The first structurally characterised example of silicon in an S_6 coordination sphere.

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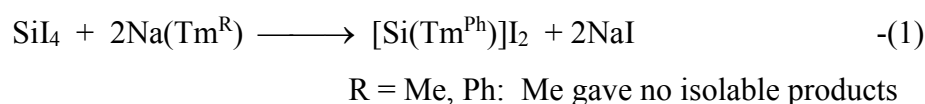E-mail: j.reglinski@strath.ac.uk m.d.spicer@strath.ac.uk

Abstract

The reaction of sodium hydro-tris(phenylthioimidazolyl)borate (NaTm^{Ph}) with silicon tetraiodide gives rise to the first crystallographically characterised molecular silicon compounds, [Si(Tm^{Ph})$_2$] 2X (X = I$^-$ and I$_3^-$), in which the silicon is found in a regular S_6 environment. The [Si(Tm^{Ph})$_2$]$^{2+}$ cation is subjected to analysis using DFT methods to explain why an S_6 coordination motif is preferred to an S_4 coordination motif.

Introduction

The scope of the coordination chemistry of the poly(thioimidazolyl)borate anions (Tm^R) commonly known as the soft scorpionates is extensive and comparable to that of the paternal pyrazolyl based ligand system [1]. By design the soft scorpionates generate compounds with soft metals [1]. However, the quixotic qualities of the sulphur donors allows the formation of *bona-fide* complexes with partners which can be quite surprising such as the alkali metals and transition metals in high formal oxidation states.[2-6] Not only can these Tm^R anions be combined with a wide range of elements, their chemistry also generates some intriguing motifs. For example, shortly after the thioimidazolylborates were first reported, Hill et al were able to synthesis and isolate stable boratranes [7]. Indeed this family of ligands (Tm^R) has since proved to be a rich source of these elusive entities. In complete contrast, our studies with carbon based electrophiles and mild oxidising agents have opened up new avenues in heterocyclic chemistry.[8,9] This success with carbon centred electrophiles left silicon as the

only member of group 14 to be tested.[10-12] However silicon presented an intriguing puzzle. Few structurally characterised sulphur donor adducts of silicon are known, but the mono- and bis-thiolates adopt a simple S_4 tetrahedral motif.[13-15] However, a number of structures and reports have appeared which suggest that under certain circumstances the coordination number at silicon centres containing sulfur donor atoms can rise to six, although no species with S_6-donor sets are known. [16-20] Among these six coordinate species are the halo-silylene adducts of methimazole which are reminiscent of our scorpionate compounds [16-18]. These observations, coupled with our general interest in the group 14 adducts of hydrotris(methimazolyl)borate anion, encouraged us to explore the reaction of Tm^R with silicon tetraiodide [10, 11].

Results and Discussion

$$SiI_4 + 2Na(Tm^R) \longrightarrow [Si(Tm^{Ph})]I_2 + 2NaI \qquad -(1)$$
$$R = Me, Ph: \text{ Me gave no isolable products}$$

Initial attempts to generate a scorpionate adduct of silicon using $NaTm^{Me}$ did not lead to a pure isolable product (equation 1), although ^{29}Si NMR did show a single peak at -145.1 ppm which is believed to arise from the desired product (vide infra). Previous studies on the complexation of Tm^R ligands has clearly demonstrated that the reaction profile of Tm^{Me} differs markedly from that of Tm^{Ph}. Indeed the observed chemistry suggested that Tm^{Ph} complexes are often more robust. For instance, while the Tm^{Me} anion does not form well defined Pb(II) complexes, the phenyl analogue yields crystallographically characterised complexes.[10]

The reaction of SiI_4 with $NaTm^{Ph}$ resulted in the successful generation of a scorpionate adduct of silicon(IV). ^{29}Si NMR studies suggest quantitative conversion of SiI_4 to a single Si containing species, with δ_{Si} = -148.3 ppm, which is in the middle of the range of chemical shifts for six-coordinate silicon (ca -110 to -200 ppm). The isolated yields of the complex were modest, but we were able to isolate a mixture of two types of crystals suitable for analysis by X-ray diffraction methods (figure 1).
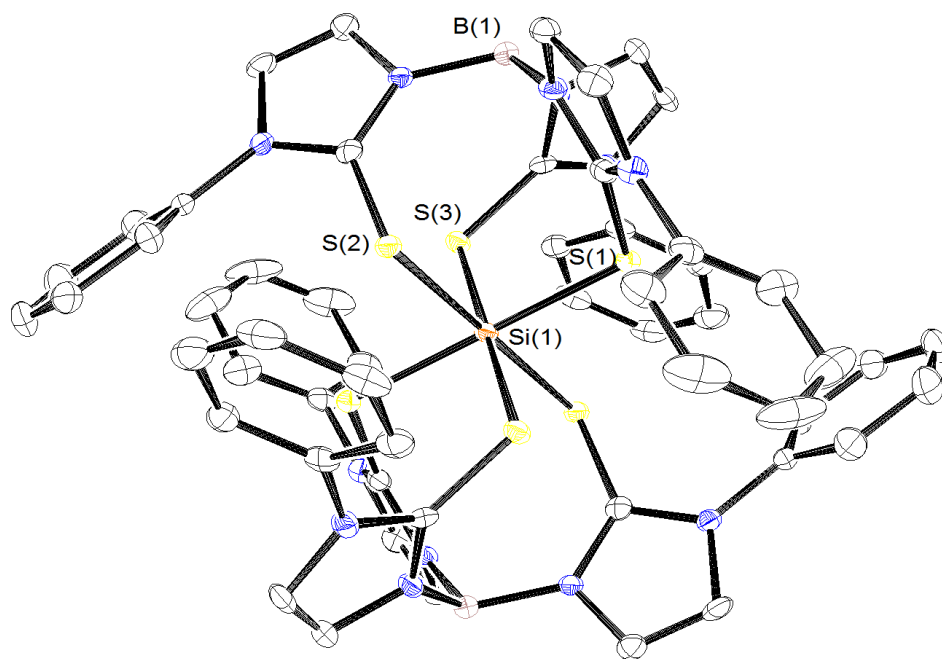
Figure 1. The molecular structure of $[Si(Tm^{Ph})_2]^{2+}$ derived from X-ray diffraction. The thermal ellipsoids are shown at the 50% probability level. The H-atoms, solvent of crystallisation (DCM) and iodide counterions are omitted for clarity. The central $[Si(Tm^{Ph})_2]^{2+}$ cation is isostructural in the colourless iodide species (shown) and the red tri-iodide species (not shown). Selected Bond distances (Å) and angles (°): Si(1) – S(1) = 2.3185(10), Si(1) – S(2) = 2.3214(10), Si(1) – S(3) = 2.3129(9),), S(1) – Si(1) – S(2) = 96.55(4), S(1) – Si – S(2)' = 83.45(4) S(2) – Si(1) – S(S3) = 95.46(3), S(2) – Si(1) – S(3)' = 84.54(3), , S(1) – Si – S(S3) = 96.24(3), S(1) – Si – S(S3) = 83.76(3).

The structures obtained from both reveal the species $[Si(Tm^{Ph})_2]^{2+}$ in which silicon atom has an S_6 coordination sphere (figure 1), the first structurally characterised example. The counter-anions were iodide and triiodide. Scorpionate compounds are typically defined by two short central atom to sulphur distances (the pincers) and a third longer central atom to sulphur distance (the sting). The compounds isolated here do not conform to this image, having all the Si-S distances equidistant (at 2.3176 Å av). However, while the Si-S distances are highly regular, the S-Si-S angles show some variation, resulting in a distortion of the S_6 octahedron (figure 1) as seen previously. The $[E(\kappa^3-Tm^R)_2]^{n+}$ motif, with an S_6 octahedral coordination mode, is extremely common in the chemistry of the soft scorpionates. A previous analysis of this motif in main group compounds has shown a linear relationship between ionic radii and the corresponding E-S bond lengths (figure 2). This relationship would seem to hold for silicon despite the fact that the compound reported here is derived from Tm^{Ph} rather that Tm^{Me}. That the behaviour of $[Si(Tm^{Ph})_2]^{2+}$ is consistent with the other $[E(Tm^R)_2]^{n+}$ cations is further evidence of the covalent character of this compound. Silicon is the smallest atom (r Si^{4+} = 54 pm) which has yet been found in a soft scorpionate S_6 coordination environment.

This coupled with the Si-S distance of 2.3176 Å, makes this motif the most compact of these sandwich complexes. It is notable that such a compact motif can be achievable with Tm^{Ph}, which is commonly described as a 'bulky' ligand.*[21]
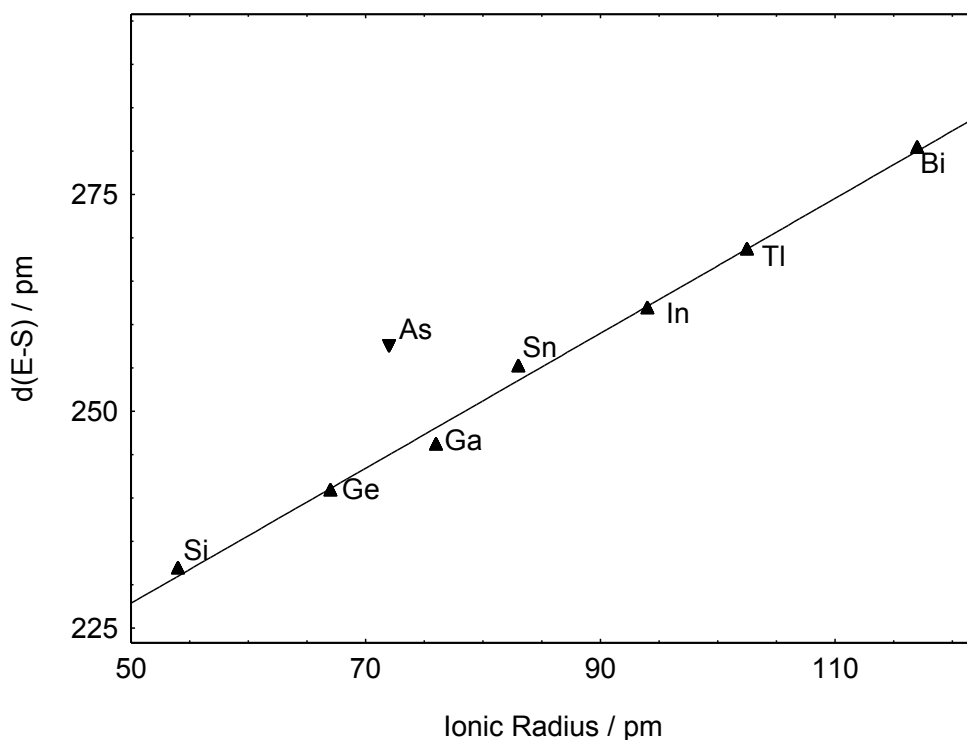

Figure 2. Plot of E–S bond length (pm) against ionic radius (pm) for the p-block complexes $[E(\kappa^3\text{-}Tm^R)_2]^{n+}$ (R = Ph, n = 2, E = Si; R = Me, n = 3, E = As, In, Tl, Bi; n = 4, E = Ge, Sn). Adapted from Spicer & Reglinski 2009.[1]

Silicon-sulfur chemistry is dominated by low coordinate species.[13-15] Higher coordination numbers involving mixed donor sets including sulphur are rare. Amongst these, however, are species based on amine-thiones which are the precursors of the ligand system discussed here.[16-18] Indeed, the silylene compounds reported by Wagler et al could be described as inverse scorpionates or silatranes. However, what remains intriguing is the stability of the S_6 motif over a simpler 4 coordinate motif i.e. one closer to that more commonly found for the combination of silicon with sulfur donors [22] and one which has previously been reported for the soft scorpionates of tellurium.[23]

In an attempt to understand the bonding and stability of the observed S_6 environment displayed by $[Si(Tm^{Ph})_2]^{2+}$ we subjected the cation to analysis using DFT calculations. We used the molecular coordinates from the $[Si(Tm^{Ph})_2]^{2+}$ cation (figure 1) to generate a model of the parent species (figure 3). In an attempt to understand the preferred coordination number i.e. six over four, we used the previously reported four coordinate tellurium compound

($Te(Tm^{Me})_2]^{2+}$) to produce a viable model of a putative tetrahedral S_4 species (figure 2).[23] The molecular coordinates of $[Te(Tm^{Me})_2]^{2+}$ were loaded into GaussView and the tellurium replaced by a silicon.[24] Once this had been achieved the methyl groups were replaced by phenyl groups and one of the resulting Tm^{Ph} units rotated by 90° to achieve the tetrahedral environment (figure 3) which is most favoured by SiS_4 species.[22] After structure optimisation, a comparison of the models revealed that the total energy of the SiS_6 motif is lower than that of the SiS_4 motif by ca 38 kcal mol^{-1}.[25]
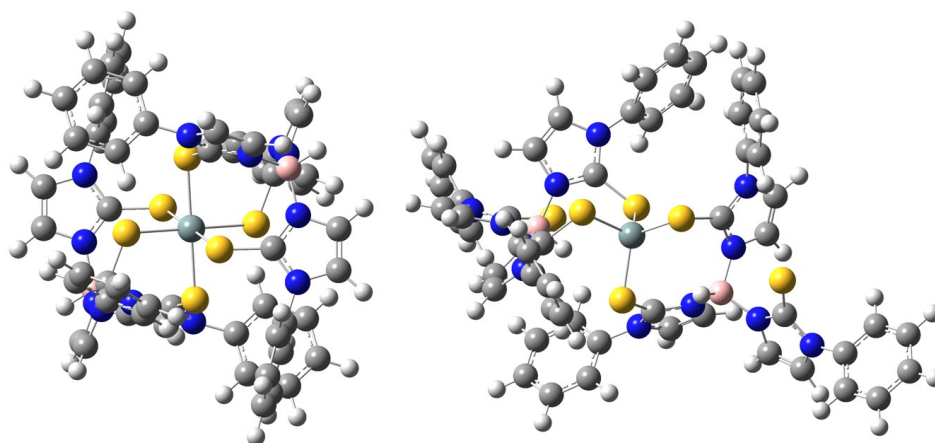

Figure 3. The *in-silico* derived structures of $[E(Tm^R)_2]^{n+}$ in an octahedral (left) and a tetrahedral coordination geometry. The octahedral conformation is ca 38 kcal mol^{-1} more stable that the tetrahedral conformation

The calculated S_6 structure compares well with the structures obtained experimentally. The Si – S bond distances obtained are in the range 2.3825 – 2.3838 Å, a little longer than the experimental distances (2.3176 Å (av)). The S-Si-S bond angles are consistent with the slightly flattened octahedral structures observed in $[M(Tm^R)_2]^{n+}$, with the intra-ligand angles being slightly less than 90 ° (calculated 84.57 – 84.59 °; experimental 83.45(4) – 84.54(3) °) and the inter-ligand angles greater than 90 ° (calculated 95.40 – 95.43 °; experimental 95.46(3) – 96.55(4) °). The S_4 structure has shorter Si-S bond distances (2.1703 – 2.1996 Å), as might be expected with fewer donor atoms, while the bond angles reveal a distorted tetrahedral geometry with S-Si-S angles in the range 99.56 – 114.55 °). Molecular orbital surfaces were calculated, and a comparison of the two models is of some interest (figure 4). The LUMO of each species is dominated by silicon-sulfur antibonding interactions. This

observation is probably a factor in the poor stability of the species. The orbitals which have
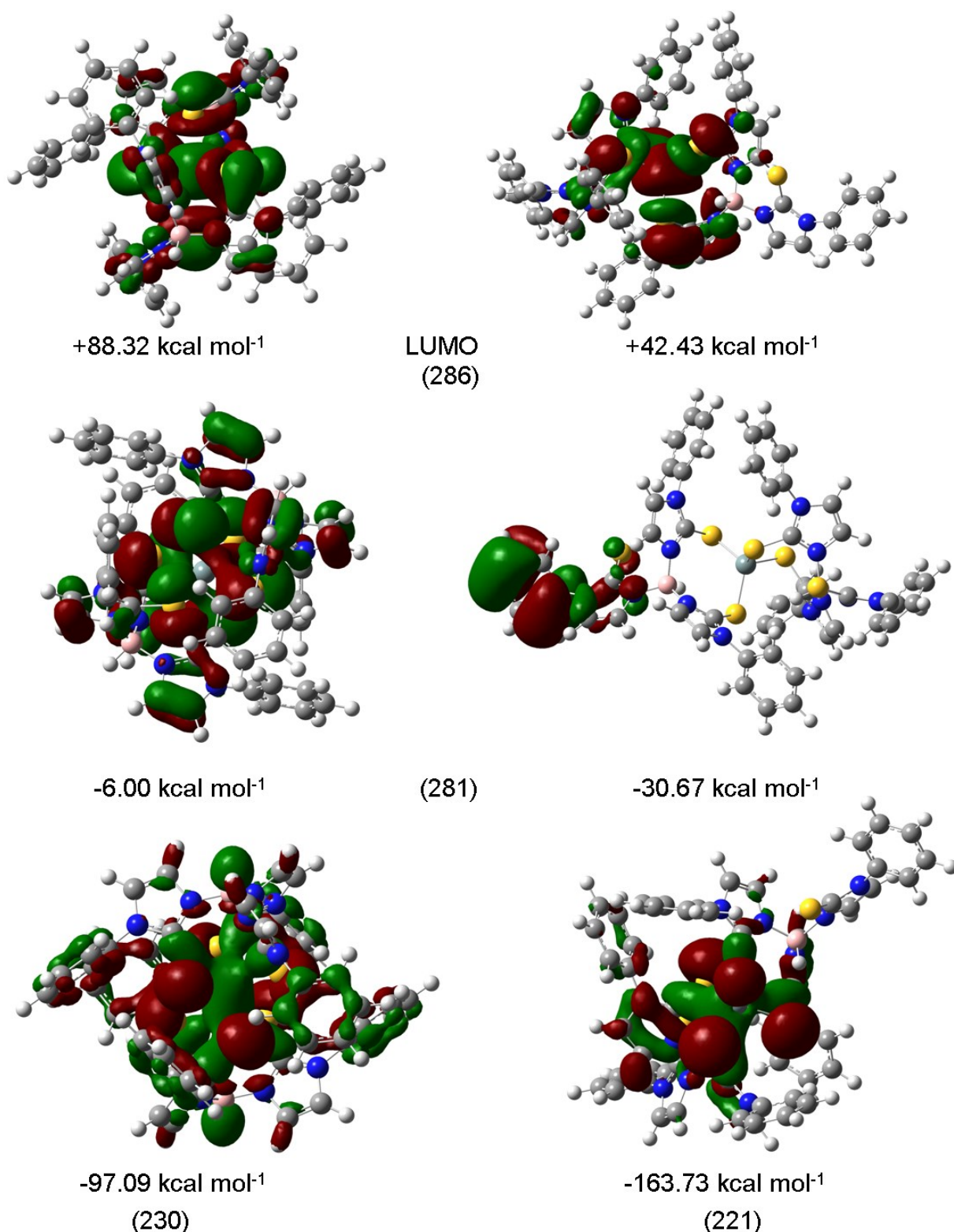

+88.32 kcal mol⁻¹ — LUMO (286) — +42.43 kcal mol⁻¹

-6.00 kcal mol⁻¹ — (281) — -30.67 kcal mol⁻¹

-97.09 kcal mol⁻¹ (230) — -163.73 kcal mol⁻¹ (221)

Figure 4. Selected molecular orbital diagrams for the [Si(Tm^{Ph})$_2$]$^{2+}$ cation where the silicon is in a S$_6$ (left) and an S$_4$ (right) coordination sphere. The orbital energies are given relative to the HOMO in each species which has arbitrarily been set at 0 kcal mol⁻¹. Top, the LUMO (M.O. 286) middle a representative of the orbitals (M. O. 281) found close to the HOMO and bottom, the highest energy silicon sulphur bonding interaction in each compound.

energies close to the HOMO on the two species are however, of distinctively different character. For the S_4 conformation, the orbitals in this region of the calculation are all discreetly associated with the non-coordinating thioimidazolyl ring (figure 3, M.O. 281). The calculated Mulliken charges on these two non-coordinating sulfurs are -0.282 and -0.304 respectively. The silicon atom has a Mulliken charge of +0.53. However, intriguingly the four sulfurs in the coordination sphere of the silicon all carry small positive charges (+0.016, +0.050, +0.052 and +0.075). The orbitals which correspond in the molecular orbital calculations on the S_6 motif (figure 3, M.O. 281) are understandably more concentrated around the central core of the molecule. Unlike the orbitals in the corresponding region of the S_4 system, they are highly distributed with mixing occurring between adjacent thioimidazolyl rings. The Mulliken charges on the sulfur atoms and silicon in the S_6 motif are -0.079 and +0.371 respectively. These data suggest that there is a propensity for greater inter-nuclear silicon-sulfur repulsion in the core of the S_4 ion compared to the S_6 species. Furthermore the S_4 motif can be classed as a zwitterion and that the inclusion of the third ring in the coordination motif might be favoured. Of some obvious interest is the relative positioning of any silicon sulfur bonding interactions. In both conformations these interactions are found to very low energy (figure 4) M.O. 230 and M.O. 221 respectively).

Concluding remarks:

The attempt to synthesise a soft scorpionate complex of silicon has been successful. Reaction of SiI_4 with $NaTm^{Ph}$ results in the octahedral $[Si(Tm^{Ph})_2]^{2+}$ cation, which, to our knowledge is the first example of silicon in a regular S_6 coordination environment. Considering the size of silicon (ionic radius 54 pm) this compound probably marks the limit at which soft scorpionates can accommodate their favoured S_6-octahedral geometry. Computational studies revealed that the octahedral S_6-coordination geometry is more stable than the corresponding tetrahedral S_4-isomer by almost 40 Kcal mol^{-1}.

Experimental

$NaTm^{Me}$ and $NaTm^{Ph}$ were synthesised according to literature methods. [26, 27] NMR analysis was carried out on a Bruker DPX 400 spectrometer, operating at 400 MHz for ^1H, 100.13 MHz for ^{13}C and 79.48 MHz for ^{29}Si. All spectra were referenced to TMS. The ^{29}Si NMR spectra were acquired using a 30 second relaxation delay. Crystals were coated in

mineral oil and mounted on glass fibres. Data were collected at 123 K on an Oxford Diffraction Xcalibur diffractometer using graphite monochromated Mo-Kα radiation. Full matrix least squares refinement was based on F^2 with all non-hydrogen atoms anisotropic. While the hydrogen atoms were mostly observed by difference syntheses, they were placed in calculated positions and modelled as riding on the parent atoms. The structure solution and refinement used the SHELX programs and the graphical interface WinGX [28, 29]

Preparation of bis(hydrotris(phenylthioimidazolyl)borato)silicon iodide/ bis-tri-iodide: A flame dried Schlenk flask was charged with dry DCM (25 mL), silicon tetraiodide (0.1934, 0.36 mmol) and NaTm^{Ph} (0.2022 g, 0.36 mmol) under a blanket of nitrogen. The solution was stirred for 72 hrs during which time a red colour developed. The solution was filtered to remove NaI and the resulting DCM solution crystallised by vapour diffusion with diethyl ether to give a mixture of white crystals interspersed with a small amount of red crystals (ca 0.10 g). These were identified by X-ray crystallography as, respectively, the iodide and tri-iodide salts of the desired silicon adduct. Anal. Calc. for $C_{54}H_{44}N_{12}B_2S_6SiI_2.2CH_2Cl_2$: C, 44.04; H, 3.17; N, 11.01. Found: C, 42.39; H, 2.82; N, 11.84%. The low values returned are attributed to the presence of the tri-iodide in the bulk sample. ^{1}H NMR (400 MHz, CDCl$_3$): δ_H 7.71 (1H, q, -BH), 7.61 (6H, br d, arom), 7.52 (6H, br t, arom), 7.45 (3H, br d, arom), 6.91 (3H, d, CH), 6.83 (3H, br s, CH). ^{13}C NMR (100.58 MHz, d$_6$-DMSO) δ_C 115.3 (C$_{im}$), 119.3 (C$_{im}$), 125.6 (C$_{Ar}$), 127.5 (C$_{Ar}$), 128.6 (C$_{Ar}$), 135.2 (C$_{Ar}$), 148.9 (C$_{C=S}$). ^{29}Si NMR (79.47 MHz, d$_6$-DMSO), δ_{Si} -148.3. FT-IR (KBr, cm^{-1}): 2470, 1495, 1200, 750, 690.

Calculations were performed using the Gaussian 09 program.[25] The molecular species were subjected to geometry optimisation at the DFT level B3LYP using a 6-311G** basis set.[30-36] The optimized species were subjected to a frequency analysis which confirmed no negative modes.

Footnotes:
* The concept of steric bulk in Tm^R compounds is discussed in detail in another report in this volume [21]

Supporting information for this article, including a table of crystallographic data and atomic coordinates from the calculated structures, is available on the WWW under http://www.eurjic.org/ or from the author. CCDC-1434690 and 1434691 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Entry for the Table of Contents

FULL PAPER

Reaction of NaTm^{Ph} with SiI$_4$ results in an octahedral Silicon complex in an S$_6$ ligand environment. The resulting compound has been characterised crystallographically and been the subject of DFT calculations.
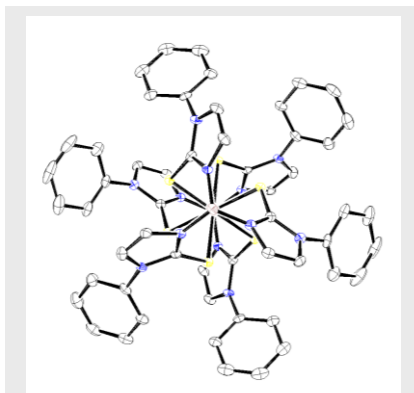
Silicon in an S$_6$ donor set

A. Marckwordt, R. R.Nair, G.Steel, A. R. Kennedy, J. Reglinski* and M. D. Spicer*

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