

The synthesis and characterisation of di- and trinuclear vinylsilicon-(tertiary phosphine) complexes of platinum(0) and nickel(0)

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Abstract

Reaction of the platinum(0) complex $[\{\text{Pt}(\eta\text{-ViSiMe}_2)_2\}_2(\mu\text{-ViSiMe}_2)_2\text{O}]$ with a bis- or tris-tertiary phosphine yields, by displacement of the bridging vinylsiloxane ligand, complexes featuring both a bridging phosphine and a terminal vinylsiloxane.

The zinc reduction of $[\text{NiCl}_2(\text{PPh}_3)_2]$ in the presence of the vinylsilane Vi_2SiMe_2 yields a dinuclear heteroleptic nickel(0) complex having a bridging vinylsilane.

X-ray molecular structures of the complexes $[\{\overline{\text{Pt}}(\overline{\text{LL}})\}_2(\text{dppe})]$, $[\{\overline{\text{Pt}}(\overline{\text{LL}})\}_3(\text{TRIPHOS})]$, $[\{\overline{\text{Pt}}(\overline{\text{LL}})\}_3(\text{TRIPHOS}')]$ and $[\{\text{Ni}(\mu\text{-Vi}_2\text{SiMe}_2)(\text{PPh}_3)\}_2]$ show a trigonal planar environment around the metal atoms and a chair conformation for the $\overline{\text{Pt}}(\overline{\text{LL}})$ units [$\text{LL} = (\eta\text{-ViSiMe}_2)_2\text{O}$, $\text{dppe} = (\text{Ph}_2\text{PCH}_2)_2$, $\text{TRIPHOS} = (\text{Ph}_2\text{PCH}_2)_3\text{CMe}$, $\text{TRIPHOS}' = \text{PhP}(\text{CH}_2\text{CH}_2\text{PPh}_2)_2$].

Keywords: Tetramethyldivinylsiloxane; Divinyl(dimethyl)silane; Platinum(0); Nickel(0); Phosphine

1. Introduction

The simplest divinylsiloxane molecule $(\text{CH}_2=\text{CHSiMe}_2)_2\text{O}$ ($=\text{LL}$) has previously been shown to be present as a ligand in the Pt(0) complex believed to be the active component in the industrially important Karstedt hydrosilylation catalyst [1–4].

Karstedt's catalyst is obtained by reacting the Pt(IV) complex $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$ (Speier's catalyst) with LL. Earlier studies at Sussex established that the reaction mixture obtained by mixing these two components, described as solution A, contained a Pt(0) species featuring LL as a ligand, as evident from (a) the isolation and characterisation (including the X-ray structure) of the platinum(0) complex $[\overline{\text{Pt}}(\overline{\text{LL}})(\text{PBU}_3)]$ [1], (b) ^{195}Pt NMR spectroscopy [1] and (c) the isolation of a principal product from solution A, namely the dinuclear Pt(0) complex $[\{\overline{\text{Pt}}(\overline{\text{LL}})\}_2(\mu\text{-LL})]$ [3]. Item (c) demonstrated, inter alia, that: (i) the new ligand LL was capable of functioning not only in a chelating mode (i.e. as a terminal ligand), but also could operate in a bridging

fashion between two platinum atoms; (ii) the formation of $[\overline{\text{Pt}}(\overline{\text{LL}})\text{PBU}_3]$ upon addition of a phosphine to solution A proceeded via the displacement of a bridging vinylsiloxane ligand from $[\{\overline{\text{Pt}}(\overline{\text{LL}})\}_2(\mu\text{-LL})]$. Similarly, in preliminary publications, it was shown that treatment of the latter with (i) maleic anhydride yielded $[\overline{\text{Pt}}(\overline{\text{LL}})\{\eta^2\text{-CHC}(\text{O})\text{OC}(\text{O})\text{CH}\}]$ [3], (ii) styrene gave $[\overline{\text{Pt}}(\overline{\text{LL}})(\eta^2\text{-CH}_2\text{CHPh})]$ or (iii) LL afforded $[\overline{\text{Pt}}(\overline{\text{LL}})(\text{LL})]$ [4]. It is evident that $\overline{\text{Pt}}(\overline{\text{LL}})$ complexes favour a three-coordinate metal environment.

We have recently reported that the reaction between $[\{\overline{\text{Pt}}(\overline{\text{LL}})\}_2(\mu\text{-LL})]$ and a mono-tertiary phosphine led to complexes of the type $[\overline{\text{Pt}}(\overline{\text{LL}})(\text{PR}_3)]$ ($\text{R} = \text{C}_6\text{H}_4\text{Me}$ or Cy) [5]. We have now extended this study to include related reactions involving a bis- or tris(tertiary phosphine).

We previously showed that the reaction between (a) nickel atoms and LL gave the macrocyclic complex $[\text{Ni}(\text{CH}_2=\text{CHSiMe}_2\text{OSiMe}_2\text{CH}=\text{CHSiMe}_2\text{OSiMe}_2\text{CH}=\text{CH}_2)]$ $[\text{Ni}(\text{LL}'\text{L})]$ [6,7] and (b) the reaction between (*trans, trans, trans*-cyclododeca-1,5,9-triene)nickel(0) and LL gave the dinuclear complex $[\{\overline{\text{Ni}}(\overline{\text{LL}})\}_2(\mu\text{-LL})]$ [5,8], which with a mono(tertiary phosphine) gave $[\overline{\text{Ni}}(\overline{\text{LL}})(\text{PR}_3)]$ ($\text{R} = \text{Cy}$, $\text{C}_6\text{H}_4\text{Me}$ or

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Ph) [5]. An alternative synthetic route to the latter was by the zinc reduction of $[\text{NiCl}_2(\text{PPh}_3)_2]$ in the presence of LL. We now also describe a related reaction in which the simplest divinylalkylsilane Vi_2SiMe_2 replaces the divinylsiloxane LL. The reaction of $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$ with successively Vi_2SiMe_2 and aqueous NaHCO_3 gave both a Pt(0) olefin complex (which with PPh_3 yielded $[\text{Pt}(\text{Vi}_2\text{SiMe}_2)(\text{PPh}_3)]$) and $[\{\text{Pt}(\mu\text{-C1})(\mu\text{-Vi}_2\text{SiMe}_2)(\text{CH}_2\text{CH}_2\text{SiMe}_2\text{Vi})\}_2]$ [9]; this paper also described reactions between $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$ and either LL or 1,3,5,7-(ViMeSiO)₄ (see also Ref. [1]).

2. Results and discussion

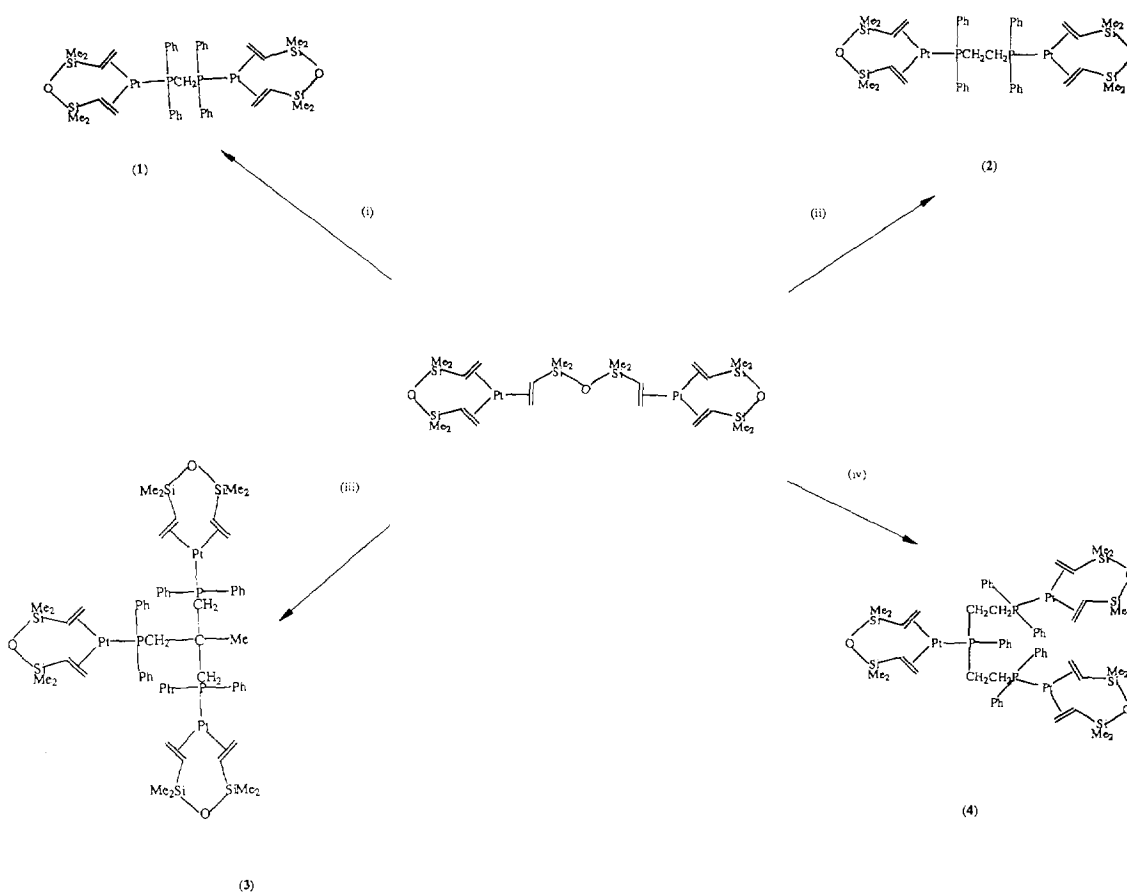
The isolation of complexes of the type $[\overline{\text{Pt}(\text{LL})}]_2 \text{L}'$ from the reaction between the dinuclear complex $[\{\overline{\text{Pt}(\text{LL})}\}_2(\mu\text{-LL})]$ and a phosphine ($\text{L}' = \text{PR}_3$) or another monofunctional ligand L' showed that the bridging ligand was displaceable to give heteroleptic complexes. This reaction is now extended to include a bis- or a tris(tertiary phosphine). Regarding the former, it had earlier been shown that the addition of an excess of bis(diphenylphosphino)ethane (dppe) to solution **A** yielded the platinum(0) complex

$[\text{Pt}(\text{dppe})_2]$ [1]. Another bis(tertiary phosphine), bis(diphenylphosphino)methane (dppm) is also widely used in platinum(0) chemistry, usually as a source of bridged binuclear complexes such as $[\text{Pt}_2(\mu\text{-dppm})_3]$ **1** (showing the relatively large $^{195}\text{Pt}\text{-}^{195}\text{Pt}$ coupling of 1183 Hz) [10]. The two tridentate ligands upon which we now report are 1,1,1-tris(diphenylphosphinomethyl)ethane (TRIPHOS) and bis(diphenylphosphinoethyl)phenylphosphine (TRIPHOS'), both of which have had many applications as ligands in transition metal chemistry. The reactions of these four di- or triphosphines with $[\{\overline{\text{Pt}(\text{LL})}\}_2(\mu\text{-LL})]$ are summarised in Scheme 1.

The dinuclear platinum complexes $[\{\overline{\text{Pt}(\text{LL})}\}_2(\text{dppm})]$ (**1**) and $[\{\overline{\text{Pt}(\text{LL})}\}_2(\text{dppe})]$ (**2**) were synthesised by the reaction of $[\{\overline{\text{Pt}(\text{LL})}\}_2(\mu\text{-LL})]$ with the appropriate phosphine in a 1:1 molar ratio.

The $^{29}\text{Si}\{^1\text{H}\}$, $^{31}\text{P}\{^1\text{H}\}$ and $^{195}\text{Pt}\{^1\text{H}\}$ NMR spectra for **2** in $[\text{C}_6\text{H}_6]$ toluene showed a single Si, P or Pt environment, indicating that in **2** the dppe ligand was bridging two three-coordinate platinum centres rather than acting in its more usual fashion as a chelating ligand.

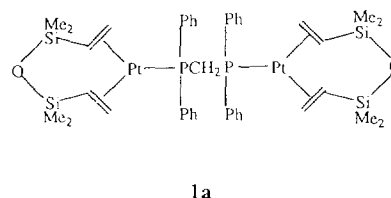
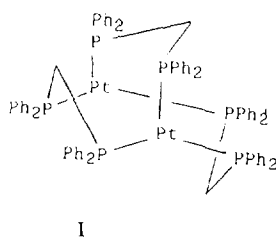
The structure of **1** was also deduced from its $^{31}\text{P}\{^1\text{H}\}$ and $^{195}\text{Pt}\{^1\text{H}\}$ NMR spectra in $[\text{C}_6\text{H}_6]$ toluene, keeping in mind the presence of isotopomers containing the spin-



Scheme 1. Di- and trinuclear vinylsiloxane complexes derived from $[\{\overline{\text{Pt}(\text{LL})}\}_2(\mu\text{-LL})]$. Reagents and conditions: (i) 1/2 dpmm, toluene, 25 °C, 1 h; (ii) 1/2 dppe, toluene, 25 °C, 1 h; (iii) 1/3 TRIPHOS, toluene, 25 °C, 1 h; (iv) 1/3 TRIPHOS', toluene, 0 °C, 1 h.

active ^{31}P and ^{195}Pt nuclei in relative natural abundance of 11:11:3 for $\text{Pt}-^{31}\text{PCH}_2^{31}\text{P}-\text{Pt}$, $^{195}\text{Pt}-^{31}\text{PCH}_2^{31}\text{P}-\text{Pt}$ and $^{195}\text{Pt}-^{31}\text{PCH}_2^{31}\text{P}-^{195}\text{Pt}$, respectively. That dppm is acting as a bridging ligand in **1** is not unexpected; dppm is well known to generate A-frame-type Pt_2 or Rh_2 complexes or related structures, e.g. **I**, having the two metals close to one another. However, the ^1H NMR

spectrum of **1** had the appearance of a 'septet' signal for the CH_2 protons of dppm , due to splitting by each of two equivalent ^{31}P and ^{195}Pt nuclei. Thus, we propose that **1** has the structure **1a** and is not of A-frame type, cf. the propellane structure **I** [10]; i.e. **1**, unlike **I**, showed only a small $^{195}\text{Pt}-^{195}\text{Pt}$ coupling of 17 Hz, established by a PANIC simulation program.



The X-ray structure of crystalline **2** is shown in Fig. 1; structural parameters and atomic coordinates are listed in Tables 1 and 2 respectively. Each platinum centre is in a trigonal planar environment, with each chelating LL ligand adopting a chair conformation, and the two positioned trans to each other, so as to minimise the repulsive interactions.

Complex **2** was shown to react with an excess of dppm to form $[\text{Pt}_2(\mu\text{-dppm})_3]$, a result consistent with

the isolation of $[\text{Pt}(\text{dppe})_2]$ from the reaction between solution **A** and an excess of dpe [1].

The complexes $[\{\text{Pt}(\text{LL})\}_3(\text{TRIPHOS})]$ (**3**) and $[\{\text{Pt}(\text{LL})\}_3(\text{TRIPHOS}')]$ (**4**) were obtained by the reaction between $[\{\text{Pt}(\text{LL})\}_2(\mu\text{-LL})]$ and the phosphine in a 3:2 molar ratio. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra indicated that in each case a mixture of products had formed, although only the trinuclear platinum(0) complexes **3** and **4** were isolated, both in good yield.

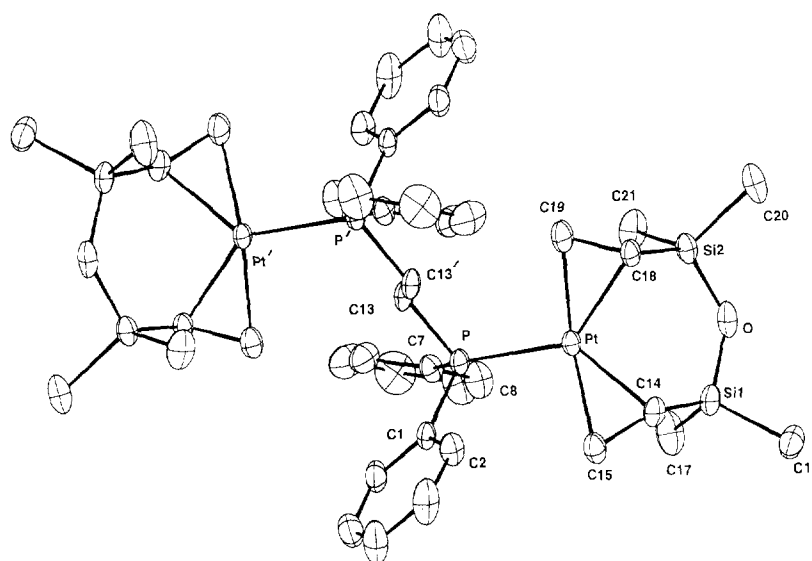


Fig. 1. The molecular structure of $[\{\text{Pt}(\eta\text{-CH}_2=\text{CHSiMe}_2)_2\text{O}\}_2(\mu\text{-dppm})]$ (**2**). Selected bond lengths (Å) and angles (deg): $\text{Pt}-\text{P} = 2.282$, $\text{Pt}-\text{C}(14) = 2.156(5)$, $\text{Pt}-\text{C}(15) = 2.144(7)$, $\text{Pt}-\text{C}(18) = 2.148(5)$, $\text{Pt}-\text{C}(19) = 2.126(6)$; $\text{Si}(1)-\text{O}-\text{Si}(2) = 136.2(2)$.

The $^{195}\text{Pt}\{^1\text{H}\}$ and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra for **3** each showed a single Pt and P environment. These findings indicate that of all the possible coordination modes for the tridentate phosphine, only the structure shown in Scheme 1 is valid. Complex **4** gave similar multinuclear NMR spectra; likewise, only the structure with a triply bridging 'TRIPHOS' ligand, as shown in Scheme 1, is compatible with the data. Full assignments of NMR spectra (see Section 3), taking account of isotopomers,

were facilitated by use of the Bruker Spectrospin PANIC simulation program.

The X-ray molecular structures of **3** and **4** are shown in Figs. 2 and 3 respectively and indicate that the structures observed in solution (NMR spectra) are retained in the crystals. Structural parameters and atomic coordinates are given in Tables 3 and 4 respectively for **3** and Tables 5 and 6 respectively for **4**. In **3** and **4** the tridentate ligand adopts a propeller-type geometry which

Table 1
Bond lengths (Å) and angles (deg) for **2**

<i>Bond lengths</i>			
Pt–P	2.282(1)	Pt–C(14)	2.156(5)
Pt–C(15)	2.144(7)	Pt–C(18)	2.148(5)
Pt–C(19)	2.126(6)	P–C(1)	1.823(6)
P–C(7)	1.824(5)	P–C(13)	1.832(5)
Si(1)–O	1.638(5)	Si(1)–C(14)	1.849(5)
Si(1)–C(16)	1.846(6)	Si(1)–C(17)	1.853(6)
Si(2)–O	1.641(4)	Si(2)–C(18)	1.851(5)
Si(2)–C(20)	1.857(6)	Si(2)–C(21)	1.855(7)
C(1)–C(2)	1.402(8)	C(1)–C(6)	1.379(6)
C(2)–C(3)	1.388(10)	C(3)–C(4)	1.377(7)
C(4)–C(5)	1.364(11)	C(5)–C(6)	1.394(11)
C(7)–C(8)	1.380(7)	C(7)–C(12)	1.396(7)
C(8)–C(9)	1.399(10)	C(9)–C(10)	1.342(9)
C(10)–C(11)	1.357(9)	C(11)–C(12)	1.400(10)
C(14)–C(15)	1.405(6)	C(18)–C(19)	1.413(6)
C(13)–C(13')	1.550(9)	Pt–M(1)	2.032
Pt–M(2)	2.016		
<i>Bond angles</i>			
P–Pt–C(14)	131.5(1)	P–Pt–C(15)	93.6(1)
P–Pt–C(18)	133.0(1)	P–Pt–C(19)	94.5(1)
C(14)–Pt–C(15)	38.1(2)	C(14)–Pt–C(18)	95.3(2)
C(14)–Pt–C(19)	133.9(2)	C(15)–Pt–C(18)	133.4(2)
C(15)–Pt–C(19)	171.8(2)	C(18)–Pt–C(19)	38.6(2)
Pt–P–C(1)	116.2(1)	Pt–P–C(7)	112.7(1)
Pt–P–C(13)	116.7(1)	C(1)–P–C(7)	106.7(2)
C(1)–P–C(13)	101.5(2)	C(7)–P–C(13)	101.4(2)
O–Si(1)–C(14)	109.9(2)	O–Si(1)–C(16)	106.5(3)
O–Si(1)–C(17)	109.8(3)	C(14)–Si(1)–C(16)	110.4(3)
C(14)–Si(1)–C(17)	111.0(2)	C(16)–Si(1)–C(17)	109.0(3)
O–Si(2)–C(18)	110.9(3)	O–Si(2)–C(20)	104.3(2)
O–Si(2)–C(21)	110.1(2)	C(18)–Si(2)–C(20)	113.8(2)
C(18)–Si(2)–C(21)	107.0(2)	C(20)–Si(2)–C(21)	110.7(3)
Si(1)–O–Si(2)	136.2(2)	P–C(1)–C(2)	117.5(3)
P–C(1)–C(6)	124.9(5)	C(2)–C(1)–C(6)	117.4(6)
C(1)–C(2)–C(3)	121.0(4)	C(2)–C(3)–C(4)	120.0(6)
C(3)–C(4)–C(5)	119.9(7)	C(4)–C(5)–C(6)	120.3(5)
C(1)–C(6)–C(5)	121.3(6)	P–C(7)–C(8)	118.8(4)
P–C(7)–C(12)	123.4(4)	C(8)–C(7)–C(12)	117.7(5)
C(7)–C(8)–C(9)	121.0(5)	C(8)–C(9)–C(10)	120.3(6)
C(9)–C(10)–C(11)	120.4(7)	C(10)–C(11)–C(12)	120.6(5)
C(7)–C(12)–C(11)	119.9(5)	Pt–C(14)–Si(1)	112.2(3)
Pt–C(14)–C(15)	70.4(3)	Si(1)–C(14)–C(15)	126.3(4)
Pt–C(15)–C(14)	71.4(4)	Pt–C(18)–Si(2)	111.3(2)
Pt–C(18)–C(19)	69.9(3)	Si(2)–C(18)–C(19)	124.7(5)
Pt–C(19)–C(18)	71.5(3)	P–C(13)–C(13')	111.6(5)
P–Pt–M(1)	113	P–Pt–M(2)	114
M(1)–Pt–M(2)	134		

The symmetry element σ' is: $1 - x, 1 - y, 1 - z$. M(1) is the centre of C(14) and C(15). M(2) is the centre of C(18) and C(19).

Table 2
Atomic coordinates ($\times 10^4$) for **2**

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
Pt	3463.2(2)	3010.2(2)	8357.4(2)	29.31(5)
P	3244(1)	5103(1)	6563(1)	31(1)
Si(1)	1701(1)	1483(1)	11313(1)	40(1)
Si(2)	2573(1)	-37(1)	9572(1)	37(1)
O	1949(3)	2063	10905(3)	44(3)
C(1)	3670(5)	6534(4)	6635(4)	35(4)
C(2)	4802(5)	6245(5)	7166(5)	45(4)
C(3)	5250(6)	7299(6)	7164(5)	64(5)
C(4)	4567(7)	8647(6)	6657(5)	69(5)
C(5)	3455(7)	8948(6)	6150(6)	64(6)
C(6)	3013(6)	7896(5)	6131(5)	50(5)
C(7)	1576(5)	5704(5)	6166(4)	38(4)
C(8)	551(6)	5110(6)	7108(6)	58(6)
C(9)	-734(6)	5489(7)	6832(7)	78(7)
C(10)	-993(6)	6440(7)	5639(7)	82(7)
C(11)	-13(6)	7051(8)	4688(6)	77(7)
C(12)	1285(6)	6689(7)	4930(5)	61(6)
C(13)	4249(5)	5160(5)	5002(4)	36(4)
C(14)	3057(5)	2487(5)	10423(4)	38(4)
C(15)	2911(6)	3939(5)	9699(5)	48(5)
C(16)	1678(7)	676(7)	13098(5)	67(6)
C(17)	71(6)	2613(7)	10954(6)	68(7)
C(18)	3972(5)	895(4)	8606(4)	35(4)
C(19)	4086(5)	1818(5)	7259(5)	43(4)
C(20)	3050(6)	-1956(5)	10184(6)	56(5)
C(21)	1299(6)	669(6)	8508(5)	60(6)

*U*_{eq} is defined as one-third of the trace of the orthogonalised *U*_{*ij*} tensor.

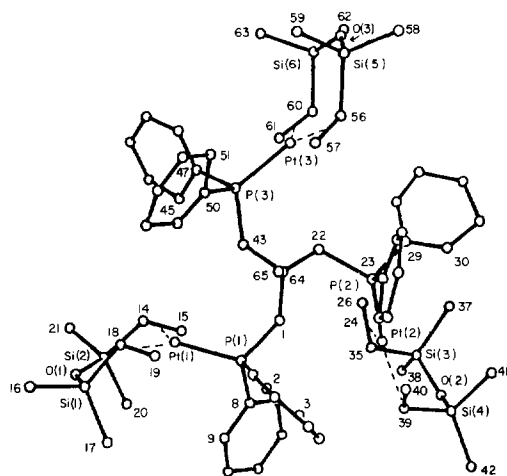


Fig. 2. The molecular structure of $[\{\text{Pt}(\eta\text{-CH}_2=\text{CHSiMe}_2)_2\text{O}\}_3(\text{TRIPHOS})]$ (**3**). Selected bond lengths (Å) and angles (deg): Pt(1)–P(1) = 2.308(7), Pt(2)–P(2) = 2.299(7), Pt(3)–P(3) = 2.293(7), Pt(1)–C(14) = 2.12(2), Pt(1)–C(15) = 2.14(3), Pt(1)–C(18) = 2.13(3), Pt(1)–C(18) = 2.13(3), Pt(2)–C(35) = 2.14(3), Pt(2)–C(36) = 2.10(3), Pt(2)–C(39) = 2.17(3), Pt(2)–C(40) = 2.16(3), Pt(3)–C(56) = 2.15(3), Pt(3)–C(57) = 2.18(3), Pt(3)–C(60) = 2.16(3), Pt(3)–C(61) = 2.12(4); Si(1)–O(1)–Si(2) = 133(1), Si(3)–O(2)–Si(4) = 134(1), Si(5)–O(3)–Si(6) = 135(1).

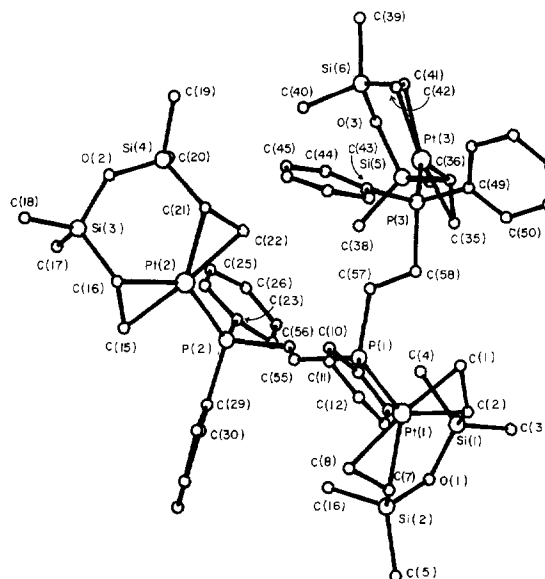


Fig. 3. The molecular structure of $[\{\text{Pt}(\eta\text{-CH}_2=\text{CHSiMe}_2)_2\text{O}\}_3(\text{TRIPHOS}')]$ (**4**). Selected bond lengths (Å) and angles (deg): Pt(1)–P(1) = 2.282(6), Pt(2)–P(2) = 2.266(7), Pt(3)–P(3) = 2.267(6), Pt(1)–C(1) = 2.12(2), Pt(1)–C(2) = 2.12(2), Pt(1)–C(7) = 2.11(2), Pt(1)–C(8) = 2.12(2), Pt(2)–C(15) = 2.08(2), Pt(2)–C(16) = 2.10(3), Pt(2)–C(21) = 2.14(2), Pt(2)–C(22) = 2.13(2), Pt(3)–C(35) = 2.18(2), Pt(3)–C(36) = 2.14(3), Pt(3)–C(14) = 2.16(2), Pt(3)–C(42) = 2.22(2); Si(1)–O(1)–Si(2) = 136(1), Si(3)–O(2)–Si(4) = 135(1), Si(5)–O(3)–Si(6) = 133.7(9).

minimises interaction between each of the trigonal planar Pt atoms and its pendant vinylsiloxane ligand. The molecules are chiral.

A recent review [14] identifies 15 types of ligation for a triphosphine, only one of which being the trinuclear triligate type now found for **3** and **4**. This type of bonding for the TRIPHOS and TRIPHOS' ligands, in which they bridge three metal atoms, observed in **3** and **4** appears to be uncommon and may be due to the substantial steric demands of the LL ligand. It is more usual that such a P₃ ligand is bonded to one (then referred to as a 'tripodal' ligand) or two metal atoms but rarely (in the absence of metal–metal bonds) three, cf. Ref. [14] and $[\text{Ni}(\text{CO})(\text{TRIPHOS})]$ [15]; exceptions include $[\text{NiCl}_2]\{\mu_3\text{-(Ph}_2\text{PCH}_2\text{CH}_2)_3\text{CMe}\}$ [16].

Table 7 shows selected bond lengths and angles for those bonds nearest to the platinum centres for complexes **2–4** and some related $\text{Pt}^0(\text{LL})\text{-phosphine}$ complexes. It is evident that the parameters are broadly similar and each complex has platinum in an approximately trigonal planar environment, with bonds to a phosphorus and the two centroids M of the vinyl groups; the sum of the bond angles at Pt is close to 360°. Other common features are that (i) the vinyl carbons and a phosphorus lie in the M₂PtP plane and (ii) each PtMSiOSiM ring has the chair conformation, with axial and equatorial methyl groups on each silicon. The biggest difference between the LL parameters in these

Table 3
Bond lengths (Å) and angles (deg) for **3**

<i>Bond lengths</i>			
Pt(1)–M1	2.01	Pt(1)–M2	2.02
Pt(1)–P(1)	2.308(7)	Pt(1)–C(14)	2.12(2)
Pt(1)–C(15)	2.14(3)	Pt(1)–C(18)	2.13(3)
Pt(1)–C(19)	2.15(3)	Pt(2)–M3	1.98
Pt(2)–M4	2.04	Pt(2)–P(2)	2.299(7)
Pt(2)–C(35)	2.14(3)	Pt(2)–C(36)	2.10(3)
Pt(2)–C(39)	2.17(3)	Pt(2)–C(40)	2.16(3)
Pt(3)–M5	2.05	Pt(3)–M6	2.03
Pt(3)–P(3)	2.293(7)	Pt(3)–C(56)	2.15(3)
Pt(3)–C(57)	2.18(3)	Pt(3)–C(60)	2.16(3)
Pt(3)–C(61)	2.12(4)	P(1)–C(1)	1.88(3)
P(1)–C(2)	1.87(3)	P(1)–C(8)	1.81(2)
P(2)–C(22)	1.90(3)	P(2)–C(23)	1.79(3)
P(2)–C(29)	1.74(3)	P(3)–C(43)	1.82(2)
P(3)–C(44)	1.80(3)	P(3)–C(50)	1.89(3)
Si(1)–O(1)	1.69(2)	Si(1)–C(14)	1.83(2)
Si(1)–C(16)	1.92(3)	Si(1)–C(17)	1.86(4)
Si(2)–O(1)	1.62(2)	Si(2)–C(18)	1.87(3)
Si(2)–C(20)	1.86(3)	Si(2)–C(21)	1.88(4)
Si(3)–O(2)	1.64(2)	Si(3)–C(35)	1.85(3)
Si(3)–C(37)	1.93(5)	Si(3)–C(38)	1.97(6)
Si(4)–O(2)	1.61(3)	Si(4)–C(39)	1.82(4)
Si(4)–C(41)	1.87(4)	Si(4)–C(42)	1.85(4)
Si(5)–O(3)	1.62(2)	Si(5)–C(56)	1.85(3)
Si(5)–C(58)	1.86(4)	Si(5)–C(59)	1.82(3)
Si(6)–O(3)	1.65(2)	Si(6)–C(60)	1.84(3)
Si(6)–C(62)	1.81(4)	Si(6)–C(63)	1.85(3)
O(4)–C(69)	1.44(10)	C(1)–C(64)	1.59(3)
C(2)–C(3)	1.36(4)	C(2)–C(7)	1.37(4)
C(3)–C(4)	1.42(5)	C(4)–C(5)	1.36(5)
C(5)–C(6)	1.36(4)	C(6)–C(7)	1.41(4)
C(8)–C(9)	1.39(4)	C(8)–C(13)	1.31(4)
C(9)–C(10)	1.40(4)	C(10)–C(11)	1.34(4)
C(11)–C(12)	1.43(5)	C(12)–C(13)	1.44(5)
C(14)–C(15)	1.41(4)	C(18)–C(19)	1.41(4)
C(22)–C(64)	1.48(3)	C(23)–C(24)	1.41(4)
C(23)–C(28)	1.35(4)	C(24)–C(25)	1.42(5)
C(25)–C(26)	1.42(4)	C(26)–C(27)	1.34(4)
C(27)–C(28)	1.42(5)	C(29)–C(30)	1.35(4)
C(29)–C(34)	1.43(4)	C(30)–C(31)	1.39(5)
C(31)–C(32)	1.49(6)	C(32)–C(33)	1.46(5)
C(33)–C(34)	1.30(5)	C(35)–C(36)	1.51(4)
C(39)–C(40)	1.43(4)	C(43)–C(64)	1.66(3)
C(44)–C(45)	1.48(4)	C(44)–C(49)	1.40(4)
C(45)–C(46)	1.43(4)	C(46)–C(47)	1.36(4)
C(47)–C(48)	1.40(5)	C(48)–C(49)	1.39(5)
C(50)–C(51)	1.41(4)	C(50)–C(55)	1.27(4)
C(51)–C(52)	1.41(5)	C(52)–C(53)	1.24(6)
C(53)–C(54)	1.37(6)	C(54)–C(55)	1.45(5)
C(56)–C(57)	1.38(5)	C(60)–C(61)	1.40(5)
C(64)–C(65)	1.57(4)	C(66)–C(67)	1.78(8)
C(67)–C(68)	1.03(8)	C(68)–C(69)	1.26(13)
<i>Bond angles</i>			
M1–Pt(1)–M2	131.9	M1–Pt(1)–P(1)	120.4
M2–Pt(1)–P(1)	107.2	M3–Pt(2)–M4	131.4
M3–Pt(2)–P(2)	106.3	M4–Pt(2)–P(2)	122.0
M5–Pt(3)–M6	132.0	M5–Pt(3)–P(3)	119.7
M6–Pt(3)–P(3)	108.2	Pt(1)–P(1)–C(1)	119.2(8)
Pt(1)–P(1)–C(2)	122.3(9)	Pt(1)–P(1)–C(8)	108.1(9)
C(1)–P(1)–C(2)	103(1)	C(1)–P(1)–C(8)	101(1)
C(2)–P(1)–C(8)	99(1)	Pt(2)–P(2)–C(22)	117.3(9)

Table 3 (continued)

<i>Bond angles</i>			
Pt(2)–P(2)–C(23)	121.2(8)	Pt(2)–P(2)–C(29)	105.9(8)
C(22)–P(2)–C(23)	104(1)	C(22)–P(2)–C(29)	104(1)
C(23)–P(2)–C(29)	103(1)	Pt(3)–P(3)–C(43)	115.8(8)
Pt(3)–P(3)–C(44)	110(1)	Pt(3)–P(3)–C(50)	120.0(9)
C(43)–P(3)–C(44)	103(1)	C(43)–P(3)–C(50)	106(1)
C(44)–P(3)–C(50)	99(1)	O(1)–Si(1)–C(14)	109(1)
O(1)–Si(1)–C(16)	106(1)	O(1)–Si(1)–C(17)	113(1)
C(14)–Si(1)–C(16)	112(1)	C(14)–Si(1)–C(17)	109(2)
C(16)–Si(1)–C(17)	107(2)	O(1)–Si(2)–C(18)	111(1)
O(1)–Si(2)–C(20)	109(1)	O(1)–Si(2)–C(21)	106(1)
C(18)–Si(2)–C(20)	110(1)	C(18)–Si(2)–C(21)	110(1)
C(20)–Si(2)–C(21)	111(2)	O(2)–Si(3)–C(35)	108(1)
O(2)–Si(3)–C(37)	110(2)	O(2)–Si(3)–C(38)	107(2)
C(35)–Si(3)–C(37)	112(2)	C(35)–Si(3)–C(38)	109(2)
C(37)–Si(3)–C(38)	112(2)	O(2)–Si(4)–C(39)	110(1)
O(2)–Si(4)–C(41)	110(2)	O(2)–Si(4)–C(42)	111(2)
C(39)–Si(4)–C(41)	107(2)	C(39)–Si(4)–C(42)	111(2)
C(41)–Si(4)–C(42)	107(2)	O(3)–Si(5)–C(56)	111(1)
O(3)–Si(5)–C(58)	106(1)	O(3)–Si(5)–C(59)	109(1)
C(56)–Si(5)–C(58)	111(2)	C(56)–Si(5)–C(59)	107(1)
C(58)–Si(5)–C(59)	113(2)	O(3)–Si(6)–C(60)	109(1)
O(3)–Si(6)–C(62)	105(1)	O(3)–Si(6)–C(63)	114(1)
C(60)–Si(6)–C(62)	111(2)	C(60)–Si(6)–C(63)	108(1)
C(62)–Si(6)–C(63)	110(2)	Si(1)–O(1)–Si(2)	133(1)
Si(3)–O(2)–Si(4)	134(1)	Si(5)–O(3)–Si(6)	135(1)
P(1)–C(1)–C(64)	122(2)	P(1)–C(2)–C(3)	119(2)
P(1)–C(2)–C(7)	119(2)	C(3)–C(2)–C(7)	122(3)
C(2)–C(3)–C(4)	120(3)	C(3)–C(4)–C(5)	118(3)
C(4)–C(5)–C(6)	121(3)	C(5)–C(6)–C(7)	121(3)
C(2)–C(7)–C(6)	117(3)	P(1)–C(8)–C(9)	118(2)
P(1)–C(8)–C(13)	123(2)	C(9)–C(8)–C(13)	119(2)
C(8)–C(9)–C(10)	123(3)	C(9)–C(10)–C(11)	116(3)
C(10)–C(11)–C(12)	123(3)	C(11)–C(12)–C(13)	116(3)
C(8)–C(13)–C(12)	121(3)	Si(1)–C(14)–C(15)	124(2)
Si(2)–C(18)–C(19)	118(2)	P(2)–C(22)–C(64)	118(2)
P(2)–C(23)–C(24)	123(2)	P(2)–C(23)–C(28)	123(2)
C(24)–C(23)–C(28)	114(3)	C(23)–C(24)–C(25)	123(2)
C(24)–C(25)–C(26)	118(3)	C(25)–C(26)–C(27)	122(3)
C(26)–C(27)–C(28)	116(3)	C(23)–C(28)–C(27)	127(3)
P(2)–C(29)–C(30)	123(2)	P(2)–C(29)–C(34)	128(3)
C(30)–C(29)–C(34)	110(3)	C(29)–C(30)–C(31)	132(4)
C(30)–C(31)–C(32)	109(3)	C(31)–C(32)–C(33)	125(3)
C(32)–C(33)–C(34)	111(3)	C(29)–C(34)–C(33)	132(3)
Si(3)–C(35)–C(36)	118(2)	Si(4)–C(39)–C(40)	123(3)
P(3)–C(43)–C(64)	118(2)	P(3)–C(44)–C(45)	122(2)
P(3)–C(44)–C(49)	117(2)	C(45)–C(44)–C(49)	119(3)
C(44)–C(45)–C(46)	115(2)	C(45)–C(46)–C(47)	124(3)
C(46)–C(47)–C(48)	118(3)	C(47)–C(48)–C(49)	122(3)
C(44)–C(49)–C(48)	121(3)	P(3)–C(50)–C(51)	112(2)
P(3)–C(50)–C(55)	124(2)	C(51)–C(50)–C(55)	124(3)
C(50)–C(51)–C(52)	110(3)	C(51)–C(52)–C(53)	122(3)
C(52)–C(53)–C(54)	132(4)	C(53)–C(54)–C(55)	104(3)
C(50)–C(55)–C(54)	127(3)	Si(5)–C(56)–C(57)	129(2)
Si(6)–C(60)–C(61)	129(2)	C(1)–(64)–C(22)	108(2)
C(1)–C(64)–C(43)	106(2)	C(1)–C(64)–C(65)	113(2)
C(22)–C(64)–C(43)	107(2)	C(22)–C(64)–C(65)	118(2)
C(43)–C(64)–C(65)	104(2)	C(66)–C(67)–C(68)	93(6)
C(67)–C(68)–C(69)	128(8)	O(4)–C(69)–C(68)	133(8)

M1, M2, M3, M4, M5, and M6 are the mid-points of the C=C bonds 14–15, 18–19, 35–36, 39–40, 56–57 and 60–61 respectively.

Table 4
Atomic coordinates ($\times 10^4$) for **3**

	x	y	z
Pt(1)	1908.1(7)	70.3(3)	2927.4(8)
Pt(2)	-218.0(8)	1577.0(3)	1938.8(9)
Pt(3)	3757.1(7)	1493.0(3)	5426.9(8)
P(1)	1245(5)	509(2)	2076(5)
P(2)	1300(5)	1682(2)	2612(5)
P(3)	3550(5)	962(2)	5029(5)
Si(1)	2286(6)	-693(2)	2556(6)
Si(2)	1017(6)	-547(2)	4079(7)
Si(3)	-2264(8)	1821(3)	2524(8)
Si(4)	-1962(7)	1892(3)	432(7)
Si(5)	5273(6)	2100(2)	5910(7)
Si(6)	4080(6)	1931(2)	7470(7)
O(1)	1659(13)	-769(4)	3475(15)
O(2)	-2552(14)	1879(6)	1342(16)
O(3)	4798(13)	2145(5)	6899(14)
C(1)	1206(19)	902(6)	2730(19)
C(2)	1560(19)	629(6)	854(19)
C(3)	907(18)	779(7)	201(20)
C(4)	1118(23)	860(9)	-746(24)
C(5)	2019(26)	832(6)	-915(20)
C(6)	2674(24)	684(6)	-255(21)
C(7)	2465(22)	588(8)	675(21)
C(8)	7(16)	419(6)	1726(18)
C(9)	-242(21)	139(7)	1261(22)
C(10)	-1170(22)	51(8)	937(27)
C(11)	-1831(20)	262(7)	1105(22)
C(12)	-1629(24)	558(11)	1614(26)
C(13)	-650(21)	631(8)	1891(22)
C(14)	2866(18)	-304(5)	2765(21)
C(15)	2918(19)	-75(6)	2017(24)
C(16)	3163(22)	-1039(6)	2556(28)
C(17)	1552(26)	-689(9)	1332(27)
C(18)	1503(18)	-130(7)	4224(20)
C(19)	897(21)	125(7)	3919(22)
C(20)	-197(21)	-537(8)	3414(24)
C(21)	1059(24)	-739(9)	5322(24)
C(22)	1867(18)	1396(7)	3588(21)
C(23)	2196(16)	1748(5)	1853(17)
C(24)	2180(20)	1607(6)	922(24)
C(25)	2905(24)	1654(6)	341(21)
C(26)	3682(24)	1842(8)	741(22)
C(27)	3733(24)	1979(6)	1629(24)
C(28)	2941(25)	1939(8)	2121(29)
C(29)	1267(16)	2044(8)	3235(20)
C(30)	987(24)	2320(8)	2778(28)
C(31)	947(29)	2633(7)	3109(32)
C(32)	1183(26)	2635(8)	3196(33)
C(33)	1441(34)	2353(7)	4803(27)
C(34)	1484(28)	2098(9)	4266(26)
C(35)	-1383(19)	1496(6)	2709(20)
C(36)	-491(19)	1557(7)	3394(20)
C(37)	-1787(34)	2216(12)	3141(35)
C(38)	-3404(37)	1678(14)	3032(37)
C(39)	-1112(22)	1566(11)	538(23)
C(40)	-159(17)	1611(9)	382(18)
C(41)	-1295(21)	2276(9)	455(29)
C(42)	-2740(29)	1878(12)	-754(31)
C(43)	2451(16)	860(6)	4276(19)
C(44)	3516(21)	725(7)	6121(19)
C(45)	2753(21)	497(8)	6211(20)
C(46)	2843(22)	321(7)	7111(23)
C(47)	3650(21)	306(7)	7757(20)

Table 4 (continued)

	x	y	z
C(48)	4399(22)	501(10)	7587(23)
C(49)	4344(27)	701(7)	6777(21)
C(50)	4494(19)	735(7)	4496(18)
C(51)	5370(20)	888(6)	4687(28)
C(52)	6068(22)	694(11)	4371(32)
C(53)	5880(30)	437(11)	3932(29)
C(54)	5095(27)	247(6)	3840(24)
C(55)	4377(23)	458(6)	4116(23)
C(56)	4454(16)	1904(8)	4936(21)
C(57)	4612(22)	1651(8)	4332(23)
C(58)	5578(24)	2512(10)	5537(28)
C(59)	6287(23)	1839(8)	6165(26)
C(60)	3173(19)	1750(8)	6562(23)
C(61)	2854(22)	1433(8)	6505(25)

Table 5
Bond lengths (Å) and angles (deg) for **4**

Bond lengths			
Pt(1)–M1	2.01	Pt(1)–M2	1.99
Pt(1)–P(1)	2.282(6)	Pt(1)–C(1)	2.12(2)
Pt(1)–C(2)	2.13(2)	Pt(1)–C(7)	2.11(2)
Pt(1)–C(8)	2.12(2)	Pt(2)–M3	1.97
Pt(2)–M4	2.01	Pt(2)–P(2)	2.266(7)
Pt(2)–C(15)	2.08(2)	Pt(2)–C(16)	2.10(3)
Pt(2)–C(21)	2.14(2)	Pt(2)–C(22)	2.13(2)
Pt(3)–M5	2.03	Pt(3)–M6	2.07
Pt(3)–P(3)	2.267(6)	Pt(3)–C(35)	2.18(2)
Pt(3)–C(36)	2.14(3)	Pt(3)–C(41)	2.16(2)
Pt(3)–C(42)	2.22(2)	P(1)–C(9)	1.85(2)
P(1)–C(55)	1.86(3)	P(1)–C(57)	1.85(2)
P(2)–C(23)	1.88(2)	P(2)–C(29)	1.81(2)
P(2)–C(56)	1.85(3)	P(3)–C(43)	1.82(3)
P(3)–C(49)	1.80(3)	P(3)–C(58)	1.85(2)
Si(1)–O(1)	1.66(2)	Si(1)–C(2)	1.87(3)
Si(1)–C(3)	1.79(3)	Si(1)–C(4)	1.89(3)
Si(2)–O(1)	1.58(2)	Si(2)–C(5)	1.87(3)
Si(2)–C(6)	1.84(3)	Si(2)–C(7)	1.86(3)
Si(3)–O(2)	1.65(2)	Si(3)–C(16)	1.87(2)
Si(3)–C(17)	1.85(3)	Si(3)–C(18)	1.87(4)
Si(4)–O(2)	1.62(2)	Si(4)–C(19)	1.84(2)
Si(4)–C(20)	1.88(3)	Si(4)–C(21)	1.92(2)
Si(5)–O(3)	1.63(2)	Si(5)–C(36)	1.87(3)
Si(5)–C(37)	1.91(4)	Si(5)–C(38)	1.79(3)
Si(6)–O(3)	1.63(2)	Si(6)–C(39)	1.89(3)
Si(6)–C(40)	1.86(3)	Si(6)–C(41)	1.85(3)
C(1)–C(2)	1.38(3)	C(7)–C(8)	1.47(4)
C(9)–C(10)	1.36(4)	C(9)–C(14)	1.35(3)
C(10)–C(11)	1.38(3)	C(11)–C(12)	1.34(4)
C(12)–C(13)	1.34(5)	C(13)–C(14)	1.45(4)
C(15)–C(16)	1.38(3)	C(21)–C(22)	1.44(4)
C(23)–C(24)	1.37(3)	C(23)–C(28)	1.38(4)
C(24)–C(25)	1.38(4)	C(25)–C(26)	1.36(5)
C(26)–C(27)	1.40(4)	C(27)–C(28)	1.37(4)
C(29)–C(30)	1.40(3)	C(29)–C(34)	1.41(3)
C(30)–C(31)	1.43(3)	C(31)–C(32)	1.40(4)
C(32)–C(33)	1.39(4)	C(33)–C(34)	1.39(3)
C(35)–C(36)	1.46(3)	C(41)–C(42)	1.40(3)
C(43)–C(44)	1.35(4)	C(43)–C(48)	1.44(3)
C(44)–C(45)	1.38(4)	C(45)–C(46)	1.34(4)
C(46)–C(47)	1.35(4)	C(47)–C(48)	1.42(4)
C(49)–C(50)	1.35(4)	C(49)–C(54)	1.38(3)
C(50)–C(51)	1.41(4)	C(51)–C(52)	1.42(4)

Table 5 (continued)

C(52)–C(53)	1.33(5)	C(53)–C(54)	1.43(4)
C(55)–C(56)	1.56(3)	C(57)–C(58)	1.52(4)
<i>Bond angles</i>			
M1–Pt(1)–M2	132.4	M1–Pt(1)–P(1)	117.8
M2–Pt(1)–P(1)	109.8	M3–Pt(2)–M4	134.3
M3–Pt(2)–P(2)	116.6	M4–Pt(2)–P(2)	109.1
M5–Pt(3)–M6	133.3	M5–Pt(3)–P(3)	112.2
M6–Pt(3)–P(3)	114.0	Pt(1)–P(1)–C(9)	114.2(8)
Pt(1)–P(1)–C(55)	112.1(7)	Pt(1)–P(1)–C(57)	121.8(9)
C(9)–P(1)–C(55)	102(1)	C(9)–P(1)–C(57)	104(1)
C(55)–P(1)–C(57)	100(1)	Pt(2)–P(2)–C(23)	113.0(8)
Pt(2)–P(2)–C(29)	119.3(8)	Pt(2)–P(2)–C(56)	114.7(7)
C(23)–P(2)–C(29)	106(1)	C(23)–P(2)–C(56)	99(1)
C(29)–P(2)–C(56)	102(1)	Pt(3)–P(3)–C(43)	117.0(7)
Pt(3)–P(3)–C(49)	111.0(7)	Pt(3)–P(3)–C(58)	116.3(8)
C(43)–P(3)–C(49)	105(1)	C(43)–P(3)–C(58)	102(1)
C(49)–P(3)–C(58)	104(1)	O(1)–Si(1)–C(2)	107.9(8)
O(1)–Si(1)–C(3)	107(1)	O(1)–Si(1)–C(4)	112(1)
C(2)–Si(1)–C(3)	112(1)	C(2)–Si(1)–C(4)	109(1)
C(3)–Si(1)–C(4)	109(1)	O(1)–Si(2)–C(5)	106(1)
O(1)–Si(2)–C(6)	111(1)	O(1)–Si(2)–C(7)	108(1)
C(5)–Si(2)–C(6)	110(1)	C(5)–Si(2)–C(7)	110(1)
C(6)–Si(2)–C(7)	110(1)	O(2)–Si(3)–C(16)	110(1)
O(2)–Si(3)–C(17)	110(1)	O(2)–Si(3)–C(18)	107(1)
C(16)–Si(3)–C(17)	108(1)	C(16)–Si(3)–C(18)	113(1)
C(17)–Si(3)–C(18)	109(2)	O(2)–Si(4)–C(19)	107(1)
O(2)–Si(4)–C(20)	109(1)	O(2)–Si(4)–C(21)	108.4(9)
C(19)–Si(4)–C(20)	109(1)	C(19)–Si(4)–C(21)	111(1)
C(20)–Si(4)–C(21)	112(1)	O(3)–Si(5)–C(36)	110.7(9)
O(3)–Si(5)–C(37)	105(1)	O(3)–Si(5)–C(38)	110(1)
C(36)–Si(5)–C(37)	110(1)	C(36)–Si(5)–C(38)	110(1)
C(37)–Si(5)–C(38)	112(2)	O(3)–Si(6)–C(39)	106(1)
O(3)–Si(6)–C(40)	106(1)	O(3)–Si(6)–C(41)	112(1)
C(39)–Si(6)–C(40)	115(1)	C(39)–Si(6)–C(41)	110(1)
C(40)–Si(6)–C(41)	108(1)	Si(1)–O(1)–Si(2)	136(1)
Si(3)–O(2)–Si(4)	135(1)	Si(5)–O(3)–Si(6)	133.7(9)
Si(1)–C(2)–C(1)	123(2)	Si(2)–C(7)–C(8)	125(2)
P(1)–C(9)–S(10)	122(2)	P(1)–C(9)–C(14)	116(2)
C(10)–C(9)–C(14)	122(2)	C(9)–C(10)–C(11)	120(2)
C(10)–C(11)–C(12)	122(3)	C(11)–C(12)–C(13)	118(2)
C(12)–C(13)–C(14)	123(3)	C(9)–C(14)–C(13)	115(3)
Si(3)–C(16)–C(15)	127(2)	Si(4)–C(21)–C(22)	123(2)
P(2)–C(23)–C(24)	115(2)	P(2)–C(23)–C(28)	119(2)
C(24)–C(23)–C(28)	125(2)	C(23)–C(24)–C(25)	117(3)
C(24)–C(25)–C(26)	121(3)	C(25)–C(26)–C(27)	118(3)
C(26)–C(27)–C(28)	123(3)	C(23)–C(28)–C(27)	114(2)
P(2)–C(29)–C(30)	122(1)	P(2)–C(29)–C(34)	119(2)
C(30)–C(29)–C(34)	118(2)	C(29)–C(30)–C(31)	117(2)
C(30)–C(31)–C(32)	123(2)	C(31)–C(32)–C(33)	119(2)
C(32)–C(33)–C(34)	118(2)	C(29)–C(34)–C(33)	124(2)
Si(5)–C(36)–C(35)	122(2)	Si(6)–C(41)–C(42)	130(2)
P(3)–C(43)–C(44)	122(2)	P(3)–C(43)–C(48)	120(2)
C(44)–C(43)–C(48)	119(2)	C(43)–C(44)–C(45)	120(2)
C(44)–C(45)–C(46)	123(3)	C(45)–C(46)–C(47)	119(3)
C(46)–C(47)–C(48)	121(3)	C(43)–C(48)–C(47)	118(2)
P(3)–C(49)–C(50)	121(2)	P(3)–C(49)–C(54)	124(2)
C(50)–C(49)–C(54)	116(2)	C(49)–C(50)–C(51)	121(2)
C(50)–C(51)–C(52)	123(3)	C(51)–C(52)–C(53)	118(3)
C(52)–C(53)–C(54)	120(3)	C(49)–C(54)–C(53)	122(3)
P(1)–C(55)–C(56)	108(2)	P(2)–C(56)–C(55)	112(2)
P(1)–C(55)–C(58)	115(1)	P(3)–C(58)–C(57)	110(2)

M1, M2, M3, M4, M5, and M6 are the midpoints of the vinyl C=C bonds C(1)–C(2), C(7)–C(8), C(15)–C(16), C(21)–C(22), C(35)–C(36) and C(41)–C(42) respectively.

Table 6

Atomic coordinates ($\times 10^4$) for 4

	x	y	z	U_{eq}
Pt(1)	–766.9(8)	–1781.1(6)	2176.4(5)	48.7(3)
Pt(2)	2101.9(7)	1627.5(6)	1370.9(4)	42.5(3)
Pt(3)	556.8(7)	2441.7(7)	4681.0(5)	50.3(3)
P(1)	–898(5)	–311(4)	2058(3)	44(2)
P(2)	2188(4)	147(4)	1456(3)	43(2)
P(3)	–1025(5)	2204(4)	3901(3)	48(3)
Si(1)	630(7)	–2934(5)	3100(4)	74(4)
Si(2)	394(6)	–3819(5)	1588(3)	67(3)
Si(3)	3265(6)	3186(5)	836(4)	69(3)
Si(4)	3185(6)	3816(5)	2328(4)	60(3)
Si(5)	2863(6)	1513(5)	4929(4)	64(3)
Si(6)	2966(6)	3619(5)	5186(4)	66(3)
O(1)	658(13)	–3755(11)	2363(7)	80(8)
O(2)	3342(14)	3929(10)	1617(8)	72(8)
O(3)	3420(11)	2600(10)	5188(7)	61(7)
C(1)	725(22)	–1391(15)	3234(11)	83(12)
C(2)	–658(19)	–2364(15)	2983(9)	55(10)
C(3)	715(22)	–3528(19)	3721(12)	88(14)
C(4)	1800(23)	–1993(22)	3384(17)	129(18)
C(5)	33(28)	–5108(18)	1081(17)	120(18)
C(6)	1557(22)	–3356(20)	1356(13)	99(14)
C(7)	785(22)	–3130(17)	1435(12)	77(13)
C(8)	–812(23)	–2374(17)	1120(12)	76(13)
C(9)	2237(15)	–140(16)	1590(11)	52(10)
C(10)	–2419(20)	639(17)	1390(11)	73(12)
C(11)	–3424(20)	712(21)	1026(12)	96(14)
C(12)	–4247(19)	51(20)	877(14)	92(14)
C(13)	–4038(23)	741(23)	1036(15)	107(17)
C(14)	–3019(17)	–843(18)	1450(13)	75(12)
C(15)	2210(21)	1260(15)	357(11)	68(12)
C(16)	2142(18)	2228(17)	601(11)	62(11)
C(17)	4530(24)	2601(25)	786(14)	114(18)
C(18)	3083(27)	3912(24)	252(14)	132(19)
C(19)	2991(22)	5004(17)	2887(13)	81(13)
C(20)	4442(19)	3393(19)	2740(12)	75(13)
C(21)	1943(18)	2940(16)	2132(10)	60(11)
C(22)	1946(21)	2163(16)	2404(12)	73(12)
C(23)	3448(15)	26(16)	2052(11)	55(10)
C(24)	4302(18)	669(17)	2155(13)	77(12)
C(25)	5243(21)	606(19)	2588(15)	101(15)
C(26)	5329(23)	–74(23)	2894(16)	116(17)
C(27)	4437(21)	–734(19)	2744(15)	96(15)
C(28)	3481(20)	–719(17)	2313(11)	74(12)
C(29)	2034(17)	–874(14)	688(10)	46(9)
C(30)	2787(19)	–1555(17)	609(11)	63(12)
C(31)	2576(21)	–2334(16)	–19(13)	76(13)
C(32)	1655(24)	–2447(21)	–541(14)	105(16)
C(33)	918(20)	–1764(17)	–452(11)	68(12)
C(34)	1150(19)	–979(17)	139(10)	62(11)
C(35)	557(20)	937(15)	4586(12)	74(12)
C(36)	1484(19)	1496(15)	5101(12)	66(11)
C(37)	3777(24)	884(21)	5460(19)	133(19)
C(38)	2788(27)	973(25)	4036(15)	125(19)
C(39)	3919(24)	4559(19)	5907(16)	110(16)
C(40)	2921(24)	3683(20)	4318(14)	105(16)
C(41)	1580(19)	3707(15)	5328(13)	69(12)
C(42)	683(19)	4017(16)	4976(12)	67(12)
C(43)	–1194(19)	2950(14)	3360(11)	59(10)
C(44)	–342(18)	3361(16)	3237(11)	60(11)
C(45)	–502(21)	3854(20)	2779(14)	93(15)
C(46)	–1480(23)	3984(19)	2453(12)	90(14)
C(47)	–2356(22)	3636(18)	2589(12)	97(14)

Table 6 (continued)

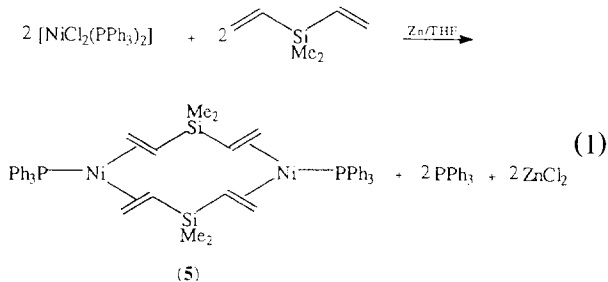
	x	y	z	U_{eq}
C(48)	-2262(21)	3101(17)	3043(11)	72(12)
C(49)	-2144(18)	2390(15)	4311(11)	57(11)
C(50)	-2668(19)	1654(16)	4392(13)	75(12)
C(51)	-3481(23)	1813(18)	4768(15)	105(15)
C(52)	-3869(22)	2649(20)	4981(15)	101(15)
C(53)	-3369(21)	3402(19)	4919(16)	109(15)
C(54)	-2508(19)	3272(16)	4570(12)	67(12)
C(55)	9(16)	-86(13)	1532(10)	46(9)
C(56)	1185(16)	-187(15)	1879(10)	55(10)
C(57)	-556(17)	795(15)	2802(11)	55(10)
C(58)	-1356(17)	997(16)	3261(12)	61(11)

U_{eq} is defined as one-third of the trace of the orthogonalised U_{ij} tensor.

phosphine complexes and the chelating LL ligand in $[\{\text{Pt}(\overline{\text{LL}})\}_2(\mu\text{-LL})]$ is in the M–Pt–M bond angles, 124° in the latter but significantly longer in the phosphine complexes.

We have previously reported on the synthesis of nickel(0) complexes containing phosphines and vinylsiloxanes as co-ligands. The complex $[\text{Ni}(\overline{\text{LL}})(\text{PPh}_3)]$ was prepared by either (i) the displacement of a bridging vinylsiloxane ligand from $[\{\text{Ni}(\overline{\text{LL}})\}_2(\mu\text{-LL})]$ or (ii) the zinc reduction of the nickel(II) complex $[\text{NiCl}_2(\text{PPh}_3)_2]$ in the presence of the vinylsiloxane.

The zinc reduction of $[\text{NiCl}_2(\text{PPh}_3)_2]$ in the presence of the divinylsilane Vi_2SiMe_2 yielded the dinuclear complex $[\{\text{Ni}(\mu\text{-Vi}_2\text{SiMe}_2)\text{PPh}_3\}_2]$ (**5**), Eq. (1).



The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopic data for **5** showed only one sharp signal (even down to 143 K) for

the protons and carbons of the SiMe_2 groups, due to the presence of an axis of symmetry bisecting the silicon atoms. Thus, unlike for complexes **1–4**, which show axial and equatorial methyl groups on silicon, the methyl groups on silicon are not differentiated.

Figs. 4 and 5 show the molecular structure of **5** (the carbon atoms of the phenyl groups are numbered sequentially around the rings starting with the *ipso*-C atom); structural parameters and atomic coordinates are listed in Tables 8 and 9 respectively. Fig. 4 shows that, as in the Pt(0) complexes, the vinylsilane and phosphine ligands are coordinated in a trigonal planar geometry about each nickel atom. Fig. 5 shows the non-planarity of the vinyl groups on each silane ligand. This view shows how a methyl group on a silicon atom can be described as being axial to one coordination plane and equatorial to the other.

3. Experimental

3.1. Synthesis of bis(tetramethyldivinylsiloxane)- $\{(\text{bis}(\text{diphenylphosphino})\text{methane})\text{diplatinum}(0)$ (**1**)

Bis(diphenylphosphino)methane (0.34 g, 0.90 mmol) was added slowly to a rapidly stirring solution of tris(tetramethyldivinylsiloxane)diplatinum(0) (0.85 g, 0.90 mmol) in toluene (10 ml) at 0°C . The mixture was allowed to warm to room temperature and was stirred for 1 h. The solvent was removed in vacuo to leave a white oil. Addition of *n*-pentane (5 ml) induced precipitation of a colourless solid. The mixture was filtered, the solid was washed with *n*-pentane (2×3 ml), and dried in vacuo to yield the colourless solid title compound **1** (680 mg, 0.60 mmol, 66%). A further portion of **1** (180 mg, 0.16 mmol) was obtained from the filtrate by cooling to -30°C for ca. 12 h. Colourless crystals of **1**, m.p. $164\text{--}166^\circ\text{C}$ were obtained by recrystallisation from *n*-pentane.

Anal. Found: C, 42.7; H, 5.1. $\text{C}_{41}\text{H}_{58}\text{O}_2\text{P}_2\text{Pt}_2\text{Si}_4$ calc.: C, 43.0; H, 5.1%. ^1H NMR (C_7D_8 , 303 K,

Table 7
Selected bond lengths and angles for some Pt(LL)–phosphine complexes

Complex	Average Pt–M ^a /Å	Average C=C /Å	Average Pt–P /Å	Average M ^a –Pt–P /deg	Average M–Pt–M ^a /deg	Average Si–O–Si /deg	Ref.
$[\text{Pt}(\text{LL})(\text{PBu}_3)_2]$	— ^c	— ^c	2.384(2)	— ^c	— ^c	129.9(4)	[1]
$[\text{Pt}(\text{LL})(\text{P}(\text{C}_6\text{H}_4\text{Me-}p)_3)]$	2.023	1.42(1)	2.292(2)	113.5	133	134.5(4)	[5]
$[\text{Pt}(\text{LL})(\text{PPh}_2\text{CH}_2\text{CBu}_2\text{OH})]$	2.035	1.42(4)	2.308(5)	118.5, 112.8	128.4	132.2(9)	[5]
$[\text{Pt}(\text{LL})(\text{PPh}_3)_2]$	— ^c	1.43(2)	2.282(3)	— ^c	— ^c	135.3(5)	[17]
$[\{\text{Pt}(\text{LL})\}_2(\mu\text{-dppe})]$ 2	2.024	1.409(6)	2.282(1)	113.5	134	136.2	— ^b
$[\{\text{Pt}(\text{LL})\}_2(\mu_3\text{-TRIPHOS})]$ 3	2.02	1.41(5)	2.300(7)	120.7, 107.2	131.8	134(1)	— ^b
$[\{\text{Pt}(\text{LL})\}_3(\mu_3\text{-TRIPHOS})]$ 4	2.01	1.42(4)	2.272(7)	116.1, 110.4	133.3	135(1)	— ^b

^a M is the midpoint of a chelating Vi.

^b This work.

^c Not cited.

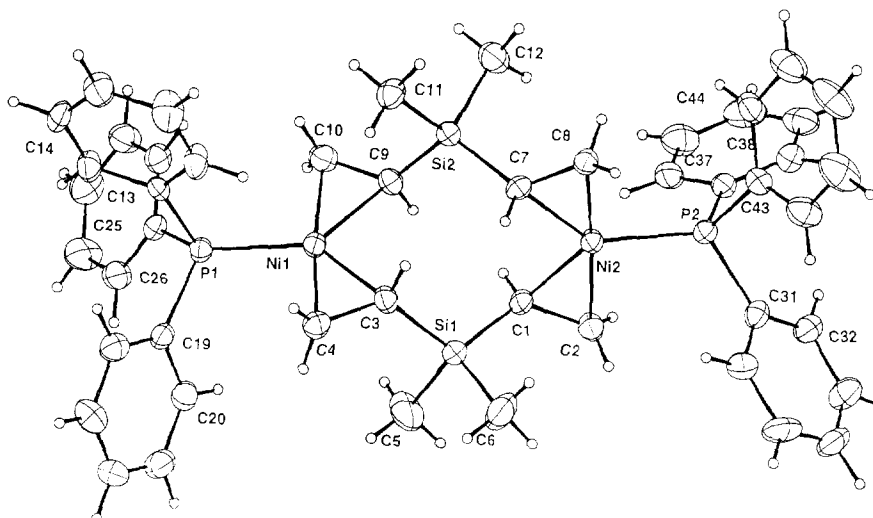


Fig. 4. The molecular structure of $[\{\text{Ni}(\mu\text{-ViSiMe}_2)(\text{PPh}_3)\}_2]$ (**5**). Selected bond lengths (Å) and angles (deg): Ni(1)–P(1) = 2.170(1), Ni(2)–P(2) = 2.167(1), Ni(1)–C(3) = 2.028(5), Ni(1)–C(4) = 1.990(5), Ni(1)–C(9) = 2.028(4), Ni(1)–C(10) = 2.005(5), Ni(2)–C(1) = 2.026(4), Ni(2)–C(2) = 1.999(5), Ni(2)–C(7) = 2.018(4), Ni(2)–C(8) = 1.981(5); C(1)–Si(1)–C(3) = 117.2(2), C(7)–Si(2)–C(9) = 116.4(2).

360 MHz) (labelling: (i) Vi: Si–C₁H₁=C₂H₂H₃ with H₁ trans to H₃; (ii) e = equatorial, a = axial) δ –0.42 (s, Me_e, 12H), 0.41 (s, Me_a, 12H), 2.08 (dd, H₃, 4H), 2.26 (m, H₁, 4H), 2.49 (dd, H₂, 4H), 3.96 (m, CH₂, 2H), 6.8–7.3 (m, Ph, 20H), $^3J(^1\text{H}_1\text{--}^1\text{H}_2)$ = 11.86 Hz, $^3J(^1\text{H}_1\text{--}^1\text{H}_3)$ = 13.76 Hz, $^2J(^1\text{H}_2\text{--}^1\text{H}_3)$ = 13.76 Hz, $^2J(^1\text{H}_2\text{--}^{195}\text{Pt})$ = 52 Hz, $^2J(^1\text{H}_1\text{--}^{195}\text{Pt})$ = 52 Hz, $^3J(\text{CH}_2\text{--}^{195}\text{Pt})$ = 33.4 Hz, $^2J(\text{CH}_2\text{--}^{31}\text{P})$ = 9.5 Hz. $^{13}\text{C}\{^1\text{H}\}$ NMR (C₇D₈, 303 K, 90 MHz): δ –2.0 (s, Me_e), 1.5 (s, Me_a), 32.2 (m, CH₂), 47.1 (d, C₂), 52.4 (s, C₁), 120–130 (m, Ph), $^1J(^{13}\text{C}_1\text{--}^{195}\text{Pt})$ = 164 Hz, $^1J(^{13}\text{C}_2\text{--}^{195}\text{Pt})$ = 116 Hz, $^2J(^{13}\text{C}_2\text{--}^{31}\text{P})$ = 10.9 Hz. $^{31}\text{P}\{^1\text{H}\}$ NMR (C₇D₈, 303 K, 32 MHz): δ 6.6 (s)

$^1J(^{31}\text{P}\text{--}^{195}\text{Pt})$ = 3700 Hz, $^3J(^{31}\text{P}\text{--}^{195}\text{Pt})$ = 34 Hz, $^2J(^{31}\text{P}\text{--}^{31}\text{P})$ = 22 Hz. $^{195}\text{Pt}\{^1\text{H}\}$ NMR (C₇D₈, 303 K, 17 MHz): δ –5541 (d), $^1J(^{195}\text{Pt}\text{--}^{31}\text{P})$ = 3705 Hz, $^3J(^{195}\text{Pt}\text{--}^{31}\text{P})$ = 34 Hz, $^4J(^{195}\text{Pt}\text{--}^{195}\text{Pt})$ = 17 Hz (from the Bruker Spectroscopic PANIC simulation program).

The ^{195}Pt chemical shifts for **1**, **2**, **3**, and **4** are reported relative to external aqueous K₂[PtCl₄].

3.2. Synthesis of bis(tetramethyldivinyldisiloxane)-bis(diphenylphosphino)ethane)diplatinum(0) (**2**)

This was prepared (0.19 g, 0.17 mmol, 63%) by a procedure similar to that described in Section 3.1.

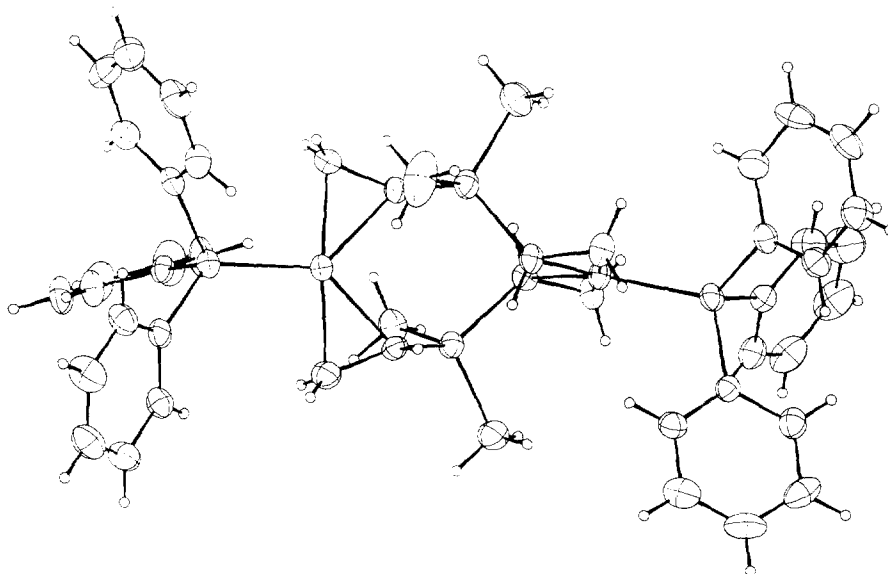


Fig. 5. The molecular structure of $[\{\text{Ni}(\mu\text{-ViSiMe}_2)(\text{PPh}_3)\}_2]$ (**5**). This view shows the non-planarity of the two vinyl coordination sites.

Table 8
Bond lengths (Å) and angles (deg) for 5

Bond lengths			
Ni(1)–C(3)	2.028(5)	Ni(1)–C(4)	1.990(5)
Ni(1)–C(9)	2.028(4)	Ni(1)–C(10)	2.005(5)
Ni(1)–P(1)	2.170(1)	Ni(1)–M(2)	1.883(5)
Ni(1)–M(4)	1.892(5)	Ni(2)–C(1)	2.026(4)
Ni(2)–C(2)	1.999(5)	Ni(2)–C(7)	2.018(4)
Ni(2)–C(8)	1.981(5)	Ni(2)–P(2)	2.167(1)
Ni(2)–M(1)	1.886(5)	Ni(2)–M(3)	1.874(5)
P(1)–C(13)	1.833(5)	P(1)–C(19)	1.834(5)
P(1)–C(25)	1.847(5)	P(2)–C(31)	1.832(5)
P(2)–C(37)	1.825(5)	P(2)–C(43)	1.836(5)
Si(2)–C(7)	1.859(5)	Si(2)–C(9)	1.862(5)
Si(2)–C(12)	1.862(5)	Si(2)–C(11)	1.883(5)
Si(1)–C(1)	1.837(5)	Si(1)–C(6)	1.859(6)
Si(1)–C(3)	1.860(5)	Si(1)–C(5)	1.874(6)
C(1)–C(2)	1.405(6)	C(3)–C(4)	1.399(6)
C(7)–C(8)	1.394(6)	C(9)–C(10)	1.390(7)
C(13)–C(18)	1.362(6)	C(13)–C(14)	1.382(6)
C(14)–C(15)	1.373(7)	C(15)–C(16)	1.365(7)
C(16)–C(17)	1.380(7)	C(17)–C(18)	1.399(7)
C(19)–C(24)	1.379(7)	C(19)–C(20)	1.385(6)
C(20)–C(21)	1.393(7)	C(21)–C(22)	1.372(8)
C(22)–C(23)	1.357(8)	C(23)–C(24)	1.382(7)
C(25)–C(30)	1.386(6)	C(25)–C(26)	1.388(6)
C(26)–C(27)	1.377(7)	C(27)–C(28)	1.364(7)
C(28)–C(29)	1.369(7)	C(29)–C(30)	1.374(7)
C(31)–C(32)	1.374(6)	C(31)–C(36)	1.384(6)
C(32)–C(33)	1.393(6)	C(33)–C(34)	1.354(7)
C(34)–C(35)	1.369(8)	C(35)–C(36)	1.399(6)
C(37)–C(42)	1.381(6)	C(37)–C(38)	1.390(6)
C(38)–C(39)	1.394(7)	C(39)–C(40)	1.384(8)
C(40)–C(41)	1.355(8)	C(41)–C(42)	1.369(7)
C(43)–C(48)	1.378(7)	C(43)–C(44)	1.384(6)
C(44)–C(45)	1.382(7)	C(45)–C(46)	1.377(8)
C(46)–C(47)	1.370(8)	C(47)–C(48)	1.377(7)
C(54)–C(55)	1.26(2)		
Bond angles			
M(2)–Ni(1)–M(4)	132.4(2)	M(3)–Ni(2)–M(1)	135.4(2)
P(1)–Ni(1)–M(2)	112.5(2)	P(2)–Ni(2)–M(1)	110.3(2)
P(1)–Ni(1)–M(4)	114.8(2)	P(2)–Ni(2)–M(3)	114.2(2)
C(13)–P(1)–C(19)	104.5(2)	C(13)–P(1)–C(25)	100.6(2)
C(19)–P(1)–C(25)	101.5(2)	C(13)–P(1)–Ni(1)	110.8(2)
C(19)–P(1)–Ni(1)	115.5(2)	C(25)–P(1)–Ni(1)	121.9(2)
C(37)–P(2)–C(32)	106.0(2)	C(37)–P(2)–C(43)	101.5(2)
C(31)–P(2)–C(43)	101.2(2)	C(37)–P(2)–Ni(2)	109.8(2)
C(7)–Si(2)–C(9)	116.4(2)	C(43)–P(2)–Ni(2)	120.1(2)
C(9)–Si(2)–C(12)	116.9(2)	C(7)–Si(2)–C(12)	107.6(2)
C(9)–Si(2)–C(11)	108.4(2)	C(7)–Si(2)–C(11)	106.9(3)
C(1)–Si(1)–C(6)	108.7(2)	C(12)–Si(2)–C(11)	108.1(2)
C(6)–Si(1)–C(3)	108.6(2)	C(1)–Si(1)–C(3)	117.2(2)
C(6)–Si(1)–C(5)	108.3(3)	C(1)–Si(1)–C(5)	106.9(3)
C(6)–Si(1)–C(5)	108.2(3)	C(3)–Si(1)–C(5)	107.3(2)
C(2)–C(1)–Si(1)	123.1(3)	C(4)–C(3)–Si(1)	121.8(4)
C(8)–C(7)–Si(2)	122.3(3)	C(10)–C(9)–Si(2)	123.7(4)
C(18)–C(13)–C(14)	118.2(5)	C(18)–C(13)–P(1)	119.0(4)
C(14)–C(13)–P(1)	122.8(4)	C(15)–C(14)–C(13)	121.2(5)
C(16)–C(15)–C(14)	120.3(5)	C(15)–C(16)–C(17)	119.9(5)
C(16)–C(17)–C(18)	119.0(5)	C(13)–C(18)–C(17)	121.5(5)
C(24)–C(19)–C(20)	117.7(4)	C(24)–C(19)–P(1)	124.4(4)
C(20)–C(19)–P(1)	117.8(4)	C(19)–C(20)–C(21)	121.3(5)
C(22)–C(21)–C(20)	119.4(5)	C(23)–C(22)–C(21)	119.9(5)
C(22)–C(23)–C(24)	120.9(6)	C(19)–C(24)–C(23)	120.8(5)
C(30)–C(25)–C(26)	117.9(4)	C(30)–C(25)–P(1)	118.5(4)
C(26)–C(25)–P(1)	123.6(3)	C(27)–C(26)–C(25)	120.1(5)

Table 8 (continued)

Bond angles			
C(28)–C(27)–C(26)	121.4(5)	C(27)–C(28)–C(29)	119.0(5)
C(28)–C(29)–C(30)	120.5(5)	C(29)–C(30)–C(25)	121.0(5)
C(32)–C(31)–C(36)	118.9(4)	C(32)–C(31)–P(2)	124.0(4)
C(36)–C(31)–P(2)	117.1(4)	C(31)–C(32)–C(33)	120.5(5)
C(34)–C(33)–C(32)	119.9(5)	C(33)–C(34)–C(35)	121.0(5)
C(34)–C(35)–C(36)	119.2(5)	C(31)–C(36)–C(35)	120.3(5)
C(42)–C(37)–C(38)	118.0(4)	C(42)–C(37)–P(2)	119.1(4)
C(38)–C(37)–P(2)	122.9(4)	C(37)–C(38)–C(39)	120.3(5)
C(40)–C(39)–C(38)	119.8(5)	C(41)–C(40)–C(39)	119.6(5)
C(40)–C(41)–C(42)	120.9(6)	C(41)–C(42)–C(37)	121.4(5)
C(48)–C(43)–C(44)	117.2(5)	C(48)–C(43)–P(2)	123.6(4)
C(44)–C(43)–P(2)	119.1(4)	C(45)–C(44)–C(43)	121.6(5)
C(46)–C(45)–C(44)	119.9(5)	C(47)–C(46)–C(45)	119.2(6)
C(46)–C(47)–C(48)	120.4(6)	C(47)–C(48)–C(43)	121.7(5)
C(55)–C(54)–C(53)	108.8(11)	C(55)–C(54)–C(49)	130.8(11)

Table 9
Atomic coordinates ($\times 10^4$) for 5

	x	y	z	U_{eq}
Ni(1)	1499.0(5)	3233.9(4)	2788.9(4)	36(1)
Ni(2)	2691.4(5)	1412.5(4)	5332.1(4)	35(1)
P(1)	1043.1(11)	3939.2(9)	1697.4(7)	37(1)
P(2)	3513.2(11)	802.5(9)	6361.2(7)	38(1)
Si(1)	1425.5(13)	861.8(10)	3379.7(9)	45(1)
Si(2)	2426.4(12)	3784.3(10)	4785.3(8)	37(1)
C(1)	2757(4)	1146(3)	4128(3)	37(1)
C(2)	3111(4)	370(4)	4560(3)	44(1)
C(3)	684(4)	1948(4)	3270(3)	42(1)
C(4)	68(4)	2063(4)	2522(3)	48(2)
C(5)	1805(6)	501(5)	2361(3)	101(2)
C(6)	394(5)	–312(4)	3637(4)	94(2)
C(7)	1823(4)	2544(3)	5214(3)	35(1)
C(8)	2131(4)	2415(4)	6030(3)	42(1)
C(9)	2812(4)	3632(4)	3748(3)	37(1)
C(10)	2893(4)	4419(4)	3232(3)	49(2)
C(11)	1326(4)	4587(4)	4764(3)	51(2)
C(12)	3739(4)	4536(4)	5507(3)	58(2)
C(13)	293(4)	4966(3)	1920(3)	37(1)
C(14)	195(4)	5739(4)	1418(3)	49(1)
C(15)	–333(5)	6522(4)	1620(3)	57(2)
C(16)	–788(5)	6542(4)	2323(3)	64(2)
C(17)	–706(5)	5780(5)	2836(3)	72(2)
C(18)	–160(4)	4993(4)	2621(3)	56(2)
C(19)	62(4)	3027(3)	861(3)	40(1)
C(20)	398(5)	2147(4)	563(3)	53(2)
C(21)	–314(5)	1399(4)	–54(3)	67(2)
C(22)	–1386(5)	1514(4)	–352(3)	69(2)
C(23)	–1734(5)	2361(5)	–53(3)	71(2)
C(24)	–1015(4)	3123(4)	541(3)	50(2)
C(25)	2146(4)	4664(3)	1151(3)	40(1)
C(26)	2258(4)	4331(4)	362(3)	52(2)
C(27)	3094(5)	4923(4)	–9(3)	70(2)
C(28)	3832(5)	5839(4)	386(3)	66(2)
C(29)	3730(5)	6175(4)	1165(3)	57(2)
C(30)	2898(4)	5598(4)	1544(3)	47(1)
C(31)	3361(4)	–633(3)	6263(3)	40(1)
C(32)	4257(4)	–1092(4)	6454(3)	48(2)
C(33)	4067(5)	–2192(4)	6373(3)	63(2)
C(34)	2988(5)	–2816(4)	6124(3)	64(2)
C(35)	2080(5)	–2384(4)	5917(3)	68(2)
C(36)	2271(4)	–1280(4)	5975(3)	51(2)
C(37)	5057(4)	1417(3)	6552(3)	38(1)

Table 9 (continued)

	x	y	z	U_{eq}
C(38)	5772(4)	1364(4)	7268(3)	51(2)
C(39)	6943(5)	1861(4)	7384(4)	64(2)
C(40)	7398(5)	2403(4)	6779(4)	66(2)
C(41)	6696(5)	2457(4)	6084(4)	68(2)
C(42)	5545(4)	1975(4)	5968(3)	50(2)
C(43)	3140(4)	1036(4)	7378(3)	39(1)
C(44)	3480(4)	2052(4)	7790(3)	52(2)
C(45)	3197(5)	2280(5)	8547(3)	69(2)
C(46)	2526(5)	1492(6)	8894(3)	82(2)
C(47)	2174(5)	484(6)	8491(4)	87(2)
C(48)	2477(5)	262(5)	7743(3)	64(2)
C(49)	3649(5)	-2368(6)	8501(3)	229(6)
C(50)	3350(6)	-3423(6)	8158(3)	297(9)
C(51)	4199(9)	-3966(6)	8106(4)	248(6)
C(52)	5346(8)	-3454(9)	8396(4)	358(8)
C(53)	5644(5)	-2399(9)	8739(4)	280(8)
C(54)	4796(6)	-1856(6)	8791(4)	256(8)
C(55)	5274(18)	-891(12)	9043(10)	397(15)

Colourless crystals of **2**, m.p. 168–170 °C (decomp.), suitable for X-ray diffraction were obtained from a concentrated solution in pentane.

Anal. Found: C, 43.1; H, 3.59. $C_{42}H_{60}O_2P_2PtSi_4$ calc.: C, 44.05; H, 3.49%. 1H NMR (C_7D_8 , 298 K, 360 MHz): δ -0.23 (s, Me_e , 12H), 0.44 (s, Me_a , 12H), 2.77 (m, CH_2 , 4H), 2.32 (m, H_3 , 4H), 2.53 (m, H_1 , 4H), 2.63 (m, H_2 , 4H), 6.92–7.34 (m, Ph, 20H), $^3J(^1H_1-^1H_2) = 11.92$ Hz, $^3J(^1H_1-^1H_3) = 13.47$ Hz, $^3J(^1H_1-^{31}P) = 6.76$ Hz, $^2J(^1H_1-^{195}Pt) = 52.82$ Hz, $^3J(^1H_2-^{31}P) = 6.37$ Hz, $^2J(^1H_2-^{195}Pt) = 51.77$ Hz, $^3J(^1H_3-^{31}P) = 7.15$ Hz, $^2J(^1H_3-^{195}Pt) = 79.90$ Hz. $^{13}C\{^1H\}$ NMR (C_7D_8 , 298 K, 62.8 MHz): δ -1.4 (s, Me_e), 1.6 (s, Me_a), 26.6 (m, CH_2), 46.7 (s, C_2), 49.7 (s, C_1), 128.6–132.5 (m, Ph), $^2J(^{13}C_1-^{31}P) = 4.28$ Hz, $^1J(^{13}C_1-^{195}Pt) = 157.94$ Hz, $^2J(^{13}C_2-^{31}P) = 5.45$ Hz, $^1J(^{13}C_2-^{195}Pt) = 116.56$ Hz. $^{29}Si\{^1H\}$ NMR (C_7D_8 , 298 K, 49.7 MHz): δ 2.36 (s). $^{31}P\{^1H\}$ NMR (C_7D_8 , 298 K, 101 MHz): δ 14.53 (s), $^3J(^{31}P-^{31}P) = 43.81$ Hz, $^1J(^{31}P-^{195}Pt) = 3585.54$ Hz. $^{195}Pt\{^1H\}$ NMR (C_7D_8 , 298 K, 54 MHz): δ -5570.65 (s), $^1J(^{195}Pt-^{31}P) = 3587.40$ Hz.

3.3. Synthesis of tris(tetramethyldivinylsiloxane)-{1,1,1-tris(diphenylphosphinomethyl)ethane}triplatinum(0) (**3**)

1,1,1-Tris(diphenylphosphinomethyl)ethane (0.12 g, 0.20 mmol) was added slowly to a rapidly stirring solution of tris(tetramethyldivinylsiloxane)diplatinum(0) (0.28 g, 0.29 mmol) in toluene (5 ml) at 0 °C. The reaction mixture was allowed to warm up to ambient temperature and was stirred for 12 h. The solvent was removed in vacuo to give a yellow-white solid, which was extracted into toluene (10 ml) and the extract was filtered through Celite. The solvent was removed from

the filtrate in vacuo to yield the colourless solid title compound **3** (0.25 g, 0.14 mmol, 72%), which was washed with *n*-pentane (3 × 3 ml) and dried in vacuo. Crystals, m.p. 158–160 °C, suitable for X-ray diffraction were obtained by dissolving the solid in a 1:1 dichloromethane–ethanol mixture, and leaving the mixture at 25 °C for ca. 48 h.

Anal. Found: C, 44.1; H, 5.5. $C_{62}H_{87}O_3P_3Pt_3Si_6$ calc.: C, 44.1; H, 5.3%. 1H NMR (CD_2Cl_2 , 303 K, 360 MHz): δ -0.46 (s, Me_e , 18H), 0.22 (s, Me_p , 3H), 0.32 (s, Me_a , 18H), 2.14 (d, H_3 , 6H), 2.45 (dd, H_1 , 6H), 2.76 (d, H_2 , 6H), 3.20 (m, CH_2 , 6H), 7.0–7.3 (m, Ph, 30H). $^3J(^1H_1-^1H_2) = 11.7$ Hz, $^3J(^1H_1-^1H_3) = 13.2$ Hz. $^{31}P\{^1H\}$ NMR (C_7D_8 , 303 K, 32 MHz): δ 6.6 (s), $^1J(^{31}P-^{195}Pt) = 3700$ Hz, $^3J(^{31}P-^{195}Pt) = 34$ Hz, $^2J(^{31}P-^{31}P) = 22$ Hz, $^1J(^{195}Pt-^{195}Pt) = 17$ Hz, 6.7 (s) $^1J(^{31}P-^{195}Pt) = 3540$ Hz. $^{195}Pt\{^1H\}$ NMR (C_7D_8 , 303 K, 17 MHz): δ -5572 (d), $^1J(^{195}Pt-^{31}P) = 3540$ Hz.

3.4. Synthesis of tris(tetramethyldivinylsiloxane)-{bis(diphenylphosphinoethyl)phenylphosphine}platinum(0) (**4**)

This was prepared (0.79 g, 0.47 mmol, 72%) by a procedure similar to that described in Section 3.3. Colourless crystals of **4**, m.p. 136–138 °C (decomp.), suitable for X-ray diffraction were obtained from a concentrated solution in pentane at -30 °C.

Anal. Found: C, 41.8; H, 5.42. $C_{58}H_{87}O_3P_3Pt_3Si_6$ calc.: C, 41.5; H, 5.18%. 1H NMR (C_7D_8 , 298 K, 360 MHz): δ -0.23 (s, Me_e , 6H), -0.21 (s, Me_c , 6H), -0.19 (s, Me_e , 6H), 0.22 (s, Me_a , 3H), 0.46 (s, Me_a , 6H), 0.47 (s, Me_a , 9H), 2.02–2.67 (m, vinyl and methylene, 26H), 6.91–7.34 (m, Ph, 25H). $^{13}C\{^1H\}$ NMR (C_7D_8 , 298 K, 62.8 MHz): δ -1.3 (s, Me_e), -1.2 (s, Me_c), 1.6 (s, Me_a), 24.4 (s, CH_2), 26.5 (s, CH_2), 45.8 (d, C_2), 46.6 (d, C_2), 47.5 (d, C_1), 49.5 (d, C_1), 128.7–133.3 (m, Ph). $^2J(^{13}C_1-^{31}P) = 8.61$ Hz, $^2J(^{13}C_1-^{195}Pt) = 5.7$ Hz, $^1J(^{13}C_1-^{195}Pt) = 114.8$ Hz, $^2J(^{13}C_2-^{31}P) = 11.48$ Hz, $^2J(^{13}C_2-^{195}Pt) = 14.35$ Hz. $^{29}Si\{^1H\}$ NMR (C_7D_8 , 298 K, 49.7 MHz): δ 3.07 (s), 3.17 (s). $^{31}P\{^1H\}$ NMR (C_7D_8 , 298 K, 101 MHz): δ 17.79 (t) 22.16 (d), $^3J(^{31}P-^{31}P) = 39.9$ Hz (1P), $^1J(^{31}P-^{195}Pt) = 3566$ Hz, $^3J(^{31}P-^{31}P) = 39.9$ Hz (2P), $^1J(^{31}P-^{195}Pt) = 3587$ Hz. $^{195}Pt\{^1H\}$ NMR (C_7D_8 , 298 K, 54 MHz): δ -5563.7 (d), -5572 (d).

3.5. Synthesis of bis((divinyldimethylsilane)(triphenylphosphine)nickel(0)) (**5**)

Bis(triphenylphosphine)nickel(II) chloride (0.70 g, 1.07 mmol) was suspended in THF (10 ml). Divinyldimethylsilane (0.5 ml) was added, followed by zinc metal (1 g) and the reaction mixture was allowed to stir at ambient temperature for 2 h, during which time

Table 10
Crystal data and structural refinement parameters for **2**, **3**, **4** and **5**

	2	3	4	5
Formula	C ₄₂ H ₆₀ O ₂ Si ₄ P ₂ Pt ₂	C ₆₅ H ₉₃ O ₃ P ₃ Pt ₃ Si ₆	C ₅₈ H ₇₇ O ₃ P ₃ Pt ₃ Si ₆	C ₅₅ H ₆₂ Ni ₂ P ₂ Si ₂
<i>M</i>	1161.4	1841.3	1669.0	958.6
Crystal system	Triclinic	Monoclinic	Triclinic	Triclinic
<i>a</i> /Å	10.694(5)	14.430(17)	12.755(3)	12.135(2)
<i>b</i> /Å	11.130(3)	41.712(9)	14.858(6)	13.074(3)
<i>c</i> /Å	11.779(7)	13.772(7)	21.200(12)	16.681(2)
α /deg	61.47(3)		108.50(4)	94.80(2)
β /deg	73.68(4)	98.04(5)	102.04(3)	98.17(1)
γ /deg	73.12(3)		90.94(2)	103.72(2)
<i>U</i> /Å ³	1161.8	8207.9	3711.4	2525.9
<i>Z</i>	1	4	2	2
<i>D_c</i> /g cm ⁻³	1.66	1.49	1.49	1.26
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i> (No. 14)	<i>P</i> $\bar{1}$ (No. 2)	<i>P</i> $\bar{1}$ (No. 2)
θ_{\max} for data collection/deg	25	22	22	25
Unique reflections	4073	10291	9087	8881
Reflections with <i>I</i> > <i>n</i> σ (<i>I</i>)	3594, <i>n</i> = 2	6667, <i>n</i> = 1	5347, <i>n</i> = 3	4729, <i>n</i> = 2
<i>R</i> 1 [for <i>I</i> > <i>n</i> σ (<i>I</i>)]	0.025	0.077	0.057	0.063
<i>R</i> ' [for <i>I</i> > 2 σ (<i>I</i>)]	0.030	0.120	0.074	
w <i>R</i> 2 (for all data)	—	—	—	0.134

the purple suspension became a yellow solution. The volatiles were removed under reduced pressure, the residue was extracted with toluene (2 × 5 ml) and after storing at -30 °C for 24 h, deep yellow crystals of **5** (0.38 g, 0.889 mmol, 83%) deposited. Crystals, m.p. 90–94 °C (decomp.), suitable for X-ray diffraction were grown from a mixture of toluene and pentane at ambient temperature over a period of 48 h.

Anal. Found: C, 66.3; H, 6.16. C₅₅H₆₂Ni₂P₂Si₂ calc.: C, 66.5; H, 6.24. ¹H NMR (C₇D₈, 298 K, 500 MHz): δ 0.23 (s, Me, 12H), 2.75 (dd, H₃, 4H), 3.23 (m, H₁, 4H), 3.49 (dd, H₂, 4H) 7.14–7.63 (m, Ph, 30H), ³*J*(¹H₁–¹H₂) = 12.6 Hz, ³*J*(¹H₁–¹H₃) = 16.6 Hz, ³*J*(¹H₁–³¹P) = 4.7 Hz, ³*J*(¹H₁–³¹P) = 11.2 Hz, ³*J*(¹H₃–³¹P) = 6.7 Hz. ¹³C{¹H} NMR (C₇D₈, 298 K, 125 MHz): δ 0.4 (d, Me), 59.2 (d, C₁), 62.9 (d, C₂), 129.3–136.5 (m, Ph), ⁴*J*(¹³C_{Me}–³¹P) = 4.4 Hz, ²*J*(¹³C₁–³¹P) = 5.33 Hz, ²*J*(¹³C₂–³¹P) = 1.9 Hz. ²⁹Si{¹H} NMR (C₇D₈, 298 K, 99.4 MHz): δ 3.1 (d), ³*J*(²⁹Si–³¹P) = 2.1 Hz. ³¹P{¹H} NMR (C₇D₈, 298 K, 101 MHz): δ 43.90 (s).

3.6. X-ray structure determinations for **2**, **3**, **4** and **5**

Intensities were measured on an Enraf–Nonius diffractometer at 293 K with monochromated Mo K α radiation ($\lambda = 0.71073$ Å). Corrections for absorption were applied using DIFABS [11] for **2**, **3** and **4** and using psi-scan measurements for **5**. Refinement was by full-matrix least squares, on *F* using Enraf–Nonius MOLEN [12] programs for **2**, **3** and **4** and on *F*² using all reflections and SHELXL-93 [13] for **5**. Non-hydrogen atoms were refined anisotropically. For **2**, **3** and **4**

hydrogen atoms were fixed at calculated positions, except for the vinyl H atoms which were freely refined. For **5**, H atoms were included in riding mode.

Crystal and refinement data are in Table 10.

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