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Stitching together SN_x units in the coordination sphere of zirconium: assembly of a tris(imido)sulfite and a hydrazidobis(imido)sulfite†

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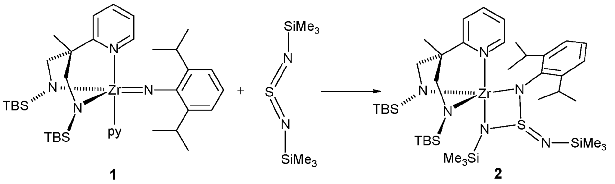
Reaction of a zirconium imido and a hydrazinediido complex with bis(trimethylsilyl)sulfur diimide yielded the corresponding formal [2 + 2] cycloaddition products, the trisimidosulfito complex and the hydrazidobis(imido)sulfito complex containing an unprecedented SN_2(N–N) unit.

The coupling of the multiply bonded nitrogen ligand in group 4 metal imides and hydrazinediides with unsaturated organic substrates has given rise to a multitude of new types of chemical transformations.[1,2] These not only have attracted interest in their own right but as key steps in catalytic reactions such as hydroaminations,[3] hydrohydrazinations[4] or more complex catalytic domino reactions.[5] Whereas the formation of N–C bonds has been the focus of these studies, the M=N unit may also undergo coupling reactions with other main group elements,[6,7] with the potential of forming main group imides.

Sulfur nitrogen compounds have been the focus of much interest for more than half a century,[8] initially for their own sake and later in investigations of their properties as non-metal conducting materials.[9] They have also played an important role in developing the isoelectronic principle based *inter alia* on the synthesis of analogues of the ubiquitous sulfur oxygen compounds.[10] Iminosulfindiamides,[10a,11] frequently referred to as triimidosulfites $S(NR)_3^{2-}$, have been studied both in terms of their S–N bonding[12] and as tridentate capping ligands for alkali and coinage metals.[13] They are typically generated by addition of a lithiated amine to a sulfur diimide and may be coordinated to other metals in subsequent transmetallations. These types of sulfur nitrogen compounds have not been generated within the coordination sphere of a transition metal, and the highly reactive nature of the imido and hydrazinediido ligands in group 4 metal complexes suggests the possibility of this type of buildup.

Reaction of the zirconium imido complex $[Zr(N_2{}^{TBS}N^{py})(=N^{DIPP})(py)]$ (**1**), stabilized by a tripodal diamido-pyridyl ligand previously employed in this field of group 4 metal complex chemistry,[1a,14] with one molar equivalent of bis(trimethylsilyl)sulfur diimide immediately generated the trisimidosulfito complex $[Zr(N_2{}^{TBS}N^{py})\kappa^2\text{-}N,N'(TMS\text{–}N\text{–}S(=N\text{–}TMS)N^{DIPP})]$ (**2**) (Scheme 1). In complex **2** the $S(NR)_3^{2-}$ ligand is coordinated in a κ^2-*N*,*N* fashion with the aryl-N unit derived from the imido ligand being located next to the coordinating pyridyl ring of the ancillary tripod such that the *ortho* CH of the pyridine ring is directed to the deshielding segment of the anisotropy cone of the 2,6-diisopropylphenyl substituent. This gives rise to an unusually high field shifted resonance (8.35 ppm compared to 9–10 ppm in most related complexes) of this proton.



Scheme 1 Synthesis of the tris(imido)sulfito-zirconium complex **2** by formal [2 + 2] cycloaddition of the imido complex **1** with bis(trimethylsilyl)sulfur diimide.

Details of the molecular structure of complex **2** were established by X-ray diffraction (Fig. 1).‡ The tris(imido)sulfito ligand adopts the expected non-planar arrangement [$\Sigma\angle(NSN) = 308.8°$], due to a stereochemically active lone pair at the sulfur atom. There are two independent molecules in the asymmetric unit which are related to one another essentially by inversion of configuration of S(1). The S–N bond lengths indicate the bonding within this fragment. The distances between the sulfur atom and the nitrogen atoms connected to the metal centre are in agreement with bond lengths characteristic for S–N single bonds (S(1)–N(4): 1.727(2) Å [1.723(2) Å for the second independent molecule in the unit cell] and S(1)–N(5): 1.670(2) [1.682(3)] Å), while the significantly shorter S(1)–N(6) bond is consistent with a double bond (1.554(2) [1.535(3)] Å).[8,10]

The corresponding reaction of the previously reported hydrazinediido complex $[Zr(N_2{}^{TBS}N^{py})(=NNPh_2)(py)]$ (**3**)[6] with one molar equivalent of bis(trimethylsilyl)sulfur diimide yielded the corresponding formal [2 + 2] cycloaddition product $[Zr(N_2{}^{TBS}N^{py})\kappa^2\text{-}N,N'(TMS\text{–}N\text{–}S(=N\text{–}TMS)NNPh_2)]$ (**4**) (Scheme 2).

Whereas previous cycloaddition products of hydrazinediido-zirconium complexes displayed the tendency to undergo thermal N–N bond cleavage and subsequent transformations,[5e,6,7]

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† Electronic supplementary information (ESI) available: Characterisation and crystallographic data for **1**, **3** and **4**; computational details and further discussion. CCDC 857217 and 857218. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2cc17594k

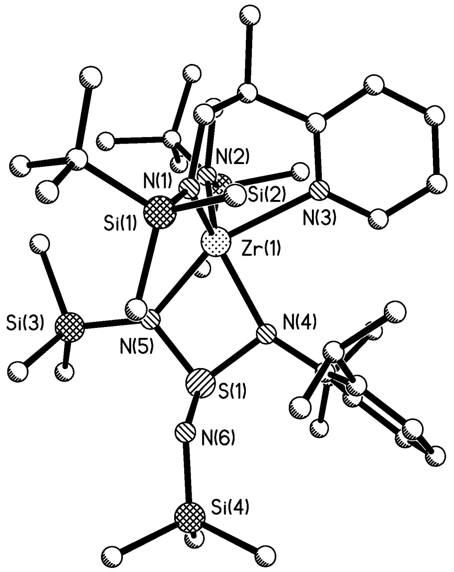
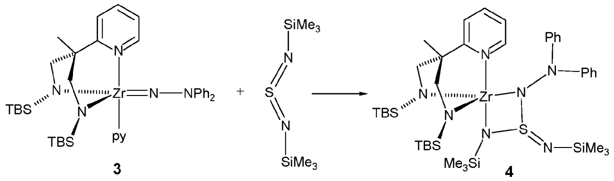


Fig. 1 Molecular structure of complex **2**. The asymmetric unit contains two independent molecules. Selected bond lengths (Å) and angles (°) [data for the second independent molecules given in brackets]: Zr(1)–N(4) 2.139(2) [2.117(2)], Zr(1)–N(5) 2.117(2) [2.133(2)], S(1)–N(4) 1.727(2) [1.723(2)], S(1)–N(5) 1.670(2) [1.682(3)], S(1)–N(6) 1.544(2) [1.535(3)], Zr(1)–N(4)–S(1) 98.7(1) [98.8(1)], Zr(1)–N(5)–S(1) 101.5(1) [100.8(1)], N(4)–S(1)–N(6) 109.4(1) [109.39(14)], N(4)–S(1)–N(5) 90.6(1) [90.8(1)], N(5)–S(1)–N(6) 108.9(1) [108.8(1)].



Scheme 2 Synthesis of the hydrazidobis(imido)sulfito-zirconium complex **4** by formal [2 + 2] cycloaddition of the hydrazinediido complex **3** with bis(trimethylsilyl)sulfur diimide.

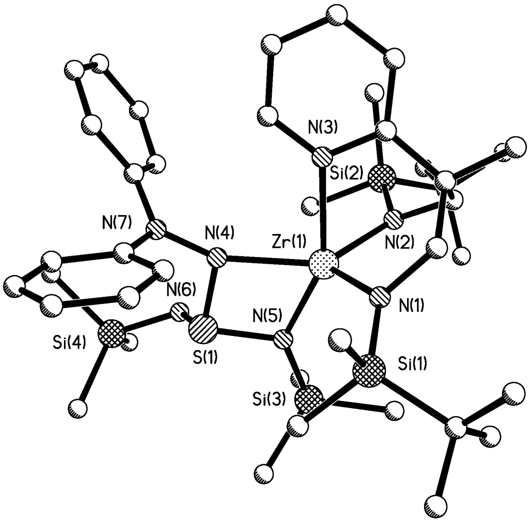


Fig. 2 Molecular structure of complex **4**. Selected bond lengths (Å) and angles (°): Zr(1)–N(1) 2.052(2), Zr(1)–N(3) 2.346(2), Zr(1)–N(4) 2.176(2), Zr(1)–N(5) 2.119(2), S(1)–N(4) 1.725(2), S(1)–N(5) 1.686(2), S(1)–N(6) 1.542(2), Zr(1)–N(4)–S(1) 100.20(8), Zr(1)–N(5)–S(1) 103.80(9), N(4)–S(1)–N(6) 110.08(11), N(4)–S(1)–N(5) 88.26(9), N(5)–S(1)–N(6) 108.39(10).

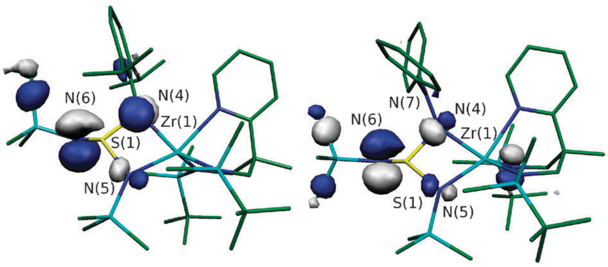


Fig. 3 Kohn–Sham molecular orbitals (HOMO-4) illustrate the localised π-bond between N(6) and S(1) with only non-bonding contributions at N(4) and N(5) in **2** (left) and **4** (right).

complex **4** proved to be thermally highly stable and could be fully characterized.

The hydrazidobis(imido)sulfite ligand in **4** is the first such fragment to be generated. Based on the spectroscopic data its coordination mode remained ambiguous. In order to clarify this aspect and to establish the structural details of the coordinated S–N fragment in **4** a single crystal X-ray structure analysis was carried out (Fig. 2).‡

The geometry of the non-planar hydrazidobis(imido)sulfite ligand in **4** is similar to that observed for the tris(imido)sulfite in **2** [$\Sigma\angle$(NSN) = 306.7°]. The hydrazido unit is directly bonded to the Zr centre through the N_α atom. The S–N units connected to the metal centre are again consistent with the presence of S–N single bonds (S(1)–N(4): 1.725(2) Å; S(1)–N(5): 1.686 Å) and the non-coordinated S(1)–N(6) unit having multiple bond character (1.552(2) Å).

More details related to the intra-ligand bonding were obtained by a DFT study carried out for both **2** and **4** at the B3PW91/6-31G(d) level of theory.[15] The analysis of the Kohn–Sham molecular frontier orbitals established weak π-bonding between S(1) and N(6) with non-bonding contributions at N(4) and N(5) in both cases, which may be attributed to a localised S(1)–N(6) double bond (Fig. 3). This interpretation is further supported by the Wiberg indices for the relevant bonds [S(1)–N(6) 1.33 (**2**), 1.31 (**4**), S(1)–N(4) 0.73 (**2**), 0.73 (**4**), S(1)–N(5) 0.87 (**2**), 0.88 (**4**)]. The Wiberg index for N(4)–N(7) of 1.08 is consistent with an N–N single bond within the hydrazido fragment. (See ESI† for details.)

The small Wiberg indices for the S–N bonds which include the nitrogen atoms ligating the metal centre are indicative of strongly polar bonds. The electron density in these bonds is polarised towards the electronegative nitrogen atoms, an effect which is further amplified by the influence of the positively charged zirconium atom (ligand–metal π-donation). The resulting electron deficiency at the sulfur atom is stabilised by conjugation with N(6). Stalke *et al.* have previously shown that tris(imido)sulfito ligands provide several resonance forms stabilising the negative charge by delocalisation.[12,13,16] In the case at hand a localised resonance structure with terminal partial charges and a single S═N bond accounts for the most significant contribution (Fig. 4, left).[17] The bis(imido)hydrazidosulfite fragment on its own lacks the competition for electron density, hence delocalisation is observed and all S–N bonds exhibit Wiberg indices close to 1.

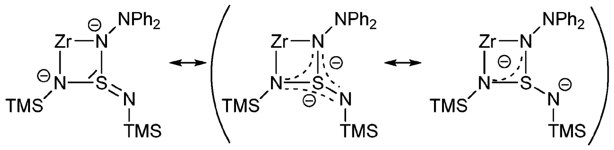


Fig. 4 The negative charges may be stabilised by delocalisation within the π-system. In the metal complex the resonance form on the left accounts for the most significant contribution resulting in virtually localised charges on the nitrogen atoms bonded to the metal centre.

The preparation of complexes **2** and **4** has demonstrated that the pattern of formal [2 + 2] cycloaddition at the highly polar M=N bonds of group 4 metal imides and hydrazinediides may be employed for the assembly of imido-derivatives of 3rd row main group element imides and hydrazides and thus element-N coupling in a broader sense.

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Notes and references

‡ Crystal data for **2**: $C_{39}H_{76}N_6SSi_4Zr$, M = 864.70, orthorhombic, space group $P2_12_12$, a = 24.884(11), b = 27.141(12), c = 14.484(6) Å, V = 9782(7) Å^3, Z = 8. T = 100(2) K, 209 306 reflections measured, 24 252 unique [R_{int} = 0.090] which were used in all calculations. Final R indices: $R(F)$ [$F_o > 4\sigma(F_o)$] = 0.0398, w$R(F^2)$ [all data] = 0.0874. *Flack* absolute structure parameter 0.01(2). Crystal data for **4**: $C_{39}H_{69}N_7SSi_4Zr$, M = 871.65, orthorhombic, space group $P2_12_12_1$, a = 10.222(5), b = 19.352(10), c = 23.638(13) Å, V = 4676(4) Å^3, Z = 4. T = 100(2) K, 110 828 reflections measured, 14 274 unique [R_{int} = 0.086] which were used in all calculations. Final R indices: $R(F)$ [$F_o > 4\sigma(F_o)$] = 0.0374, w$R(F^2)$ [all data] = 0.0788. *Flack* absolute structure parameter −0.05(2).

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