)_2$, $Me(H)Si(mt)_2$, $PhMeSi(mt)_2 \cdot 0.5$toluene, $Ph(H)Si(mt)_2$, $Ph_2Si(mt)_2 \cdot 0.5$toluene, $EtSi(mt)_3 \cdot CH_2Cl_2$, $PhSi(mt)_3 \cdot$toluene, $PhClSi(mt)_2 \cdot$toluene, $PhCl_2Si(mt)$, and $ClSi(mt)_3$, Which Are Affected by the S−Si Capping[a]

compd	S	*trans* to	*d*(Si−S)	N	*d*(Si−N)	Si−N−C(S)	Si−N−C(C)
$Me_3Si(mt)$	S1	C	3.451(1)			125.9(1)	126.2(1)
				N1	1.800(2)		
$Me_2Si(mt)_2$	**S1**	**N3**	**3.367(1)**	**N3**	**1.780(2)**	123.4(1)	128.6(1)
	S2	C	3.500(1)			127.7(1)	124.1(1)
				N1	1.775(2)		
$Me(H)Si(mt)_2$	S1	C	3.321(1)			122.2(2)	128.5(2)
	S2	**N1**	**3.180(1)**	**N1**	**1.771(2)**	119.1(1)	132.6(2)
				N3	1.768(2)		
$PhMeSi(mt)_2$	S1	C	3.426(1)			126.0(1)	126.0(1)
	S2	**N1**	**3.300(1)**	**N1**	**1.785(1)**	122.3(1)	129.5(1)
				N3	1.769(1)		
$Ph(H)Si(mt)_2$	S1	C	3.292(1)			121.6(1)	128.8(1)
	S2	**N1**	**3.167(1)**	**N1**	**1.776(1)**	119.2(1)	132.3(1)
				N3	1.759(1)		
$Ph_2Si(mt)_2$	S1	C	3.480(1)			127.0(1)	124.3(1)
	S2	C	3.452(1)			127.2(1)	124.5(1)
				N1	1.769(2)		
				N3	1.765(2)		
$EtSi(mt)_3$	**S1**	**N3**	**3.419(1)**	**N3**	**1.767(1)**	125.1(1)	125.3(1)
	S2	**N5**	**3.385(1)**	**N5**	**1.761(1)**	125.0(1)	126.1(1)
	S3	**N1**	**3.319(1)**	**N1**	**1.777(1)**	122.3(1)	129.0(1)
$PhSi(mt)_3$	S1	C	3.422(1)			126.3(1)	125.1(1)
	S2	**N1**	**3.349(1)**	**N1**	**1.756(1)**	123.5(1)	126.9(1)
	S3	**N3**	**3.353(1)**	**N3**	**1.763(1)**	123.5(1)	126.9(1)
				N5	1.751(1)		
$PhClSi(mt)_2$	S1	C	3.403(1)			125.2(1)	125.9(1)
	S2	Cl	3.317(1)			122.9(1)	128.5(1)
				N1	1.752(2)		
				N3	1.751(2)		
$PhCl_2Si(mt)$	S1	Cl	3.243(1)			120.9(1)	130.3(1)
				N1	1.753(1)		
$ClSi(mt)_3$	**S1**	**N3**	**3.386(1)**	**N3**	**1.742(1)**	124.9(1)	126.3(1)
	S2	Cl	3.331(1)			123.8(1)	127.6(1)
	S3	**N1**	**3.302(1)**	**N1**	**1.752(1)**	121.7(1)	126.9(1)
				N5	1.735(1)		

[a] *Trans*-N Si−S separations and their respective *trans*-disposed Si−N bonds are highlighted in bold. The structure of $Si(mt)_4$ suffers effects of disorder, thus the structural parameters are not listed.

Scheme 4



NMR signal to higher field (with respect to molecular systems that lack the additional donor sites).[11] Comparison of the ^{29}Si NMR data of some of above methimazolylsilanes with structurally related molecules that lack the capping S-donor function, however, does not support a concept of Si-hypercoordination in terms of significantly upfield-shifted ^{29}Si resonances upon coordination of the additional donors: The ^{29}Si NMR shift of $Me_3Si(mt)$ (15.8 ppm) is similar to that of trimethylsilylimidazole (14.1 ppm);[12] the resonances of $PhCl_2Si(mt)$ (−17.0 ppm) and $PhClSi(mt)_2$ (−28.5 ppm) are slightly upfield-shifted with reference to the indolyl-substituted silanes $(indolyl)SiPhCl_2$ (−12.6 ppm)[13] and $(indolyl)_2SiPhCl$ (−23.7 ppm).[13] These differences, however, do not represent any significant hint at hypercoordination because replacement of one indolyl group of the latter by pyrrole causes an even greater upfield shift of (indolyl)(pyrrolyl)SiPhCl (−31.7 ppm).[13] Hence, although X-ray diffraction data hint at intramolecular Si−S interactions, these effects exert only marginal impact on the ^{29}Si NMR properties of methimazolylsilanes. In this context we need to point out that ^{29}Si NMR data reported in our paper are solution-state NMR data, and the molecular architectures as found crystallographically do not persist in solution (only one set of signals was found ^{1}H and ^{13}C NMR spectroscopically for the mt moieties of the bis-, tris-, and tetrakis(methimazolyl) silanes). Nonetheless, rotation of the methimazolyl moiety about the Si−N bond should retain the sulfur atoms in close proximity to the Si atom. This was confirmed by a potential energy surface scan (PES) of a rotation about the Si−N bond of $Cl_3Si(mt)$ (Figure 3). According to the only slightly altered Si−S separations along the rotation coordinate (ranging between 3.39 and 3.60 Å), similar shielding of the Si nucleus can be expected. The energy barrier associated with the rotation about the Si−N bond of our model compound $Cl_3Si(mt)$ (ca. 8 kcal/mol), which may furthermore be lowered by solvent effects, indicates both the possibility of rotation in solution and

(11) For reviews on hypercoordinate silicon compounds see for example: (a) Chuit, C.; Corriu, R. J. P.; Reye, C.; Young, J. C. *Chem. Rev*. **1993**, *93*, 1371. (b) Tacke, R.; Pülm, M.; Wagner, B. *Adv. Organomet. Chem*. **1999**, *44*, 221. (c) Kost, D.; Kalikhman, I. *Adv. Organomet. Chem*. **2004**, *50*, 1. (d) Voronkov, M. G.; Trofimova, O. M.; Bolgova, Yu. I.; Chernov, N. F. *Russ. Chem. Rev*. **2007**, *76*, 825.

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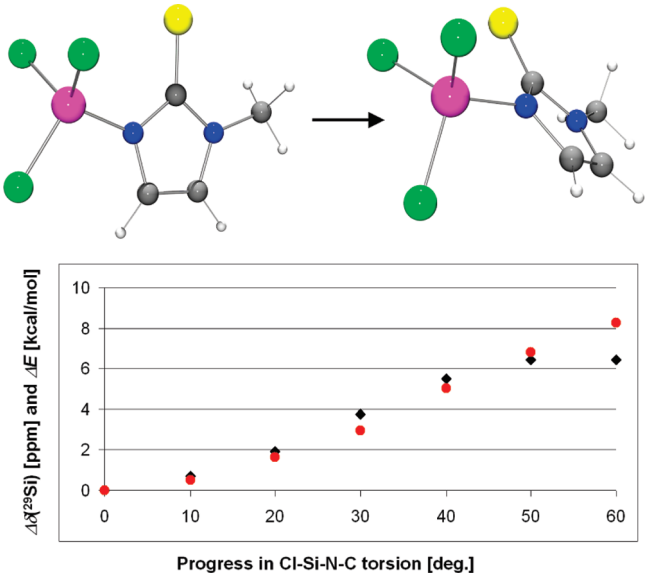
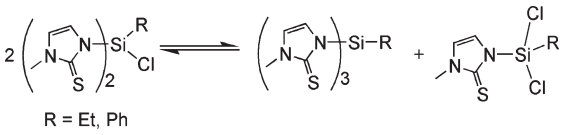


Figure 3. Potential energy surface scan (PES) of a torsion about the Si−N bond in $Cl_3Si(mt)$ by 60° in steps of 10°, calculated at the PBE-D+ZORA/TZ2P level. Red spots represent the relative energies ΔE (in kcal/mol); black diamonds represent the calculated difference in ^{29}Si NMR shift $\Delta\delta$ (in ppm).

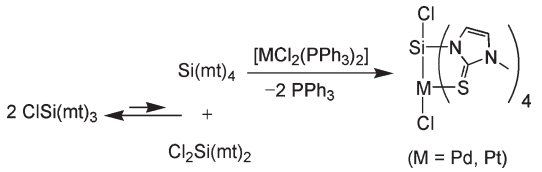
a preference for the conformations with S-capped tetrahedral faces in the Si coordination sphere. The latter should render the ^{29}Si NMR shifts in solution similar to those of the solids, as the predominant conformation will contribute predominantly to $\delta^{29}Si$. Accordingly, for $ClSi(mt)_3$ (which exhibits chemically different mt ligands in the solid state, i.e., *trans*-S-capped and noncapped Si−N bonds) only one mt-related set of signals was detected in solution ^1H and ^{13}C NMR spectra, and ^{29}Si NMR spectroscopy revealed similar chemical shifts in solution (−50.5 ppm in $CDCl_3$) and the solid state (−50.1 ppm).

Although the methimazolylsilanes $Ph_2Si(mt)_2$, $EtSi(mt)_3$, and $PhSi(mt)_3$ require the presence of *N*-methylimidazole (NMI) as catalyst when prepared in THF solution, their formation seems favored in chlorinated solvents such as chloroform or dichloromethane. Whereas donors such as NMI may support nucleophilic substitution reactions at Si by formation of reactive higher-coordinate Si complexes,[14] solvents such as $CHCl_3$ may support ionic Si−Cl bond dissociation,[15] thus also supporting nucleophilic substitution reactions at Si. When dissolved in $CDCl_3$ compound $PhClSi(mt)_2$ gives rise to three signals of similar intensity in the ^{29}Si solution NMR spectrum (δ −17.0, −28.5, and −39.9 ppm for $PhCl_2Si(mt)$, $PhClSi(mt)_2$, and $PhSi(mt)_3$, respectively) (Scheme 5).[4] Assignment was made by analyzing these compounds separately in thf or toluene solution, where they remained the predominant species for many hours. The same effect has been observed for $EtClSi(mt)_2$ in $CDCl_3$ (signals at δ 0.0, −12.6, and −24.0 ppm, which were assigned to $EtCl_2Si(mt)$, $EtClSi(mt)_2$, and $EtSi(mt)_3$, respectively, according to the systematic upfield shift by ca. 10 ppm upon replacing one Si-bound Cl atom by a mt

Scheme 5



Scheme 6



substituent), and we also reported it for $ClSi(mt)_3$ in $CDCl_3$ (δ −41.2, −50.5, and −59.1 ppm, assigned to $Cl_2Si(mt)_2$, $ClSi(mt)_3$, and $Si(mt)_4$, respectively).[5] For the latter we have now shown that in the solid state only $ClSi(mt)_3$ is present (one signal at −50.1 ppm), whereas the three signals emerge upon dissolution in $CDCl_3$.

This feature of multicomponent solutions in $CDCl_3$, which has only been observed for those methimazolylsilanes bearing both N−Si and Cl−Si bonds, was ascribed to ligand scrambling since those methimazolylsilanes devoid of Cl−Si bonds were found to produce only one set of signals in their ^1H and ^{13}C NMR spectra as well as only one ^{29}Si NMR peak. The latter observation excludes traces of water being the source of the reproducible emerging of the sets of signals (e.g., signals of silanols or siloxanes), since Cl-free methimazolylsilanes were also found to be highly sensitive toward moisture and other OH-protic reagents such as alcohols and would therefore have to exhibit similar behavior. Whereas ligand scrambling at Cl−Si-functionalized methimazolylsilanes represents a potential disadvantage of these compounds with respect to their applicability as stable ligands in coordination chemistry, this ligand scrambling has however proven useful for providing the ligand scrambling products as starting materials in a decelerated fashion. It renders them useful precursors when slow crystallization is preferred rather than spontaneous precipitation, e.g., in the synthesis of metallasilatranes, Scheme 6.

In addition, the facile N−Si versus Cl−Si exchange within the methimazolylsilane systems opens further routes toward methimazolylsilanes. Instead of synthesizing methimazolylsilanes along the base-supported route as depicted in Scheme 3, a transsilylation between $Me_3Si(mt)$ and a chlorosilane might prove the better alternative, especially when the product reveals poor solubility in THF and might precipitate with the byproduct Et_3NHCl. In a particular case, i.e., the synthesis of $ClSi(mt)_3$, $SiCl_4$ was successfully reacted with $Me_3Si(mt)$ to give the desired product in good yield and without Et_3NHCl as potential impurity.

In conclusion, we have found that a variety of methimazolylsilanes are accessible via straightforward syntheses from methimazole and the respective chlorosilane in the presence of triethylamine as sacrificial base, whereas more bulky substituents at the silicon atom required a catalyst (NMI) to promote complete methimazolyl substitution. The silanes reported herein add to this essentially unexplored class of N-silylated methimazoles, which represent tempting "scorpionate"-like systems for further investigation as ligands in transition metal coordination chemistry. In addition to

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exhibiting interesting molecular structural features by means of S-capped tetrahedral Si coordination spheres, the Si−N bonds of methimazolylsilanes appeared to be both kinetically labile and thermodynamically capable of undergoing intermolecular mt versus Cl ligand exchange reactions. This feature renders methimazolylsilanes potential methimazolyl transfer reagents. The latter was proven both in the syntheses of the first methimazolyl-bridged metallasilatranes[5] and by the successful synthesis of $ClSi(mt)_3$ along a transsilylation route, namely, starting from $SiCl_4$ and $Me_3Si(mt)$. The applicability of methimazolylsilanes as methimazolyl-transfer reagents for syntheses of silicon-free methimazolyl-bridged complexes such as $ClSn(\mu\text{-}mt)_4PdCl$,[16] which could only be prepared in traces so far, will be explored in further studies.

Experimental Section

General Considerations. Unless otherwise indicated, the chemicals used were commercially available. Due to the general hydrolytic sensitivity of both chlorosilanes and methimazolylsilanes, all following manipulations were carried out under an inert atmosphere of dry argon. Toluene and THF were distilled from sodium/benzophenone prior to use. Triethylamine and dichloromethane were distilled from calcium hydride, and chloroform was dried over 4 Å molecular sieves.

NMR spectra were recorded on a Varian Inova 500 or Inova 300 spectrometer ($SiMe_4$ as internal standard). Elemental analyses were carried out by the RSC microanalytical services. Single-crystal X-ray diffraction data were collected on a NONIUS KappaCCD diffractometer. Structures were solved with direct methods and refined with full-matrix least-squares methods. All non-hydrogen atoms were anisotropically refined. C-Bound hydrogen atoms were placed in idealized positions and isotropically refined (riding model). The Si-bound hydrogen atom in the structure of $Me(H)Si(mt)_2$ was located on residual electron density maps and isotropically refined without restraints. The absolute configuration of the non-centrosymmetric structure of $Me_2Si(mt)_2$ was determined (Flack parameter: −0.05(6)) Structure solution and refinement of F^2 against all reflections were done with the software SHELXS-97 and SHELXL-97 (G. M. Sheldrick, Universität Göttingen, 1986−1997). Data of structure determination and refinement for the herein presented crystal structures can be found in the respective part of analytical data for each compound. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Centre as supplementary publication nos. CCDC 773420−773426. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: (int.) +44-1223/336-033; e-mail: deposit@ccdc.cam.ac.uk].

The syntheses of $PhClSi(mt)_2$,[4] $PhCl_2Si(mt)$,[4] $ClSi(mt)_3$,[5] $Si(mt)_4$,[5] and $Ph(H)Si(mt)_2$[6] have been recently reported elsewhere.

An alternative **Synthesis of $ClSi(mt)_3$**, via transsilylation, proceeds as follows: To a solution of $Me_3Si(mt)$ (10.0 g, 53.8 mmol) in THF (20 mL) was added $SiCl_4$ (3.00 g, 17.6 mmol) at room temperature. Within 1 day crystallization of $ClSi(mt)_3$ commenced. Upon storage at room temperature for 7 days the crystals were separated from the supernatant by decantation, washed with THF (5 mL), and dried under vacuum. Yield: 6.22 g (15.4 mmol, 87%). ^1H, ^{13}C, and ^{29}Si NMR data correspond to those previously reported for $ClSi(mt)_3$; ^{29}Si CP/MAS NMR (δ_{iso} −50.1 ppm) confirmed the presence of only one Si species in the solid state.

Synthesis of $Me_3Si(mt)$. To a suspension of methimazole (8.0 g, 70 mmol) in diethyl ether (150 mL) were added triethylamine (10.0 g, 99 mmol) and chlorotrimethylsilane (9.0 g, 83 mmol), and the mixture was stirred at room temperature for 1 h. The hydrochloride precipitate was then filtered off and washed with ether (100 mL). From the combined filtrate and washings the volatiles were removed under reduced pressure, and the resulting solid was recrystallized from hexane (50 mL). Upon storage at room temperature for 1 day, the crystals were separated from the supernatant by decantation and dried in vacuo. Yield: 11.6 g (62.2 mmol, 89%). Mp: 58 °C. Anal. Found (%): C 44.72, H 7.53, N 15.09. Calcd for $C_7H_{14}N_2SSi$: C 45.12, H 7.57, N 15.03. ^1H NMR ($CDCl_3$, 300 MHz): δ 0.59 (s, 9 H, $SiCH_3$), 3.58 (s, 3 H, NCH_3), [6.57 (d, 1 H, 2.4 Hz), 6.72 (d, 1 H, 2.4 Hz)(methimazole)]. ^{13}C NMR ($CDCl_3$, 300 MHz): δ −0.6 ($SiCH_3$), 34.5 (NCH_3), 117.8, 119.8 (methimazole CH), 167.1 (C=S). ^{29}Si NMR ($CDCl_3$, 300 MHz): δ 15.8. Crystal structure analysis of $Me_3Si(mt)$: $C_7H_{14}N_2SSi$, CCDC-773426, T 100(2) K, orthorhombic, *Pnma*, a 13.9036(6) Å, b 7.0905(2) Å, c 21.1015(9) Å, V 2080.26(14) Å^3, Z 8, μ(Mo Kα) 0.373 mm^{-1}, θ_{max} 32°, 16 935 reflections (3838 unique, R_{int} 0.0602), 133 parameters, S 1.042, R_1/wR_2 [$I > 2\sigma(I)$] 0.0354/0.0577, R_1/wR_2 (all data) 0.0793/0.0857, residual electron density (highest peak, deepest hole) 0.462/−0.408 e Å^{-3}.

Synthesis of $Me_2Si(mt)_2$. A solution of methimazole (0.80 g, 7.0 mmol) and triethylamine (1.2 g, 12 mmol) in THF (20 mL) was stirred at ambient temperature, and dimethyldichlorosilane (0.47 g, 3.6 mmol) was added dropwise. Immediately a precipitate of triethylammonium chloride formed. The mixture was stored in a refrigerator (4 °C) overnight and then filtered, and the hydrochloride washed with THF (10 mL). Removal of the solvent from the filtrate provided a white powder, recrystallization of which from toluene (10 mL) afforded colorless crystals of $Me_2Si(mt)_2$. The solution was decanted, and the crystals were dried in vacuo. Yield: 0.85 g (3.00 mmol, 85%). Mp: 168−170 °C. Anal. Found (%): C 42.02, H 5.86, N 19.45. Calcd for $C_{10}H_{16}N_4S_2Si$: C 42.22, H 5.67, N 19.70. ^1H NMR ($CDCl_3$, 500 MHz): δ 1.18 (s, 6 H, Si-CH_3), 3.55 (s, 6 H, N-CH_3), 6.70−6.74 (m, 4 H, methimazole). ^{13}C NMR ($CDCl_3$, 500 MHz): δ −1.0 ($SiCH_3$), 34.4 (NCH_3), 119.0, 120.0 (methimazole CH), 167.6 (C=S). ^{29}Si NMR ($CDCl_3$, 500 MHz): δ 3.75. Crystal structure analysis of $Me_2Si(mt)_2$: $C_{10}H_{16}N_4S_2Si$, CCDC-773420, T 200(2) K, orthorhombic, $Pna2_1$, a 16.8497(3) Å, b 11.5975(2) Å, c 7.1424(1) Å, V 1395.73(4) Å^3, Z 4, μ(Mo Kα) 0.452 mm^{-1}, θ_{max} = 32°, 34 433 reflections (4767 unique, R_{int} 0.0682), 154 parameters, S 1.060, R_1/wR_2 [$I > 2\sigma(I)$] 0.0384/0.0690, R_1/wR_2 (all data) 0.0751/0.0833, x(Flack) −0.05(6), residual electron density (highest peak, deepest hole) 0.228/−0.368 e Å^{-3}.

Synthesis of $Me(H)Si(mt)_2$. At −5 °C a solution of methimazole (0.80 g, 7.0 mmol) and triethylamine (1.2 g, 12 mmol) in THF (20 mL) was added dropwise to a solution of methyldichlorosilane (0.42 g, 3.6 mmol) in THF (10 mL). Immediately a precipitate of triethylammonium chloride formed. The mixture was stored in a refrigerator (4 °C) for 2 h and then filtered, and the hydrochloride washed with THF (10 mL). Removal of the solvent from the filtrate provided a white powder, which upon recrystallization from toluene (10 mL) afforded colorless crystals of $Me(H)Si(mt)_2$. The solution was decanted, and the crystals were dried in vacuo. Yield: 0.80 g (2.96 mmol, 84%). Mp: 170−174 °C. Anal. Found (%): C 39.29, H 5.34, N 20.42. Calcd for $C_9H_{14}N_4S_2Si$: C 39.97, H 5.22, N 20.72. ^1H NMR ($CDCl_3$, 500 MHz): δ 1.23 (d, 3 H, 3 Hz, $SiCH_3$), 3.55 (s, 6 H, NCH_3), 5.78 (q, 1 H, 3 Hz, SiH), 6.74 (d, 2 H, 2.8 Hz), 6.84 (d, 2 H, 2.8 Hz) (methimazole). ^{13}C NMR ($CDCl_3$, 500 MHz): δ −3.3 ($SiCH_3$), 34.3 (NCH_3), 119.6, 120.3 (methimazole CH), 167.7 (C=S). ^{29}Si NMR ($CDCl_3$, 500 MHz): δ −18.2 (d, $^1J_{SiH}$ 264 Hz). Crystal structure analysis of $Me(H)Si(mt)_2$: $C_9H_{14}N_4S_2Si$, CCDC-773421, T 100(2) K, monoclinic, $P2_1/c$, a 7.4489(2) Å, b 19.7998(8) Å, c 8.7347(3) Å, β 100.361(2)°, V 1267.25(8) Å^3, Z 4, μ(Mo Kα) 0.494 mm^{-1}, θ_{max} 27.5°, 21 341 reflections (2918 unique, R_{int} 0.1106), 149 parameters, S 1.034, R_1/wR_2 [$I > 2\sigma(I)$] 0.0433/0.0664, R_1/wR_2 (all data) 0.0893/0.0958, residual electron density (highest peak, deepest hole) 0.349/−0.323 e Å^{-3}.

Synthesis of $PhMeSi(mt)_2$. A solution of methimazole (0.80 g, 7.0 mmol) and triethylamine (1.2 g, 12 mmol) in THF (20 mL)

(16) Wagler, J.; Hill, A. F.; Heine, T. *Eur. J. Inorg. Chem.* **2008**, 4225.

was stirred at ambient temperature, and methylphenyldichlorosilane (0.68 g, 3.6 mmol) was added dropwise. Immediately a precipitate of triethylammonium chloride formed. The mixture was stirred at 60 °C for 30 min, then stored in a refrigerator (4 °C) overnight. The hydrochloride was filtered and washed with THF (10 mL). Removal of the solvent from the filtrate provided a colorless foam, which upon recrystallization from toluene (10 mL) afforded colorless crystals of the solvate $PhMeSi(mt)_2 \cdot (toluene)_{0.5}$. The solution was decanted, and the crystals were briefly dried in vacuo. Yield: 1.20 g (3.06 mmol, 87%). Anal. Found (%): C 54.86, H 5.25, N 14.77. Calcd for $C_{37}H_{44}N_8S_4Si_2$: C 56.60, H 5.65, N 14.27. (The slightly lower content in C and H as well as the higher content in N may result from partial loss of toluene from the crystals.) ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.61 (s, 3 H, $SiCH_3$), 3.56 (s, 6 H, NCH_3), [6.30 (d, 2 H, 2.5 Hz), 6.68 (d, 2 H, 2.5 Hz)(methimazole)], 7.40−7.60 (m, 5 H, phenyl). ^{13}C NMR ($CDCl_3$, 500 MHz): δ −1.9 ($SiCH_3$), 34.5 (NCH_3), 119.5, 120.2 (methimazole CH), 128.5 (o,m), 128.9 (i), 131.3 (p), 134.3 (o,m), 168.0 (C=S). ^{29}Si NMR ($CDCl_3$, 500 MHz): δ −8.9. Crystal structure analysis of $(PhMeSi(mt)_2)_2 \cdot$ toluene: $C_{37}H_{44}N_8S_4Si_2$, CCDC-773422, T 200(2) K, monoclinic, $P2_1/c$, a 12.5018(2) Å, b 7.6542(1) Å, c 21.4230(3) Å, β 97.356(2)°, V 2033.12(5) Å^3, Z 2, μ(Mo Kα) 0.330 mm^{-1}, θ_{max} = 32°, 43 207 reflections (7034 unique, R_{int} 0.0522), 263 parameters, S 1.062, R_1/wR_2 [$I > 2\sigma(I)$] 0.0470/0.0695, R_1/wR_2 (all data) 0.1263/0.1362, residual electron density (highest peak, deepest hole) 0.514/−0.415 e Å^{-3}.

Synthesis of $Ph_2Si(mt)_2$. A solution of methimazole (0.80 g, 7.0 mmol), triethylamine (2.0 g, 20 mmol), and *N*-methylimidazole (0.1 g) in THF (20 mL) was stirred at ambient temperature, and diphenyldichlorosilane (0.90 g, 3.6 mmol) was added dropwise. Immediately a precipitate of triethylammonium chloride formed. The mixture was stirred at 60 °C for 1 h, then stored in a refrigerator (4 °C) overnight. The hydrochloride was filtered off and washed with THF (5 mL). Removal of the solvent from the filtrate delivered a colorless foam, which upon recrystallization from toluene (20 mL) afforded colorless crystals of the solvate $Ph_2Si(mt)_2 \cdot (toluene)_{0.5}$. The solution was decanted, and the crystals were briefly dried in vacuo. Yield: 1.21 g (2.66 mmol, 76%). Anal. Found (%): C 59.04, H 5.14, N 12.82. Calcd for $C_{47}H_{48}N_8S_4Si_2$: C 62.08, H 5.32, N 12.32. (The lower content in C and H as well as the higher content in N may result from partial loss of toluene from the crystals.) ^{1}H NMR ($CDCl_3$, 500 MHz): δ 3.56 (s, 6 H, N-CH_3), [6.63 (d, 2 H, 2.5 Hz), 6.70 (d, 2 H, 2.5 Hz)(methimazole)], [7.40−7.55 (m, 6 H), 7.84 (dd, 4 H, 8.0 Hz, 1.5 Hz)(phenyl)]. ^{13}C NMR ($CDCl_3$, 500 MHz): δ 34.7 (N-CH_3), 120.2, 120.6 (methimazole CH), 128.0 (o,m), 128.3 (i), 131.2 (p), 136.3 (o,m) (phenyl), 168.8 (C=S). ^{29}Si NMR ($CDCl_3$, 500 MHz): δ −22.5. Crystal structure analysis of $(Ph_2Si(mt)_2)_2 \cdot$ toluene: $C_{47}H_{48}N_8S_4Si_2$, CCDC-773423, T 200(2) K, triclinic, $P\bar{1}$, a 9.4659(2) Å, b 10.2308(3) Å, c 12.0804(3) Å, α 99.860(2)°, β 97.936(1)°, γ 91.312(1)°, V 1140.28(5) Å^3, Z 1, μ(Mo Kα) 0.305 mm^{-1}, θ_{max} = 28.5°, 25 025 reflections (5702 unique, R_{int} 0.0444), 272 parameters, S 1.053, R_1/wR_2 [$I > 2\sigma(I)$] 0.0432/0.0639, R_1/wR_2 (all data) 0.1077/0.1166, residual electron density (highest peak, deepest hole) 0.487/−0.390 e Å^{-3}.

Synthesis of $PhSi(mt)_3$. A solution of methimazole (10.0 g, 87.7 mmol), triethylamine (10.0 g, 99 mmol), and *N*-methylimidazole (0.2 g) in THF (120 mL) was stirred at ambient temperature, and phenyltrichlorosilane (6.25 g, 29.6 mmol) was added dropwise. Immediately, a precipitate of triethylammonium chloride formed. The mixture was stirred at 50 °C for 1.5 h, then stored in a refrigerator (4 °C) overnight. The hydrochloride was filtered off and washed with THF (100 mL). From the filtrate the solvent was removed under reduced pressure, and the resultant white foam was dissolved in hot toluene (40 mL). After storage at room temperature for 1 day followed by storage at 4 °C for 5 days the solid product ($PhSi(mt)_3$.toluene) was filtered off, washed with toluene (20 mL), and briefly dried in vacuo. Yield: 12.6 g (23.5 mmol, 80%). Anal. Found (%): C 51.06, H 5.01, N 15.93. Calcd for $C_{25}H_{28}N_6S_3Si$: C 55.94, H 5.26, N 15.66. (The lower content in C and H as well as the higher content in N may result from partial loss of toluene from the crystals.) ^{1}H NMR ($CDCl_3$, 500 MHz): δ 3.52 (s, 9 H, N-CH_3), [6.72 (d, 3 H, 2.5 Hz), 6.90−7.05 (br, 3 H)(methimazole)], [7.40−7.50 (m, 3 H), 7.92 (dd, 2 H, 7.5 Hz, 1.0 Hz)(phenyl)]. ^{13}C NMR ($CDCl_3$, 500 MHz): δ 34.6 (NCH_3), 120.4, 121.6 (methimazole), 125.8(i), 128.0 (o,m), 131.9 (p), 136.3 (o,m)(phenyl), 168.4 (C=S). ^{29}Si ($CDCl_3$, 500 MHz): δ −39.9. Crystal structure analysis of $PhSi(mt)_3 \cdot$ toluene: $C_{25}H_{28}N_6S_3Si$, CCDC-773425, T 100(2) K, monoclinic, $P2_1/n$, a 12.7358(2) Å, b 14.5040(3) Å, c 14.6495(3) Å, β 93.037(1)°, V 2702.26(9) Å^3, Z 4, μ(Mo Kα) 0.345 mm^{-1}, θ_{max} = 41°, 119 198 reflections (17 784 unique, R_{int} 0.0793), 316 parameters, S 1.082, R_1/wR_2 [$I > 2\sigma(I)$] 0.0421/0.0766, R_1/wR_2 (all data) 0.1042/0.1128, residual electron density (highest peak, deepest hole) 0.663/−0.480 e Å^{-3}.

Synthesis of $EtClSi(mt)_2$. A solution of methimazole (2.50 g, 21.9 mmol) and triethylamine (3.0 g, 29.7 mmol) in THF (70 mL) was stirred at 0 °C, and ethyltrichlorosilane (1.83 g, 11.2 mmol) was added dropwise. Immediately a precipitate of triethylammonium chloride formed. The mixture was stored in a refrigerator (4 °C) overnight. The hydrochloride was filtered and washed with THF (30 mL). Removal of the solvent from the filtrate delivered a white powder, which upon recrystallization from toluene (12 mL) afforded a white powder of $EtClSi(mt)_2$. The solution was decanted, and the solid was dried in vacuo. Yield: 2.33 g (7.32 mmol, 67%). The ^{1}H and ^{13}C NMR spectra ($CDCl_3$) reveal the presence of at least three chemically independent ethyl moieties, while the ^{29}Si NMR ($CDCl_3$) spectrum is consistent with the presence of $EtCl_2Si(mt)$, $EtClSi(mt)_2$, and $EtSi(mt)_3$ suggested by the presence of three signals (δ 0.0, −12.6, −24.0) in approximate intensity ratio 1:2:1.

Synthesis of $EtSi(mt)_3$. From the above crude $EtClSi(mt)_2$ crystalline $EtSi(mt)_3$ was obtained as dichloromethane solvate by dissolution of $EtClSi(mt)_2$ (1.36 g, 4.27 mmol) in dichloromethane (5.5 mL) followed by addition of diethyl ether (4 mL). Within 1 day large crystals of $EtSi(mt)_3.CH_2Cl_2$ formed, which were separated by decantation and briefly dried in vacuo. Yield: 0.51 g (1.06 mmol, 50%) with respect to the formation of $EtCl_2Si(mt)$ as byproduct. Anal. Found (%): C 37.24, H 4.60, N 17.56. Calcd for $C_{15}H_{22}Cl_2N_6S_3Si$: C 37.41, H 4.60, N 17.45. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.25 (t, 3 H, 7.8 Hz, $SiCH_2CH_3$), 2.32 (q, 2 H, 7.8 Hz, $SiCH_2CH_3$), 3.55 (s, 9 H, NCH_3), [6.71 (d, 3 H, 2.4 Hz), 6.74 (d, 3 H, 2.4 Hz)(methimazole)]. ^{13}C NMR ($CDCl_3$, 300 MHz): δ 7.2, 7.6 ($SiCH_2CH_3$), 34.6 (NCH_3), 120.3, 120.6 (methimazole CH), 167.9 (C=S). ^{29}Si NMR ($CDCl_3$, 500 MHz): δ −24.0. Crystal structure analysis of $EtSi(mt)_3 \cdot CH_2Cl_2$: $C_{15}H_{22}Cl_2N_6S_3Si$, CCDC-773424, T 100(2) K, monoclinic, $P2_1/n$, a 10.8429(1) Å, b 17.0694(3) Å, c 12.8979(2) Å, β 113.057(1)°, V 2196.47(6) Å^3, Z 4, μ(Mo Kα) 0.649 mm^{-1}, θ_{max} 45°, 117 337 reflections (18 099 unique, R_{int} 0.0550), 248 parameters, S 1.049, R_1/wR_2 [$I > 2\sigma(I)$] 0.0365/0.0586, R_1/wR_2 (all data) 0.0861/0.0923, residual electron density (highest peak, deepest hole) 0.764/−1.156 e Å^{-3}.

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Supporting Information Available: X-ray crystallographic files in CIF format (for structure determinations of $Me_3Si(mt)$, $Me_2Si(mt)_2$, $Me(H)Si(mt)_2$, $PhMeSi(mt)_2 \cdot 0.5$toluene, $Ph_2Si(mt)_2 \cdot 0.5$toluene, $EtSi(mt)_3 \cdot CH_2Cl_2$, and $PhSi(mt)_3 \cdot$ toluene) and a pdf document containing ORTEP diagrams of $Ph(H)Si(mt)_2$, $PhClSi(mt)_2$, $PhCl_2Si(mt)$, $ClSi(mt)_3$, and $Si(mt)_4$ as well as details of the computational analyses are deposited with the ACS. This information is available free of charge via the Internet at http://pubs.acs.org.