

Bis(silylaminodiarylphosphoranylsilylmethyl-*C,N*)-tin(II) and
-lead(II) complexes and their precursors; structures of H(LL'), H(LL''),
Sn(LL'')₂ and Pb(LL'')₂; [LL']⁻ = [CH(SiMe₃)P(Ph)₂=NSiMe₃]⁻,
[LL'']⁻ = [CH(SiMe₃)P(Ph){=NSi(Me₂)C₆H₄-1,2}]⁻

Peter B. Hitchcock^a, Michael F. Lappert^{a,*}, Zhong-Xia Wang^{a,b}

^a Department of Chemistry, University of Sussex, Brighton BN1 9QJ, UK

^b Department of Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, PR China

Received 19 December 2005; received in revised form 8 February 2006; accepted 8 February 2006

Available online 23 February 2006

Abstract

We report a series (a)–(d) of tandem reactions involving the conversion of: (a) 2CH₂(SiMe₃)P(Ph)₂=NSiMe₃ [≡2H(LL')] (**III**) into successively [Li(LL')]₂ (**1a**) and [Pb(LL'')]₂ (**3a**); (b) **1a** in turn into [LiCH(SiMe₃)P(Ph){=NSi(Me₂)C₆H₄-1,2}]₂ {≡[Li(LL'')]₂} (**2**) and [Pb(LL'')]₂ (**4**); (c) **1a** successively into Sn(LL')Cl (**5**) and [Sn(LL'')]₂ (**6**); (d) 2Li[CH(SiMe₂NEt₂)P(Ph)₂=NSiMe₃] (**1b**) into Pb[CH(SiMe₂NEt₂)P(Ph)₂=NSiMe₃]₂ (**3b**). Experimental details for the preparation and characterisation (including elemental analysis and multinuclear NMR spectra in C₆D₆ and EI mass spectra) of **1a**, **2**, **3a**, **3b**, **4**, **6**, **III** (a new synthesis) and **IV** are provided. The X-ray structures of crystalline **4**, **6**, **III** and **IV** are presented; those of **1a**, **2** and **3a** were previously published.
© 2006 Elsevier B.V. All rights reserved.

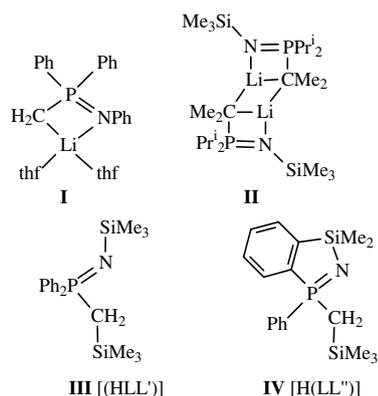
Keywords: 1-Aza-2-phospha(V)allyls; Lithium; Tin(II); Lead(II)

1. Introduction

1-Aza-2-phospha(V)allyl ligands have featured extensively in coordination chemistry [1,2]. The structure of the crystalline lithium compound **I** dates from 1995 [3]. The crystalline neutral donor-free binuclear compound **II** has a ladder structure in which the ligand is both *N,C*-chelating and via the 3-C site bridging [1].

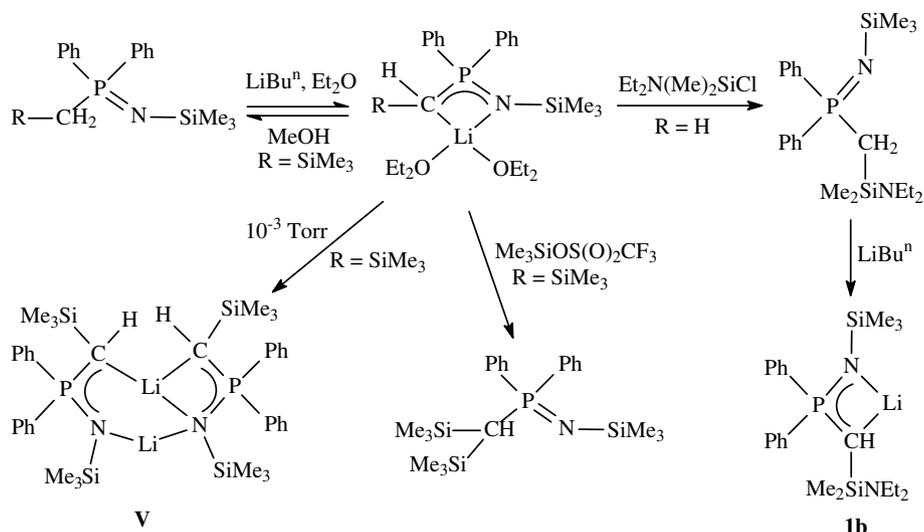
In a preliminary communication we reported that the conjugate acid **III** of such a ligand (abbreviated as H[LL']) is a convenient precursor to its Li(LL') (**1a**), (KLL') and Pb(LL')₂ (**3a**) derivatives, and also of two *ortho*-cyclosilylated compounds: the [Li(LL'')] (**2**) and Pb(LL'')]₂ (**4**) complexes, [H(LL'') = **IV**]; the crystalline **2** and **3a** were X-ray-characterised [4]. While **III** was originally obtained from [(Me₃Si)₂NP(Me)Ph₂]I and LiBuⁿ [5],

it was more conveniently prepared by the Staudinger reaction of CH₂(SiMe₃)PPh₂ with Me₃SiN₃ [6].



In a follow-up paper we described the synthesis and structures of the crystalline compounds [Li(LL')(OEt₂)₂] and the

* Corresponding author. Tel.: +44 1273 678316; fax: +44 1273 677196.
E-mail address: m.f.lappert@sussex.ac.uk (M.F. Lappert).



Scheme 1. [7].

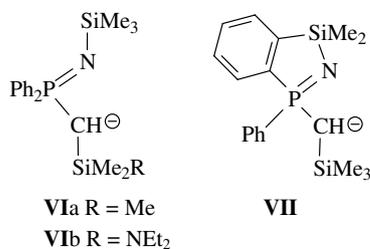
binuclear ether-free compound **V**, as well as the conversion of the former into: (i) $\text{CH}(\text{SiMe}_3)_2\text{P}(\text{Ph})_2=\text{NSiMe}_3$ and (ii) the phosphinimine $\text{CH}_2\{\text{SiMe}_2(\text{NEt}_2)\}\text{P}(\text{Ph})_2=\text{NSiMe}_3$ and its lithium salt **1b**, as summarised in Scheme 1 [7].

We now report details not available in our earlier communication [4] regarding compounds **1a**, **2** and **3a** [5], and extensions to the synthesis and characterisation of other Sn(II) and Pb(II) complexes of the ligands $[\text{LL}']^-$ and $[\text{LL}'']^-$, as well as the structures of the crystalline polymeric ligands **III** $[\text{H}(\text{LL}')]^-$ and **IV** $[\text{H}(\text{LL}'')]^-$.

2. Results and discussion

2.1. Objectives

As indicated in the preceding section, we have previously reported on complexes derived from the 1-aza-2-phospha(V)allyl ligands $[\text{LL}']^-$ (**VI**) and $[\text{LL}'']^-$ (**VII**) [4,6,7]. The principal focus of this paper is on the synthesis and structures of the corresponding homoleptic tin(II) and lead(II) complexes, $\text{M}(\text{LL}')_2$ and $\text{M}(\text{LL}'')_2$.

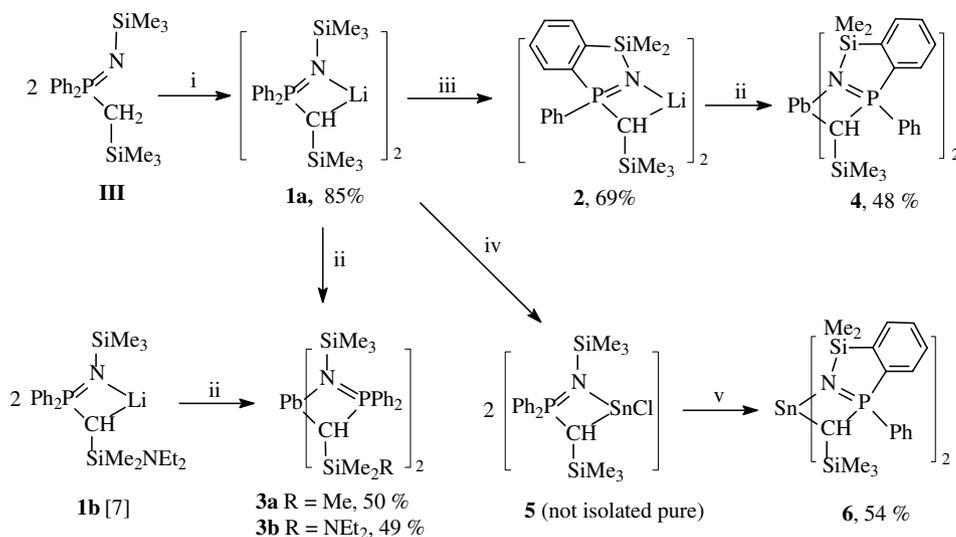


2.2. Synthesis of lithium, tin(II) and lead(II) silyliminodiarlylphosphoranylsilylmethyls

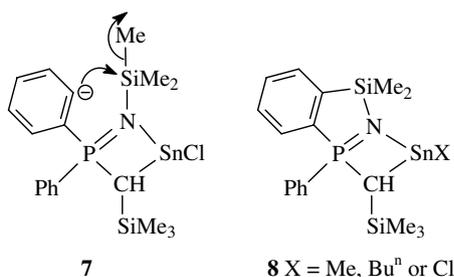
The preparation of compounds $[\text{Li}(\text{LL}')_2]$ (**1a**), $[\text{Li}(\text{LL}'')]_2$ (**2**), $[\text{Pb}(\text{LL}')_2]$ (**3a**), $[\text{Pb}\{\text{CH}(\text{SiMe}_2\text{NEt}_2)\text{P}(\text{Ph})_2=\text{NSiMe}_3\}_2]$

(**3b**), $[\text{Pb}(\text{LL}'')_2]$ (**4**) and $[\text{Sn}(\text{LL}'')_2]$ (**6**) is summarised in Scheme 2. Thus, treatment of $\text{H}(\text{LL}')$ (**III**) [7] with LiBu'' afforded (i in Scheme 2) **1a**. From the latter or **1b** [7] and PbCl_2 there was obtained (ii in Scheme 2) **3a** or **3b**, respectively. Treatment of **1a** with LiBu'' yielded (iii in Scheme 2) **2**, which with PbCl_2 gave (iv in Scheme 2) **4**. Whereas $[\text{Li}(\text{LL}'')_2]$ (**2**) was thus an effective ligand transfer reagent for securing the homoleptic Pb(II) compound **4**, curiously this proved not to be the case (possibly for steric reasons) for the tin(II) analogue **6**. The latter was, however, conveniently obtained by treating $[\text{Li}(\text{LL}')_2]$ (**1a**) successively (iv and v in Scheme 2) with equivalent portions of SnCl_2 and LiBu'' .

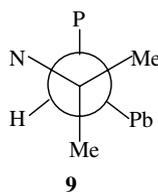
The transformation of the ligand $[\text{LL}']^-$ (**VIa**) into the cyclosilylated $[\text{LL}'']^-$ (**VII**) has previously been explained [4] by proposing that the reaction of $\text{Li}(\text{LL}')^-$ (**1a**) with LiBu'' proceeded via an *ortho*-lithiated intermediate which underwent an intramolecular displacement of Me^- at silicon by the *o*-carbanion thus generating $1/2[\text{Li}(\text{LL}'')]_2$ (**2**) and LiMe [4]; the reaction was shown to be catalytic in LiBu'' , interpreted as due to the eliminated LiMe formed in the initiation step being able to participate in the propagation cycle. We now suggest that a similar mechanism is operative in step v of Scheme 2 in the conversion of **1a** into **6** [**1a** $\xrightarrow{\text{iv}}$ $\text{SnCl}(\text{LL}')^-$ (**5**) $\xrightarrow{\text{v}}$ $1/2\text{SnCl}(\text{LL}'')_2$ (**6**)]. The evidence for the intermediacy of **5** rests on mass spectral evidence (molecular ion $[\text{5}]^+$ observed on the volatiles-free sample) and the ^1H NMR spectrum which showed that the sample in C_6D_6 had the appropriate signals for **5**, albeit with minor impurities; attempts to crystallise **5** from various solvents (C_6H_{14} , Et_2O or C_6H_6) failed. As for step v, we suggest that **5** with LiBu'' forms a transient *ortho*-lithiated intermediate **7**, which upon cyclosilylation generates **8**, which disproportionates yielding $1/2(\text{6})$ with oligomeric SnMe_2 , SnBu_2'' or SnCl_2 as coproduct. Metallation of an iminophosphorane was first demonstrated by Stuckwisch, as in $\text{Ph}_3\text{P}=\text{NPh}$ with successively LiPh , CO_2 and H_2O giving $\text{Ph}_2\text{P}(\text{O})\text{C}_6\text{H}_4\text{CO}_2\text{H}-2$ [8].



Scheme 2. Synthesis of (silyliminodiaryldiaryldiarylsilylmethyl-C,N)tin(II) or -lead(II) complexes **3-6** and their lithium precursors **1a**, **1b** [7] and **2**. Reagents and conditions: (i) 2LiBuⁿ, hexane, -20 °C to 20 °C; (ii) PbCl₂, Et₂O, -45 °C to ca. 20 °C, 15 h; (iii) 2LiBuⁿ, hexane, reflux, 4 h; (iv) 2SnCl₂, Et₂O, -45 °C to ca. 20 °C, 15 h; (v) 2LiBuⁿ, -78 °C to ca. 20 °C, 4 h.



Crystalline compounds **1a**, **2**, **3a**, **3b**, **4** and **6** gave satisfactory microanalytical data (C, H, N) as well as ¹H (for **1a**, see also [4]), ¹³C{¹H}, ³¹P{¹H}, ⁷Li{¹H} (for **1a** and **2**), ²⁹Si{¹H} (for **6**), ¹¹⁹Sn{¹H} (for **6**) and ²⁰⁷Pb{¹H} (for **3a**, **3b** and **4**) NMR spectra; for such data on **1b**, see [7]. The ⁷Li{¹H} NMR spectral chemical shift in C₆D₆ for **1b** (δ -0.76) was at significantly lower frequency than for Li(LL') (**1a**) or [Li(LL'')]₂ (**2**), which may be due to a close Et₂N···Li contact in **1b**. Each of the two methyl groups attached to the silicon atom of the five-membered CCPNSi ring of each of the compounds [Li(LL'')]₂ (**2**), [Pb(LL'')]₂ (**4**) and [Sn(LL'')]₂ (**6**) was magnetically distinct as evident from both their ¹H and ¹³C{¹H} NMR spectra in C₆D₆, one being *endo*- and the other *exo*- in conformation. Likewise, such spectra showed that the two silylmethyl groups of the SiMe₂NEt₂ moiety of [Pb{CH(SiMe₂NEt₂)P(Ph)₂=NSiMe₃}₂] (**3b**) are diastereotopic as illustrated in **9**, a Newman projection taken through the α-C—Si vector.

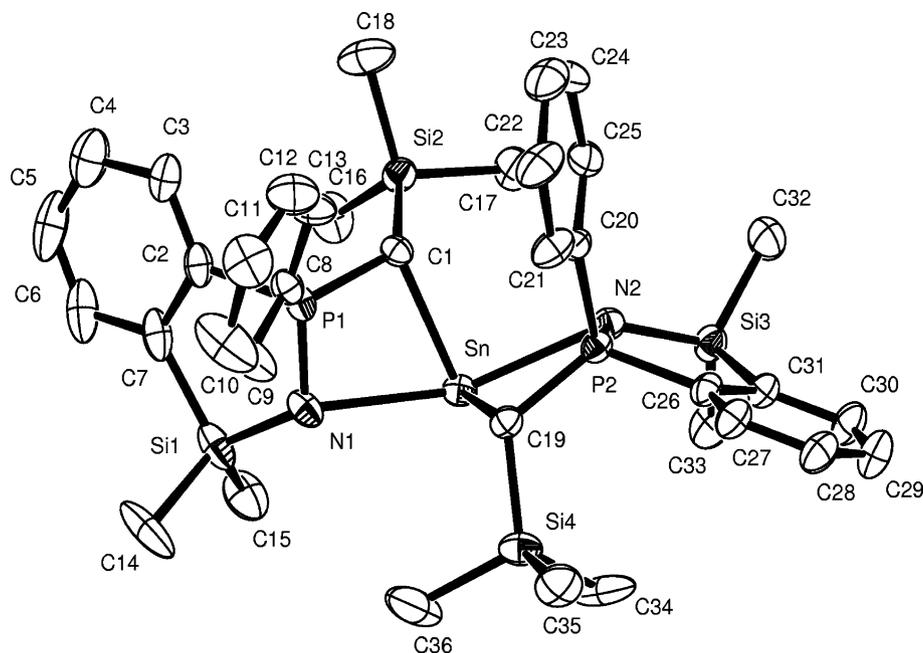


The ³¹P{¹H} NMR spectra of **3a**, **3b** and **4** showed singlets at δ 19.5, 17.05 and 40.3, respectively, with satellites due to ²J(³¹P—²⁰⁷Pb). The ²⁰⁷Pb{¹H} NMR spectra revealed triplets centred at δ 2787.6 (**3a**), 2936.9 (**3b**) and 1998.3 (**4**). Thus, it is evident that **3a** and **3b** had the closer ³¹P and ²⁰⁷Pb chemical shifts. This indicates that this disparity for **4** is determined principally by the fused bicyclic structure of the ligand in **4**, and that the different substituents on silicon in **3a** and **3b** have little influence on these parameters. The EI-MS of each of **3a**, **3b** and **4** gave a weak parent ion.

The ¹¹⁹Sn{¹H} NMR spectrum of **6** displayed a triplet due to coupling with two equivalent phosphorus atoms, ²J(¹¹⁹Sn—³¹P) = 162.5 Hz. The ³¹P{¹H} spectrum showed a singlet with satellites due to ^{119/117}Sn coupling, ²J(³¹P—^{119/117}Sn) = 162.6 Hz. The ²⁹Si{¹H} NMR spectrum comprised two sets of signals: the first, a singlet with ^{119/117}Sn satellites, ²J(²⁹Si—^{119/117}Sn) = 53.5 Hz; and the second, a doublet due to coupling to phosphorus, ²J(²⁹Si—³¹P) = 7.3 Hz. The EI-mass spectrum of **6** showed a weak [Sn(LL'')]₂⁺ parent and a strong [Sn₂(LL'')₂-2]⁺ ion; the latter may have arisen from a recombination of fragments in the mass spectrometer.

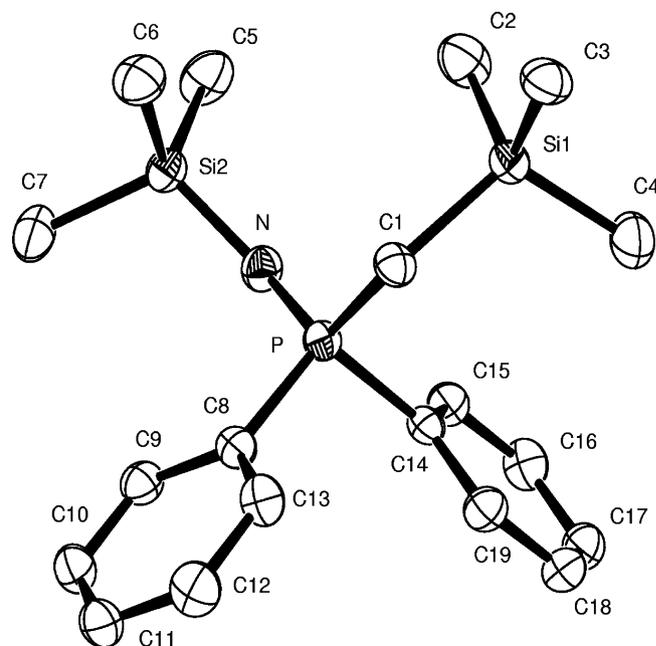
2.3. The X-ray structures of the crystalline compounds **4**, **6**, **III** and **IV**

The molecular structure of the crystalline lead(II) complex [Pb(LL'')]₂ (**4**) is illustrated in Fig. 1 and selected geometric parameters are listed in Table 1. The four-coordinate lead atom is the centre of a distorted trigonal bipyramid, the N1 and N2 atoms axial and the C1 and C19 atoms with the stereochemically active lone pair occupying the equatorial sites. The central five-membered ring of each Pb(LL'') moiety is coplanar with its fused *ortho*-phenylene ring. The dihedral angle between: (a) the

Fig. 2. Molecular structure of $[\text{Sn}(\text{LL}'')_2]$ (**6**).Table 2
Selected bond lengths (Å) and angles (°) for **6**

Bond length (Å)			
Sn—C(1)	2.335(6)	Si(1)—N(1)	1.705(6)
Sn—C(19)	2.353(6)	Si(1)—C(15)	1.841(9)
Sn—N(1)	2.480(6)	Si(1)—C(14)	1.866(9)
Sn—N(2)	2.525(6)	Si(1)—C(7)	1.886(10)
P(1)—N(1)	1.599(6)	Si(2)—C(1)	1.870(6)
P(1)—C(1)	1.751(6)	Si(3)—N(2)	1.711(6)
P(1)—C(8)	1.811(7)	Si(3)—C(33)	1.847(9)
P(1)—C(2)	1.812(8)	Si(3)—C(32)	1.861(9)
P(2)—N(2)	1.592(6)	Si(3)—C(31)	1.899(8)
P(2)—C(19)	1.749(7)	Si(4)—C(19)	1.853(7)
P(2)—C(20)	1.817(7)	C(2)—C(7)	1.401(11)
P(2)—C(26)	1.830(7)	C(26)—C(31)	1.395(9)
Bond angle (°)			
C(1)—Sn—C(19)	93.8(2)	C(19)—P(2)—C(26)	117.6(3)
C(1)—Sn—N(1)	68.4(2)	C(20)—P(2)—C(26)	105.6(3)
C(19)—Sn—N(1)	89.3(2)	P(2)—C(19)—Sn	92.0(3)
C(1)—Sn—N(2)	88.8(2)	C(31)—C(26)—P(2)	111.1(5)
C(19)—Sn—N(2)	67.5(2)	N(1)—Si(1)—C(7)	97.9(4)
N(1)—Sn—N(2)	146.73(18)	N(2)—Si(3)—C(31)	97.9(3)
N(1)—P(1)—C(1)	107.9(3)	P(1)—N(1)—Si(1)	114.6(4)
N(1)—P(1)—C(8)	112.5(3)	P(1)—N(1)—Sn	90.6(2)
C(1)—P(1)—C(8)	110.8(3)	Si(1)—N(1)—Sn	131.2(3)
N(1)—P(1)—C(2)	103.5(4)	P(2)—N(2)—Si(3)	114.6(3)
C(1)—P(1)—C(2)	117.1(3)	P(2)—N(2)—Sn	89.8(2)
C(8)—P(1)—C(2)	104.9(3)	Si(3)—N(2)—Sn	134.3(3)
N(2)—P(2)—C(19)	108.4(3)	P(1)—C(1)—Si(2)	123.4(4)
N(2)—P(2)—C(20)	112.9(3)	P(1)—C(1)—Sn	91.9(3)
C(19)—P(2)—C(20)	108.6(3)	Si(2)—C(1)—Sn	110.0(3)
N(2)—P(2)—C(26)	103.9(3)		

diethyl ether (9:1) at $-25\text{ }^\circ\text{C}$. The molecular structure is shown in Fig. 3, selected geometric parameters being listed in Table 3. The phosphorus atom is in a distorted tetrahedral environment, the N—P—C1 and C8—P—C14 bond angles being the widest and narrowest, respectively; the former is

Fig. 3. Molecular structure of $\text{H}(\text{LL}')$ (**III**).Table 3
Selected bond lengths (Å) and angles (°) for **III**

Bond length (Å)			
P—N	1.544(2)	P—C(8)	1.825(2)
P—C(1)	1.803(2)	Si(1)—C(1)	1.892(2)
P—C(14)	1.818(2)	Si(2)—N	1.680(2)
Bond angle (°)			
N—P—C(1)	117.28(11)	C(1)—P—C(8)	106.17(10)
N—P—C(14)	109.95(10)	C(14)—P—C(8)	103.29(10)
C(1)—P—C(14)	104.64(11)	P—N—Si(2)	143.89(13)
N—P—C(8)	114.21(10)	P—C(1)—Si(1)	119.60(3)

much wider than the N–P–C_{sp3} bond angle in the strained four-membered ring of [Li(LL')(OEt₂)₂] [110.2(1)°] [7], **4** or **6** and the 114.7(3) in the open-chain compound **XI** [12]. The P–C(H)₂ bond length is close to that of the P–C(H)₂ bond of 1.807 ± 0.002 Å in –[CH₂P(Ph)₂=N(SiMe₃)₂] (XI), but much longer than in **4**, **6** or [Li(LL')(OEt₂)₂], 1.702(3) Å [7]. The P–N bond in the latter, 1.592(2) Å, **4** and **6** are of similar magnitude but much longer than the 1.537 ± 0.007 Å of **XI** [12] which is close to the value in **III**.

Single crystals of CH₂(SiMe₃)P(Ph){=NSi(Me₂)C₆H₄-1,2}, H(LL''), **IV**, were obtained adventitiously from the in situ prepared Pb complex Pb(LL'')₂ under aerobic conditions. The molecular structure is illustrated in Fig. 4, with some geometric parameters listed in Table 4. The bicyclic moiety, comprising the *ortho*-phenylene ring and its fused C8PNSiC9 neighbour are almost coplanar. The phosphorus atom is in a distorted tetrahedral environment with the N–P–C1 and the N–P–C8 angles the widest and narrowest, respectively. The former is only very slightly narrower than the corresponding N–P–C_{sp3} angle of **III**. Likewise, the P–C1 [P–C(H)₂] bond lengths in the two compounds are virtually identical. The principal points of

difference between the two, attributable to the silylphenylation in **IV**, resides in the environment at the nitrogen atom, the P–N bond being appreciably longer in **IV** than **III** and the P–N–Si1 bond angle significantly narrower in **IV**; however both these parameters in **IV** are close to the corresponding values in **4** and **6**.

3. Experimental

All reactions were performed under argon using standard Schlenk techniques. The THF and diethyl ether were dried using sodium-benzophenone; hexane and pentane were dried using sodium–potassium alloy. The compounds Li(LL') (**1b**) [4] and HLL' (**III**) [7] were prepared by published methods. The NMR spectra were recorded on Bruker AC-P250, DPX 300, WM-360 or AMX-500 instruments, and the solvent resonances were used as the internal references for ¹H and ¹³C{¹H} spectra; H₃PO₄ (85% aqueous solution), SnMe₄ and PbMe₄ were the external references for ³¹P{¹H}, ¹¹⁹Sn{¹H} and ²⁰⁷Pb{¹H} NMR spectra, respectively; unless other stated, spectra were recorded at 298 K in C₆D₆ at 360.1 (¹H), 62.9 (¹³C), 97.3 (⁷Li), 99.4 (²⁹Si), 101.3 (³¹P), 93.3 (¹¹⁹Sn) or 52.1 (²⁰⁷Pb) MHz. Elemental analyses were carried out by Medac Ltd., Brunel University. Melting points were determined under argon in sealed capillaries on an electrothermal apparatus and were uncorrected.

3.1. Synthesis of [Li{CH(SiMe₃)P(Ph)₂=NSiMe₃}] (**1a**)

A solution of LiBuⁿ (2.3 cm³ of a 1.6 mol dm⁻³ solution in hexane, 3.68 mmol) was added dropwise to a stirred solution of HLL' (**III**) (1.27 g, 3.54 mmol) in hexane (30 cm³) at –20 °C. The solution was allowed to warm to room temperature and was stirred for 3 h. The solution was concentrated in vacuo to ca. 3 cm³, yielding colourless crystals of compound **1a** (85%), m.p. 135–138 °C. ¹H NMR: δ 0.10 (s, 9 H, SiMe₃), 0.13 (s, 9 H, SiMe₃), 0.17 (d, 1 H, *J* = 13.8 Hz, CH); 7.19 (s), 7.21 (s), 7.89 (m) (Ph); ¹³C{¹H} NMR: δ 3.68 (d, *J* = 3.5 Hz, SiMe₃), 4.13 (d, *J* = 4.6 Hz, SiMe₃), 14.92 (d, *J* = 68.6 Hz, CH), 127.65 (d, *J* = 10.3 Hz), 128.28 (s), 132.12 (d, *J* = 9.8 Hz), 147.93 (d, *J* = 84.2 Hz) (Ph); ⁷Li{¹H} NMR: δ 2.23; ³¹P{¹H} NMR (101.3 MHz): δ 33.32. EI-MS [*m/z* (%): (assignment)]: 359 (32) [M – Li + 1]⁺, 344 (100) [M – Me – Li + 1]⁺, 272 (26) [M – Li – CHSiMe₃]⁺, 135 (29) [M – Li – 2SiMe₃ – Ph]⁺, 73 (22) [SiMe₃]⁺. Elemental analysis for C₁₉H₂₉LiNPSi₂: found % (calculated %), C 62.3 (62.4), H 8.02 (8.00), N 3.95 (3.83).

3.2. Synthesis of [Li{CH(SiMe₃)P(Ph){=NSi(Me₂)C₆H₄-1,2}}] (**2**)

A solution of LiBuⁿ (2.8 cm³ of a 1.6 mol dm⁻³ solution in hexane, 4.38 mmol) was added to a stirred solution of Li(LL') (**1a**) (1.60 g, 4.38 mmol) in hexane (30 cm³) at room temperature. The solution was stirred for 1 h and then refluxed for 4 h. The pale yellow solution was concentrated

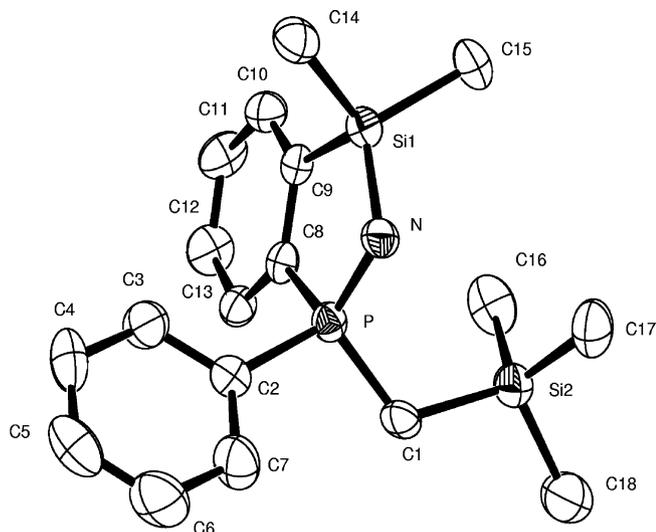


Fig. 4. Molecular structure of H(LL'') (**IV**).

Table 4
Selected bond lengths (Å) and angles (°) for **IV**

Bond length (Å)			
P–N	1.587(5)	Si(1)–N	1.689(5)
P–C(1)	1.779(6)	Si(1)–C(9)	1.884(6)
P–C(2)	1.816(6)	Si(2)–C(1)	1.887(6)
P–C(8)	1.819(6)	C(8)–C(9)	1.387(8)
Bond angle (°)			
N–P–C(1)	116.0(3)	N–Si(1)–C(9)	99.5(3)
N–P–C(2)	113.0(3)	P–N–Si(1)	112.8(3)
C(1)–P–C(2)	106.4(3)	P–C(1)–Si(2)	116.3(3)
N–P–C(8)	105.1(3)	C(9)–C(8)–P	110.4(4)
C(1)–P–C(8)	109.0(3)	C(8)–C(9)–Si(1)	112.0(4)
C(2)–P–C(8)	106.9(3)		

to ca. 3 cm³, yielding colourless crystals of compound **2** (1.05 g, 69%), m.p. 214–217 °C. ¹H NMR: δ -0.02 (s, 9 H, SiMe₃), 0.32 [s, 3 H, Si(CH₃)Me], 0.59 (s, 3 H, Si(Me)CH₃), 0.92 (d, 1 H, *J* = 4.9 Hz, CH), 7.03–7.15 (m, 5 H, Ph), 7.44–7.56 (m, 2 H, C₆H₄) and 7.77–7.83 (m, 2 H, C₆H₄); ¹³C{¹H} NMR (75.5 MHz): δ 2.28 (d, *J* = 5.1 Hz, Me), 2.77 (d, *J* = 4.0 Hz, Me), 2.91 (d, *J* = 2.1 Hz, Me), 6.50 (d, *J* = 86.6 Hz), 127.80 (s), 128.37 (d, *J* = 10.8 Hz), 128.75 (d, *J* = 5.5 Hz), 128.93 (s), 129.25 (d, *J* = 2.9 Hz), 129.58 (d, *J* = 9.8 Hz), 130.03 (d, *J* = 2.6 Hz), 130.79 (d, *J* = 15.9 Hz), 140.81 (d, *J* = 86.9 Hz), 147.01 (d, *J* = 29.0 Hz), 148.57 (d, *J* = 84.6 Hz); ⁷Li{¹H} NMR (97.3 MHz): δ 2.05; ³¹P{¹H} NMR: δ 48.70. EI-MS [*m/z* (%) (assignment)]: 342 (58) [M - Li]⁺, 328 (44) [M - Me - Li + 1]⁺, 256 (100) [M - Li - CHSiMe₃]⁺, 180 (25) [PhP(CH)NSiMe₂]⁺, 137 (17) [PhP(CH)N]⁺. Elemental analysis for C₃₆H₅₀Li₂N₂P₂Si₄: found % (calculated %), C 60.9 (61.8), H 7.27 (7.21), N 3.15 (4.01).

3.3. Synthesis of [Pb{CH(SiMe₃)P(Ph)₂=NSiMe₃}₂] (**3a**)

PbCl₂ (0.37 g, 1.33 mmol) was added at -45 °C to a stirred diethyl ether solution of [Li{CH(SiMe₃)P(Ph)₂=NSiMe₃}] (**1a**), prepared from CH₂(SiMe₃)P(Ph)₂=NSiMe₃ (0.96 g, 2.67 mmol) and LiBuⁿ (1.7 cm³ of a 1.6 mol dm⁻³ solution in hexane, 2.72 mmol). The mixture was allowed to warm to room temperature and was stirred overnight. Volatiles were removed in vacuo. The residue was extracted with pentane and the extract was filtered. The filtrate was concentrated in vacuo to afford yellow crystals of complex **3a** (0.62 g, 50%), m.p. 148–152 °C. ¹H NMR: δ -0.01 (s, 18 H, SiMe₃), 0.20 (s, 18 H, SiMe₃), 1.37 (d, 2 H, *J* = 15.8 Hz, CH); 7.00–7.05 (m), 7.15–7.22 (m), 7.64–7.69 (m), 7.79–7.85 (m) (Ph); ¹³C{¹H} NMR: δ 3.26 (d, *J* = 4.2 Hz, SiMe₃), 4.01 (d, *J* = 3.8 Hz, SiMe₃), 39.47 (d, *J* = 70.5 Hz, CH); 128.20 (d, *J* = 4.3 Hz), 128.37 (d, *J* = 3.9 Hz), 130.78 (s), 131.03 (d, *J* = 10.5 Hz), 131.92 (d, *J* = 10.4 Hz), 140.20 (d, *J* = 83.7 Hz), 144.17 (d, *J* = 84.9 Hz) (Ph); ³¹P{¹H} NMR: δ 19.5 (s, with satellite peaks, *J* = 308 Hz); ²⁰⁷Pb{¹H} NMR: δ 2787.6 (t, *J* = 306 Hz). EI-MS [*m/z* (%) (assignment)]: 924 (1%) ([M]⁺). Elemental analysis for C₃₈H₅₈N₂P₂PbSi₄: found % (calculated %), C 49.2 (49.4), H 6.36 (6.32), N 2.90 (3.03).

3.4. Synthesis of [Pb{CH(SiMe₂NEt₂)P(Ph)₂=NSiMe₃}₂] (**3b**)

Complex **3b** was obtained similarly as for **3a**. [Li{CH(SiMe₂NEt₂)P(Ph)₂=NSiMe₃}] (**1b**) (0.84 g, 1.99 mmol) was treated with PbCl₂ (0.27 g, 0.97 mmol) to yield the yellow crystalline complex **3b** (0.51 g, 49%), m.p. 148–152 °C. ¹H NMR: δ 0.02 (s, 18 H, SiMe₃), 0.17 (s, 6 H, SiMe), 0.28 (s, 6 H, SiMe), 1.03 (t, 12 H, *J* = 7.0 Hz, Me), 1.28 (d, 2 H, *J* = 14.6 Hz, CH), 2.97 (m, 8 H, NEt₂); 7.05 (s), 7.20–7.28 (m), 7.73–7.77 (m), 7.85–7.90 (m) (Ph); ¹³C{¹H} NMR: δ 0.48 (d, *J* = 2.8 Hz, SiMe), 2.36 (d, *J* = 3.2 Hz, SiMe), 3.25 (d, *J* = 4.5 Hz, SiMe₃), 15.79 (s, NCH₂), 39.20 (d, *J* = 70.9 Hz, CH), 40.13 (s, Me); 128.03 (d, *J* = 16.3 Hz),

128.13 (d, *J* = 11.1 Hz), 130.32 (s), 130.57 (d, *J* = 13.0 Hz), 131.15 (d, *J* = 10.2 Hz), 131.60 (d, *J* = 10.3 Hz), 131.87 (d, *J* = 10.6 Hz), 141.85 (d, *J* = 82.8 Hz), 143.17 (d, *J* = 86.5 Hz) (Ph); ³¹P{¹H} NMR: δ 17.05 (s, with satellite peaks, *J* = 304.7 Hz); ²⁰⁷Pb{¹H} NMR: δ 2936.9 (t, *J* = 303 Hz). EI-MS [*m/z* (%) (assignment)]: 1038 (0.1%) ([M]⁺). Elemental analysis for C₄₄H₇₂N₄P₂PbSi₄: found % (calculated %), C 50.8 (50.9), H 7.16 (6.99), N 5.47 (5.39).

3.5. Synthesis of [Pb{CH(SiMe₃)P(Ph){=NSi(Me₂)C₆H₄-1,2)}₂] (**4**)

Complex **4** was prepared similarly as for **3a**. [LiCH(SiMe₃)P(Ph){=NSi(Me₂)C₆H₄-1,2}]₂ (**2**) (0.57 g, 1.63 mmol) was treated with PbCl₂ (0.23 g, 0.82 mmol) to produce colourless crystals of complex **4** (0.35 g, 48%), m.p. 90–92 °C. ¹H NMR: δ 0.31 (s, 18 H, SiMe₃), 0.53 (s, 6 H, SiMe), 0.69 (s, 6 H, SiMe), 1.43 (d, 2H, *J* = 9.5 Hz, CH); 7.06–7.25 (m), 7.54–7.65 (m) (Ph + C₆H₄). ¹³C{¹H} NMR: δ 1.63 (d, *J* = 6.2 Hz, SiMe), 2.01 (d, *J* = 3.9 Hz, SiMe₃), 2.39 (d, *J* = 2.4 Hz, SiMe), 28.22 (d, *J* = 61.9 Hz, CH); 127.05 (d, *J* = 13.4 Hz), 128.54 (d, *J* = 11.2 Hz), 129.14 (d, *J* = 10.2 Hz), 129.66 (d, *J* = 2.8 Hz), 129.87 (d, *J* = 2.8 Hz), 131.10 (d, *J* = 16.5 Hz), 141.26 (d, *J* = 86.9 Hz), 147.96 (d, *J* = 30.8 Hz), 153.65 (d, *J* = 77.0 Hz) (Ph + C₆H₄); ³¹P{¹H} NMR: δ 40.3 (s, with satellite peaks, *J* = 311.8 Hz). ²⁰⁷Pb{¹H} NMR: δ 1998.3 (t, *J* = 313.3 Hz). EI-MS [*m/z* (%) (assignment)]: 892 (5%) ([M]⁺). Elemental analysis for C₃₆H₅₀N₂P₂PbSi₄: found % (calculated %), C 47.9 (48.5), H 5.65 (5.65), N 3.09 (3.14).

3.6. Synthesis of [Sn{CH(SiMe₃)P(Ph){=NSi(Me₂)C₆H₄-1,2)}₂] (**6**)

SnCl₂ (0.58 g, 3.05 mmol) was added to a diethyl ether (ca. 30 cm³) solution of [Li{CH(SiMe₃)P(Ph)₂=NSiMe₃}] (**1a**) (1.10 g, 3.01 mmol) at -78 °C with stirring. The mixture was allowed to warm to room temperature and was stirred overnight. The stirred mixture was recooled to -78 °C and LiBuⁿ (1.9 cm³ of a 1.6 mol dm⁻³ hexane solution, 3.04 mmol) was added dropwise. Stirring was continued for 4 h at room temperature. Solvent was removed in vacuo and the solid residue was extracted with hexane. The extract was filtered and the filtrate was concentrated to afford colourless crystals of **6** (0.65 g, 54%), m.p. 183–186 °C. ¹H NMR: δ 0.27 (s, 18 H, SiMe₃), 0.43 (s, 6 H, SiMe), 0.69 (s, 6 H, SiMe), 1.77 (d, 2H, *J* = 10.8 Hz, CH); 6.92–7.02 (m), 7.39–7.49 (m) (Ph + C₆H₄); ¹³C{¹H} NMR: δ 0.74 (d, *J* = 6.2 Hz, SiMe), 1.60 (d, *J* = 3.8 Hz, SiMe₃), 2.63 (d, *J* = 2.1 Hz, SiMe), 18.94 (d, *J* = 54.7 Hz, CH); 127.47 (d, *J* = 13.5 Hz), 128.55 (d, *J* = 10.0 Hz), 128.71 (d, *J* = 11.5 Hz), 129.05 (d, *J* = 10.5 Hz), 129.78 (d, *J* = 2.6 Hz), 129.91 (d, *J* = 2.5 Hz), 131.62 (d, *J* = 16.5 Hz), 140.55 (d, *J* = 85.7 Hz), 148.31 (d, *J* = 75.3 Hz), 149.71 (d, *J* = 30.2 Hz) (Ph + C₆H₄); ³¹P{¹H} NMR: δ 44.9 (s, with satellite peaks, *J* = 162.3, 155.5 Hz); ¹¹⁹Sn{¹H} NMR: δ -121.4 (t, *J* = 162.6 Hz); ²⁹Si{¹H}

NMR: δ -0.42 (s, with satellite peaks, $J = 53.5$ Hz), 8.53 (d, $J = 7.3$ Hz). EI-MS [m/z (%)] (assignment): 804 (10%) ($[M]^+$), 920 (38%) ($[\text{Sn}_2(\text{LL}'')_2-2]^+$). Elemental analysis for $\text{C}_{36}\text{H}_{50}\text{N}_2\text{P}_2\text{Si}_4\text{Sn}$: found % (calculated %), C 53.0 (53.8), H, 6.18 (6.27), N, 3.13 (3.48).

3.7. A new synthesis of $\text{CH}_2(\text{SiMe}_3)\text{P}(\text{Ph})_2=\text{NSiMe}_3$ (**III**) (by P.G.H. Uiterweerd)

Compound **1a** (1.38 g, 3.78 mmol) was dissolved in hexane (20 cm³) and cooled to 0 °C. Methanol (0.2 cm³, 4.94 mmol) was added dropwise. The reaction mixture was allowed to warm to room temperature and then stirred for 1 h. The mixture was filtered and the volatiles from the filtrate were removed in vacuo, yielding **III** (1.22 g, 90%) as a white solid, m.p. 38.5–41.0 °C. ¹H NMR (300.1 MHz): δ 0.01 (s, 9 H, CSiMe_3), 0.31 (s, 9 H, NSiMe_3), 1.44 [d, 1 H, $^2J(^1\text{H}, ^{31}\text{P}) = 15.2$ Hz, CH], 7.04–7.08 (m, 6 H, Ph), 7.54–7.60 (m, 4 H, Ph); ³¹P{¹H} NMR (121.1 MHz): δ 0.46 (s). X-ray quality crystals were obtained from a mixture of methylcyclohexane:diethyl ether (9:1) at -25 °C.

3.8. Synthesis of $\text{CH}_2(\text{SiMe}_3)\overline{\text{P}(\text{Ph})\{\text{NSi}(\text{Me}_2)\text{C}_6\text{H}_4-1,2\}}$ (**IV**)

PbCl_2 (0.29 g, 1.04 mmol) was added to a stirred solution of $[\text{Li}(\text{LL}'')_2]$ (**2**) (0.75 g, 2.15 mmol) in diethyl ether (ca. 20 cm³) at -40 °C. The mixture was stirred for ca. 12 h at room temperature. Volatiles were removed in vacuo and the residue was extracted with pentane. The extract was filtered in the open laboratory and the filtrate was concentrated in vacuo yielding colourless crystals of **IV** (0.41 g, 56%). ¹H NMR: δ 0.04 (s, 9 H, SiMe_3), 0.54 (s, 3 H, SiMe), 0.62 (s, 3 H, SiMe), 1.17 (t, 1H, $J = 15.7$ Hz, CH), 1.51 (t, 1H, $J = 14.3$ Hz, CH); 7.03–7.17, 7.32–7.55, 7.82–7.87 (m, Ph + C_6H_4); ¹³C{¹H} NMR: δ 0.32 (d, $J = 2.9$ Hz, SiMe_3), 2.66 (d, $J = 6.6$ Hz, SiMe), 2.95 (d, $J = 4.0$ Hz, SiMe), 19.66 (d, $J = 62.2$ Hz, CH), 126.93 (d, $J = 11.3$ Hz), 128.26

(d, $J = 9.2$ Hz), 128.42 (d, $J = 11.4$ Hz), 129.81 (d, $J = 2.9$ Hz), 130.45 (d, $J = 9.5$ Hz), 130.63 (d, $J = 2.8$ Hz), 131.61 (d, $J = 17.9$ Hz), 138.67 (d, $J = 92.1$ Hz), 147.07 (d, $J = 80.7$ Hz), 152.30 (d, $J = 33.3$ Hz); ³¹P{¹H} NMR: δ 32.0. X-ray quality crystals were grown from a hexane solution.

3.9. Crystallographic data and structure refinement for **3a**, **6**, **III** and **IV**

Diffraction data were collected on an Enraf Nonius CAD4 diffractometer using monochromated Mo K α radiation ($\lambda = 0.71073$ Å) with crystals sealed in capillaries for **4**, **6** and **IV**, or for **III** coated in oil and directly mounted on the diffractometer under a stream of cold nitrogen gas. The structures were refined on all F^2 using SHELXL-97 [13]. Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 289180 (**4**), 189181 (**6**), 289178 (**III**) and 289179 (**IV**). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk, www: <http://www.ccdc.cam.ac.uk> (see Table 5).

Acknowledgements

We are grateful to Dr. P.G.N. Uiterweerd for supplying single crystals of **III** and to the British Council and the Chinese Government for financial support.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.02.011.

Table 5
Crystal data and refinements for complexes **3a**, **6**, **III** and **IV**

	3a	6	III	IV
Formula	$\text{C}_{36}\text{H}_{50}\text{N}_2\text{P}_2\text{PbSi}_4$	$\text{C}_{36}\text{H}_{50}\text{N}_2\text{P}_2\text{Si}_4\text{Sn}$	$\text{C}_{19}\text{H}_{30}\text{NPSi}_2$	$\text{C}_{18}\text{H}_{26}\text{NPSi}_2$
M	892.3	803.77	359.59	343.6
Temperature (K)	293(2)	293(2)	173(2)	293(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Tetragonal
Space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$I4_1/a$ (No. 88)
a (Å)	12.757(2)	12.681(5)	9.907(2)	21.635(6)
b (Å)	10.763(4)	10.705(2)	22.965(6)	21.635(6)
c (Å)	31.388(7)	31.343(9)	10.143(3)	16.915(5)
β (°)	96.85(2)	96.66(2)	111.36(2)	90
U (Å ³)	4279(2)	4226(2)	2149(1)	7917(4)
Z	4	4	4	16
μ (Mo K α) (mm ⁻¹)	4.16	0.82	0.24	0.26
Reflections collected	10714	7757	3993	2571
Independent reflections [R_{int}]	10282 [0.040]	7413 [0.032]	3769 [0.021]	2412 [0.046]
Reflections with $I > 2\sigma(I)$	4736	4325	3122	1494
Final R indices [$I > 2\sigma(I)$]	R_1 0.060, wR_2 0.098	R_1 0.054, wR_2 0.133	R_1 0.041, wR_2 0.100	R_1 0.066, wR_2 0.140
R indices (all data)	R_1 0.164, wR_2 0.131	R_1 0.113, wR_2 0.171	R_1 0.053, wR_2 0.108	R_1 0.124, wR_2 0.167

References

- [1] A. Müller, B. Neumüller, K. Dehnicke, *Chem. Ber.* 129 (1996) 253.
- [2] (a) P. Imhoff, R. van Asselt, C.J. Elsevier, M.C. Zoutberg, C.H. Stam, *Inorg. Chim. Acta* 184 (1991) 73;
(b) P. Imhoff, C.J. Elsevier, *J. Organomet. Chem.* 361 (1989) C61;
(c) C.J. Elsevier, P. Imhoff, *Phosphorus Sulfur* 49/50 (1990) 405;
(d) M.W. Avis, K. Vrieze, H. Kooijman, N. Veldman, A.L. Spek, C.J. Elsevier, *Inorg. Chem.* 34 (1995) 4092;
(e) P. Imhoff, S.C.A. Nefkins, C.J. Elsevier, *Organometallics* 10 (1991) 1421;
(f) P. Imhoff, R. van Asselt, J.M. Ernsting, K. Vrieze, C.J. Elsevier, W.J.J. Smeets, A.L. Spek, A.P.M. Kentgens, *Organometallics* 12 (1993) 1523;
(g) M.W. Avis, K. Vrieze, J.M. Ernsting, C.J. Elsevier, N. Veldman, A.L. Spek, K.V. Katti, C.L. Barnes, *Organometallics* 15 (1996) 2376;
(h) P. Imhoff, J.H. Gülpen, K. Vrieze, W.J.J. Smeets, A.L. Spek, C.J. Elsevier, *Inorg. Chim. Acta* 235 (1995) 77;
(i) K. Izod, *Coordin. Chem. Rev.* 227 (2002) 153;
(j) A. Steiner, S. Zacchini, P.I. Richards, *Coordin. Chem. Rev.* 227 (2002) 193.
- [3] F. López-Ortiz, E. Peláez-Arango, B. Tejerina, E. Pérez-Carreno, S. Gareia-Granda, *J. Am. Chem. Soc.* 117 (1995) 9972.
- [4] P.B. Hitchcock, M.F. Lappert, Z.-X. Wang, *J. Chem. Soc., Chem. Commun.* (1997) 1113.
- [5] J.C. Wilburn, R.H. Neilson, *Inorg. Chem.* 18 (1979) 347.
- [6] P.B. Hitchcock, M.F. Lappert, Z.-X. Wang, *J. Chem. Soc., Dalton Trans.* (1997) 1953.
- [7] P.B. Hitchcock, M.F. Lappert, P.G.H. Uiterweerd, Z.-X. Wang, *J. Chem. Soc., Dalton Trans.* (1999) 3413.
- [8] C.G. Stuckwisch, *J. Org. Chem.* 41 (1976) 1173.
- [9] U. Kilimann, M. Noltemeyer, F.T. Edelman, *J. Organomet. Chem.* 443 (1993) 35.
- [10] A. Müller, M. Möhlen, B. Neumüller, N. Faza, W. Massa, K. Dehnicke, *Z. Anorg. Allg. Chem.* 625 (1999) 1748.
- [11] Z.-X. Wang, C.-Y. Qi, *Dalton Trans.* (2005) 996.
- [12] F. Weller, H.-C. Kang, W. Massa, T. Rubenstahl, F. Kunkel, K. Dehnicke, *Z. Naturforsch. B* 50 (1995) 1050.
- [13] G.M. Sheldrick, *SHELXL-97*, Program for Crystal Structure Refinement, University of Göttingen, Göttingen, Germany, 1997.