

The synthesis and characterisation of some nickel(0) complexes with π -bounded vinylsilicon ligands; the molecular structure of $[\text{Ni}\{\text{P}(\text{C}_6\text{H}_5)_3\}_2\{\eta^2\text{-CH}_2=\text{CHSi}(\text{CH}_3)_3\}]$

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Abstract

Reactions of the nickel(0) complexes $[\text{Ni}(\text{cod})_2]$ (in the presence of PP or $[\text{Ni}(\text{PPh}_3)_2\text{C}_2\text{H}_4]$ with vinyl-siloxanes, -silanes or -silazanes yield, by displacement of alkene ligand, the new nickel π -complexes $[\text{Ni}(\text{PPh}_3)_2(\eta\text{-CH}_2=\text{CHSi}(\text{OSiMe}_3)_3)]$ (**2**), $[\{\text{Ni}(\text{PPh}_3)_2\{\mu\text{-}(\eta\text{-}(\text{CH}_2=\text{CH})_2\text{SiMe}_2\text{O})\}\}]$ (**4**), $[\text{Ni}(\text{PPh}_3)\{\eta^4\text{-CH}_2=\text{CHSi}(\text{Me})(\mu\text{-O})\}_3]$ (**5**), $[\{\text{Ni}(\eta\text{-CH}_2=\text{CHSiMe}_2)_2\text{O}\}(\eta\text{-CH}_2=\text{CHSiMe}_3)]$ (**7**) and the known complexes $[\text{Ni}(\text{PPh}_3)_2(\eta\text{-CH}_2=\text{CHSiMe}_3)]$ (**1**), $[\{\text{Ni}(\text{PPh}_3)_2\{\mu\text{-}(\eta\text{-}(\text{CH}_2=\text{CH})_4\text{Si})\}\}]$ (**3**), $[\{\text{Ni}(\text{PPh}_3)(\eta\text{-CH}_2=\text{CHSiMe}_2)_2\text{NH}\}]$ (**6**) obtained by a simple one pot synthesis, more efficiently than in hitherto published reports. The X-ray crystal structure of (**1**) shows a trigonal planar environment around the nickel atom.

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Keywords: Nickel complexes; Vinylsilanes; π -Complexes; X-ray crystal structure

1. Introduction

Transition metal–alkene π -complexes have attracted much attention because of their significance in organometallic synthesis and catalysis [1–4]. A lot of examples of complexes with π -bounded ligands are known but those containing vinyl derivatives of organosilicon compounds are still rare. On the ground of traditional Dewar–Chatt–Duncanson model [5,6] alkene–metal centre bond could be explained in terms of ligand to metal σ donation and metal to ligand π back donation. When vinylsilicon ligands are used in such complexes there have been reports of their enhanced thermal stability relative to that of their silicon-free analogues [7]. A suggested reason for this fact invoked an interaction be-

tween the silicon atom and the C=C bond, allowing delocalisation of electron density from the alkene π^* -orbital onto the d orbitals of the silicon atom, which enhanced the back-bonding component of the system.

The interest in the chemistry of transition metal complexes containing vinyl derivatives of organosilicon compounds as π -ligands is fully justified not only by the particular nature of the bond between vinylsilicon derivatives and transition metals, but mainly by the possible application of this kind of complexes to catalysis of hydrosilylation processes [8–11].

Hydrosilylation is also used to a much greater extent in industry to produce cross-linked products [12]; for example silicone industry extensively uses highly active platinum complexes, e.g., Karstedt catalyst [13] containing both bridging and chelating divinyl ligands $[\{\text{Pt}(\eta\text{-CH}_2=\text{CHSiMe}_2)_2\text{O}\}_2\{\mu\text{-}(\eta\text{-CH}_2=\text{CHSiMe}_2)_2\text{O}\}]$ [14,15]. High reactivity of this complex has led to synthesis of other Pt(0) complexes containing both divinyltetramethyldisiloxane (LL) and maleic anhydride, styrene

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[15] or various tertiary phosphines [16,17]. There are also known vinylsiloxane-complexes of palladium [18,19] and rhodium [20,21]. Besides vinylsiloxanes, vinylsilanes have also been used for synthesis of metal π -complexes, e.g., Pt [22,23], Fe [24–27], Ru [28], Rh [21,29–33], Co [25,34].

The TM complexes with vinylsilicon ligands include a number of organosilicon derivative-containing nickel complexes as well. Nickel equivalent of Karstedt catalyst [$\{\text{Ni}(\eta\text{-CH}_2=\text{CHSiMe}_2)_2\text{O}\}_2\{\mu\text{-(}\eta\text{-CH}_2=\text{CHSiMe}_2)_2\text{-O}\}$] has been synthesised in the reaction of (*trans,trans*-cyclododeca-1,5,9-triene) nickel(0) [16,36] or bis(cycloocta-1,5-diene) nickel(0) [37] with LL. There are known examples of phosphine–vinylsiloxane nickel(0) complexes $[\text{Ni}(\text{LL})(\text{PR}_3)]$ [16,36,38]. The reaction between nickel atoms and LL under metal vapour synthesis conditions yielded the tris(alkene) nickel(0) complex $[\text{Ni}(\text{CH}_2=\text{CHSiMe}_2\text{OSiMe}_2\text{CH}=\text{CHSiMe}_2)_3\text{SiMe}_2\text{CH}=\text{CH}_2]$ [39]. Other silicon derivatives which have been employed as ligands in nickel chemistry include vinylsilanes [40], e.g., $(\text{CH}_2=\text{CH})_2\text{-SiMe}_2$ [17] and vinylsilazane [36,41]. Our recent contribution to this field has brought the first examples of the nickel complexes with cyclic π -vinylsilicon ligands, which have been fully spectroscopically and structurally characterised. Cyclo-tetrakis[vinyl(methyl)siloxane] and cyclo-tetrakis[vinyl(methyl)silazane] have been used to generate the nickel complexes $[\{\text{Ni}(\text{PR}_3)_2\}_2\{\mu\text{-(}\eta\text{-CH}_2=\text{CH}(\text{Me})\text{Si}(\mu\text{-O}))_4\}]$ [38] and $[\{\text{Ni}(\text{PR}_3)_2\}_2\{\mu\text{-(}\eta\text{-CH}_2=\text{CH}(\text{Me})\text{Si}(\mu\text{-NH}))_4\}]$ [42], respectively, where R = Ph, $\text{C}_6\text{H}_4\text{Me-4}$, $\text{C}_6\text{H}_{11}\text{-c}$. The first one is similar to the earlier described platinum complex [14].

The aim of this study was to synthesise and characterise new nickel–vinylsilicon π -complexes and synthesise the known complexes but by different, simpler and more efficient methods using $[\text{Ni}(\text{cod})_2]$ or $[\text{Ni}(\text{PR}_3)_2\text{C}_2\text{H}_4]$ as precursors.

2. Experimental

2.1. General procedures

All reagents were dried and purified before use by the usual procedures. $[\text{Ni}(\text{cod})_2]$ and $[\text{Ni}(\text{PR}_3)_2(\text{CH}_2=\text{CH}_2)]$ were prepared as described in the literature [43,44]. Organosilicon compounds were purchased from Gelest. Other chemicals were purchased from Fluka. The NMR spectra (^1H , ^{13}C , ^{31}P , ^{29}Si) were recorded on a Varian Gemini 300 VT spectrometer. In all cases C_6D_6 was used as a solvent.

2.2. Synthesis of complexes

2.2.1. Synthesis of $[\text{Ni}(\text{PPh}_3)_2(\eta\text{-CH}_2=\text{CHSiMe}_3)]$ (1)

Bis(triphenylphosphine)ethylenenickel(0) $[\text{Ni}(\text{PPh}_3)_2\text{C}_2\text{H}_4]$ (0.33 g, 0.54 mmol) was dissolved in benzene (5 ml) and to this solution, $\text{CH}_2=\text{CHSiMe}_3$ (1 ml, 6.9 mmol)

was added. The reaction mixture was allowed to stir for 24 h. The colour of the solution changed from orange to brown. The volatiles were removed under vacuum to yield brown oil which was dissolved in pentane (5 ml) and stored at -30°C for 24 h, to yield orange crystals of **1** (0.35 g, 5.1 mmol, 95%). Orange crystals of **1**, m.p. 124–128 $^\circ\text{C}$ (decomp.) suitable for X-ray diffraction were obtained from a concentrated solution in pentane.

Anal. Found: C, 71.59; H, 9.42%. $\text{C}_{41}\text{H}_{42}\text{NiP}_2\text{Si}$ Calc.: C, 72.05; H, 9.06.

^1H NMR (C_6D_6 , 298 K, 300 MHz), $\delta(\text{ppm})$: 0.07(s, 9H), 2.63(d, 1H), 2.77(m, 1H), 2.95(d, 1H), 6.97–7.60(m, 30H).

^{13}C NMR (C_6D_6 , 298 K, 75.5 MHz), $\delta(\text{ppm})$: 51.91(s, $=\text{CH-}$), 57.38(s, $=\text{CH}_2$), 129.18(s, Ph), 131.95(s, Ph), 134.36(s, Ph), 134.80(s, Ph).

^{31}P NMR (C_6D_6 , 298 K, 101.2 MHz), $\delta(\text{ppm})$: 32.83(dd), $^2J_{\text{P-P}} = 37.3$ Hz.

^{29}Si NMR (C_6D_6 , 298 K, 99.4 MHz), $\delta(\text{ppm})$: $-4.20(\text{s})$.

2.2.2. Synthesis of $[\text{Ni}(\text{PPh}_3)_2(\eta\text{-CH}_2=\text{CHSi}(\text{OSiMe}_3)_3)]$ (2)

Bis(cyclooctadiene)nickel(0) $[\text{Ni}(\text{cod})_2]$ (0.11 g, 0.4 mmol) and PPh_3 (0.21 g, 0.8 mmol) were dissolved in ethyl ether (5 ml) and to this suspension, $\text{CH}_2=\text{CHSi}(\text{OSiMe}_3)_3$ (1.15 mmol) was added. The reaction mixture was allowed to stir for 24 h. The colour of the solution changed from orange to brown. The volatiles were removed under vacuum to yield brown oil which was dissolved in pentane (5 ml) and stored at -30°C for 2 days, to yield pale yellow crystals (0.35 g, 0.39 mmol, 96%).

Anal. Found: C, 61.98; H, 6.85%. $\text{C}_{47}\text{H}_{60}\text{NiO}_3\text{P}_2\text{Si}_4$ Calc.: C, 62.31; H, 6.68.

^1H NMR (C_6D_6 , 298 K, 300 MHz), $\delta(\text{ppm})$: 0.19(s, 27H), 2.20–2.43(m, 3H), 6.92–7.06(m, 18H, Ph), 7.42–7.59(m, 12H, Ph).

^{13}C NMR (C_6D_6 , 298 K, 75.5 MHz), $\delta(\text{ppm})$: 2.29(s, Me), 45.30(d, $=\text{CH-}$), 54.18(s, $-\text{CH}_2$), 127.8–134.3(m, Ph).

^{31}P NMR (C_6D_6 , 298 K, 101.2 MHz), $\delta(\text{ppm})$: 30.80(dd).

2.2.3. Synthesis of $[\{\text{Ni}(\text{PPh}_3)_2\}_2\{\mu\text{-(}\eta\text{-}\{(\text{CH}_2=\text{CH})_4\text{-Si}\})\}]$ (3)

To a solution of 0.16 g (0.58 mmol) $[\text{Ni}(\text{cod})_2]$ in 6 ml of benzene, 0.15 g (0.58 mmol) PPh_3 was added giving a blood red solution. Next, 0.25 ml (1.16 mmol) of tetravinylsilane $(\text{CH}_2=\text{CH})_4\text{Si}$ was added; the colour of the solution changed from red to brown. The mixture was stirred at room temperature for 24 h. The volatiles were removed under reduced pressure to give a brown oil moved into pentane and filtered through Celite. After concentration of the solution, it was left at -30°C for 2 days to yield a yellow solid (**3**) (0.21 g, 0.27 mmol, 92%).

Anal. Found: C, 67.39; H, 5.90%. $\text{C}_{44}\text{H}_{42}\text{Ni}_2\text{P}_2\text{Si}$ Calc.: C, 67.91; H, 5.44.

^1H NMR (C_6D_6 , 298 K, 300 MHz), $\delta(\text{ppm})$: 2.86(dd, 4H), 3.26(dd, 4H), 3.49(m, 4H), 7.04–7.55 (m, 30H) $^3J(\text{H}_1\text{--H}_2) = 12.8$ Hz, $^3J(\text{H}_1\text{--H}_3) = 16.6$ Hz, $^3J(\text{H}_1\text{--P}) = 4.2$ Hz, $^3J(\text{H}_2\text{--P}) = 12.2$ Hz, $^3J(\text{H}_3\text{--P}) = 7.1$ Hz.

^{13}C NMR (C_6D_6 , 298 K, 75.5 MHz), $\delta(\text{ppm})$: 55.25(s, $=\text{CH-}$), 64.36(s, $=\text{CH}_2$), 129.30(s, Ph), 131.48(d, Ph), 132.49(d, Ph), 133.96(d, Ph).

^{31}P NMR (C_6D_6 , 298 K, 101.2 MHz), $\delta(\text{ppm})$: 41.95(s).

2.2.4. Synthesis of $[\{\text{Ni}(\text{PPh}_3)_2\}_2\{\mu-(\eta-(\text{CH}_2=\text{CH})_2\text{-SiMe}_2)_2\text{O}\}]$ (**4**)

To a solution of 0.14 g (0.5 mmol) $[\text{Ni}(\text{cod})_2]$ in 7 ml of benzene, 0.13 g (0.5 mmol) PPh_3 was added giving blood red solution. Next, 0.25 ml (2.5 mmol) of tetra-vinyl-dimethyldisiloxane $\{(\text{CH}_2=\text{CH})_2\text{SiMe}_2\}_2\text{O}$ was added; a colour of solution changing from red to brown. A mixture was stirred at room temperature for 24 h. The volatiles were removed under reduced pressure to give a brown oil. This was taken up into pentane and filtered through Celite. After concentration of the solution, it was left at -30°C for 2 days to yield yellow crystals of (**4**) (0.19 g, 0.23 mmol, 89%).

Anal. Found: C, 64.44; H, 5.75%. $\text{C}_{46}\text{H}_{48}\text{Ni}_2\text{O}_2\text{P}_2\text{Si}_2$ Calc.: C, 64.82; H, 5.68.

^1H NMR (C_6D_6 , 298 K, 300 MHz), $\delta(\text{ppm})$: 0.11(s, 6H, Me), 2.84(dd, 4H), 3.18(dd, 4H), 3.29(m, 4H) 6.70–7.45(m, 30H) $^3J(\text{H}_1\text{--H}_2) = 11.9$ Hz, $^3J(\text{H}_1\text{--H}_3) = 16.4$ Hz, $^3J(\text{H}_1\text{--P}) = 4.7$ Hz, $^3J(\text{H}_2\text{--P}) = 10.8$ Hz, $^3J(\text{H}_3\text{--P}) = 6.1$ Hz.

^{13}C NMR (C_6D_6 , 298 K, 75.5 MHz), $\delta(\text{ppm})$: -1.76 (s, Me), 60.83(s, $=\text{CH-}$), 64.00(s, $=\text{CH}_2$), 129.4(s, Ph), 131.8(s, Ph), 133.8(d, Ph), 135.8(d, Ph).

^{31}P NMR (C_6D_6 , 298 K, 101.2 MHz), $\delta(\text{ppm})$: 37.5(s).

^{29}Si NMR (C_6D_6 , 298 K, 99.4 MHz), $\delta(\text{ppm})$: -8.63 (s).

2.2.5. Synthesis of $[\text{Ni}(\text{PPh}_3)_2\{\eta^4\text{-CH}_2=\text{CHSi}(\text{Me})(\mu\text{-O})\}_3]$ (**5**)

Cyclotris[vinyl(methyl)siloxane] (1.0 ml) was added slowly to a stirred red suspension of $[\text{Ni}(\text{cod})_2]$ (0.14 g, 0.5 mmol) and PPh_3 (0.13 g, 0.5 mmol) in diethyl ether (10 ml) at ambient temperature, yielding a yellow solution. The reaction mixture was allowed to stir overnight and the volatiles were removed under reduced pressure to yield a yellow oil. This was taken up into pentane (2×2 ml) and filtered through Celite. Concentration of the filtrate and cooling to -30°C yielded yellow crystals of (**5**) (yield 90%).

Anal. Found: C, 55.56; H, 5.94%. Calc. for $(\text{C}_{27}\text{H}_{33}\text{NiO}_3\text{Si}_3)$: C, 55.96; H, 5.74.

^1H NMR (C_6D_6 , 298 K, 300 MHz), $\delta(\text{ppm})$: 0.58(s, 3H, Me), 0.66(s, 6H, Me), 2.66(td, 2H), 3.11(dd, 4H), 5.90–6.27(m, 3H), 7.04–7.77(m, 15H), $^3J(\text{H}_1\text{--H}_2) = 12.6$ Hz, $^3J(\text{H}_1\text{--H}_3) = 16.9$ Hz, $^3J(\text{H}_1\text{--P}) = 4.4$ Hz, $^3J(\text{H}_2\text{--P}) = 8.8$ Hz, $^3J(\text{H}_3\text{--P}) = 4.9$ Hz.

^{13}C NMR (C_6D_6 , 298 K, 75.5 MHz), $\delta(\text{ppm})$: 0.01(s, Me), 0.59(s, Me) 58.45(s, $=\text{CH=}$), 63.87(s, $=\text{CH}_2$), 129.4(s, Ph), 131.8(s, Ph), 132.2(s, $=\text{CH-}$), 133.8(d, Ph), 135.8(d, Ph), 139.2(s, $=\text{CH}_2$).

^{31}P NMR (C_6D_6 , 298 K, 101.2 MHz), $\delta(\text{ppm})$: 38.15(d).

2.2.6. Synthesis of $[\{\text{Ni}(\text{PPh}_3)(\eta\text{-CH}_2=\text{CH-SiMe}_2)_2\text{NH}\}]$ (**6**)

Divinyltetramethyldisilazane (1.0 ml) was added slowly to a stirred red suspension of $[\text{Ni}(\text{cod})_2]$ (0.56 g, 2.5 mmol) and PPh_3 (0.66 g, 2.5 mmol) in diethyl ether (10 ml) at ambient temperature, yielding a yellow solution. The reaction mixture was allowed to stir overnight and the volatiles were removed under reduced pressure to yield yellow oil. This was taken up into pentane (2×2 ml) and filtered through Celite. Concentration of the filtrate and cooling to -30°C yielded yellow crystals of (**6**) (yield 90%), m.p. 123–128 $^\circ\text{C}$ (dec).

Anal. Found: C, 61.28; H, 6.93%. $\text{C}_{26}\text{H}_{34}\text{NNiPSi}_2$ Calc.: C, 61.67; H, 6.77.

^1H NMR (C_6D_6 , 298 K, 300 MHz): δ -0.07 (s, 6H), 0.42(s, 6H), 2.63(dd, 2H), 2.87(m, 2H), 3.12(dd, 2H), 6.92–7.41(m, 15H), $^3J(\text{H}_1\text{--H}_2) = 11.8$ Hz, $^3J(\text{H}_1\text{--H}_3) = 15.2$ Hz, $^3J(\text{H}_1\text{--P}) = 3.2$ Hz, $^3J(\text{H}_2\text{--P}) = 8.8$ Hz, $^3J(\text{H}_3\text{--P}) = 6.9$ Hz.

^{13}C NMR (C_6D_6 , 298 K, 75.5 MHz): δ 0.1(s, Me), 0.9(s, Me), 58.7(d, $=\text{CH-}$), 62.3(s, $=\text{CH}_2$), 125.2–137.1(m, Ph).

^{31}P NMR (C_6D_6 , 298 K, 101.2 MHz): δ 41.72(s).

^{29}Si NMR (C_6D_6 , 298 K, 99.4 MHz): δ -1.5 (d).

2.2.7. Synthesis of $[\{\text{Ni}(\eta\text{-CH}_2=\text{CHSiMe}_2)_2\text{O}\}(\eta\text{-CH}_2=\text{CHSiMe}_3)]$ (**7**)

A mixture of divinyltetramethyldisiloxane (0.54 ml, 2.4 mmol) and vinyltrimethylsilane (0.68 ml, 4.7 mmol) was added to 0.13 g (0.47 mmol) $[\text{Ni}(\text{cod})_2]$. The suspension was dissolved and a yellow–orange solution was obtained. The reaction mixture was stirred for 48 h, and then 5 ml of ether was added (for deposition of unreacted $[\text{Ni}(\text{cod})_2]$). After filtration, the volatile were removed in vacuo to give a red oil (yield 85%).

Anal. Found: C, 44.96; H, 8.98%. Calc. for $(\text{C}_{13}\text{H}_{30}\text{NiOSi}_3)$: C, 45.22; H, 8.76.

^1H NMR (C_6D_6 , 298 K, 300 MHz), $\delta(\text{ppm})$: -0.28 (s, 6H), 0.46(s, 6H), 0.14(s, 9H), 1.35(s, 3H), 2.98–3.97(m, 6H).

^{13}C NMR (C_6D_6 , 298 K, 75.5 MHz), $\delta(\text{ppm})$: -1.17 (s, Me), 1.86(s, Me), 67.06(s), 67.29(s), 67.49(s), 67.86(s), 68.4(s).

^{29}Si NMR (C_6D_6 , 298 K, 99.4 MHz), $\delta(\text{ppm})$: -0.86 (s), 4.16(s), 5.21(s).

2.3. X-ray structure determination of **1**

All data were measured using monochromatic Mo K α radiation ($\lambda = 0.71073$ Å). The diffraction data were

collected at 100(1) K by the ω -scan technique on a KUMA-KM4CCD diffractometer equipped with CCD camera [45] with graphite-monochromatized Mo K α radiation ($\lambda = 0.71073$ Å). The temperature was controlled by an Oxford Instruments Cryosystem cooling device. The data were corrected for Lorentz-polarization effects [46,47] as well as for absorption [46,48]. Accurate unit-cell parameters were determined by a least-squares fit of 6738. The structure was solved with SHELXS97 [49] and refined with the full-matrix least-squares procedure on F^2 by SHELXL97 [50]. Scattering factors incorporated in SHELXL93 were used. The function $\sum w(|F_o|^2 - |F_c|^2)^2$ was minimized, with $w^{-1} = [\sigma^2(F_o)^2 + (A \cdot P)^2 + BP]$ ($P = [\text{Max}(F_o^2, 0) + 2F_c^2]/3$). No empirical extinction corrections were applied. The final values of A and B are listed in Table 1. All non-hydrogen atoms were refined anisotropically. In **1** the hydrogen atoms were found in subsequent ΔF maps and their positions and isotropic thermal parameters were refined. Relevant crystal data are listed in Table 1, together with refinement details.

Table 1
Crystal data, data collection and structure refinement

Compound	1
Formula	Ni(PPh ₃) ₂ (CH ₂ CHSiMe ₃),
Formula weight	683.49
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a (Å)	9.4096(7)
b (Å)	10.3294(7)
c (Å)	20.6740(12)
α (°)	98.472(5)
β (°)	92.389(5)
γ (°)	114.480(7)
V (Å ³)	1797.0(2)
Z	2
D_x (g cm ⁻³)	1.263
μ (mm ⁻¹)	0.690
Crystal size (mm)	0.4 × 0.2 × 0.2
θ Range (°)	3–30
hkl Range	$-12 \leq h \leq 12$, $-14 \leq k \leq 13$, $-28 \leq l \leq 28$
Reflections	
Collected	17750
unique (R_{int})	8956 (0.0320)
with $I > 2\sigma(I)$	6871
Number of parameters	568
Weighting scheme	
A	0.020
B	0.80
$R(F)$ [$I > 2\sigma(I)$]	0.0339
$wR(F^2)$ [$I > 2\sigma(I)$]	0.0636
$R(F)$ (all data)	0.0480
$wR(F^2)$ (all data)	0.0672
Goodness-of-fit	0.985
Max/min $\Delta\rho$ (e Å ⁻³)	0.78/−0.38

3. Results and discussion

3.1. Synthetic studies

All the known nickel–vinylsilicon complexes have been prepared by two methods:

(i) Displacement of one or two alkene ligands from nickel(0) complexes e.g., [Ni(C₂H₄)₃], [Ni(CDT)], [Ni(cod)₂] or by displacement of the bridging vinylsiloxane ligand LL from Karstedt's type complex $\{[\text{Ni}(\text{LL})]_2(\mu\text{-LL})\}$, (ii) by the zinc (or alkylaluminium compounds) reduction of the nickel(II) complexes [NiCl₂(PPh₃)₂] (or [Ni(acac)₂]) in the presence of the vinylsilicon ligands.

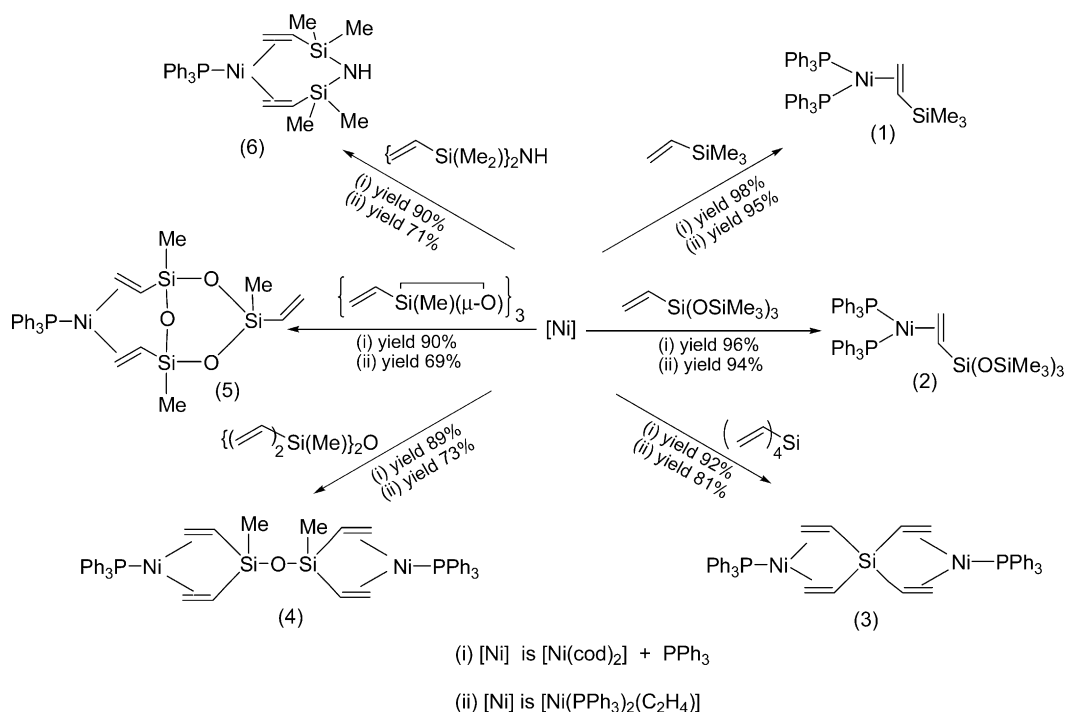
The isolation of the phosphine–nickel complexes with cyclo-siloxane [38] and -silazane [42] from the reaction between [Ni(cod)₂], appropriate organosilicon compounds and tertiary phosphines has shown that cyclo-octadiene is a labile ligand which readily undergoes displacement by many ligands. This reaction is now extended to include vinylsilanes and linear vinyl-siloxanes or -silazanes. For synthesis of these complexes we have also used other nickel(0) complex [Ni(PPh₃)₂-(C₂H₄)]. Platinum counterpart of the latter has been used by Fitch for synthesis of several platinum complexes with vinylsilicon ligands [22,23].

The reaction of mono-vinylsilanes with these Ni precursors has led to the same complex [Ni(PPh₃)₂(η^2 -CH₂=CHSiR₃)]. In the first step of the reaction between [Ni(cod)₂] and tertiary phosphines, only one cyclooctadiene ligand is replaced by two molecules of phosphine to form [Ni(PR₃)₂(cod)]. Phosphines stabilise this complex similarly to [Ni(PR₃)₂C₂H₄] but olefinic ligands in both complexes undergo displacement by vinylsilanes, according to Scheme 1.

The displaced volatile cyclo-octadiene or ethylene were easily removed in vacuo, providing the essentially pure residue of the appropriate complexes **1** or **2** in quantitative yield.

In a similar fashion, but using tetravinylsilane or tetravinylsiloxane, instead of mono-vinylsilane, binuclear nickel(0) complexes (**3**) and (**4**) were obtained. These complexes are similar to nickel complexes with cyclo-tetrakis[vinyl(methyl)siloxane] and cyclotetrakis[vinyl(methyl)silazane] which we have described earlier [38,42]. In all of these complexes tetravinyl silicon derivatives act as chelating and bridging ligands contrary to divinylsilicon ligands which operate as chelating (divinyl- tetramethyldisiloxane) or bridging (divinyl-dimethylsilane) ligands. Exemplary complexes [Ni(PPh₃)₂(η^4 -CH₂=CHSiMe₂)₂O}] and $\{[\text{Ni}(\text{PPh}_3)(\mu\text{-}\eta^2\text{-CH}_2\text{=CH})_2\text{SiMe}_2]\}_2$ were synthesised by the Lappert group [16,17].

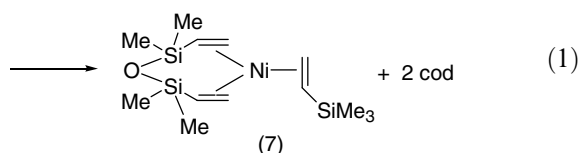
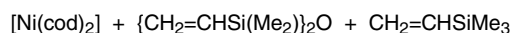
Very interesting is the complex [Ni(PPh₃)₂(η^4 -(CH₂=CHSi(Me)(μ -O))₃)] (**5**) synthesised using cyclo-tris[vinyl(methyl)siloxane], in which two vinyl groups



Scheme 1.

are coordinated to the metal centre but the third one is still free. Besides vinyl-silanes and -siloxanes, we have also used divinyltetramethyldisilazane for synthesis of phosphine–nickel–vinylsilicon complexes. Complexes of this type have been synthesised previously by zinc reduction of $[\text{NiCl}_2(\text{PPh}_3)_2]$ in the presence of vinylsilazane [36,41]. Our method of synthesis is more convenient and leads to the complex $[\text{Ni}(\text{PPh}_3)\{\eta^4\text{-CH}_2=\text{CHSi}(\text{Me})_2\text{NH}\}]$ (**6**) obtained in a high yield.

$[\text{Ni}(\text{cod})_2]$ can also be a good nickel precursor for synthesis of non-phosphine complexes. Earlier, we have described a synthesis of nickel equivalent of Karstedt catalyst $[\{\text{Ni}(\eta\text{-CH}_2=\text{CHSiMe}_2)_2\text{O}\}_2\{\mu\text{-}(\eta\text{-CH}_2=\text{CHSiMe}_2)_2\text{O}\}]$ [37]. The bridging divinylsiloxane ligand in this complex can be replaced by other ligands, however, it is not necessary to isolate Karstedt type catalyst because in direct equimolar reaction between $[\text{Ni}(\text{cod})_2]$, divinyltetramethyldisiloxane and other vinylsilicon derivatives, an appropriate nickel complex is formed. In this way, we have synthesised a few complexes (e.g., with styrene, maleate or fumarate derivatives), of which $[\{\text{Ni}(\eta\text{-CH}_2=\text{CHSiMe}_2)_2\text{O}\}(\eta\text{-CH}_2=\text{CHSiMe}_3)]$ (**7**) is a good example;



All kinds of analyses of the synthesised complexes **1–7** have brought satisfactory results. In the ^1H NMR spectra of complexes **1–7**, the signals assigned to the vinyl protons are in the expected region 2–3.5 ppm which is a typical of nickel π -complexes. The signals assigned to free vinyl groups at 5–6.5 ppm are not observed, except for the spectrum of complex **5**, in which, due to the one non-coordinated vinyl group, the signal at 5.90–6.27 ppm occurred.

The signals assigned to the protons of phosphine co-ligands in complexes **1–6** appear in expected regions and have expected intensities.

The ^{13}C NMR spectra of all complexes have confirmed the formation of π -complexes by the signals assigned to the coordinated vinyl groups in the region 50–65 ppm. Additionally for the complex **5** the signals at 130–140 ppm from non-coordinated vinyl group were observed.

The ^{31}P NMR spectroscopic data for the complexes synthesised illustrate the usual shift to a higher frequency on coordination of the phosphine ligands, due to deshielding effects, however, the shift is smaller for the complexes **1** and **2**, with monovinylsilanes, then for the complexes with multi-vinyl ligands.

Also in the ^{29}Si NMR spectra, the signals are shifted to a higher frequency as compared to those for the free ligands.

3.2. The X-ray molecular structure of $[\text{Ni}\{\text{P}(\text{C}_6\text{H}_5)_3\}_2\{\eta^2\text{-CH}_2\text{CHSi}(\text{CH}_3)_3\}]$ (**1**)

The majority of nickel–alkene complexes stabilised by tertiary phosphines adopt a trigonal shape. To the best

of our knowledge, complex **1** is the first example of a fully characterised nickel complex with mono-vinylsilane as a ligand.

Anisotropic ellipsoid representation of molecule **1** is presented in Fig. 1. Table 2 lists relevant geometrical parameters.

The midpoint of the double bond was considered as a coordination centre. In complex **1** the coordination number of the central Ni atom is 3, and nickel lies very close (0.036(1) Å) to the plane defined by P1, P2 and X (midpoint of the double C=C bond) – so the coordination is trigonal.

It has been found that Ni–P distances in the crystal structures show the bimodal distribution with the mean values around 2.187 and 2.321 Å, without apparent chemical distinction between these two groups [51]. The Ni–P distances in **1** belong to the group with shorter bond lengths (2.16–2.17 Å).

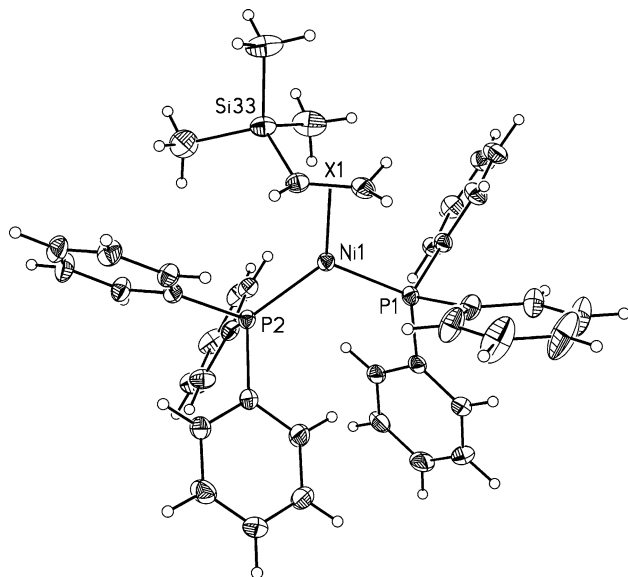


Fig. 1. Anisotropic ellipsoid representation of complex **1**. The ellipsoids are drawn at 50% probability level, hydrogen atoms are depicted as spheres with arbitrary radii. X1 is the middlepoints of C=C bonds.

Table 2
Relevant geometrical parameters (Å, °)

	1
Ni–P	2.1648(5) 2.1703(5)
Ni–X	1.860(2)
⟨P–C⟩	1.841(8)
⟨C–Si⟩	1.870(8)
P–Ni–P	116.96(2)
P–Ni–X	115.62(6) 127.33(6)

X denotes the midpoint of the double bond, regarded as the coordination site.

The phenyl rings are almost ideally planar (maximum deviation from the least square plane is 0.020(2) Å). Their mutual arrangement can be described by the dihedral angles between their planes or by the dihedral angles between the phenyl ring and the P–Ni–P plane. The latter values in **1** are low (mean values are 63°).

4. Conclusions

- (1) [Ni(cod)₂] and [Ni(PR₃)₂C₂H₄] are a good starting materials for synthesis of various nickel(0) complexes containing vinyl-siloxanes, -silanes or -silazanes as ligands.
- (2) New nickel(0) complexes (**2**, **4**, **5**, **7**) were fully, spectroscopically characterised. The other complexes (**1**, **3**, **6**) were synthesised by a simple, more efficient method than described in the literature.
- (3) The complex [Ni(PPh₃)₂(η-CH₂=CHSiMe₃)] (**1**) is the first example of nickel complex with mono-vinylsilane whose crystal structure has been determined.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre: No. CCDC 232294. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK. Fax: +44-1223-336-033, e-mail: deposit@ccdc.cam.ac.uk, or <http://www.ccdc.cam.ac.uk>.

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References

- [1] L.S. Hegedus, *Transition Metals in the Synthesis of Complex Organic Molecules*, University Science Book, Mill Valley, 1994.
- [2] G.W. Parschall, S.D. Ittel, *Homogeneous Catalysis*, Wiley Interscience, New York, 1992.
- [3] D.S. Frohnapfel, J.L. Templeton, *Coord. Chem. Rev.* 206–207 (2000) 199.
- [4] R.H. Crabtree, *The Organometallic Chemistry of the Transition Metals*, Wiley, New York, 1994.
- [5] M.J.S. Dewar, *Bull. Soc. Chim. Fr.* 18 (1951) C71.
- [6] J. Chatt, L.A. Duncanson, *J. Chem. Soc.* (1953) 2939.
- [7] J.W. Fitch, D.P. Flores, J.E. Guorge, *J. Organometal. Chem.* 29 (1971) 263.

- [8] B. Marciniec (Ed.), *Comprehensive Handbook on Hydrosilylation*, Pergamon Press, Oxford, 1992.
- [9] B. Marciniec, in: B. Cornils, W.A. Herrman (Eds.), *Applied Homogeneous Catalysis with Organometallic Compounds*, Verlag Chemie, Weinheim, 2002 (Chapter 2.6).
- [10] I. Ojima, Z. Li, J. Zhu, in: Z. Rappoport, Y. Apeloig (Eds.), *The Chemistry of Organic Silicon Compounds*, Wiley, New York, 1998.
- [11] M.A. Brook, *Silicon in Organic, Organometallic and Polymer Chemistry*, Wiley, New York, 2000.
- [12] L.N. Lewis, J. Stein, Y. Gao, R.E. Colborn, G. Hutchins, *Platinum Met. Rev.* 4 (12) (1997) 66.
- [13] B.D. Karstedt, US Patent 377 54 52 (1973).
- [14] G. Chandra, P.Y. Lo, P.B. Hitchcock, M.F. Lappert, *Organometallics* 6 (1987) 191.
- [15] P.B. Hitchcock, M.F. Lappert, N.J.W. Warhurst, *Angew. Chem., Int. Ed. Engl.* 30 (1991) 438.
- [16] P.B. Hitchcock, M.F. Lappert, C. MacBeath, F.P.E. Scott, N.J.W. Warhurst, *J. Organometal. Chem.* 528 (1997) 186.
- [17] P.B. Hitchcock, M.F. Lappert, C. MacBeath, F.P.E. Scott, N.J.W. Warhurst, *J. Organometal. Chem.* 534 (1997) 139.
- [18] J. Krause, K.-J. Haack, G. Cestarić, R. Goddard, K.-R. Pörschke, *Chem. Commun.* (1998) 1291.
- [19] J. Krause, G. Cestarić, K.-J. Haack, K. Seevogel, W. Storm, K.-R. Pörschke, *J. Am. Chem. Soc.* 121 (1999) 9807.
- [20] S.S.D. Brown, S.N. Heaton, M.H. Moore, R.N. Perutz, G. Wilson, *Organometallics* 15 (1996) 1392.
- [21] C.J. Cardin, P.B. Hitchcock, M.F. Lappert, C. MacBeath, N.J.W. Warhurst, *J. Organometal. Chem.* 584 (1999) 366.
- [22] E.M. Haschke, J.W. Fitch, *J. Organomet. Chem.* 57 (1973) C93.
- [23] J.W. Fitch, K.C. Chan, J.A. Froelich, *J. Organomet. Chem.* 160 (1978) 477.
- [24] R.D. Kelly, G.B. Young, *J. Organometal. Chem.* 361 (1989) 123.
- [25] J.W. Fitch, H.E. Herbold, *Inorg. Chem.* 9 (1970) 1926.
- [26] H. Sakurai, Y. Kamiyama, Y. Nakadaira, *J. Organomet. Chem.* 184 (1980) 13.
- [27] M.I. Rybinskaya, L.V. Rybin, A.A. Pogrebnyak, G.V. Nurtdinova, V.P. Yur'ev, *J. Organomet. Chem.* 217 (1981) 373.
- [28] T. Takao, M. Amako, H. Suzuki, *Organometallics* 20 (2001) 3406.
- [29] J.W. Fitch, W.T. Osterloch, *J. Organomet. Chem.* 213 (1981) 493.
- [30] J.W. Fitch, D. Westmoreland, *J. Organomet. Chem.* 268 (1984) 269.
- [31] S.T. Belt, S.B. Duckett, D.M. Haddleton, R.N. Perutz, *Organometallics* 8 (1989) 748.
- [32] C.P. Lenges, P.S. White, M. Brookhart, *J. Am. Chem. Soc.* 121 (1999) 4385.
- [33] P. Błażejewska-Chadyniak, M. Kubicki, H. Maciejewski, B. Marciniec, *Inorg. Chim. Acta* 350 (2003) 603.
- [34] C.P. Lenges, M. Brookhart, B.E. Grant, *J. Organomet. Chem.* 528 (1997) 199.
- [35] C.P. Lenges, P.S. White, M. Brookhart, *J. Am. Chem. Soc.* 120 (1998) 6965.
- [36] B. Proft, Ph.D. Dissertation, University of Dusseldorf, 1993.
- [37] H. Maciejewski, B. Marciniec, I. Kownacki, *J. Organomet. Chem.* 597 (2000) 175.
- [38] P.B. Hitchcock, M.F. Lappert, H. Maciejewski, *J. Organomet. Chem.* 605 (2000) 221.
- [39] F.G.N. Cloke, P.B. Hitchcock, M.F. Lappert, C. MacBeath, G.O. Mepsted, *J. Chem. Soc., Chem. Commun.* (1995) 87.
- [40] I.S. Isaeva, T.A. Peganova, P.V. Petrovskii, F.F. Kayumov, F.G. Yusupova, V.P. Yur'ev, *J. Organomet. Chem.* 248 (1983) 375.
- [41] C. MacBeath, Ph.D. Thesis, University of Sussex, 1996.
- [42] H. Maciejewski, M. Kubicki, B. Marciniec, A. Sydor, *Polyhedron* 21 (2002) 1261.
- [43] D.J. Krysan, P.B. Mackenzie, *J. Org. Chem.* 55 (1990) 4229.
- [44] C.A. Dolman, W.A. Riggs, W.J. Lim, C.M. King, R.C. Wendt, *Inorg. Chem.* 12 (1973) 2770.
- [45] CRYALISCCD, User Guide Vers. 168, Kuma Diffraction, Wrocław, Poland, 1999.
- [46] KUMA, KUMA KM4 Software, Version 5.0. KUMA Diffraction, Wrocław, Poland, 1992.
- [47] CRYALISRED, Program for Reduction of the Data from Kuma CCD Diffractometer, Kuma Diffraction, Wrocław, Poland, 1999.
- [48] R.H. Blessing, *J. Appl. Crystallogr.* 22 (1989) 396.
- [49] G.M. Sheldrick, *Acta Cryst. A* 46 (1990) 467.
- [50] G.M. Sheldrick, *SHELXL-97*, Program for the Refinement of Crystal Structures, University of Göttingen, Göttingen Germany, 1997.
- [51] F.H. Allen, O. Kennard, D.G. Watson, L. Brammer, G. Orpen, R. Taylor, *J. Chem. Soc., Dalton Trans.* (1987) S1.