$(2,5\text{-}C_4Bu^t{}_2H_2N)_2Sn$: a New Heterostannocene

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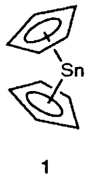
The stable 1,1′-diazastannocene **6** is obtained by the reaction of lithiated 2,5-di-*tert*-butylpyrrole **5** and $SnCl_2$; the X-ray structure of **6** is reported.

In the past 35 years, there has been much progress in stannocene chemistry[1] starting with the discovery of stannocene **1** itself by Fischer and Grubert.[2] On the other hand, only two examples of heterostannocene derivatives have been reported as yet, namely a tetradecker sandwich compound containing 1,3-diborolenyl ligands **2**[3] and the 1,2-azaborolenyl complex **3**.[4]



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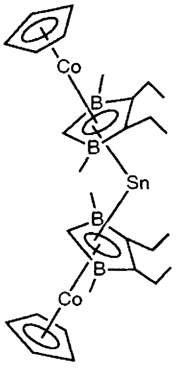

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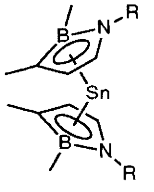

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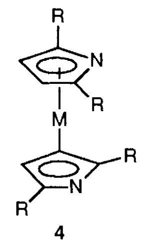

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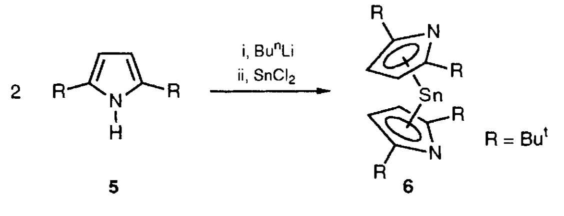

As reported recently, shielding of the nitrogen atoms by bulky substituents in the α-position causes a remarkable stabilisation of transition metal diazametallocene structures (**4**; M = Fe, Co).[5] In fact, steric overcrowding is also a suitable method to stabilise the diazastannocene system; **6** is obtained

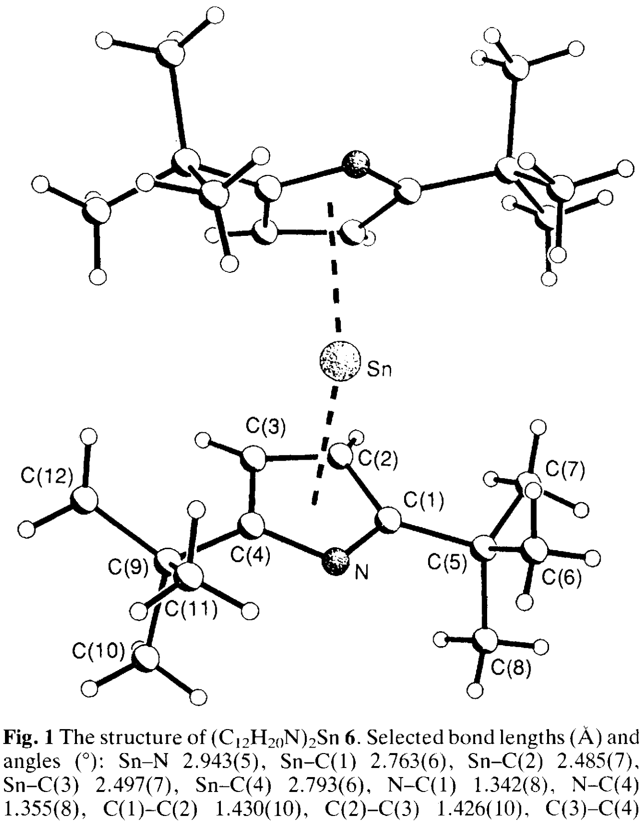

Fig. 1 The structure of $(C_{12}H_{20}N)_2Sn$ **6**. Selected bond lengths (Å) and angles (°): Sn–N 2.943(5), Sn–C(1) 2.763(6), Sn–C(2) 2.485(7), Sn–C(3) 2.497(7), Sn–C(4) 2.793(6), N–C(1) 1.342(8), N–C(4) 1.355(8), C(1)–C(2) 1.430(10), C(2)–C(3) 1.426(10), C(3)–C(4) 1.417(9), pyr(centre)–Sn 2.428, pyr(centre)···pyr′(centre) 4.599; N–C(1)–C(2) 110.7(6), N–C(4)–C(3) 109.9(6), C(1)–N–C(4) 108.4(5), C(1)–C(2)–C(3) 104.7(6), C(2)–C(3)–C(4) 106.3(6), pyr–pyr′ 65.6, pyr(centre)–Sn–pyr′(centre) 142.5, N–pyr(centre)–pyr′(centre)–N′–1.1.

by reaction of lithiated 2,5-di-*tert*-butylpyrrole **5** with $SnCl_2$ as pale-yellow crystals in good yield.[†]

Crystals of **6** contain monomeric molecules lying on a twofold rotation axis imposed by crystallographic symmetry (4_2).[‡] As expected, the molecular geometry (Fig. 1) shows a bent structure typical of group 14 metallocenes.[6] The unusually small bending angle of 114.4° between the normals to the planes defined by the azacyclopentadienyl rings may be interpreted both in terms of steric and electronic interaction.[7] As a consequence from ring slippage, we observe a marked difference in the Sn–C bond lengths [2.485(7)–2.793(6) Å]. As well as in **2**[3] and **3**[4] the distances are markedly shortened by comparison with carbocyclic stannocene structures.[1] The Sn–N distance [2.943(5) Å] is at the upper end but clear inside the scale of covalent bond lengths. In contrast with $(C_5Me_5)_2Sn$,[7a] the conformation of the ring ligands is near to being eclipsed [N–pyr(centre)–pyr′(centre)–N′ −1.1.°]; this may be a consequence of low interaction between the C-3,4-substituents in **6**.

Compound **6** is remarkably soluble in organic solvents, including n-pentane. The NMR spectra show coupling patterns similar to that observed for the carbocyclic analogue $(1,3\text{-}C_5H_3Bu^t{}_2)_2Sn$.[8] The mass spectrum is indicative of monomeric molecules in the vapour phase.

The structure of the diazastannocene **6** parallels that of $(2,5\text{-}C_4Bu^t{}_2H_2N)_2Pb$ reported by us recently.[9] In summary, our results demonstrate the stabilisation modes of azacyclopentadienyl transition metal complexes[10] to be valid also for main group centres.

Financial support by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged.

Received, 30th December 1991; Com. 1/06478I

[†] Stoichiometric amounts of $SnCl_2$ are added to 3.57 g (19.3 mmol) lithium 2,5-di-*tert*-butylpyrrolide (obtained from **5** and n-butyllithium) in 60 ml toluene and 3 ml tetrahydrofuran. The mixture is evaporated after 2 h and extracted with 50 ml n-pentane. Crystallisation from n-pentane at −78 °C gives 75% of **6** as pale yellow crystals. ^1H NMR (C_6D_6): δ 1.39 (s, 36H, Bu^t), 5.47 [s, 4H, azacyclopentadienyl H, ^2J (^{119}Sn, ^1H) 15.6 Hz]; ^{13}C NMR (C_6D_6): δ 32.01 (Me), 33.78 (quaternary C), 100.51 [C-3,4, ^1J(^{119}Sn, ^{13}C) 33.2 Hz], 162.30 (C-2, 5); ^{119}Sn NMR (C_6D_6, $SnMe_4$ ext.); δ −1889. MS (70 eV): *m/z* = 475 (1%, M^+), 297 (64, M^+ − pyr), 164 (100, pyr^+ − Me) and further fragments.

[‡] *Crystal data* for $(2,5\text{-}C_4H_2Bu^t{}_2N)_2Sn$ **6**: $M = 475.27$, tetragonal, space group $P4_2/n$, $a = 13.906(4)$, $c = 12.721(4)$ Å, $U = 2459.95$ Å^3, $T = 153$ K, $Z = 4$, $D_c = 1.283$ g cm^{-3}, $\mu = 1.05$ mm^{-1} reflections *hkl*, $l = 2n + 1$ very weak, empirical absorption correction. The structure analysis is based on 974 independent reflections (l even, Mo-Kα, $2\theta_{max}$ 54°), 894 of which were observed [$F_o \geqslant 2\sigma(F_o)$]. The structure was solved using Patterson methods and refined to $R = 0.029$, $R_w = 0.031$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

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