

The synthesis and characterisation of some divinylsiloxane–(tertiary phosphine) complexes of platinum(0) and nickel(0)¹

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Abstract

Reaction of the platinum(0) complex $[\{\overline{\text{Pt}}(\text{LL})\}_2(\mu\text{-LL})]$ [LL = (ViMe₂Si)₂O] with PR₃ (R = C₆H₄Me-*p* or C₆H₁₁-*c*) or PPh₂CH₂CBu^t₂OH yields, by displacement of the bridging vinylsiloxane ligand, complexes having both a phosphine and a vinylsiloxane as co-ligands. There is evidence for interaction between the platinum atom and the OH moiety in $[\overline{\text{Pt}}(\text{LL})(\text{PPh}_2\text{CH}_2\text{CBu}_2\text{OH})]$.

Reaction of the analogous nickel(0) complex $[\{\overline{\text{Ni}}(\text{LL})\}_2(\mu\text{-LL})]$ with a tertiary phosphine yields $[\overline{\text{Ni}}(\text{LL})\text{PR}_3]$ (R = Ph, C₆H₁₁-*c* or C₆H₄Me-*p*). The zinc reduction of $[\text{Ni}(\text{PPh}_3)_2\text{Cl}_2]$ in the presence of (ViPh₂Si)₂O (PLL) yields the complex $[\text{Ni}(\text{PLL})\text{PPh}_3]$.

X-ray molecular structures of the crystalline complexes $[\overline{\text{Pt}}(\text{LL})\text{P}(\text{C}_6\text{H}_4\text{Me-}p)_3]$, $[\overline{\text{Pt}}(\text{LL})(\text{PPh}_2\text{CH}_2\text{CBu}_2\text{OH})]$, $[\overline{\text{Ni}}(\text{LL})(\text{P}(\text{C}_6\text{H}_{11}\text{-}c)_3)]$ and $[\overline{\text{Ni}}(\text{PLL})(\text{PPh}_3)]$ show a trigonal planar metal environment and chair conformation for the $\overline{\text{M}}(\text{LL})$ and $\overline{\text{M}}(\text{PLL})$ units.

Keywords: Tetramethyldivinylsiloxane; Platinum(0); Nickel(0); Phosphine

1. Introduction

Probably the most important catalyst for hydrosilylation is H₂[PtCl₆]·xH₂O, Speier's catalyst, discovered in the mid-1950s [1]. It soon became apparent that for this to operate efficiently a 'solvent' was required in order to overcome the long and variable induction periods and the exothermic reactions. Such a solvent-modified system is the Karstedt catalyst [2], which incorporates the simplest divinylsiloxane molecule (CH₂=CHSiMe₂)₂O (≡LL). The generally accepted mechanism (Chalk–Harrod) of hydrosilylation postulated that the initiator was a Pt(0) species, probably formed by reduction of the chloroplatinic acid by the silane HSiX₃.

It was shown in 1987 that H₂[PtCl₆]·xH₂O with LL affords a solution **A** containing Pt(0) [3]. The evidence was that (i) treatment of solution **A** with a tertiary phosphine led to recognisable Pt(0) species, e.g. $[\text{Pt}(\text{PPh}_3)_3]$ when PPh₃ was employed; (ii) reaction with

PBu^t₃ gave the X-ray-characterised platinum(0) complex $[\overline{\text{Pt}}(\text{LL})(\text{PBu}_3)]$ [3]; and (iii) the ¹⁹⁵Pt{¹H} NMR spectrum of solution **A** showed a signal indicative of a platinum(0) complex.

Subsequently, a crystalline material was isolated from solution **A**, the X-ray structure of which established it to be the binuclear Pt(0) complex of formula $[\{\overline{\text{Pt}}(\text{LL})\}_2(\mu\text{-LL})]$ [4]. This demonstrated inter alia that the new ligand LL was capable of functioning not only in a chelating mode (i.e. as a terminal ligand), but could also operate in a bridging mode, and moreover that in this context it was a reducing agent.

This complex was also formed from LL and K₂[PtCl₄], $[\{\overline{\text{Pt}}(\text{C}_2\text{H}_4)\text{Cl}(\mu\text{-Cl})\}_2]$, $[\text{Pt}(\text{COD})_2]$ or *cis*- $[\text{Pt}(\eta^2\text{-CH}_2=\text{CHPh})_2\text{Cl}_2]$. The last of these reactions was proposed to proceed by the exchange between Pt(II) and Si of a Cl with a CH=CH₂ ligand [5], this mechanism explaining the action of LL as a reducing agent in the formation of Karstedt's catalyst.

The complex $[\overline{\text{Pt}}(\text{LL})\text{PPh}_3]$ has been prepared from $[\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2]$ [6].

The reaction between nickel atoms and LL under metal vapour synthesis conditions yielded the tris(alkene)nickel(0) complex $[\text{Ni}(\text{CH}_2=\text{CHSiMe}_2\text{O-SiMe}_2\text{CH}=\text{CHSiMe}_2\text{OSiMe}_2\text{CH}=\text{CH}_2)]$, $[\overline{\text{Ni}}(\text{LL})\text{L}]$

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¹ Dedicated to Professor Malcolm Green as a mark of esteem and friendship on the occasion of his 60th birthday.

Table 1
Crystal data for 1, 3, 5 and 7

Formula	1 C ₂₉ H ₃₉ OPPtSi ₂	3 C ₃₀ H ₄₉ O ₂ PPtSi ₂	5 C ₂₆ H ₅₁ NiOPSi ₂	7 C ₄₆ H ₄₁ NiOPSi ₂
<i>M</i>	685.9	724.0	525.5	958.6
Crystal system	monoclinic	triclinic	triclinic	triclinic
<i>M</i>	685.9	724.0	525.5	958.6
<i>a</i> (Å)	14.202(4)	9.207(2)	9.945(3)	11.778(2)
<i>b</i> (Å)	14.960(19)	12.929(6)	12.561(3)	13.983(2)
<i>c</i> (Å)	14.775(5)	14.736(3)	12.738(4)	14.399(3)
α (°)	90	83.39(3)	91.15(2)	88.620(10)
β (°)	104.47(2)	84.13(2)	111.43(3)	66.910(10)
γ (°)	90	68.68(2)	94.52(2)	67.920(10)
<i>U</i> (Å ³)	3039.5	1619.8	1474.6	2000.2
<i>Z</i>	4	2	2	2
<i>D</i> _c (g cm ⁻³)	1.50	1.48	1.18	1.26
Space group	<i>P</i> 2 ₁ / <i>n</i> (No. 14)	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$ (No. 2)	<i>P</i> $\bar{1}$ (No. 2)
θ_{\max} (°) for data collection	25	25	30	25
Unique reflections	5570	5693	8570	8880
Reflections with <i>I</i> > 2 σ (<i>I</i>)	3638	4744	5581	6541
<i>R</i> ₁ [for <i>I</i> > 2 σ (<i>I</i>)]	0.036	0.071	0.051	0.063
<i>R</i> ' [for <i>I</i> > 2 σ (<i>I</i>)]	0.042	—	—	—
<i>wR</i> ₂ (for all data)	—	0.380	0.128	0.134

[7]. An interesting feature of the ligand LL'L was its ability to undergo a novel dynamic process involving dissociation–rotation then reassociation of both terminal and internal alkene units [8]. A similar process, involving the terminal vinyl groups of LL, had been observed for [Pt(LL)PBu₃] [9].

2. Results and discussion

Reaction of [$\overline{\text{Pt}(\text{LL})}_2(\mu\text{-LL})$] with either P(C₆H₄Me-*p*)₃ or P(C₆H₁₁-*c*)₃ yielded the mononuclear complex [Pt(LL)PR₃] [R = C₆H₄Me-*p* (1) or C₆H₁₁-*c* (2)]. The crystalline complex 1 has been characterised by X-ray crystallography (crystal data in Table 1); the vinylsiloxane-metal ring adopts a chair conformation, Fig. 1. This structure renders the methyl groups on the silicon atoms to be inequivalent, axial and equatorial. This is reflected in both the ¹H and ¹³C{¹H} NMR spectra, which show that there are two equal intensity methyl environments for the LL ligand.

Similarly, treatment with the phosphino-alcohol PPh₂CH₂CBu₂OH yielded [Pt(LL)(PPh₂CH₂CBu₂OH)] (3). In the ¹H NMR spectrum of 3, the OH group of the phosphino-alcohol gave rise to a doublet with ¹⁹⁵Pt satellites at δ 3.36 [*J*(¹H–³¹P) = 5.8 Hz, *J*(¹H–¹⁹⁵Pt) = 18.6 Hz], Fig. 2. The chemical shift of the OH group was verified by recording the ¹H NMR spectrum of 3 in a 10% [²H₄]methanol/[²H₈]toluene solution; the OH group underwent OH/OD chemical exchange in solution, causing disappearance of the signal at 3.36. The coupling indicates that there is a Pt···HOR or Pt···O(H)R interaction in the solution.

The X-ray molecular structure of 3 is illustrated in Fig. 3 (crystal data in Table 1) and shows that the ¹H–¹⁹⁵Pt coupling for the OH signal probably operates via a 'through space' spin–spin coupling mechanism. The related Rh(I) complex, *trans*-[Rh(CO)(Cl)(PMe₂CH₂CBu₂OH)₂] has been X-ray characterised and a similar M···HOR interaction (M = Rh) was indicated [10].

Complexes of the type [Ni(LL)PR₃] [R = Ph (4), C₆H₁₁-*c* (5) or C₆H₄Me-*p* (6)] were prepared by the

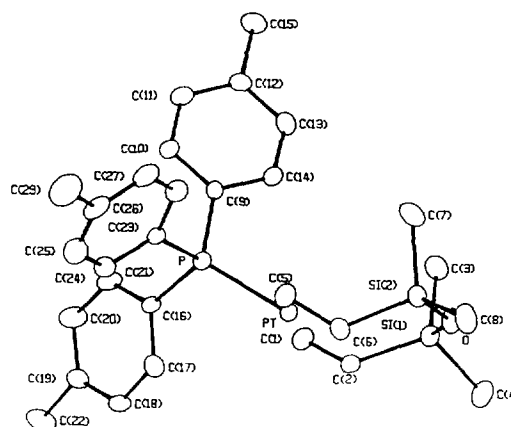


Fig. 1. The molecular structure of [Pt((η -CH₂=CHSiMe₂)₂O)P(C₆H₄Me-*p*)₃] (1). Selected bond distances (Å) and angles (°): Pt–P = 2.292(2), Pt–C(1) = 2.144(8), Pt–C(2) = 2.150(8), Pt–C(5) = 2.123(8), Pt–C(6) = 2.160(7); M1–Pt–M2 = 133.0, M1–Pt–P = 112.5, M2–Pt–P = 114.5, Si(1)–O–Si(2) = 134.5(4). M1 and M2 are the midpoints of the C(1)–C(2) and C(5)–C(6) bonds respectively.

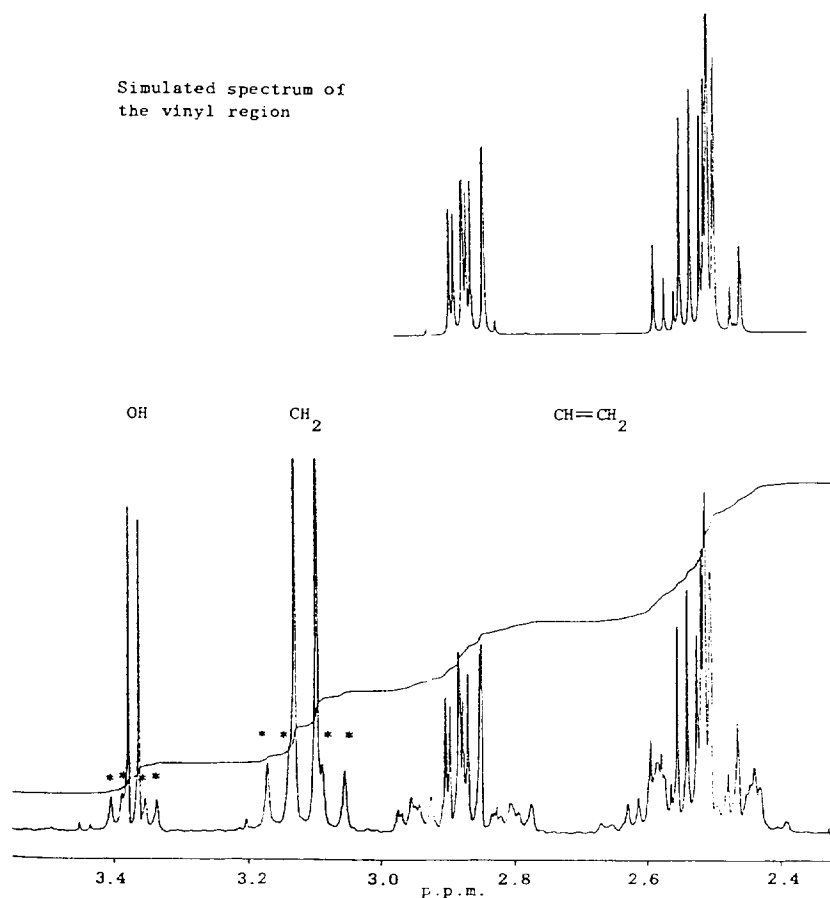


Fig. 2. The ^1H NMR spectrum of $[\text{Pt}(\{\eta\text{-CH}_2=\text{CHSiMe}_2\}_2\text{O})\text{PPh}_2\text{CH}_2\text{CBu}_2\text{OH}]$ (3) in the region δ 2.4–3.4, with simulation of the spectrum in the vinyl region. Recorded in $[\text{D}_8\text{H}_6]$ toluene at 303 K, 360 MHz. * Pt satellites.

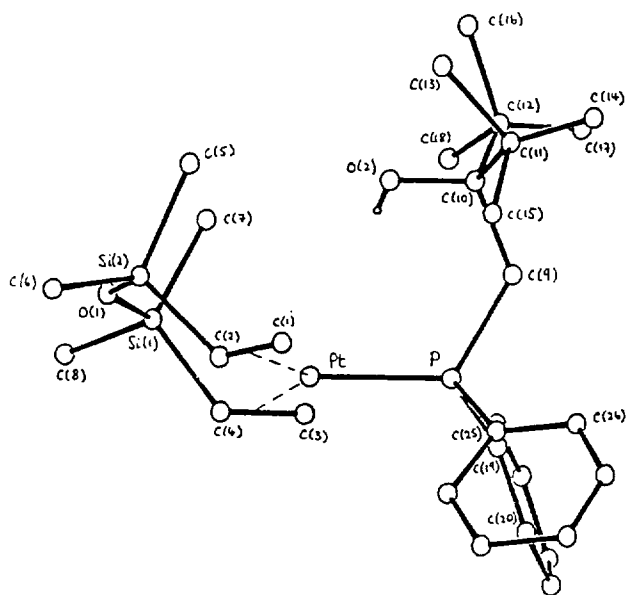
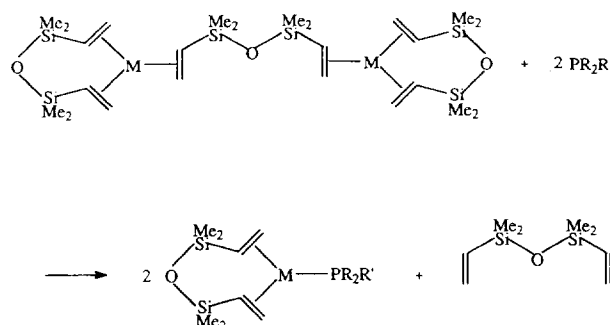


Fig. 3. The molecular structure of $[\text{Pt}(\{\eta\text{-CH}_2=\text{CHSiMe}_2\}_2\text{O})\text{PPh}_2\text{CH}_2\text{CBu}_2\text{OH}]$ (3). Selected bond lengths (\AA) and angles ($^\circ$): Pt–P = 2.308(5), Pt–C(1) = 2.08(3), Pt–C(2) = 2.20(2), Pt–C(3) = 2.15(3), Pt–C(4) = 2.16(2); M1–Pt–M2 = 128.4, M1–Pt–P = 118.5, M2–Pt–P = 112.8, Si(1)–O–Si(2) = 132.2(2). M1 and M2 are the midpoints of the C1–C2 and C3–C4 bonds respectively.

addition of the appropriate phosphine in a similar procedure to that used for the Pt(0) complexes 1–3.

These syntheses are summarised in Scheme 1.

The binuclear complex $[\{\text{Ni}(\text{LL})\}_2(\mu\text{-LL})]$ was prepared by the displacement, by LL, of the *trans,trans,trans*-cyclododeca-1,5,9-triene ligand from the nickel(0) complex $[\text{Ni}(t,t,t\text{-CDT})]$, and has been



M = Pt; R = R' = $\text{C}_6\text{H}_4\text{Me-p}$ (1) or $\text{C}_6\text{H}_{11\text{-c}}$ (2)

M = Pt, R = Ph, R' = $\text{CH}_2\text{CBu}_2\text{OH}$ (3)

M = Ni, R = R' = Ph (4), $\text{C}_6\text{H}_{11\text{-c}}$ (5) or $\text{C}_6\text{H}_4\text{Me-p}$ (6)

Scheme 1.

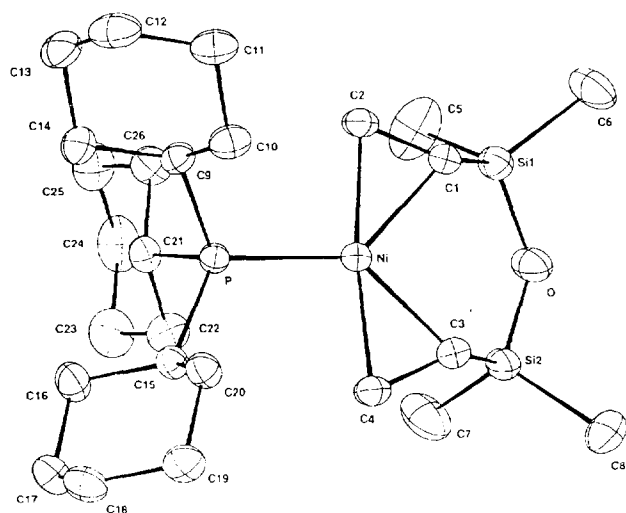


Fig. 4. The molecular structure of $[\text{Ni}\{(\eta\text{-CH}_2=\text{CHSiMe}_2)_2\text{O}\}(\text{PC}_6\text{H}_{11})_3]$ (**5**). Selected bond lengths (Å) and angles ($^\circ$): Ni–P = 2.2060(9), Ni–C(1) = 2.025(3), Ni–C(2) = 2.007(3), Ni–C(3) = 2.030(3), Ni–C(4) = 1.994(3); M1–Ni–M2 = 130.89(12), M1–Ni–P = 113.91(8), M2–Ni–P = 115.15(9), Si(1)–O–Si(2) = 131.98. M1 and M2 are the midpoints of the C(1)–C(2) and C(3)–C(4) bonds respectively.

prepared independently at the University of Düsseldorf [11].

The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of these phosphine complexes showed the methyl and vinyl resonances in similar regions to those obtained for the platinum(0) complexes or $[\text{Ni}(\text{LL}'\text{L})]$ [7,8].

The X-ray molecular structure of **5** is shown in Fig. 4 (crystal data in Table 1). As in the platinum complexes, the vinylsiloxane ligand-metal ring adopts a chair conformation, as is also the case in the heptadiene complex $[\text{Ni}(\text{C}_7\text{H}_{12})\text{PPh}_3]$ [12].

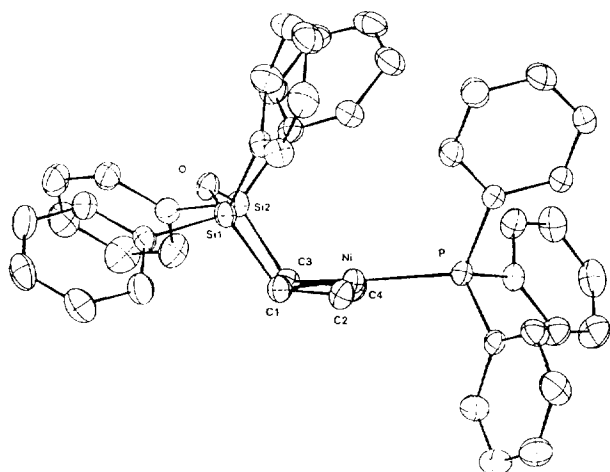
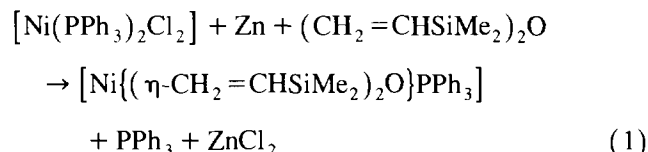


Fig. 5. The molecular structure of $[\text{Ni}\{(\eta\text{-CH}_2=\text{CHSiPh}_2)_2\text{O}\}\text{PPh}_3]$ (**7**). Selected bond lengths (Å) and angles ($^\circ$): Ni–P = 2.1801(9), Ni–C(1) = 2.107(3), Ni–C(2) = 2.004(3), Ni–C(3) = 2.021(3), Ni–C(4) = 2.000(3); M1–Ni–M2 = 132.1(1), M1–Ni–P = 111.97(8), M2–Ni–P = 115.54(8), Si(1)–O–Si(2) = 133.12(12). M1 and M2 are the midpoints of the C(1)–C(2) and C(3)–C(4) bonds respectively.

An alternative route to complex **4** was by the zinc reduction of the nickel(II) complex $[\text{Ni}(\text{PPh}_3)_2\text{Cl}_2]$ in the presence of the vinylsiloxane, as shown in Eq. (1). Such a procedure has previously been used for $[\text{Ni}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2]$ [13], although it may be the first time that it has been used to prepare a dienenickel(0) complex.



Similarly, the zinc reduction of $[\text{Ni}(\text{PPh}_3)_2\text{Cl}_2]$ in the presence of the vinylsiloxane $(\text{CH}_2=\text{CHSiPh}_2)_2\text{O}$ (\equiv PLL) yielded the X-ray characterised $[\text{Ni}(\text{PLL})(\text{PPh}_3)]$ (**7**). As in the complexes of LL, the vinylsiloxane-metal ring adopts a chair conformation upon coordination, with the phenyl groups on the silicon atoms inequivalent, as shown in Fig. 5 (crystal data in Table 1).

3. Experimental

3.1. Synthesis of $[\text{Pt}\{(\eta\text{-CH}_2=\text{CHSiMe}_2)_2\text{O}\}\text{-P}(\text{C}_6\text{H}_4\text{Me-}p)_3]$ (**1**)

A toluene solution (10 ml) of $\text{P}(\text{C}_6\text{H}_4\text{Me-}p)_3$ (0.19 g, 0.63 mmol) was added dropwise to a toluene solution (10 ml) of tris(tetramethyldivinylsiloxy)diplatinum(0) (0.30 g, 0.315 mmol) at 0°C . The reaction mixture was allowed to warm to room temperature and the pale yellow solution was stirred for 16 h. Removal of the solvent in vacuo yielded a white solid together with a yellow oil. On addition of pentane (10 ml), complex **1** (0.30 g, 0.43 mmol, 69%) precipitated as a white solid and was washed with cold pentane (4×5 ml) and dried in vacuo. The pentane washings were combined with the pale yellow mother liquor. White crystals suitable for X-ray diffraction were obtained from a concentrated solution of this mother liquor at -30°C .

Anal. Found: C, 50.3; H, 5.89. $\text{C}_{29}\text{H}_{39}\text{OPtSi}_2$ Calc.: C, 50.8; H, 5.69%. ^1H NMR (C_7D_8 , 298 K, 360 MHz): δ -0.08 (s, Me_e , 6H), 0.49 (s, Me_a , 6H), 1.99 (s, Me, 9H), 2.36 (m, H_3 , 2H), 2.63 (m, H_1 , 2H), 2.70 (m, H_2 , 2H), 6.85–7.42 (m, tol, 12H), $J(^1\text{H}_1\text{-}^1\text{H}_2) = 11.2$ Hz, $^3J(^1\text{H}_1\text{-}^1\text{H}_3) = 13.9$ Hz, $^3J(^1\text{H}_1\text{-}^{31}\text{P}) = 6.3$ Hz, $^3J(^1\text{H}_2\text{-}^{31}\text{P}) = 6.4$ Hz, $^3J(^1\text{H}_3\text{-}^{31}\text{P}) = 7.2$ Hz. $^{13}\text{C}\{^1\text{H}\}$ NMR (C_7D_8 , 298 K, 62.8 MHz): δ -1.3 (s, Me_e), 1.7 (s, Me_a), 21.0 (s, Me), 46.6 (d, C_2), 52.5 (d, C_1), 128.9–137.4 (m, tol), $^2J(^{13}\text{C}_1\text{-}^{31}\text{P}) = 5.4$ Hz, $^2J(^{13}\text{C}_1\text{-}^{195}\text{Pt}) = 162.7$ Hz, $^2J(^{13}\text{C}_2\text{-}^{31}\text{P}) = 10.8$ Hz, $J(^{13}\text{C}_2\text{-}^{195}\text{Pt}) = 119.3$ Hz. $^{29}\text{Si}\{^1\text{H}\}$ NMR (C_7D_8 , 298 K, 49.7 MHz): δ 2.3 (d), $J(^{29}\text{Si}\text{-}^{31}\text{P}) = 5.1$ Hz. $^{31}\text{P}\{^1\text{H}\}$

NMR (C_7D_8 , 298 K, 101 MHz): δ 19.3 (s), $J(^{31}P-^{195}Pt) = 3641.4$ Hz. $^{195}Pt\{^1H\}$ NMR (C_7D_8 , 298 K, 54 MHz): δ -5567.4 (s).

3.2. Synthesis of $[Pt\{\eta\text{-}CH_2=CHSiMe_2\}_2O\}P(C_6H_{11}\text{-}c)_3]$ (2)

This complex was prepared in a similar method to **1**, except that the reaction mixture was heated to 80 °C for 5 min prior to work up.

Anal. Found: C, 47.8; H, 7.2. $C_{26}H_{51}OPtSi_2$ Calc.: C, 47.4; H, 7.8%. 1H NMR (C_7D_8 , 303 K, 360 MHz): δ 0.0 (s, Me_e , 6H), 0.8 (s, Me_a , 6H), 1.1–1.8 (m, $C_6H_{11}\text{-}c$, 33H), 2.27 (m, H_3 , 2H), 2.64 (m, H_1 , 2H), 2.66 (m, H_2 , 2H), $J(^1H_1\text{-}^1H_2) = 11.8$ Hz, $^3J(^1H_1\text{-}^1H_3) = 14.3$ Hz, $^2J(^1H_2\text{-}^1H_3) = -0.7$ Hz, $^3J(^1H_1\text{-}^{31}P) = 6.8$ Hz, $^3J(^1H_2\text{-}^{31}P) = 6.7$ Hz, $^3J(^1H_3\text{-}^{31}P) = 7.2$ Hz. $^{13}C\{^1H\}$ NMR (C_7D_8 , 303 K, 90 MHz): δ -1.3 (s, Me_e), 1.9 (s, Me_a), 27.1–37.8 (m, $C_6H_{11}\text{-}c$), 42.9 (d, C_2), 45.7 (d, C_1), $^2J(^{13}C_1\text{-}^{31}P) = 6.4$ Hz, $^1J(^{13}C_1\text{-}^{195}Pt) = 153$ Hz, $^2J(^{13}C_2\text{-}^{31}P) = 10.8$ Hz, $^1J(^{13}C_2\text{-}^{195}Pt) = 110$ Hz. $^{31}P\{^1H\}$ NMR (C_7D_8 , 303 K, 40 MHz): δ 26.8 (s), $^1J(^{31}P\text{-}^{195}Pt) = 3520$ Hz. $^{195}Pt\{^1H\}$ NMR (C_7D_8 , 303 K, 77 MHz): δ -5633 (s).

3.3. Synthesis of $[Pt\{\eta\text{-}CH_2=CHSiMe_2\}_2O\}P(Ph_2CH_2CBu^tOH)]$ (3)

The phosphino-alcohol $Ph_2CH_2CBu^tOH$ (0.18 g, 0.53 mmol) in toluene (3 ml) was added dropwise to a rapidly stirring solution of tris(tetramethyldivinylsiloxane)diplatinum(0) (0.25 g, 0.26 mmol) in toluene (2 ml) at 25 °C for 3 h. The solvent was removed in vacuo to yield a white oil. Addition of pentane (3 ml) and cooling the resultant solution to -30 °C for ca. 12 h gave white crystals of **3** (0.26 g, 0.36 mmol, 68%). These were filtered off, washed with cold (-30 °C) pentane (2 ml) and dried in vacuo. Crystals suitable for X-ray diffraction were obtained by dissolving the crystals in a minimum amount of pentane and cooling the solution to -30 °C for ca. 48 h.

Anal. Found: C, 49.4; H, 6.4. $C_{29}H_{39}O_2PtSi_2$ Calc.: C, 49.7; H, 6.8%. 1H NMR (C_7D_8 , 303 K, 360 MHz): δ 0.02 (s, Me_e , 6H), 0.43 (s, Me_a , 6H), 0.99 (s, Bu^t , 18H), 2.50 (m, H_3 , 2H), 2.54 (m, H_1 , 2H), 2.87 (m, H_2 , 2H), 3.11 (s, CH_2 , 2H), 3.36 (d, OH, 1H), 6.85–7.5 (m, Ph, 10H), $^3J(^1H_1\text{-}^1H_2) = 12.2$ Hz, $^3J(^1H_1\text{-}^1H_3) = 14.5$ Hz, $^2J(^1H_2\text{-}^1H_3) = 0.4$ Hz, $^3J(^1H_1\text{-}^{31}P) = 6.8$ Hz, $^3J(^1H_2\text{-}^{31}P) = 7.2$ Hz, $^3J(^1H_3\text{-}^{31}P) = 6.2$ Hz. $^{13}C\{^1H\}$ NMR (C_7D_8 , 303 K, 90 MHz): δ -1.6 (s, Me_e), 1.7 (s, Me_a), 21.8 (s, C- CH_3), 32.7 (d, P- CH_2), 43.4 (d, C- CH_3), 49.3 (d, C_2), 54.2 (d, C_1), 81.7 (s, C-OH), 132–141 (m, Ph), $^2J(^{13}C_1\text{-}^{31}P) = 5.0$ Hz, $^1J(^{13}C_1\text{-}^{195}Pt) = 165$ Hz, $^2J(^{13}C_2\text{-}^{31}P) = 111.1$ Hz, $^1J(^{13}C_2\text{-}^{195}Pt) = 110$ Hz. $^{31}P\{^1H\}$ NMR (C_7D_8 , 303 K, 40 MHz):

δ 9.2 (s), $^1J(^{31}P\text{-}^{195}Pt) = 3471$ Hz. $^{195}Pt\{^1H\}$ NMR (C_7D_8 , 303 K, 77 MHz): δ -5582 (s).

3.4. Synthesis of $[Ni\{\eta\text{-}CH_2=CHSiMe_2\}_2O\}P(Ph_3)]$ (4)

Triphenylphosphine (0.47 g, 1.803 mmol) was dissolved in toluene (5 ml) and added slowly to a stirred solution of tris(tetramethyldivinylsiloxane)dinickel(0) (0.61 g, 0.902 mmol) in toluene (10 ml) at ambient temperature. The reaction mixture was allowed to stir overnight; the colour of the solution changed from orange to yellow. The volatiles were removed in vacuo to give a yellow oil, which was taken up into pentane and filtered through Celite (2 × 2 ml). After concentration of the solution, it was set aside at -30 °C to yield yellow crystals of **4** (0.73 g, 1.442 mmol, 80%).

Anal. Found: C, 61.4; H, 6.59. $C_{26}H_{33}NiOPSi_2$ Calc.: C, 61.6; H, 6.56%. 1H NMR (C_7D_8 , 298 K, 500 MHz): δ -0.02 (s, Me_e , 6H), 0.52 (s, Me_a , 6H), 2.77 (dd, H_3 , 2H), 2.95 (m, H_1 , 2H), 3.12 (dd, H_2 , 2H), 7.02–7.48 (m, Ph, 15H), $^3J(^1H_1\text{-}^1H_2) = 12.4$ Hz, $^3J(^1H_1\text{-}^1H_3) = 15.8$ Hz, $^3J(^1H_1\text{-}^{31}P) = 3.7$ Hz, $^3J(^1H_2\text{-}^{31}P) = 7.9$ Hz, $^3J(^1H_3\text{-}^{31}P) = 7.7$ Hz. $^{13}C\{^1H\}$ NMR (C_7D_8 , 298 K, 125.8 MHz): δ -0.4 (s, Me_e), 12.1 (s, Me_a), 62.5 (d, C_1), 63.8 (s, C_2), 128.4–136.2 (m, Ph), $^2J(^{13}C_1\text{-}^{31}P) = 6.9$ Hz. $^{29}Si\{^1H\}$ NMR (C_7D_8 , 298 K, 99.4 MHz): δ 25.8 (d), $^3J(^{29}Si\text{-}^{31}P) = 3.6$ Hz. $^{31}P\{^1H\}$ NMR (C_7D_8 , 298 K, 101.2 MHz): δ 42.0 (s).

3.5. Synthesis of $[Ni\{\eta\text{-}CH_2=CHSiMe_2\}_2O\}P(C_6H_{11}\text{-}c)_3]$ (5)

The title compound (0.45 g, 1.16 mmol, 74%) was prepared in a similar manner as **4**. Crystals suitable for X-ray diffraction were obtained by storing a solution of the compound at -30 °C for 24 h.

Anal. Found: C, 59.8; H, 9.66. $C_{26}H_{51}NiOPSi_2$ Calc.: C, 59.4; H, 9.78%. 1H NMR (C_7D_8 , 298 K, 500 MHz): δ 0.08 (s, Me_e , 6H), 0.60 (s, Me_a , 6H), 1.0–1.8 (m, $C_6H_{11}\text{-}c$, 33H), 2.63 (dd, H_2 , 2H), 2.70 (m, H_1 , 2H), 2.99 (dd, H_3 , 2H), $^3J(^1H_1\text{-}^1H_2) = 12.8$ Hz, $^3J(^1H_1\text{-}^1H_3) = 16.0$ Hz, $^2J(^1H_2\text{-}^1H_3) = 1.3$ Hz, $^3J(^1H_1\text{-}^{31}P) = 4.4$ Hz, $^3J(^1H_2\text{-}^{31}P) = 4.1$ Hz, $^3J(^1H_3\text{-}^{31}P) = 7.6$ Hz. $^{13}C\{^1H\}$ NMR (C_7D_8 , 298 K, 125.8 MHz): δ -0.2 (s, Me_e), 2.4 (s, Me_a), 27.0–36.6 (m, $C_6H_{11}\text{-}c$), 55.6 (d, C_2), 58.8 (d, C_1), $^2J(^{13}C_1\text{-}^{31}P) = 7.0$ Hz, $^2J(^{13}C_2\text{-}^{31}P) = 4.6$ Hz. $^{29}Si\{^1H\}$ NMR (C_7D_8 , 298 K, 99.4 MHz): δ 4.6 (d), $^3J(^{29}Si\text{-}^{31}P) = 3.3$ Hz. $^{31}P\{^1H\}$ NMR (C_7D_8 , 298 K, 101.2 MHz): δ 39.4 (s).

3.6. Synthesis of $[Ni\{\eta\text{-}CH_2=CHSiMe_2\}_2O\}P(C_6H_4Me\text{-}p)_3]$ (6)

The title compound (0.44 g, 0.798 mmol, 71%) was prepared in a similar manner as **4**, except that the

phosphine solution was added at 0°C and the reaction mixture was allowed to reach ambient temperature after 1 h.

Anal. Found: C, 63.1; H, 6.97. C₂₉H₃₀NiOPSi₂ Calc.: C, 63.4; H, 7.10%. ¹H NMR (C₇D₈, 298 K, 500 MHz): δ 0.05 (s, Me_c, 6H), 0.54 (s, Me_a, 6H), 2.01 (s, Me, 9H), 2.87 (dd, H₂, 2H), 2.98 (m, H₁, 2H), 3.19 (dd, H₃, 2H), 6.97–7.56 (m, tol, 12H), ³J(¹H₁–¹H₂) = 12.6 Hz, ³J(¹H₁–¹H₃) = 16.3 Hz, ³J(¹H₁–³¹P) = 4.5 Hz, ³J(¹H₂–³¹P) = 7.7 Hz, ³J(¹H₃–³¹P) = 8.2 Hz. ¹³C{¹H} NMR (C₇D₈, 298 K, 125.8 MHz): δ –0.3 (s, Me_c), 2.2 (s, Me_a), 21.1 (s, Me), 62.0 (d, C₁), 63.6 (d, C₂), 129.2–139.4 (m, tol), ²J(¹³C₁–³¹P) = 7.2 Hz, ¹J(¹³C₂–³¹P) = 2.4 Hz. ²⁹Si{¹H} NMR (C₇D₈, 298 K, 99.4 MHz): δ 3.8 (d), ³J(²⁹Si–³¹P) = 2.8 Hz. ³¹P{¹H} NMR (C₇D₈, 298 K, 101.2 MHz): δ 39.7 (s).

3.7. An alternative synthetic route to [Ni{(η-CH₂=CHSiMe₂)₂O}PPH₃] (4)

Tetramethyldivinylsiloxane (2 ml) was added to a suspension of bis(triphenylphosphine)nickel(II) chloride (1 g, 1.53 mmol) in THF (10 ml). Zinc metal (1 g) was added and the reaction mixture was allowed to stir at ambient temperature for 1 h; the purple suspension changed to a yellow solution. The volatiles were removed in vacuo and pentane was added, causing the precipitation of a white solid below a yellow solution, which was filtered through Celite (2 × 2 ml). The white precipitate was washed with pentane (2 × 5 ml) and the washings and filtrate were concentrated and stored at –30°C to yield yellow crystals of 4 (0.50 g, 0.98 mmol, 64%).

3.8. Synthesis of [Ni{(η-CH₂=CHSiPh₂)₂O}PPH₃] (7)

The title compound (0.77 g, 1.024 mmol, 67%) was prepared in a similar manner to that described in Section 3.4, except that toluene (10 ml) was used in place of pentane in the extraction of the complex. Crystals suitable for X-ray diffraction were grown from a mixture of toluene and pentane at ambient temperature over a period of 24 h.

Anal. Found: C, 72.9; H, 5.31. C₄₆H₄₃NiOPSi₂ Calc.: C, 73.0; H, 5.42%. ¹H NMR (C₇D₈, 298 K, 500 MHz): δ 3.05 (dd, H₃, 2H), 3.32 (m, H₁, 2H), 3.17 (dd, H₂, 2H), 6.92–8.12 (m, Ph, 35H), ³J(¹H₁–¹H₂) = 12.5 Hz, ³J(¹H₁–¹H₃) = 15.7 Hz, ³J(¹H₁–³¹P) = 3.8 Hz, ³J(¹H₂–³¹P) = 8.2 Hz, ³J(¹H₃–³¹P) = 7.1 Hz. ¹³C{¹H} NMR (C₇D₈, 298 K, 62.8 MHz): δ 58.7 (d, C₁), 62.9 (s, C₂), 128.7–136.1 (m, Ph), ²J(¹³C₁–³¹P) = 6.0 Hz. ²⁹Si{¹H} NMR (C₇D₈, 298 K, 99.4 MHz): δ –13.4 (d), ³J(²⁹Si–³¹P) = 2.9 Hz. ³¹P{¹H} NMR (C₇D₈, 298 K, 101.2 MHz): δ 42.36 (s).

3.9. X-ray structure determinations for 1, 3, 5 and 7

Intensities were measured on a Enraf–Nonius CAD4 diffractometer at 293 K with monochromated Mo Kα radiation (λ = 0.71073 Å). Corrections for absorption were applied using DIFABS for 1 and 3 and using psi-scan measurements for 5 and 7. Refinement was by full-matrix least-squares on *F* using reflections with *I* > 2σ(*I*) and Enraf–Nonius Molen programs for 1, and on *F*² using all reflections and SHELXL-93 for 3, 5 and 7. Non-hydrogen atoms were refined anisotropically. For 1 and 3 hydrogen atoms were fixed at calculated positions except for the vinyl H atoms in 1 and the hydroxyl H atom in 3, which were fixed at positions from a difference map. For 5 and 7 hydrogen atoms were included in riding mode except for the vinyl H atoms in 7 which were freely refined.

Complete tables of bond lengths and angles, atomic coordinates and equivalent isotropic thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

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