

The first structurally characterised σ -bonded organonickel(II) compound.

Crystal structures of $[\text{Ni}\{\text{C}(\text{SiMe}_3)_2(\text{SiMe}_2\text{C}_5\text{H}_4\text{N}-2)\}(\text{PPh}_3)]$,

$[\text{Ni}\{\text{C}(\text{SiMe}_3)(\text{SiMe}_2\text{C}_5\text{H}_4\text{N}-2)(\text{SiMe}_2\text{O})\}]_2$ and

$[\text{Pd}(\mu\text{-Cl})\{\text{C}(\text{SiMe}_3)_2(\text{SiMe}_2\text{C}_5\text{H}_4\text{N}-2)\}]_2$

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The reaction between $[\text{NiCl}_2(\text{PPh}_3)_2]$ and $[\text{Li}\{\text{C}(\text{SiMe}_3)_2(\text{SiMe}_2\text{C}_5\text{H}_4\text{N}-2)\}]$ in tetrahydrofuran gave the monomeric Ni(II) compound $[\text{Ni}\{\text{C}(\text{SiMe}_3)_2(\text{SiMe}_2\text{C}_5\text{H}_4\text{N}-2)\}(\text{PPh}_3)]$, which shows planar coordination at Ni with Ni–C 2.025(4) Å, together with the Ni(II) silanolato compound $[\text{Ni}\{\text{C}(\text{SiMe}_3)(\text{SiMe}_2\text{C}_5\text{H}_4\text{N}-2)(\text{SiMe}_2\text{O})\}]_2$ as a minor product, however, the corresponding reaction with $[\text{PdCl}_2(\text{PPh}_3)_2]$ gave $[\text{Pd}(\mu\text{-Cl})\{\text{C}(\text{SiMe}_3)_2(\text{SiMe}_2\text{C}_5\text{H}_4\text{N}-2)\}]_2$, which has a chloride-bridged structure with an unusual fold angle of 60° at the Cl...Cl axis.

Organonickel compounds have been widely studied, particularly because of their applications as catalysts.¹ Some catalytic processes are thought to involve Ni(II) intermediates² but, although triorganophosphine and amine complexes have been obtained,³ attempts to isolate organo–Ni(II) compounds commonly lead to precipitation of elemental nickel.

We have previously isolated organometallic compounds of the s-, p- and f-elements containing ligands $\text{C}(\text{SiMe}_3)_n(\text{SiMe}_2\text{X})_{3-n}$ in which the groups X have lone pairs of electrons.⁴ We reasoned that, if the substituents X had π -acceptor properties, it might be possible to obtain compounds of d-block elements without unwanted reduction. Reactions of the precursor $[\text{Li}\{\text{C}(\text{SiMe}_3)_2(\text{SiMe}_2\text{C}_5\text{H}_4\text{N}-2)\}]$ **1** to give the novel derivatives **2–4**, show that this is indeed the case.

The Ni(II) compound **2** (the first structurally characterised compound to contain a Ni(II)–C σ -bond, and, apart from the electrochemically characterised dimeric species $[\text{Cu}_2\text{R}_2]^{2+}$ [$\text{R} = \text{C}(\text{SiMe}_3)_2(\text{C}_5\text{H}_4\text{N}-2)$],^{5a} the first d⁹ σ -bonded organometallic compound) was obtained from the reaction of $[\text{NiCl}_2(\text{PPh}_3)_2]$ with 2 equivalents of **1**,† and crystals suitable for an X-ray study‡ (Fig. 1) were isolated from hexane. Compound **2** appeared to be stable in the solid state under Ar, but solutions in hexane deposited metallic nickel. The EPR spectrum in toluene at 298 K ($g = 2.239$) was broad but similar to that of $[\text{NiCl}(\text{PPh}_3)_3]$,⁶ and the magnetic moment of $1.55 \mu_B$ at room temperature was as expected for a d⁹ complex with one unpaired electron. The coordination at Ni is planar (sum of angles 360°) with a bite angle of 98° for the bidentate ligand and a wide C–Ni–P angle, reflecting the repulsion between the SiMe_3 groups and the phosphine ligand. The dihedral angle between the

pyridine ring and the NiCNP coordination plane is 22° , the Ni–P bond distance is normal, and the Ni–C and Ni–N distances, 2.025(4) and 2.007(3) Å, suggest that the covalent radius for Ni(II) is ca. 1.25 Å. Longer Ni–C and shorter Ni–N distances are found in $[\text{Ni}\{\text{C}(\text{SiMe}_3)_2(\text{C}_5\text{H}_4\text{N}-2)\}\text{Cp}]$ and $[\text{Ni}\{\text{C}(\text{SiMe}_3)_2(\text{C}_5\text{H}_4\text{N}-2)\}]_2$,⁷ reflecting the greater strain in the four-membered metallacycles than in the five-membered ring of **2**.

We have found no evidence for the presence of an alkylnickel(II) chloride in the products from the reaction between $[\text{NiCl}_2(\text{PPh}_3)_2]$ and **1**. Nevertheless such a species is probably formed at the surface of the sparingly soluble $[\text{NiCl}_2(\text{PPh}_3)_2]$ and rapidly reduced to **2** by the excess of **1**. Compound **2** is probably prevented by the steric requirements of the ligand from giving aggregates with Ni–Ni bonds and ultimately metallic nickel, and remains in solution as a Ni(II) species stabilised by the soft PPh_3 and $\text{C}_5\text{H}_4\text{N}$ ligands. Compound **2** was also the principal product from a 1:1 $[\text{NiCl}_2(\text{PPh}_3)_2]$:**1** mixture but in this case we isolated a few crystals of a second compound identified‡ as the silanolato compound **3** (Fig. 2). Our $[\text{NiCl}_2(\text{PPh}_3)_2]$ probably contained a trace of hydroxide and intra- or inter-molecular elimination of CH_4 from $[\text{Ni}(\text{OH})\{\text{C}(\text{SiMe}_3)_2(\text{SiMe}_2\text{C}_5\text{H}_4\text{N}-2)\}]$ could lead to compound **3**. Cleavage of C–Si bonds under mild conditions is highly unusual, but a few examples are known where an OH group is held in a favourable position with respect to an SiMe_3 group.^{5b,8} Trialkylsilanolato nickel derivatives have not apparently been reported before.

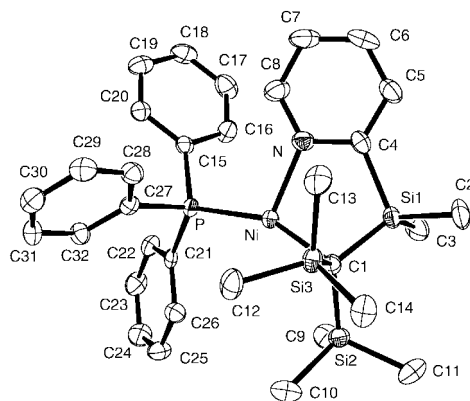
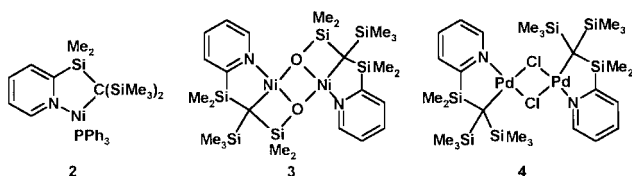


Fig. 1 The molecular structure of **2**. Selected bond lengths (Å) and angles ($^\circ$). For mean values, e.s.d.'s of individual measurements are given in parentheses: Ni–N 2.007(3), Ni–C 2.025(4), Ni–P 2.200(1), Si(1)–C(1) 1.826(4), Si(2,3)–C(1) 1.857(4), mean Si–Me 1.880(4); N–Ni–C(1) $98.28(14)$, N–Ni–P 105.81(10), C(1)–Ni–P 155.67(11), mean Si–C–Si 114.1(2), mean Me–Si–Me 105.4(2), mean C–Si–Me 113.2(2), C(1)–Si–C(4) 105.36(18), Si–C(4)–N 114.0(3), C(4)–N–Ni 111.8(3), Ni–C(1)–Si 97.20(17), Ni–C(1)–Si(3) 102.52(18), Ni–C(1)–Si(2) 112.85(18).



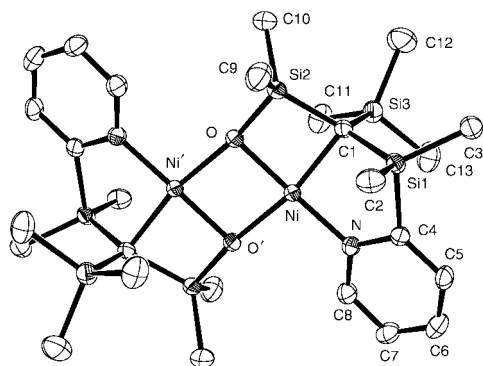


Fig. 2 The molecular structure of **3**. Selected bond lengths (Å) and angles (°): Ni–N 1.881(5), Ni–O 1.891(45), Ni–O' 1.918(4), Ni–C(1) 1.980(6), mean Si–C(1) 1.852(6), Si–Me 1.875(7), Si–O 1.651(4); O–Ni–O 84.00(18), Si–O–Ni 93.2(2), Ni–O–Ni' 96.00(18), Si–C(1)–Si 126.0(3), 115.0(3), 115.6(3), Ni–C–Si(2) 84.5(2), C(1)–Ni–O 84.2(2), Ni–O–Si(2) 93.2(2), Si(2)–C(1)–Ni 84.5(2).

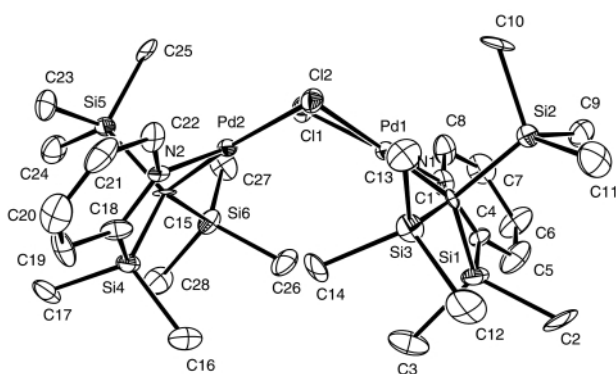


Fig. 3 The molecular structure of **4**. Selected mean bond lengths (Å) and angles (°): Pd···Pd 3.1433(15), Pd–N 2.026(10), Pd–C 2.123(12), Pd–Cl 2.325(3), 2.465(3), Si–C(1,15) 1.877(12), Si–Me 1.873(13), Si–C(py) 1.864(15), N–C(Si) 1.362(16), N–C(C) 1.329(16), N–Pd–C 89.9(4), N–Pd–Cl 92.0(3), Cl–Pd–Cl 82.62(11), C–Pd–Cl 95.6(3), Pd–Cl–Pd 81.95, Pd–C–Si(py) 100.0(5), C–Si–C(py) 102.6(6), Si–C–N 113.6(8), C(py)–N–Pd 118.7(8), Si–C–Si 112.8(6), Me–Si–Me 106.4(6). Angles between pyridyl and Pd coordination planes 26.5, 30°.

The palladium compound **4** is obtained from equimolar quantities of **1** and $[\text{PdCl}_2(\text{PPh}_3)_2]$. It is stable in the solid state under Ar but Pd metal is deposited slowly from solutions in hexane at room temperature. The dimer[‡] (Fig. 3) shows no crystallographic symmetry but there is an approximate C_2 axis perpendicular to and bisecting the Pd···Pd and Cl···Cl vectors. The coordination at Pd is square planar and the Pd–Cl bonds *trans* to C [2.465(3) Å] are longer than those *trans* to N [2.325(3) Å], as in similar compounds containing the $\text{NCPd}(\mu\text{-Cl})_2\text{PdCN}$ core. The Pd–N bond lengths are normal and the Pd–C lengths are at the upper end of the usual range. The most intriguing feature of the structure is the large fold angle (60°) at the Cl···Cl axis since most Cl-bridged Pt(II) dimers with bidentate *C,N*-ligands are planar or nearly so. Two compounds with fold angles of 37–39°, and one with a fold angle of 58°, have been reported.^{9,10} That the palladium compound **4** is much more easily isolated than the nickel analogue is in accord with the generalisation that the stabilities of M(II) organometallic compounds increase in the series from Ni to Pt.

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Notes and references

[†] Formation of complexes **2** and **3**: $(\text{Me}_3\text{Si})_2[(\text{C}_5\text{H}_4\text{N})\text{Me}_2\text{Si}]\text{CH}$ (0.63 g, 2.13 mmol) in thf (15 cm³) was treated with a solution of LiMe (2.16 mmol) in thf (10 cm³). The resulting solution of **1** was then added to a slurry of $[\text{NiCl}_2(\text{PPh}_3)_2]$ (0.70 g, 1.07 mmol) in thf (20 cm³) at –78 °C. The solution

became dark brown as it was allowed to warm to room temperature. The solvent was then removed, the solid residue extracted with hexane (40 cm³), and the extract filtered. The filtrate was reduced to 20 cm³ and kept at –30 °C, and the brown solid that separated was filtered off and recrystallised three times from hexane at –30 °C to give bright orange–red crystals of **2** (0.20 g, 30%), mp 167–168 °C (Found: C, 62.5; H, 7.1; N, 2.2. $\text{C}_{32}\text{H}_{43}\text{NNiPSi}_3$ requires C, 62.4; H, 7.0; N, 2.2%); m/z 614 (12, *M*); 599 (4, *M* – Me), 352 [43, *M* – PPh_3 (RNi)], 337 (30, RNi – Me), 322 (32, RNi – 2Me), 294 (35, R), 279 (65, R – Me), 262 (100, PPh_3), 221 (45, R – SiMe_3). The reaction between **1** (2.14 mmol), prepared as above, and $[\text{NiCl}_2(\text{PPh}_3)_2]$ (2.14 mmol) in thf also gave mainly **2** but a few deep red crystals observed in the products were separated manually and shown to be **3** (m/z 706.1181. $\text{C}_{26}\text{H}_{50}\text{N}_2\text{Ni}_2\text{O}_2\text{Si}_6$ requires 706.1195).

[‡] Crystal data: for **2**: $M = 615.6$; monoclinic, space group $P2_1/n$; $a = 16.476(2)$, $b = 9.142(3)$, $c = 21.687(5)$ Å, $\beta = 91.22(2)^\circ$, $U = 3266(1)$ Å³, $Z = 4$, $\mu = 0.77$ mm^{–1}; 5932 reflections collected, 5732 unique ($R_{\text{int}} = 0.038$), 3974 with $I > 2\sigma(I)$; $R1$, $wR2$ 0.049, 0.102 [$I > 2\sigma(I)$] and 0.089, 0.118 (all data). For **3**: $M = 708.64$; triclinic, space group $P\bar{1}$; $a = 8.8600(8)$, $b = 10.1220(10)$, $c = 10.6164(11)$ Å, $\alpha = 91.437(6)$, $\beta = 111.283(7)$, $\gamma = 92.595(5)^\circ$, $U = 885.4$ Å³, $Z = 1$; $\mu = 1.29$ mm^{–1}; 8262 reflections collected, 3091 unique ($R_{\text{int}} = 0.058$); 2618 with $I > 2\sigma(I)$; $R1$, $wR2$ 0.066, 0.154 [$I > 2\sigma(I)$], 0.079, 0.160 (all data). For **4**: $M = 873.0$; orthorhombic, space group $Pbca$; $a = 13.465(5)$, $b = 23.390(12)$, $c = 25.032(9)$ Å, $U = 7884(6)$ Å³, $Z = 8$, $\mu = 1.25$ mm^{–1}; 13619 reflections collected, 6907 unique ($R_{\text{int}} = 0.128$), 3750 with $I > 2\sigma(I)$; $R1$, $wR2$ 0.082, 0.187 [$I > 2\sigma(I)$] and 0.154, 0.226 (all data). A CAD4 diffractometer was used for **2** and **4** and a Kappa CCD diffractometer for **3**. Structures were refined by full matrix least squares refinement (SHELXL-97) with non-H atoms anisotropic and H atoms in riding mode. For **4** the structure was disordered 80:20 with only Pd sites located for the low occupancy orientation.

CCDC 182/1571. See <http://www.rsc.org/suppdata/cc/b0/b000374n/> for crystallographic files in .cif format.

§ A solution of **1** (1.22 mmol) in thf (30 cm³) was added to a slurry of $[\text{PdCl}_2(\text{PPh}_3)_2]$ (0.86 g, 1.22 mmol) in thf (25 cm³) at –78 °C and the resulting solution allowed to warm to room temperature. The solvent was pumped away, the dark brown residue extracted with hexane (3×25 cm³), and the extract filtered. The filtrate was reduced to 25 cm³ and kept at 5 °C to give pale yellow crystals of **4** (0.28 g, 53%), mp 193–195 °C (decomp.), darkens 104 °C (Found: C, 38.7; H, 6.4; N, 3.2. $\text{C}_{28}\text{H}_{56}\text{Cl}_2\text{N}_2\text{Pd}_2\text{Si}_6$ requires C, 38.7; H, 6.5; N, 2.8%); $\delta_{\text{H}}(\text{C}_6\text{D}_6)$ 0.07 (18 H, s, SiMe_3), 0.43 (6 H, s, SiMe_2), 6.70 (1 H, m, 4-H), 7.09 (1 H, t, 5-H), 7.23 (1 H, d, 3-H), 8.63 (1 H, d, 6-H); $\delta_{\text{C}}(\text{C}_6\text{D}_6)$ 1.3 ($^1J_{\text{SiC}}$ 51.8 Hz, SiMe_2), 3.4 ($^1J_{\text{SiC}}$ 51.2 Hz, SiMe_3), 15.9 ($^1J_{\text{SiC}}$ 37.1 Hz, CSi_3), 122.3 (4-C), 128.4 (5-C), 133.6 (3-C), 150.9 (6-C), 170.2 ($^1J_{\text{SiC}}$ 77.4 Hz, 2-C); $\delta_{\text{Si}}(\text{C}_6\text{D}_6)$ –6.1 ($^1J_{\text{SiC}}$ 39.4, 52.2, 77.8 Hz, SiMe_2), –0.09 ($^1J_{\text{SiC}}$ 37.4, 50.7 Hz, SiMe_3); m/z 857, (30, *M* – Me), 764 (15, *M* – SiMe_3Cl), 402, (12, RPD), 385 (22, RPD – Me), 370, (27, RPD – 2Me), 312 (100, RPD – SiMe_4), 206 (80, R – SiMe_4) [$R = \text{C}(\text{SiMe}_3)_2(\text{SiMe}_2\text{C}_5\text{H}_4\text{N})$].

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