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A convenient route to vinylsiloxane-tertiary phosphine-nickel(0) complexes; the molecular structure of $[(Ni\{P(C_6H_4Me\text{-}4)_3\})_2\{\mu\text{-}(L''L'')_2\}]$ $\{(L''L'')_2 = [CH_2{=}CH(Me)Si(\mu\text{-}O)]_4\}$

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Abstract

A simple one pot synthesis in Et_2O at ambient temperature, from the readily available starting materials $[Ni(cod)_2]$, PR_3 and LL or $(L''L'')_2$, provides an essentially quantitative route to the known vinylsiloxanenickel(0) complexes $[Ni(LL)PR_3]$ and the new binuclear analogues $[\{Ni(PR_3)\}_2\{\mu\text{-}(L''L'')_2\}]$ (**5**) $\{LL = [CH_2{=}CH(Me)_2Si]_2O$, $(L''L'')_2 = [CH_2{=}CH(Me)Si(\mu\text{-}O)]_4$ and R = Ph, $C_6H_4Me\text{-}4$ or $C_6H_{11}\text{-}c\}$. The X-ray crystal structure of **5b** (R = $C_6H_4Me\text{-}4$) shows it to be a centrosymmetric binuclear complex containing $(L''L'')_2$ as a chair-shaped bridging ligand. It is bound to each $Ni(PR_3)$ moiety by a pair of μ^2-vinyl groups (having M and M′ as centroids) and each NiMSiOSi′M′ metallacycle is also of chair conformation. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Nickel; Vinylsiloxane complexes

1. Introduction

Hydrosilylation is widely used in the silicone industry for the synthesis of monomers containing Si–C bonds, the cross-linking of polymers and as a source of various silane coupling reagents, while in organic chemistry it has a role for the synthesis of alcohols by reduction of carbonyl compounds [1]. Such processes generally require the use of a highly active platinum-containing catalyst. The silicone-soluble Karstedt catalyst is commercially important for hydrosilylation. It is obtained, in presence of the silane, by reaction of chloroplatinic acid $H_2[PtCl_6]xH_2O$ (**1**) (Speier's catalyst) with a vinylsilicon-containing compound, such as sym-divinyltetra(methyl)disiloxane $[CH_2{=}CH(Me)_2Si]_2O$ (≡LL) [2,3].

Our earlier studies had established that **1** and LL in the absence of a silane yielded a solution A [4], from which the crystalline platinum(0) complex $[\{Pt(LL)\}_2(\mu\text{-}LL)]$ (**2**) was isolated [5]. Complex **2** was shown to be a Karstedt catalyst; with styrene as substrate, transient 14-electron intermediates $[Pt(LL)(LL)]$ and $[Pt(LL)(\eta^2\text{-}CH_2{=}CHPh)]$ were identified by NMR spectroscopy [6]. Complex **2** was also shown to be a convenient source of further well characterised siloxaneplatinum(0) complexes, such as $[Pt(LL)(PR_3)]$ [4,7], $[\{Pt(LL)\}_2(\mu\text{-}dppe)]$ [8] and $[\{Pt(LL)\}_3(\mu_3\text{-}triphos)]$ [8] [dppe = $(Ph_2PCH_2)_2$, triphos = $(Ph_2PCH_2)_3CMe$ or $(Ph_2PCH_2CH_2)_2PPh$]. A series of palladium(0) complexes $[\{Pd(LL)\}_2(\mu\text{-}LL)]$ (from $[PdCl_2(cod)_2]$, Li_2cot and LL) and $[Pd(LL)D]$ (D = C_2H_4 or PR_3; R = Me, ^{i}Pr, ^{t}Bu, Ph or $C_6H_4Me\text{-}2$) has also been reported [9].

The high cost of platinum has led to much research on various nickel complexes as potential hydrosilylation catalysts [1]. Also relevant to the present study is the fact that tertiary phosphine ligands have a pervasive place in many industrially important noble metal-catalysed organic reactions, including hydrosilylation; complexes of Rh(I), Pd(0 or II) and Pt(0) are particularly prominent [10]. The other pertinent ligand component for this report relates to a vinylsilane. Previous

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work dealing with these parameters concerned the formation of (a) $[Ni(LL)(PR_3)]$ (R = Ph, C_6H_4Me-4 or C_6H_{11}-c) (**3**) from *trans,trans,trans*-cyclododecatrienenickel(0) {≡[Ni(CDDT)]} and LL [7,11], and (b) $[Ni(LL)(PPh_3)]$ or $[Ni(LPhL^{Ph})(PPh_3)]$ from $[NiCl_2(PPh_3)_2]$, zinc dust and LL or $L^{Ph}L^{Ph}$ $\{\equiv[CH_2{=}CH(Ph)_2Si]_2O\}$ [7]. The compound $[Ni\{CH_2{=}CH(Me)_2SiOSi(Me)_2CH{=}CHSi(Me)_2OSi(Me)_2\text{-}CH{=}CH_2\}]$ was obtained from nickel atoms and LL under metal vapour synthesis conditions [12]. Other vinylsilanes which have been employed as ligands in Group 10 metal chemistry include $(CH_2{=}CH)_2SiMe_2$ (≡L′L′) and $[CH_2{=}CH(Me)Si(\mu\text{-}O)]_4$ [≡(L″L″)$_2$] (**4**). Thus, $[NiCl_2(PPh_3)_2]$, zinc dust and L′L′ afforded $[\{Ni(\mu\text{-}L'L')(PPh_3)\}_2]$ [8]; and **4** has been used in platinum chemistry [7,13] to generate hydrosilylation catalysts related to **2** [13].

2. Results and discussion

2.1. Synthetic studies

Our objective was to develop convenient syntheses for nickel(0) complexes having η^2-vinylsilicon and tertiary phosphine ligands, study their structures and explore their potential as hydrosilylation catalysts; catalytic aspects will be considered in a later paper.

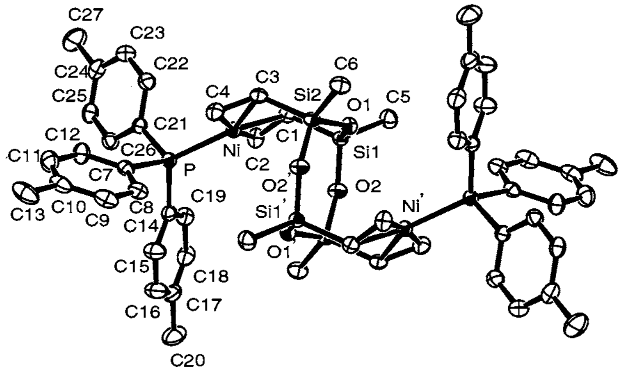


Fig. 1. The molecular structure of $[(Ni\{P(C_6H_4Me\text{-}4)_3\})_2[CH_2{=}CH(Me)Si(\mu\text{-}O)]_4$ (**5b**) with atom labelling.

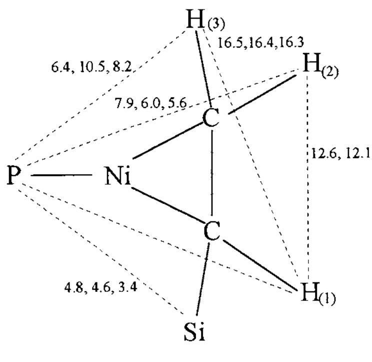


Fig. 2. Schematic representation of ^1H–^{31}P and ^{31}P–^{29}Si coupling constants (Hz), from ^1H- and ^{29}Si-NMR spectra, for **5a**, **5b**, **5c**, respectively in C_6D_6 at 298 K.

An improved synthesis (cf. [7] and [11]) of the complexes **3** was accomplished, using the readily available $[Ni(cod)_2]$ as precursor (Eq. 1). The displaced volatile cyclooctadiene was easily removed in vacuo, providing the essentially pure residue of the appropriate complex **3** in quantitative yield. Each of the crystalline complexes **3a**, **3b** and **3c** was authenticated by showing it to have identical NMR spectra to those of the previously characterised specimens [7].

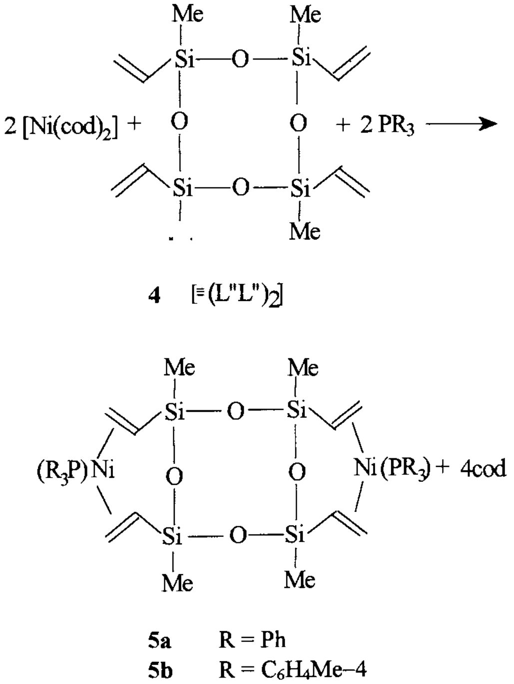
$$[Ni(cod)_2] + [CH_2{=}CH(Me)_2Si]_2O + PR_3 \longrightarrow$$

$$(\equiv LL)$$

$$[Ni(\{\eta\text{-}CH_2{=}CH(Me)_2Si\}_2O)(PR_3)] + 2\ cod$$

3a R = Ph
3b R = C_6H_4Me–4
3c R = C_6H_{11}–c (1)

In a similar fashion, but using cyclotetrakis[vinyl(methyl)siloxane] (**4**) [≡L″L″)$_2$] in place of LL, there were obtained the binuclear nickel(0) complexes **5**, Eq. (2). Each of the crystalline, yellow complexes **5a**, **5b** and **5c** gave satisfactory analyses and appropriate NMR spectra. The various ^1H–^1H, and ^1H–^{31}P and ^{31}P–^{29}Si coupling constants, Fig. 2, were similar for each of **5a**–**5c**, and also to those found for **3a**–**3c** [7]. Like their analogues **3** [7], it is interesting that **5c** is the rac-diastereoisomer in the solid state.



4 [≡(L″L″)$_2$]

5a R = Ph
5b R = C_6H_4Me–4
5c R = C_6H_{11}–c (2)

Table 1
Selected bond lengths (Å) and angles (°) for **5b**[a]

Bond lengths			
Ni–P	2.180(1)	Ni–C(1)	2.008(3)
Ni–C(2)	2.005(3)	Ni–C(3)	2.023(3)
Ni–C(4)	2.000(3)	Ni–M(1)	1.882(3)
Ni–M(2)	1.887(3)	C(1)–C(2)	1.393(4)
C(3)–C(4)	1.392(4)		
Bond angles			
M(1)–Ni–M(2)	131.85(11)	M(1)–Ni–P	111.18(9)
M(2)–Ni–P	116.00(9)	Si(1)–O(1)–Si(2)	129.08(11)
Si(1)–O(2)–Si(2)′	148.67(12)	C(2)–C(1)–Si(1)	122.4(2)
C(2)–C(1)–Ni	69.6(2)	Si(1)–C(1)–Ni	113.05(13)
C(1)–C(2)–Ni	69.8(2)	C(4)–C(3)–Si(2)	123.4(2)
C(4)–C(3)–Ni	68.9(2)	Si(2)–C(3)–Ni	113.03(13)
C(3)–C(4)–Ni	70.7(2)	C(12)–C(7)–C(8)	117.5(2)

[a] M(1) and M(2) are the centres of the C(1)–C(2) and C(3)–C(4) bonds, respectively. Symmetry transformations used to generate equivalent atoms:, $-x$, $-y$, $-z$.

A platinum analogue of **5c**, prepared from $[\overline{\mathrm{Pt(LL)}}\{P(C_6H_{11}\text{-}c)_3\}]$ and **4**, had been reported [4]; its structure was conjectured to be similar to that now established for **5b** (see Section 2.2).

2.2. The X-ray molecular structure of $[(Ni\{P(C_6H_4Me\text{-}4)_3\})_2\{\mu\text{-}(L''L'')_2\}]$ (5b)

Crystalline **5b**, obtained from benzene, is a centrosymmetric binuclear nickel(0) complex, the inversion centre being the mid-point of the chair-shaped $(SiO)_4$ ring, Fig. 1. Selected bond lengths and angles are listed in Table 1. There is a molecule of benzene solvate in a general position.

The local geometry at each three-coordinate nickel atom is planar, taking its vertices to be the phosphorus atom and the centroids M of adjacent η^2-vinyl groups. The M(1)–Ni–M(2) angle is wider [131.8(1)°] than M(1)–Ni–P [111.2(1)°] or M(2)–Ni–P [116.0(1)°]. This situation is similar to that in $[\overline{\mathrm{Ni(LL)}}\{P(C_6H_{11}\text{-}c)_3\}]$, the corresponding angles being 130.1(1), 113.9(1) and 115.1(1)° [7]. Likewise, the Ni–P and average Ni–C_α and Ni–C_β bond lengths in that compound of 2.206(1), 2.000(3) and 2.027(3) Å are close to the 2.179(1), 2.003(3) and 2.015(3) Å in **5b**. Each six-membered metallacyclic ring $[\overline{\mathrm{NiM(1)Si(1)OSi(2)M(2)}}]$ (**5b**) adopts a chair conformation, as had previously been observed for $\overline{\mathrm{(Met)M(1)Si(1)OSi(2)M(2)}}$ rings in $\overline{\mathrm{Ni(LL)}}$ [7], $\overline{\mathrm{Pt(LL)}}$ [4,5,7,8], $\overline{\mathrm{Rh(LL)}}$ [14] and $\overline{\mathrm{Rh(LPhL^{Ph})}}$ [14] complexes (Met = Ni, Pt or Rh).

3. Experimental

3.1. General procedures and starting silicon reagents

All manipulations and instruments were as described earlier [7,8,14]. The silicon reagents used in Sections 3.2, 3.3, 3.4 and 3.5 were kindly provided by Dow Corning, Ltd.

3.2. Synthesis of $[\{Ni(PPh_3)\}_2\{\mu\text{-}(\eta\text{-}\overline{CH_2{=}CH(Me)Si}(\mu\text{-}O))_4\}]$ (5a)

Cyclotetrakis[vinyl(methyl)siloxane] (1.0 ml) was added slowly to a stirred red suspension of $[Ni(cod)_2]$ (0.50 g, 1.8 mmol) and PPh_3 (0.47 g, 1.8 mmol) in diethyl ether (10 ml) at ambient temperature, yielding a yellow solution. The reaction mixture was allowed to stir overnight. The volatiles were removed in vacuo to give a yellow oil, which was extracted into pentane (2 × 2 ml). The extract was filtered through Celite. The filtrate was concentrated, then set aside at −30°C to yield the yellow solid compound **5a** (0.77 g, 0.8 mmol, 86%). Yellow crystals of **5a**, m.p. 212–214°C (dec) were obtained by recrystalisation from benzene, at ambient temperature. Anal. Found: C, 58.3; H, 5.49. $C_{48}H_{54}Ni_2O_4P_2Si_4$ Calc.: C, 58.4; H, 5.52%. ^1H-NMR (C_6D_6, 298 K, 500 MHz): δ 0.39 (s, 12H), 2.56 (td, 4H), 3.07 (dd, 8H), 7.03–7.64 (m, 30H), $^3J(^1H_1–^1H_2) = 12.6$ Hz, $^3J(^1H_1–^1H_3) = 16.5$ Hz, $^3J(^1H_1–^{31}P) = 4.8$ Hz, $^3J(^1H_2–^{31}P) = 7.9$ Hz, $^3J(^1H_3–^{31}P) = 6.4$ Hz. $^{13}C\{^1H\}$-NMR (C_6D_6, 298 K, 125.8 MHz): δ 0.61 (s, Me), 58.17 (s, =CH–), 63.15 (s, =CH_2), 127.81–136.60 (m, Ph). $^{29}Si\{^1H\}$-NMR (C_6D_6, 298 K, 99.4 MHz):δ −24.0 (d), $^3J(^{29}Si–^{31}P) = 4.0$ Hz. $^{31}P\{^1H\}$-NMR (C_6D_6, 298 K, 101.2 MHz): δ 41.2 (s).

3.3. Synthesis of $[\{NiP(C_6H_4Me\text{-}4)_3\}_2\text{-}\{\mu\text{-}(\eta\text{-}\overline{CH_2{=}CH(Me)Si}(\mu\text{-}O))_4\}]$ (5b)

Compound **5b** (0.83 g, 0.8 mmol, 85%) was prepared in a similar manner as **5a**, except that $P(C_6H_4Me\text{-}4)_3$ was used in place of PPh_3. Yellow crystals of **5b**, m.p 224–226°C (dec) suitable for X-ray diffraction, were grown from benzene at ambient temperature over a period of 24 h. Anal. Found: C, 60.7; H, 6.54. $C_{54}H_{66}Ni_2O_4P_2Si_4$ Calc.: C, 60.6; H, 6.21%. ^1H-NMR (C_6D_6, 298 K, 500 MHz): δ 0.48 (s, 12H), 2.03 (s, 9H), 2.61 (td, 4H), 3.16 (dd, 8H), 6.93–7.65 (m, 24H), $^3J(^1H_1–^1H_2) = 12.1$ Hz, $^3J(^1H_1–^1H_3) = 16.4$ Hz, $^3J(^1H_1–^{31}P) = 4.6$ Hz, $^3J(^1H_2–^{31}P) = 6.0$ Hz, $^3J(^1H_3–^{31}P) = 10.5$ Hz. $^{13}C\{^1H\}$-NMR (C_6D_6, 298 K, 125.8 MHz): δ 0.69 (s, Me), 21.01 (s, Me), 57.68 (s, =CH–), 63.00 (s, =CH_2), 127.80–139.22 (m, tol). $^{29}Si\{^1H\}$-NMR (C_6D_6, 298 K, 99.4 MHz): δ −23.9 (d), $^3J(^{29}Si–^{31}P) = 3.8$ Hz. $^{31}P\{^1H\}$-NMR (C_6D_6, 298 K, 101.2 MHz): δ 39.1 (s)

3.4. Synthesis of $[\{Ni(P(C_6H_{11}\text{-}c)_3)\}_2\text{-}\{\mu\text{-}(\eta\text{-}CH_2{=}CH(Me)Si(\mu\text{-}O))_4\}]$ ***(5c)***

Compound **5c** (0.70 g, 0.7 mmol, 76%) was prepared in similar manner as **5a**, except that $P(C_6H_{11}\text{-}c)_3$ was used in place of PPh_3. Yellow crystals of **5c**, m.p. 235–237°C (dec) were obtained by recrystalisation from benzene, at ambient temperature. Anal. Found: C, 57.3; H, 9.01. $C_{48}H_{90}Ni_2O_4P_2Si_4$ Calc.: C, 56.4; H, 8.87%. ^{1}H-NMR (C_6D_6, 298 K, 500 MHz): δ 0.51 (s, 12H), 1.1–1.8 (m, 33H), 2.53 (td, 4H), 3.06 (dd, 8H), $^3J(^1H_1\text{–}^1H_2) = 12.6$ Hz, $^3J(^1H_1\text{–}^1H_3) = 16.3$ Hz, $^3J(^1H_1\text{–}^{31}P) = 3.4$ Hz, $^3J(^1H_2\text{–}^{31}P) = 5.6$ Hz, $^3J(^1H_3\text{–}^{31}P) = 8.2$ Hz. $^{13}C\{^1H\}$-NMR (C_6D_6, 298 K, 125.8 MHz): δ 0.65 (s, Me), 26.99–36.54 (m, C_6H_{11}-c), 55.60 (s, =CH–), 58.95 (s, $=CH_2$). $^{29}Si\{^1H\}$-NMR (C_6D_6, 298 K, 99.4 MHz): δ -23.6 (d), $^3J(^{29}Si\text{–}^{31}P) = 3.2$ Hz. $^{31}P\{^1H\}$-NMR (C_6D_6, 298 K, 101.2 MHz): δ 39.4 (s).

3.5. Typical synthesis of $[Ni\{\mu\text{-}CH_2{=}CH(Me)_2Si\}_2O(PR_3)]$ ***(3)***

Divinyltetramethyldisiloxane (1.0 ml) was added slowly to a stirred red suspension of $[Ni(cod)_2]$ (0.56 g, 2.5 mmol) and PR_3 (2.5 mmol; R = Ph, C_6H_4Me-4 or C_6H_{11}-c) 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 **3**. Each of the crystalline complexes $[Ni\{\mu\text{-}CH_2{=}CH(Me)_2Si\}_2O(PPh_3)]$, (**3b**), $[Ni\{\mu\text{-}CH_2{=}CH(Me)_2Si\}_2\text{-}O\{P(C_6H_4Me\text{-}4)_3\}]$ **3a** and $[Ni\{\mu\text{-}CH_2{=}CH(Me)_2Si\}_2\text{-}O\{P(C_6H_{11}\text{-}c)_3\}]$ (**3c**) was authenticated by showing it to have identical NMR spectra to those of the previously characterised specimens [7].

3.6. X-ray structure determination of ***5b***

Intensities were measured on a Enraf–Nonius CAD 4 difractometer with monochromated Mo–K_α radiation ($\lambda = 0.71073$ Å). Structure solution was by SHELXS-86 [15]. Refinement was by full-matrix least-squares on F^2 using all reflections and SHELXL-93 [16]. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in riding mode with $U_{iso}(H)$ equal to $1.2U_{eq}(C)$ or $1.5U_{eq}(C)$ for methyl groups. The 4-tolyl methyl H atoms were included as disordered equally over two sets of positions related by a 60° rotation. Further details are in Table 2.

Table 2
Crystal data and structural refinement parameters for **5b**

Formula	$C_{54}H_{66}Ni_2O_4P_2Si_4 \cdot 2(C_6H_6)$
Formula weight	1227.0
Crystal system	Triclinic
a (Å)	10.045(5)
b (Å)	11.529(3)
c (Å)	14.179(9)
α (°)	80.65(4)
β (°)	76.86(4)
γ (°)	85.47(3)
U (Å^3)	1576.3(13)
Z	1
D_{calc} (g cm^{-3})	1.29
Space group	$P\bar{1}$ (No.2)
θ_{max} for data collection (°)	25
Unique reflections	5527
Reflections with $[I>2\sigma(I)]$	4543
R_1 [for $I>2\sigma(I)$]	0.035
wR_2 (for all data)	0.083

4. Supplementary material

Crystallographic data for the structural analysis have been deposited at the Cambridge Crystallographic Data Centre: CCDC no. 142037. Copies of this information may be obtained free of charge from The Director, CCDC, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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