Synthesis and Characterisation of a Novel Macrocyclic Vinylsiloxane-based Tris(alkene)nickel(0) Complex†

F. Geoffrey N. Cloke, Peter B. Hitchcock, Michael F. Lappert, Calum MacBeath and Gary O. Mepsted
School of Chemistry and Molecular Sciences, University of Sussex, Brighton, UK BN1 9QJ

Cocondensation of nickel atoms with the simple divinyldisiloxane molecule $[CH_2{=}CHSi(Me)_2]_2O$ yields the crystalline, volatile 16-electron X-ray-characterised nickel(0) complex $[CH_2{=}CHSi(Me)_2OSi(Me)_2CH{=}CHSi(Me)_2OSi(Me)_2CH{=}CH_2)Ni]$.

The simple divinyldisiloxane molecule $[CH_2{=}CHSi(Me)_2]_2O$ (≡LL) may have a potential role in coordination chemistry similar to that of cycloocta-1,5-diene (cod). Yet thus far it has only been established as a ligand in a small number of platinum(o) complexes, including $[Pt(LL)(PBu^t_3)]$[1] and $[\{Pt(LL)\}_2(\mu\text{-}LL)]$ **A**.[2] Unlike cod, however, LL also has the capacity to act as a reducing agent, *e.g.* in converting $H_2[PtCl_6]{\cdot}xH_2O$ into **A**, the active principle of the industrially important Karstedt hydrosilylation catalyst.[3]

We now report a further remarkable property of LL, namely its conversion by means of a nickel-template reaction into the (twelve-membered triene)nickel(o) title complex **1**. This transformation was effected under the remarkably mild conditions of a metal-vapour synthesis (MVS) experiment, nickel vapour being condensed onto a liquid nitrogen-cooled matrix of LL.‡

The new, crystalline, orange-red, trienenickel(o) complex **1** sublimed at *ca.* 65 °C/10^{-2} mbar. It was air- and moisture-sensitive both in the solid state and in solution, and readily soluble in both aliphatic and aromatic hydrocarbons. It gave satisfactory microanalysis, as well as ^1H, $^{13}C\{^1H\}$ and $^{29}Si\{^1H\}$ NMR spectroscopic§ and EI MS (parent molecular ion) data. The $^{29}Si\{^1H\}$ NMR spectrum showed two signals at δ 5.22 and 3.80 assigned to Si–CH=CH$_2$ and Si–CH=CH–Si, respectively; these values are at a higher frequency by *ca.* 7.5 and 6.1 ppm, respectively, compared to $\delta[^{29}Si\{^1H\}]$ in $[CH_2{=}CHSi(Me)_2]_2O$, consistent with deshielding[3] of the Si nuclei upon metal complexation, as had been previously observed for platinum(o) complexes such as **A**.[2]

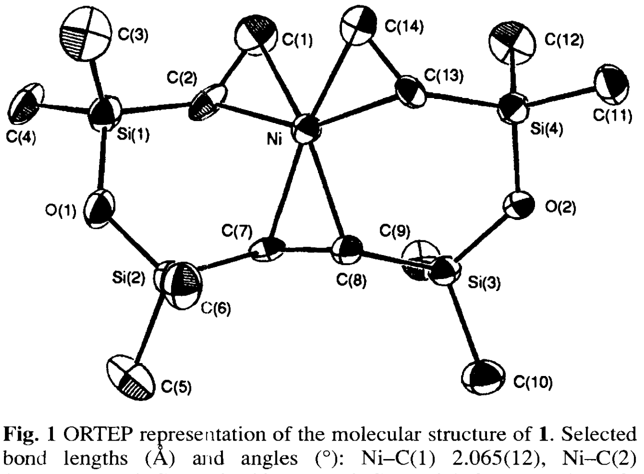


Fig. 1 ORTEP representation of the molecular structure of **1**. Selected bond lengths (Å) and angles (°): Ni–C(1) 2.065(12), Ni–C(2) 2.095(11), Ni–C(7) 2.066(10), Ni–C(8) 2.063(10), Ni–C(13) 2.075(10), Ni–C(14) 2.036(12), C(1)–C(2) 1.38(2), C(7)–C(8) 1.405(13), C(13)–C(14) 1.346(15), M(1)–Ni–M(2) 121.9, M(1)–Ni–M(3) 114.8, M(2)–Ni–M(3) 123.4, Si(1)–O(1)–Si(2) 133.8(4), Si(3)–O(2)–Si(4) 131.4(4), Si(1)–C(2)–C(1) 122.4(7), Si(2)–C(7)–C(8) 124.7(7), Si(3)–C(8)–C(7) 125.5, Si(4)–C(13)–C(14) 123.4(8). M(1), M(2) and M(3) are the midpoints of the C(1)–C(2), C(7)–C(8) and C(13)–C(14) bonds respectively.

Table 1 Comparative average selected bond lengths (Å) for some crystalline 16-electron nickel(o) complexes

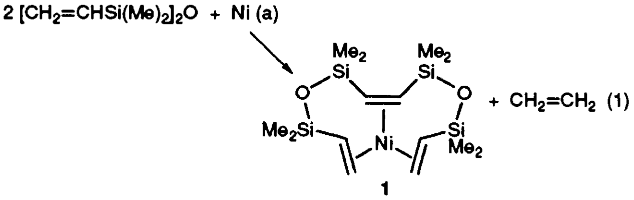
	$[Ni(bch)_3]$[5]	$[Ni(cdt)]$[4]	1
Ni–C(sp^2)	2.06	2.02	2.07
C(sp^2)–C(sp^2)	1.40	1.37	1.38
Ni–M[a]	1.95	1.92	1.95

[a] M is the midpoint of the C(sp^2)–C(sp^2) bond.

The X-ray crystal structure¶ of crystalline **1**, Fig. 1, shows that there are two independent molecules **1a** and **1b** in the unit cell of essentially the same geometry. The three alkene units are in a planar arrangement around Ni, their midpoints defining a trigonal plane around the metal. This is similar to the conformation previously established for (*trans,trans,trans*-cyclododeca-1,5,9-triene)nickel(o), [Ni(cdt)],[4] and tris(2,3-η)(bicyclo[2.2.1]hept-2-ene)nickel(o) $[Ni(bch)_3]$;[5] some comparative data are in Table 1.

Crystalline **1** may be described as a fused bicyclic molecule, the junctions comprising Ni and the midpoint of the Si–CH=CH–Si moiety, each ring adopting a chair conformation, Fig. 2, with the non-oxygen vertices being coplanar.

MVS was previously used to prepare $[Ni(\eta^2\text{-}CH_2{=}CH_2)_3]$[6] and $[Ni(\eta^2\text{-}CH_2{=}CHPh)_3]$[7] from the metal and the free ligand but C–C cleavage under MVS conditions seems to have only one precedent: $2C_5Me_6 + Mo(a) \rightarrow [Mo(\eta\text{-}C_5Me_5)_2Me_2]$.[8] The formation of **1** *may* have resulted from an alkene metathesis reaction with ethene (which was not identified) as the coproduct, eqn. (1).



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There have been recent reports of metathesis of vinyltrimethylsilane. Heterogeneous catalysts Re_2O_7/Al_2O_3 or MoO_3/Al_2O_3 provided *ca.* 10% conversion into $Me_3Si\text{-}CH{=}CHSiMe_3$ **B**,[9] whereas $[RuCl_2(PPh_3)_3]$ in C_6H_6 in a sealed tube at 130 °C gave **B** (*ca.* 50%) as the major product,[10] while conventional homogeneous metathesis catalysts proved to be inactive.[11]

The $Ni(acac)_2\text{–}AlEt_3\text{–}PPh_3$ system was catalytically active for the conversion of $CH_2{=}CHSiMe_3$ into $Me_3Si(CH_2)_2CH{=}CHSiMe_3$;[12] it is likely that a nickel(o) complex was the active species, since $Ni(acac)_2$ alone was not a catalyst.

Studies in progress include (*a*) MVS experiments with LL and other metals, (*b*) synthesis of **1** by non-MVS methods, and (*c*) preparation of the metal-free ligand.

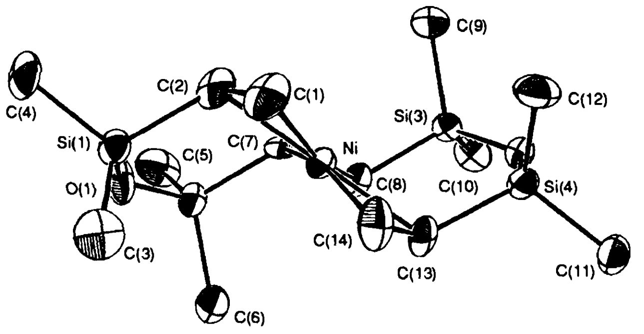

Fig. 2 An alternative view of the molecular structure of **1** demonstrating the chair conformation of each ring and the planarity at Ni

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Footnotes

† No reprints available.

‡ Cocondensation of electron-beam vaporised nickel (1.80 g) with an excess of $[CH_2{=}CHSi(Me)_2]_2O$ (25 g) at 77 K gave an orange–red matrix. After warming to room temp. the product was extracted from the reactor with hexane and the excess ligand was removed by distillation under reduced pressure. Chromatographic separation of the product on activated alumina, followed by removal of solvent and finally sublimation at 65 °C/10^{-2} mbar afforded orange crystals of **1** (0.66 g).

§ ^1H, ^{13}C *and* ^{29}Si *NMR spectroscopic data for* **1** (at *ca.* 300 K in $[^2H_6]$benzene): ^1H, δ -0.27 (s, 6H, Me), -0.10 (s, 6H, Me), 0.48 (s, 6H, Me), 0.55 (s, 6H, Me), 3.20 (d, 2H, $CH{=}CH_2$), 3.28 (t, $CH{=}CH_2$), 3.83 (s, 2H, $CH{=}CH$), 4.04 (d, 2H, $CH{=}CH_2$); $^{13}C\{^1H\}$ δ -1.43 (s, Me), -1.24 (s, Me), 1.48 (s, Me), 1.88 (s, Me), 68.34 (s, $CH{=}CH_2$), 69.69 (s, $CH{=}CH_2$), 77.86 (s, $CH{=}CH$); $^{29}Si\{^1H\}$, δ 3.80 (s, $Si{-}CH{=}CH{-}Si$), 5.22 (s, $Si{-}CH{=}CH_2$).

¶ *Crystal data for* **1** [*T* 173 K: Enraf-Nonius CAD-4 diffractometer, λ(Mo-Kα) 0.710 69 Å, no crystal decay, full-matrix least-squares refinement with non-hydrogen atoms anisotropic, $w = 1/\sigma^2(F)$]; heavy-atom method. Hydrogen atoms fixed at calculated positions $U_{iso} = 1.3$ U_{eq} for parent atom. $C_{14}H_{32}NiO_2Si_4$, $M = 403.5$, triclinic, space group $P\bar{1}$ (no. 2), $a = 6.410(3)$, $b = 12.066(5)$, $c = 29.010(12)$ Å, $\alpha = 95.76(3)$, $\beta = 96.34(3)$, $\gamma = 105.40(3)°$, $U = 2130$ Å^3, $Z = 4$, $D_c = 1.26$ g cm^{-3}, $F(000) = 864$. μ(Mo-Kα) = 11.4 cm^{-1}, specimen $0.4 \times 0.3 \times 0.2$ mm^3. 7471 unique reflections for $2 < \theta < 25°$, of which 4211 with $F^2 > 2\sigma(F^2)$ were used in the refinement, $R = 0.077$, $R' = 0.076$, $S = 1.6$. The two independent molecules have essentially the same geometry. The ORTEP drawing shows the non-H atoms as 50% thermal vibration ellipsoids. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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