

## **Ni[Sn(NBu<sup>t</sup>)<sub>2</sub>SiMe<sub>2</sub>]<sub>4</sub>: a Stable Stannylenes Analogue of Nickel tetracarbonyl**

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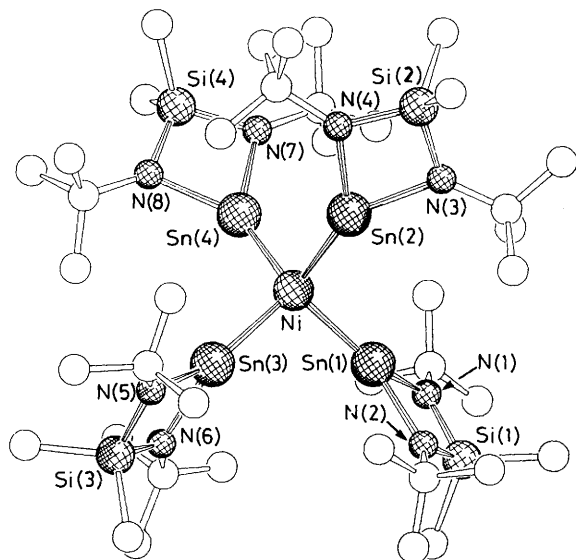
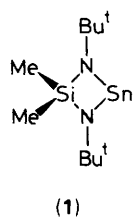
The reaction of Ni(cod)<sub>2</sub> (cod = cyclo-octadiene) with Sn(NBu<sup>t</sup>)<sub>2</sub>SiMe<sub>2</sub> has yielded Ni[Sn(NBu<sup>t</sup>)<sub>2</sub>SiMe<sub>2</sub>]<sub>4</sub>, the first binary stannylenes complex of the first transition series.

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Ni(CO)<sub>4</sub>, synthesized 100 years ago by Mond *et al.*,<sup>1</sup> was the first example of a transition metal complex with a formally zero-valent metal. Although hundreds of Ni<sup>0</sup> complexes are known today, homoleptic compounds of the metal in this oxidation state are limited to only a few π-acceptor ligands

(CO, PR<sub>3</sub>, RNC, and some alkenic systems).<sup>2</sup> We now report that stannylenes, too, can form stable binary Ni<sup>0</sup> compounds.

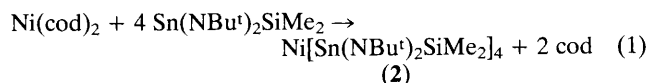
Our recent discovery that the cyclic tin(II) amide Sn(NBu<sup>t</sup>)<sub>2</sub>SiMe<sub>2</sub> (**1**),<sup>3</sup> can readily displace all PPh<sub>3</sub> ligands from RhCl(PPh<sub>3</sub>)<sub>3</sub> to give Rh[Sn(NBu<sup>t</sup>)<sub>2</sub>SiMe<sub>2</sub>]<sub>5</sub>Cl<sup>4</sup> indicated



**Figure 1.** The molecular structure and partial numbering scheme for  $\text{Ni}[\text{Sn}(\text{NBu}^t)_2\text{SiMe}_2]_4$  (**2**). For clarity, the hydrogen atoms have been omitted and the carbon atoms are drawn in outline only. Selected bond distances and angles: Ni–Sn(1) 239.9(2), Ni–Sn(2) 239.3(2), Ni–Sn(3) 239.5(2), Ni–Sn(4) 238.8(2), Sn–N (mean) 205.5(9), Si–N (mean) 172(1) pm; Sn(1)–Ni–Sn(2) 107.7(1), Sn(1)–Ni–Sn(3) 101.9(1), Sn(1)–Ni–Sn(4) 120.9(1), Sn(2)–Ni–Sn(3) 123.0(1), Sn(2)–Ni–Sn(4) 98.1(1), Sn(3)–Ni–Sn(4) 106.8(1)°.

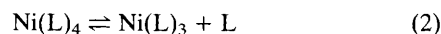
that (**1**) has remarkable ligating properties and prompted us to investigate the interaction of this cyclic diazastannylene with formally zero-valent metal centres. It was our goal to show that this subvalent tin compound can by itself stabilize metal centres in which the ligand's  $\pi$ -acceptor properties are thought to be important.

The addition of (**1**) to a toluene solution of  $\text{Ni}(\text{cod})_2$  (cod = cyclo-octadiene) according to equation (1) leads to the nearly quantitative formation of a blood-red crystalline product (**2**).<sup>†</sup>



<sup>†</sup> To a magnetically stirred solution of  $\text{Ni}(\text{cod})_2$  (0.425 g, 1.55 mmol) in toluene (50 ml) at  $-78^\circ\text{C}$ ,  $\text{Sn}(\text{NBu}^t)_2\text{SiMe}_2$  (1.96 g, 6.51 mmol) is slowly added by syringe. The initially yellow solution darkens on warming and becomes deep red at  $-30^\circ\text{C}$ . Following stirring at room temperature for 3 h, the solution is filtered and reduced in volume to 30 ml. After five days at  $-10^\circ\text{C}$ , well developed, dark red plate crystals (1.97 g, 1.47 mmol) are isolated in 95% yield, (**2**). Satisfactory elemental analysis (C, H, N) has been obtained.  $M = 1310(20)$ .<sup>5</sup> **Spectroscopic data for (2):**  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ ,  $\text{SiMe}_4$ )  $\delta$  0.437 (s, 3H, SiMe), 1.423 (s, 9H, NBu<sup>t</sup>);  $^{13}\text{C}$  NMR (75 MHz,  $\text{C}_6\text{D}_6$ , 293 K,  $\text{SiMe}_4$ )  $\delta$  8.15 (q, 1C, SiMe,  $J$  118 Hz), 37.34 (q, 3C, NBu<sup>t</sup>,  $J$  120 Hz), 54.54 (s, 1C, NBu<sup>t</sup>).

The reaction is fast, even at low temperature, and, as evidenced by  $^1\text{H}$  NMR techniques, essentially complete at  $-10^\circ\text{C}$ . The  $^1\text{H}$  and  $^{13}\text{C}$  NMR data obtained for benzene solutions of (**2**) are in accord with the formulation of compound (**2**) as a binary nickel-stannylene complex. Thus, there are only two sharp singlets at  $\delta$  0.437 and 1.423, respectively, in the  $^1\text{H}$  NMR spectrum. The presence of three signals in the  $^{13}\text{C}$  NMR spectrum also suggests that equivalent stannylenes are the only substituents on the nickel atom. The addition of excess (**1**) to an NMR solution of (**2**) did not lead to a shift in the relative positions of the NMR signals, thereby ruling out the often observed dissociation of four-co-ordinate  $\text{Ni}^0$  complexes with bulky ligands [equation (2)]. Solution molecular mass determinations support this finding.<sup>5</sup>



The colour of (**2**) is unusual for the normally colourless or light yellow  $\text{Ni}(\text{L})_4$  species. It is, however, revealing that  $\text{Ni}(\text{PPh}_3)_4$ , which like (**2**) possesses an intraligand  $\pi$ -system, is also dark red.<sup>6</sup> Compound (**2**) is air-sensitive but has a remarkable thermal stability; m.p. 178–180°C (no decomp.).

A single crystal X-ray analysis of (**2**) was carried out for unequivocal verification of the structure<sup>‡</sup> as that shown in Figure 1. As can be seen in the SCHAKAL<sup>10</sup> drawing of (**2**), the central atom is almost tetrahedrally surrounded by the stannylene ligands. The  $\text{SnN}_2\text{Si}$  planes are screwed with respect to each other, but as the two-fold axes of the  $\text{SnN}_2\text{Si}$  cycles do not match with the three-fold axes of a regular tetrahedron, there are severe distortions of the tetrahedral symmetry, as can be seen from bond angles. Thus, the smallest Sn–Ni–Sn angle measures  $98.1(1)^\circ$ , while the largest of these angles is  $123.0(1)^\circ$ . In contrast to the obvious variations in the bond angles to the central atom, the Ni–Sn bond distances are remarkably constant. The average value of 239.4(1) pm is considerably smaller than the sum of the covalent radii of tin and nickel (256 pm).<sup>11</sup> This shortening hints at a significant double bond character and may imply  $d(\pi) \rightarrow p(\pi)$  back-donation in the metal–metal interaction. § Bond distances and angles within the stannylene moieties, however, do not differ significantly from those in the 'free' molecule.<sup>3</sup>

Despite their ubiquity, stannylenes have been successfully introduced into zero-valent first-row transition metals only in the presence of stabilizing ligands,<sup>12</sup> the lone exception for the heavier transition metals being Lappert's remarkable homoleptic  $\text{M}\{\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2\}_3$  ( $\text{M} = \text{Pd}, \text{Pt}$ ) compounds.<sup>13</sup> In the case of the zero-valent palladium and platinum

<sup>‡</sup> **Crystal data for (2):**  $\text{C}_{40}\text{H}_{96}\text{N}_8\text{Si}_4\text{Sn}_4\text{Ni}$ ,  $M = 1334.97$ , triclinic,  $P\bar{1}$  (No. 2),  $a = 1391(1)$ ,  $b = 1390(1)$ ,  $c = 1981(2)$  pm,  $\alpha = 72.97(9)$ ,  $\beta = 88.37(9)$ ,  $\gamma = 61.14(9)^\circ$ ,  $U = 3179 \times 10^6$  pm<sup>3</sup>,  $Z = 2$ ,  $D_c = 1.40$  g cm<sup>-3</sup>,  $F(000) = 1352$ ,  $\mu(\text{Mo-K}\alpha) = 18.17$  cm<sup>-1</sup>,  $\lambda = 0.71069$  Å. Data were collected at 291 K on a Siemens AED 2 diffractometer equipped with a graphite monochromator. Intensities were collected from  $3\text{--}45^\circ$  in  $2\theta$ , using the  $\omega/\theta$  mode. A total of 8189 unique reflections were recorded, 6791 were used as observed,  $F_o > 2\sigma(F_o)$ , in the refinement. The structure was solved using the Patterson Methods of the SHELXS 86<sup>7</sup> program package. This yielded the position of the five heavy atoms. By using the Fourier synthesis of the SHELX 76<sup>8</sup> program all remaining non-hydrogen atoms could be located. The full-matrix least-squares refinement converged with 451 overall parameters to  $R = 0.054$ ,  $w = 1/[\sigma(F)^2 + 0.006274F^2]$ ,  $R_w = 0.062$ . The scattering factors not included in SHELX 76 were taken from standard tables.<sup>9</sup> An empirical absorption correction was applied. Hydrogen atoms were placed in calculated positions and refined with a fixed thermal parameter. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No 1.

§ This short bond can also be rationalized by invoking the use of a pure tin s-orbital in the metal–metal bond.

compounds the stannylenes most likely function mainly as  $\sigma$ -donors. For the smaller Ni<sup>0</sup> centre, with its lower ionization potential,<sup>14</sup> however, it appears likely that the  $\pi$ -acceptor properties become much more important, particularly in 18-electron complexes such as (2). The strongest evidence in support of this argument is the stability of Ni(CO)<sub>4</sub> vs. the non-existence of the Pd and Pt analogues.

We believe that both its  $\sigma$ -donor/ $\pi$ -acceptor ability and its compactness make (1) an extremely useful ligand with properties comparable to those of the phosphines. Unlike the latter molecules, however, (1) has a potentially richer chemistry (insertion, bridging function, Lewis acidity)<sup>3,15</sup> and it can be expected that this ligand will form complexes for much greater structural variety than the widely used tertiary phosphines.

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