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Synthesis and Reactivity of New Pyrazolyl-Functionalized Potassium Silanides

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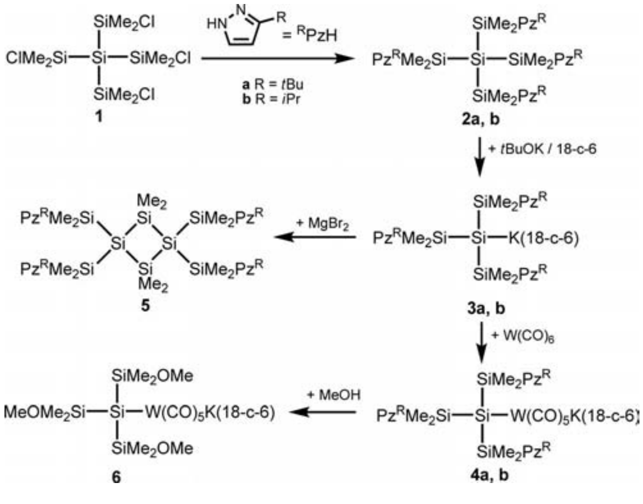
The pyrazolyl-functionalized oligosilanes $Si(SiMe_2Pz^R)_4$ (**2a** R = *t*Bu; **2b** R = *i*Pr) were prepared by the reaction of 3-R-pyrazole (R = *i*Pr, *t*Bu) with $Si(SiMe_2Cl)_4$ in the presence of NEt_3. By treatment with *t*BuOK and 18-crown-6 in THF, **2a**, **b** were converted into the new potassium silanides $(Pz^RMe_2Si)_3SiK$(18-crown-6) (**3a** R = *t*Bu; **3b** R = *i*Pr), respectively. Upon adding $W(CO)_6$ to THF solutions of **3a**, **b** the tungsten complexes $[(Pz^RMe_2Si)_3SiW(CO)_5]K$(18-crown-6) (**4a** R = *t*Bu; **4b** R = *i*Pr) were readily formed, whereas upon adding $MgBr_2$ fragmentation occurs leading to the formation of $[(Pz^RMe_2Si)_2Si\text{-}SiMe_2]_2$ **5**.

Introduction

There has been increasing interest in recent years in the chemistry of alkali-metal silanides ($R_3Si–M$)[1] as these species have shown to be useful precursors for the synthesis of main group and transition metal silanide complexes,[1a] silanols and metal siloxides,[2] unsaturated organosilicon compounds[3] and new oligosilane architectures.[4] In most of these alkali-metal silanides the central highly reactive M–Si unit is surrounded by chemically inert alkyl, phenyl or silyl substituents, whereas thermally stable alkali metal silanides with internal organic functional groups that are capable of acting as chelating ligands for metal species are rare.[5] However, recent studies by us and others have shown that in particular internal oxygen or nitrogen donors can provide new coordination modes in the chemistry of main group and transition metal silanides. Striking examples provide $[Si(SiMe_2OR)_3]Li$[6a] and $[Si^{Me,Me}Pz_3]Li$,[6b] tripodal zwitterions, in both structures the lithium cation is insulated from the silicon anion by internal donor groups. As part of our research program aimed at the coordination chemistry of novel donor substituted silanides, we report herein on the synthesis and reactivity of the first stable pyrazolyl-functionalized potassium silanides of formula $(Pz^RMe_2Si)_3SiK$(18-crown-6) (R = *t*Bu, *i*Pr).

Results and Discussion

The synthetic route to the new pyrazolyl-functionalized potassium silanide complexes is outlined in Scheme 1. The reaction of $Si(SiMe_2Cl)_4$ (**1**) with 3-*tert*-butylpyrazole (Pz^{tBu}) or 3-isopropylpyrazole (Pz^{iPr}) in the presence of triethylamine gave the neutral precursor compounds $Si(SiMe_2Pz^{tBu})_4$ (**2a**) and $Si(SiMe_2Pz^{iPr})_4$ (**2b**), the former was a white powder and the latter a colourless oil that solidified with time, both in almost quantitative yields. The solid-state structure of **2a** was determined by X-ray crystallography, and the results along with selected distances and bond angles are shown in Figure 1. After successful synthesis of **2a**, **b**, attempts were made to selectively cleave one of the Si–Si bonds using synthetic protocols developed by Marschner.[7] Neither treatment of **2a** with *t*BuOK in THF nor with *t*BuOK/18-crown-6 in toluene gave any detectable amount of potassium silanide **3a**. Even at elevated temperatures only slow conversion occurred accompanied by the formation of products resulting from partial decomposition.



Scheme 1. Synthesis of **2**–**6**.

Upon treatment of **2a** with *t*BuOK/18-crown-6 in the polar solvent THF,[8] however, potassium silanide **3a** was generated almost quantitatively after three days at room tem-

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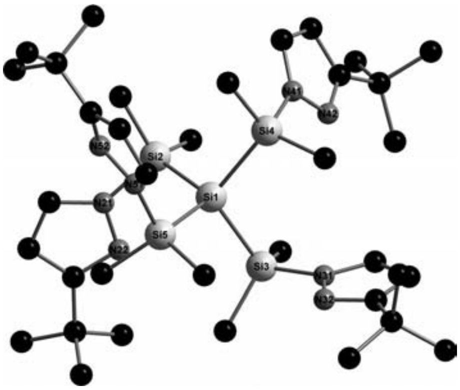


Figure 1. Molecular structure of **2a** in the crystal (black: carbon atoms; hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: Si1–Si4 2.3394(6), Si1–Si5 2.3477(6), Si1–Si2 2.3491(6), Si1–Si3 2.3549(6), Si2–N21 1.7785(14), Si3–N31 1.7810(14), Si4–N41 1.7828(14), Si5–N51 1.7871(14).

perature. Although extremely oxygen- and moisture-sensitive, **3a** is thermally stable and soluble in most organic solvents (benzene, ether, toluene, THF) except hexanes and heptanes. Through ^{1}H-, ^{13}C- and ^{29}Si-NMR spectroscopic studies in C_6D_6, the structure in solution has been assigned to be the crown ether complex $(Pz^{tBu}Me_2Si)_3SiK$(18-crown-6) (**3a**). The ^{29}Si-NMR spectroscopic data are most instructive as the signal of the central silicon drastically shifted to higher field, from –133.5 in **2a** to –197.4 ppm upon replacement of one of the silyl groups by potassium.

We next investigated whether **3a** can be used as a transmetallation reagent for the synthesis of main group or transition metal silanides. Compound **3a** reacted cleanly with $MgBr_2$ or CaI_2 in THF at room temperature; both reactions resulted in the formation of one major product according to ^{1}H NMR spectroscopic studies of the reaction mixture. However, the reaction did not produce the expected complexes, $(Pz^{tBu}Me_2Si)_3SiMgBr$ and $(Pz^{tBu}Me_2Si)_3SiCaI$; rather, the product of fragmentation, cyclotetrasilane **5**, was formed as evidenced by multinuclear NMR spectroscopic data (Scheme 1).

Accordingly, the ^{29}Si NMR spectrum of **5** showed three distinct peaks at 12.0 ($SiMe_2Pz^{tBu}$), –25.8 ($SiMe_2$) and –95.3 (*Si*Si_4) ppm, and also the ^{1}H and ^{13}C NMR spectroscopic data each exhibited two distinct peaks attributable to $SiMe_2$ and $SiMe_2Pz^{tBu}$ groups. In addition, the molecular structure of **5** was confirmed by X-ray crystallography; suitable single crystals were grown from hexane solutions. The results are shown in Figure 2 and revealed a planar four membered silicon ring as the central unit with Si–Si–Si angles being very close to 90°. The external Si2–Si3 and Si2–Si4 distances [ca. 2.33 Å] were found to be somewhat shorter than the internal ring Si–Si bond lengths with an average value of 2.36 Å, possibly due to the steric hindrance and ring strain. The proposed mechanism of this fragmentation process is shown in Scheme 2. Reaction of **3a** with $MgBr_2$ initially generates magnesium silanide, $(Pz^{tBu}Me_2Si)_3$-SiMgBr with elimination of KBr(18-crown-6). Intramolecular coordination of the internal pyrazolyl groups to the central magnesium weakens the Si–N; and this finally results in elimination of magnesium pyrazolide. The intermediately formed disilene is unstable and readily dimerizes in a head to tail fashion to finally produce cyclotetrasilane **5**. Similar fragmentation processes occurring with formation of either cyclotetrasilane[9] or stable silene adducts[10] are reported in the literature.

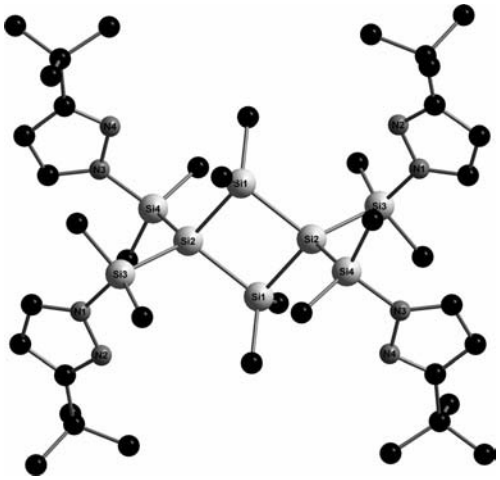
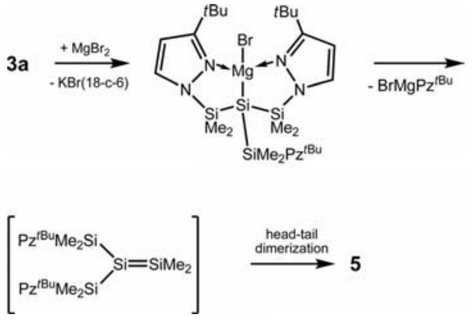


Figure 2. Molecular structure of **5** in the crystal (black: carbon atoms; hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: Si1–Si2 2.3614(8), Si1–Si2 2.3622(8), Si2–Si4 2.3249(8), Si2–Si3 2.3333(9), Si3–N1 1.7830(16), Si4–N3 1.7840(15), Si2–Si1–Si2 89.05(3), Si4–Si2–Si3 107.33(3), Si4–Si2–Si1 115.37(3), Si3–Si2–Si1 113.35(3), Si4–Si2–Si1 113.64(2), Si3–Si2–Si1 115.86(2), Si1–Si2–Si1 90.95(3).



Scheme 2. Proposed mechanism for the formation of **5**.

Since the addition of main group metal halides resulted in Si–N bond cleavage, potassium silanide **3a** was treated with $W(CO)_6$. Regardless of whether **3a** was used in pure state or generated in situ from the reaction of **2a** with *t*BuOK/18-crown-6 in THF, both reactions proceeded smoothly at room temperature with loss of one molecule of CO to quantitatively produce a yellow powder of the tungsten silanide **4a** (Scheme 1). Compound **4b**, the isopropyl analogue of **4a**, can be prepared similarly from the reaction of **2b** with *t*BuOK/18-crown-6 in THF followed by the addition of $W(CO)_6$. The structures of the new tungsten complexes were confirmed by NMR and IR data and the results of elemental analysis. The ^{29}Si NMR spectrum of **4a** showed a significant down-field shift for the central silicon (–145.6 ppm) relative to **3a**, which clearly is attributable to the formation of a W–Si bond. A ^{13}C NMR spectrum showed two resonances in a 4:1 ratio at δ = 204.3 and 206.3 ppm, the former can be assigned to the carbonyls in the *cis* position and the latter to the carbonyl in *trans* position to tungsten. Compound **4a**, whose structure was determined by X-ray crystallography (Figure 3), can be described as a monoanionic silyl tungstenate with potassium as the counter cation being coordinated by 18-crown-6 and one molecule of toluene; the latter weakly coordinates η^6. Interestingly, the oxygen of the CO ligand in *trans* position also weakly coordinates to the potassium ion with a $K–O_{CO}$ distance being 2.805 Å and a C≡O···K angle of 140°, whereas in $[Me_{11}Si_6W(CO)_5]Li(DIME)_2$[9] no coordination to the lithium cation occurred. As expected, the $W–CO_{trans}$ distance [1.965 Å] is somewhat shorter than the $W–CO_{cis}$ distances [average 2.02 Å], due to the *trans* influence of the silanide ligand, resulting in stronger W to CO_{trans} back bonding. This also increases the electron density at the CO_{trans} oxygen atom allowing it to weakly coordinate to the potassium cation. However, the W–Si [2.68 Å], the $W–C_{trans}$ [1.965 Å] and the average $W–C_{cis}$ [2.02 Å] distances of **4a** are very similar to the other related complexes $[Me_{11}Si_6W(CO)_5]Li(DIME)_2$,[11] $[(Me_3Sn)_3SiW(CO)_5]NEt_4$[12a] and $[(Me_3Si)_3SiW(CO)_5]NEt_4$.[12b] The IR spectrum ($CH_2Cl_2$) of the carbonyl region of **4a** displays four bands at 2040 cm^{-1} (m), 1954 cm^{-1} (m), 1909 cm^{-1} (vs) and 1869 cm^{-1} (s). These values are characteristic of $M[W(CO)_5X]$ species, that do not have rigorous C_{4v} geometry[13] and are very similar to the values of the tungsten silyl complexes mentioned above.[11,12]

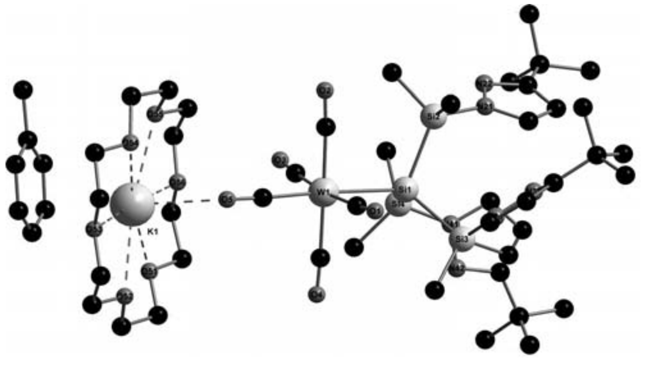


Figure 3. Molecular structure of **4a** in the crystal (black: carbon atoms; hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: W1–C5 1.965(4), W1–C3 2.015(6), W1–C4 2.025(5), W1–C1 2.020(7), W1–C2 2.028(7), W1–Si1 2.6801(10), C1–O1 1.161(8), C2–O2 1.144(8), C3–O3 1.150(7), C4–O4 1.120(6), C5–O5 1.154(5), O5 K1 2.805(4), Si1–Si2 2.3287(14), Si1–Si4 2.3509(15), Si1–Si3 2.3611(14), Si2–N21 1.803(4), Si3–N31 1.815(4), Si4–N41 1.797(3), C5–O5–K1 140.0(5).

With **4a** in hand we investigated its reactivity toward alcohols known to easily replace amino groups at the central silicon by nucleophilic substitution. The reactions were performed at room temperature in a J-Young NMR tube using [D$_6$]benzene as a solvent, and the course of the reactions was monitored periodically by ^1H NMR spectroscopy. Solutions of **4a** and *t*BuOH in C_6D_6 were surprisingly inert towards nucleophilic replacement at ambient conditions over a prolonged period of time, and even at higher temperatures no substantial conversion occurred. In contrast, MeOH reacted cleanly with **4a** (molar ratio 10:1) within 10 hours, resulting in quantitative formation of the new complex, $[(MeOMe_2Si)_3SiW(CO)_5]K$(18-crown-6) (**6**) as evidenced by multinuclear NMR and IR data (Scheme 1). The reason that the pyrazole groups in **4a** are replaced smoothly only by methanol is clearly steric in nature. Also note that cleavage of the Si–W bond did not occur, which is in line with results by Boehme and co-workers, who reported no substantial cleavage of the Si–W bond even in wet methanol.[11]

Conclusions

In summary, pyrazolyl-substituted oligosilanes were treated with *t*BuOK in the presence of 18-crown-6 to selectively generate stable pyrazolyl-substituted potassium silanides almost quantitatively. Trapping experiments of THF solutions of **3a** with $MgBr_2$ showed fragmentation processes to occur, whereas reactions with $W(CO)_6$ quantitatively produced the anionic tungsten complex **4a**. The pyrazolyl groups in **4a** are labile with respect to nucleophilic displacement and this offers new opportunities for the synthesis of various donor substituted transition metal silanides.

Acknowledgments

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[8] It seems that the bulkiness of the pyrazole groups prevents the Si–Si bond in **2a** from being cleaved by *t*BuOK in THF at all. Only the combination of the polar solvent THF and 18-crown-6, which presumably by coordination to the potassium cation causes formation of monomeric and more reactive *t*BuO$^-$, allows the Si–Si bond to be cleaved selectively.

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