



# Synthesis and characterisation of six Fe(II or III), Co(II) or Zr(IV) complexes containing the ligand $[\text{CH}(\text{SiMe}_2\text{R})\text{P}(\text{Ph})_2\text{NSiMe}_3]^-$ (R = Me, NEt<sub>2</sub>) and of $[\text{Co}\{\text{N}(\text{SiMe}_3)\text{C}(\text{Ph})\text{C}(\text{H})\text{P}(\text{Ph})_2\text{NSiMe}_3\}_2]$

Peter B. Hitchcock<sup>a</sup>, Michael F. Lappert<sup>a,\*</sup>, Zhong-Xia Wang<sup>a,b</sup>

<sup>a</sup> Department of Chemistry, University of Sussex, Brighton BN1 9QJ, UK

<sup>b</sup> Department of Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, PR China

## ARTICLE INFO

### Article history:

Received 31 July 2008

Received in revised form 5 September 2008

Accepted 10 September 2008

Available online 18 September 2008

### Keywords:

Late transition metals

C,N-Chelate ligands

N,N-Chelate ligands

Structures

Magnetism

## ABSTRACT

The C,N-(trimethylsilyliminodiphenylphosphoranyl)silylmethylmetal complexes  $[\text{Fe}(\text{L})_2]$  (**3**),  $[\text{Co}(\text{L})_2]$  (**4**),  $[\text{ZrCl}_3(\text{L})] \cdot 0.83\text{CH}_2\text{Cl}_2$  (**5**),  $[\text{Fe}(\text{L})_3]$  (**6**),  $[\text{Fe}(\text{L}')_2]$  (**7**) and  $[\text{Co}(\text{L}')_2]$  (**8**) have been prepared from the lithium compound  $\text{Li}[\text{CH}(\text{SiMe}_2\text{R})\text{P}(\text{Ph})_2\text{NSiMe}_3]$  [**1a**, (R = Me)  $\equiv \text{Li}(\text{L})$ ]; **1b**, (R = NEt<sub>2</sub>)  $\equiv \text{Li}(\text{L}')$ ] and the appropriate metal chloride (or for **7**, FeCl<sub>3</sub>). From  $\text{Li}[\text{N}(\text{SiMe}_3)\text{C}(\text{Ph})\text{C}(\text{H})\text{P}(\text{Ph})_2\text{NSiMe}_3]$  [ $\equiv \text{Li}(\text{L}'')$ ] (**2**), prepared *in situ* from  $\text{Li}(\text{L})$  (**1a**) and PhCN, and CoCl<sub>2</sub> there was obtained bis(3-trimethylsilylimino-diphenylphosphoranyl-2-phenyl-N-trimethylsilyl-1-azaallyl-N,N')cobalt(II) (**9**). These crystalline complexes **3–9** were characterised by their mass spectra, microanalyses, high spin magnetic moments (not **5**) and for **5** multinuclear NMR solution spectra. The X-ray structure of **3** showed it to be a pseudotetrahedral bis(chelate), the iron atom at the spiro junction.

© 2008 Elsevier B.V. All rights reserved.

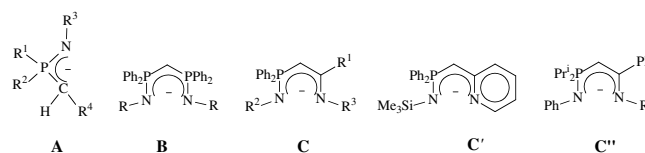
## 1. Introduction

Metal complexes containing the 1-aza-2-phospha(V)allyl ligand **A** have been much studied; for a review of such s- and p-block metal complexes, see Ref. [1]. Transition metal complexes are more scant [2]. Relevant to the present study is a report on  $[\text{Zr}\{\text{CH}(\text{C}_6\text{H}_4\text{Bu}^t\text{-4})\text{P}(\text{Ph})_2\text{NMe}_3\}(\text{NMe}_2)_3]$ , obtained from  $\text{Zr}(\text{NMe}_2)_4$  and  $\text{CH}_2(\text{C}_6\text{H}_4\text{Bu}^t\text{-4})\text{P}(\text{Ph})_2\text{NMe}_3$  (Mes = C<sub>6</sub>H<sub>2</sub>Me<sub>3</sub>-2,4,6) [3]. As far as we are aware, related iron and cobalt complexes have not previously been described.

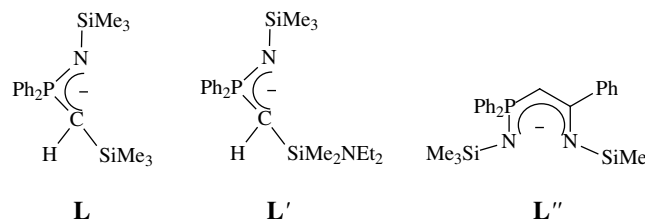
The bis(phosphinimino)methanido ligand **B** and analogues with different substituents at phosphorus have featured widely in d-block metal chemistry; for eleven pre-2005 citations, see Ref. [4]. Recent examples include complexes of yttrium [5], selected late 3d metals [6,7] and ruthenium [8]. The 3d metal complexes to have been described are  $[\text{M}(\text{B})\text{X}]$  (M = Mn, Fe or Co; R = Mes and X = N(SiMe<sub>3</sub>)<sub>2</sub> or OPh<sub>3</sub>) [6a],  $[\text{M}(\text{B})\{\text{N}(\text{SiMe}_3)_2\}]$  (M = Mn, Fe or Co, R = C<sub>6</sub>H<sub>3</sub>Pr<sup>i</sup><sub>2</sub>-2,6) [6b],  $[\text{Co}(\text{B})\text{Cl}]$  (R = C<sub>6</sub>H<sub>3</sub>Pr<sup>i</sup><sub>2</sub>-2,6 or Mes) and  $[\text{Ni}(\text{B})\text{Br}]$  (R = C<sub>6</sub>H<sub>3</sub>Pr<sup>i</sup><sub>2</sub>-2,6 or Mes) [7].

A related ligand **C** has an iminodiphenylphosphoranyl-1-azaallyl skeleton. A lithium derivative, prepared *in situ* from  $\text{R}^1\text{CH}_2\text{P}(\text{Ph})_2=\text{NPh}$  and successively  $\text{LiNPr}^i_2$  and a cyanoarene, was used for various organic transformations [9]. An iron(II) complex  $[\text{Fe}(\text{C})_2]$  was obtained from  $[\text{Fe}\{\text{N}(\text{SiMe}_3)_2\}_2]$  and 2 HC' [10]. As

shown by one of us, novel Ni(II) complexes, bearing a monoanionic P,N,P-, P,N,N-, or N,N,N-pincer ligand containing the ligand **C''**, were effective catalysts for Kumada cross-coupling reactions [11].



The precursors used in the present study,  $\text{Li}(\text{L})$  (**1a**) and  $\text{Li}(\text{L}')$  (**1b**), were prepared by metallation of H(L) [12] or H(L'); the latter was obtained from  $\text{Li}[\text{CH}_2\text{P}(\text{Ph})_2\text{NSiMe}_3]$  and  $\text{SiCl}(\text{Me})_2\text{NET}_2$  [13]. The crystalline  $[\text{Li}(\text{L})]_2$  and  $[\text{Li}(\text{L})(\text{OEt}_2)]_2$  were X-ray-characterised [13]. The compound  $\text{Li}(\text{L}'')$  (**2**), previously prepared as an oil *in situ* from **1a** and PhCN, was characterised as the crystalline potassium derivative  $[\text{K}(\text{L}'')(\text{tmeda})]_2$  [14].



\* Corresponding author. Tel.: +44 1273 678316; fax: +44 1273 677196.

E-mail address: m.f.lappert@sussex.ac.uk (M.F. Lappert).

## 2. Results and discussion

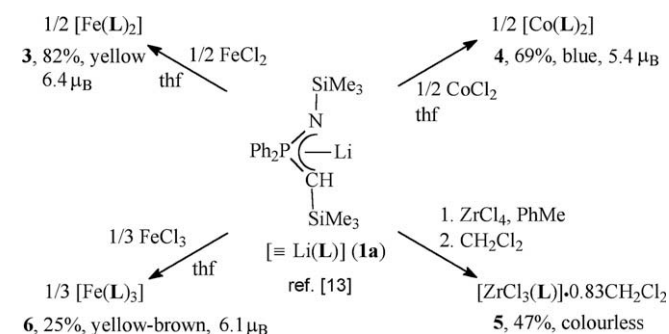
### 2.1. Trimethylsilyliminodiphenylphosphoranyltrimethylsilylmethyl-C,N-metal complexes 3–5

The synthesis of four crystalline metal complexes **3–6** derived from the ligand **L** is summarised in Scheme 1. Thus, reaction in the appropriate stoichiometry of FeCl<sub>2</sub>, CoCl<sub>2</sub>, ZrCl<sub>4</sub> or FeCl<sub>3</sub> with Li(**L**) (**1a**) in thf furnished crystals of **3** or **4** from hexane, **5** from dichloromethane or benzene, or **6** from pentane. No attempt was made to optimise yields, which for **3** or **4** were excellent, of **5** was modest and of **6** was poor. The compounds were characterised by satisfactory C, H and N microanalyses, mass spectra (parent molecular cations for **3–5** and [Fe(**L**)<sub>2</sub>]<sup>+</sup> for **6**), and for the zirconium **5** multinuclear (<sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P) NMR solution spectra. The magnetic moments of the coloured compounds **3**, **4** and **6** in benzene were examined by the Evans NMR method at ambient temperature, showing that each was high-spin. The figures for μ<sub>eff</sub> of 5.4 (**4**) to 6.3 μ<sub>B</sub> (**3**) were considerably higher than for spin-only (μ<sub>S</sub>) values (e.g., 4.9 for Fe<sup>2+</sup> and 3.9 μ<sub>B</sub> for Co<sup>2+</sup>), lower than μ<sub>J</sub> (e.g., 6.7 for Fe<sup>2+</sup> and 6.6 μ<sub>B</sub> for Co<sup>2+</sup>), but larger than μ<sub>S+L</sub> (e.g., 5.5 for Fe<sup>2+</sup> and 5.2 μ<sub>B</sub> for Co<sup>2+</sup>). The result for μ<sub>eff</sub> of **3** may be compared with those for [Fe{(N(C<sub>6</sub>H<sub>3</sub>Pr<sup>t</sup>-2,6)C(Me))<sub>2</sub>CH}{N(SiMe<sub>3</sub>)<sub>2</sub>}] [15], [Fe(**B**){N(SiMe<sub>3</sub>)<sub>2</sub>}] (R in **B** = SiMe<sub>3</sub>) [6a] and [Fe{(N(SiMe<sub>3</sub>)C(Ph))<sub>2</sub>CH<sub>2</sub>}] [16] of 4.94 μ<sub>B</sub>, 5.25 μ<sub>B</sub> and 5.06 μ<sub>B</sub>, respectively; and those of **4** with the 4.9 μ<sub>B</sub> for [Co(**B**){N(SiMe<sub>3</sub>)<sub>2</sub>}] (R in **B** = SiMe<sub>3</sub>) [6a]. The μ<sub>eff</sub> for **6** is close to the μ<sub>S</sub> for Fe<sup>3+</sup> of 5.9 μ<sub>B</sub>. We are unable to account for the high value of μ<sub>eff</sub> for **3**; it would have been useful to obtain variable temperature data on the solid sample of this compound using a SQUID magnetometer.

The molecular structure of the crystalline Fe(II) compound **3** is shown in an ORTEP representation in Fig. 1. Selected bond lengths and angles are listed in Table 1. The FeC20P2N2 ring deviates only very slightly from planarity, but the FeC1P1N1 ring somewhat more so; the dihedral angle between them is 88.74(14)°. The average Fe–N bond length of 2.08 Å is longer than values for related molecules; e.g., 1.916(4) in [Fe{CH(SiMe<sub>3</sub>)C(Bu<sup>t</sup>)NSiMe<sub>3</sub>}<sub>2</sub>] (**D**) [17]. The mean Fe–C distance of 2.185 Å is unexceptional; cf., 2.105(5) in **D** [17]. The average P–N (1.615 Å), endocyclic P–C (1.71 Å) bond lengths and the average endocyclic N–P–C angle (105°) in **3** may be compared with the corresponding data for [Zr{CH(C<sub>6</sub>H<sub>4</sub>Bu<sup>t</sup>-4)P(Ph)<sub>2</sub>N(C<sub>6</sub>H<sub>2</sub>Me<sub>3</sub>-2,4,6)(NMe<sub>2</sub>)<sub>3</sub>}] of 1.613(3) Å, 1.735(3) Å and 99.27(14)°, respectively, [3].

### 2.2. Trimethylsilyliminodiphenylphosphoranyldiethylaminodimethylsilylmethyl-C,N-metal complexes 7 and 8

The preparation in high yield of the crystalline metal compounds **7** and **8** derived from the lithium salt **1b** is outlined in Scheme 2. The outcome for **8** was unexceptional, in that it was obtained from cobalt(II) chloride and 2 Li(**L'**). The formation of **7** from



Scheme 1.

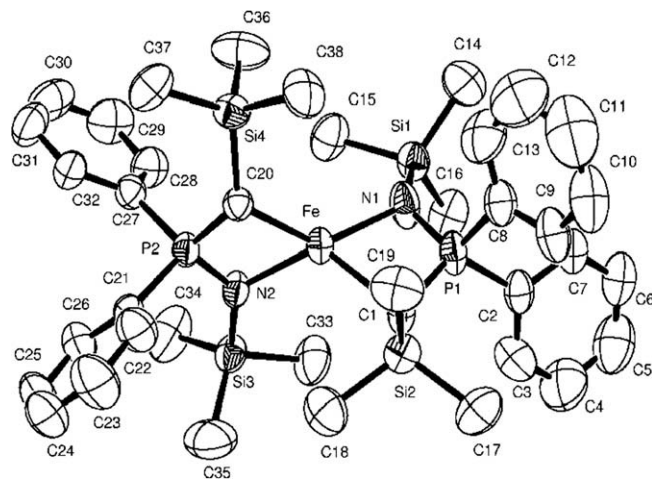
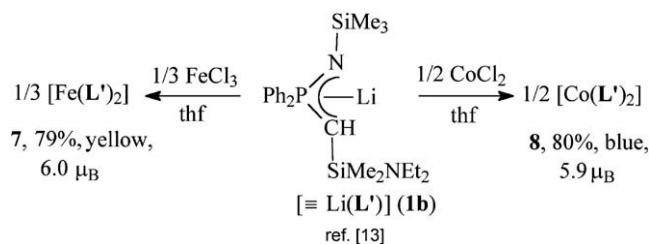


Fig. 1. Molecular structure of complex **3** (50% thermal ellipsoids).

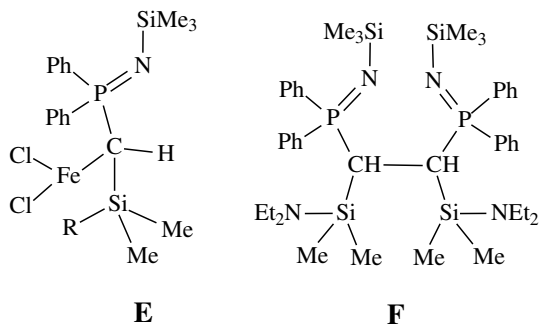
Table 1  
Selected bond distances (Å) and angles (°) for **3**

Fe–N1	2.099(3)	N1–Si1	1.739(4)
Fe–N2	2.062(3)	N2–Si3	1.719(3)
Fe–C1	2.166(4)	C1–Si2	1.804(4)
Fe–C20	2.205(4)	C20–Si4	1.835(4)
N1–P1	1.619(4)	P1–C2	1.818(5)
N2–P2	1.609(3)	P2–C21	1.822(4)
C1–P1	1.693(4)	P1–C8	1.819(5)
C20–P2	1.733(4)	P2–C27	1.809(4)
N1–P1–C1	104.9(2)	N1–P1–C8	113.2(2)
N2–P2–C20	105.12(18)	N2–P2–C27	111.33(19)
P1–C1–Fe	86.46(19)	N1–P1–C2	111.5(2)
P2–C20–Fe	84.90(16)	N2–P2–C21	111.25(18)
P1–N1–Fe	90.67(16)	C1–P1–C8	109.9(2)
P2–N2–Fe	92.96(16)	C20–P2–C27	111.79(19)
C1–Fe–N1	76.05(15)	C1–P1–C2	115.0(2)
C20–Fe–N2	76.88(14)	C20–P2–C21	113.8(2)
C1–Fe–C20	123.97(16)	C1–Fe–N2	120.76(16)
N1–Fe–N2	129.88(15)	C20–Fe–N1	136.27(16)

iron(III) chloride was, however, surprising. Thus, [Fe(**L'**)<sub>2</sub>] (**7**) was isolated by treating FeCl<sub>3</sub> with 3 Li(**L'**) in thf, using similar reaction conditions to those which had been successfully employed for the synthesis of [Fe(**L'**)<sub>3</sub>], *vide infra*. The first formed intermediate in both reactions is likely to have been **E** (R = Me or NEt<sub>2</sub>). The diethylamino substituent is believed for stereoelectronic reasons to have made the corresponding species **E** (R = NEt<sub>2</sub>) kinetically labile, homolysis furnishing FeCl<sub>2</sub> [and therefrom **7**, with 2 Li(**L'**), by analogy with the synthesis of **8** from CoCl<sub>2</sub>; the reaction FeCl<sub>2</sub> + 2 Li(**L'**) was not studied separately] and the appropriate carbon-centred radical which may have been converted to the dimer **F**. Although no attempt was made to isolate **F**, it is noted that a close analogue [Me<sub>3</sub>SiN=P(Ph)<sub>2</sub>CH<sub>2</sub>]<sub>2</sub> has long been known [18a] and is readily deprotonated [18b].



Scheme 2.



The coloured paramagnetic compounds **7** and **8** showed parent ions in their EI-mass spectra, but the C, H, N microanalyses were satisfactory only for **7**. The magnetic moments indicated that both **7** and **8** are high spin, with the  $\mu_{\text{eff}}$  values, as for **3** and **4**, significantly greater than due solely to spin-only.

### 2.3. The bis[3-trimethylsilyliminodiphenylphosphoranyl-2-phenyl-1-trimethylsilylazaallyl]cobalt(II) complex **9**

Compound **9** was prepared as shown in Scheme 3. Thus, treatment of cobalt(II) chloride with 2 Li(L') (**2**), prepared *in situ* from equivalent portions of Li(L) (**1a**) and benzonitrile in thf, and crystallisation from hexane afforded in good yield blue crystals of **9**. The rate of this reaction was slower than those for the cobalt(II) complexes **4** or **8**. If the reaction time was insufficiently long, green crystals of a presumed monosubstituted cobalt complex were formed. [Attempts to prepare an iron(II) analogue of **9** from FeCl<sub>2</sub> and 2 Li(L') were unsuccessful; unidentified mixtures of products were obtained.]

Characterisation of **9** was by C, H, N microanalysis, the mass spectrum showing the molecular cation and appropriate fragments, and the magnetic moment. The value for  $\mu_{\text{eff}}$  was similar to those found for **4** and **8**, being significantly greater than  $\mu_{\text{s}}$ .

## 3. Experimental

### 3.1. General details

Syntheses were carried out under an atmosphere of argon or in a vacuum, using Schlenk apparatus and vacuum line techniques. The solvents used were reagent grade or better and were freshly distilled under dry nitrogen gas and freeze/thaw degassed prior to use. The drying agents employed were sodium benzophenone (C<sub>6</sub>H<sub>6</sub>, C<sub>6</sub>D<sub>6</sub>, C<sub>6</sub>H<sub>5</sub>Me, Et<sub>2</sub>O, thf), sodium-potassium alloy (C<sub>5</sub>H<sub>12</sub>, C<sub>6</sub>H<sub>14</sub>), or phosphorus(V) oxide (CH<sub>2</sub>Cl<sub>2</sub>). The solvents for NMR spectroscopy (CDCl<sub>3</sub>, C<sub>5</sub>D<sub>5</sub>N) were stored over molecular sieves (A4). Elemental analyses were obtained by Medac Ltd., Brunel University. Melting points were measured in sealed capillaries. The <sup>1</sup>H-, <sup>13</sup>C{<sup>1</sup>H}- and <sup>31</sup>P{<sup>1</sup>H}-NMR spectra were recorded using a Bruker WM-360 instrument and were referenced internally (<sup>1</sup>H, <sup>13</sup>C) to residual solvent resonances, or externally (<sup>31</sup>P, with 85% aq. H<sub>3</sub>PO<sub>4</sub> as standard). Electron impact mass spectra were taken from solid samples, with a VG Auto-

spec instrument. The magnetic moments were determined by Evans' method on dilute standard solutions in C<sub>6</sub>H<sub>6</sub>/C<sub>6</sub>D<sub>6</sub> at ambient temperature, with C<sub>6</sub>H<sub>6</sub> in a sealed capillary as external standard. The compounds Li[CH(SiMe<sub>2</sub>R)P(Ph)<sub>2</sub>NSiMe<sub>3</sub>] [R = Me (**1a**), NEt<sub>2</sub> (**1b**)] were prepared as previously described [13]. The metal chlorides (FeCl<sub>2</sub>, FeCl<sub>3</sub>, CoCl<sub>2</sub>, ZrCl<sub>4</sub>) were commercial samples (Aldrich) and were rigorously dried before use.

### 3.2. Preparation of [Fe{CH(SiMe<sub>3</sub>)P(Ph)<sub>2</sub>NSiMe<sub>3</sub>}<sub>2</sub>] (**3**)

Iron(II) chloride (0.18 g, 1.42 mmol) was added to a stirred solution of the lithium compound Li(L) (**1a**) (1.04 g, 2.85 mmol) in thf (30 cm<sup>3</sup>) at -78 °C. The mixture was allowed to warm to room temperature and was stirred for *ca.* 12 h. Volatiles were removed *in vacuo* and the residue was extracted with hexane. The filtered extract was concentrated to *ca.* 3 cm<sup>3</sup>, which after *ca.* 12 h at room temperature yielded yellow crystals of **3a** (0.88 g, 82%), mp. 209 °C (decomp.),  $\mu_{\text{eff}}$  6.4  $\mu_{\text{B}}$  (C<sub>38</sub>H<sub>58</sub>FeN<sub>2</sub>P<sub>2</sub>Si<sub>4</sub> requires C, 59.0; H, 7.56; N, 3.62. Found: C, 58.5; H, 7.49; N, 3.53%). X-ray quality crystals of **3** were obtained from hexane.

### 3.3. Preparation of [Co{CH(SiMe<sub>3</sub>)P(Ph)<sub>2</sub>NSiMe<sub>3</sub>}<sub>2</sub>] (**4**)

The blue complex **4** (0.37 g, 69%), mp. 245–248 °C,  $\mu_{\text{eff}}$  5.4  $\mu_{\text{B}}$  (C<sub>38</sub>H<sub>58</sub>CoN<sub>2</sub>P<sub>2</sub>Si<sub>4</sub> requires C, 58.8; H, 7.53; N, 3.61. Found: C, 58.5; H, 7.51; N, 3.54%) was obtained, using a similar procedure to that for **3**, from **1a** (0.50 g, 1.37 mmol) and CoCl<sub>2</sub> (0.09 g, 0.69 mmol).

### 3.4. Preparation of [ZrCl<sub>3</sub>{CH(SiMe<sub>3</sub>)P(Ph)<sub>2</sub>NSiMe<sub>3</sub>}] (**5**)

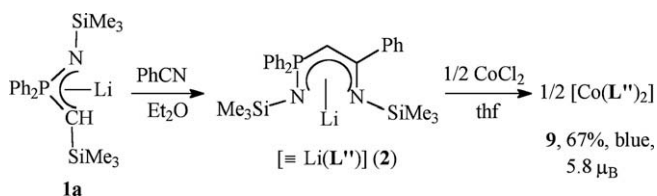
Zirconium(IV) chloride (0.72 g, 3.09 mmol) was added to a stirred solution of **1a** (1.12 g, 3.07 mmol) in toluene (30 cm<sup>3</sup>) at -50 °C. The mixture was brought to room temperature and stirred for *ca.* 20 h. Volatiles were removed *in vacuo* and the residue was extracted with dichloromethane. The filtered extract was concentrated to *ca.* 2 cm<sup>3</sup>, which after 12 h furnished the colourless crystalline complex **5** as the 0.83 CH<sub>2</sub>Cl<sub>2</sub> adduct (0.91 g, 47%), which upon being washed with benzene gave the crystalline complex as **5** as the 0.57 C<sub>6</sub>H<sub>6</sub> adduct, mp. 240–245 °C (C<sub>19</sub>H<sub>29</sub>Cl<sub>3</sub>NPSi<sub>2</sub>Zr·0.57C<sub>6</sub>H<sub>6</sub> requires C, 44.8; H, 5.44; N, 2.33. Found: C, 45.0; H, 5.34; N, 2.20%). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  -0.14 [s, 9H, CHSi(CH<sub>3</sub>)<sub>3</sub>], 0.20 [s, 9H, NSi(CH<sub>3</sub>)<sub>3</sub>], 1.64 [d, 1 H, <sup>2</sup>J (<sup>1</sup>H-<sup>31</sup>P)] 14.1 Hz, CH], 7.42 (s, 3.4H, C<sub>6</sub>H<sub>6</sub>), 7.56–7.62 (m, 6H, Ph), 7.79–7.92 (m, 4H, Ph); <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>5</sub>D<sub>5</sub>N):  $\delta$  3.04 [d, <sup>3</sup>J (<sup>13</sup>C-<sup>31</sup>P)] 4.5 Hz, Si(CH<sub>3</sub>)<sub>3</sub>], 3.90 [d, <sup>3</sup>J (<sup>13</sup>C-<sup>31</sup>P)] 3.1 Hz, Si(CH<sub>3</sub>)<sub>3</sub>], 33.4 [d, <sup>1</sup>J (<sup>13</sup>C-<sup>31</sup>P)] 39.3 Hz, CH], 129.1 [d, J (<sup>13</sup>C-<sup>31</sup>P)] 5.0 Hz], 129.2 [d, J (<sup>13</sup>C-<sup>31</sup>P)] 5.0], 131.4 [d, J (<sup>13</sup>C-<sup>31</sup>P)] 11.1 Hz], 132.4 [d, J (<sup>13</sup>C-<sup>31</sup>P)] 11.3 Hz], 133.0 (Ph); <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  25.3.

### 3.5. Preparation of [Fe{CH(SiMe<sub>3</sub>)P(Ph)<sub>2</sub>NSiMe<sub>3</sub>}<sub>3</sub>] (**6**)

Iron(III) chloride (0.13 g, 0.80 mmol) was added to a stirred solution of Li(L) (**1a**) (0.91 g, 2.49 mmol) in thf (30 cm<sup>3</sup>) at -78 °C. The mixture was brought to room temperature and stirred for *ca.* 12 h. Volatiles were removed *in vacuo* and the residue was extracted with pentane. The filtered extract was concentrated *in vacuo* to *ca.* 2 cm<sup>3</sup>, yielding after 12 h at room temperature yellow-brown crystals of **6** (0.24 g, 25%), mp. 131–133 °C,  $\mu_{\text{eff}}$  6.1  $\mu_{\text{B}}$  (C<sub>57</sub>H<sub>87</sub>FeN<sub>3</sub>P<sub>3</sub>Si<sub>6</sub> requires C, 60.5; H, 7.55; N, 3.71. Found: C, 59.4; H, 7.50; N, 3.64%).

### 3.6. Preparation of [Fe{CH(SiMe<sub>2</sub>NEt<sub>2</sub>)P(Ph)<sub>2</sub>NSiMe<sub>3</sub>}<sub>2</sub>] (**7**)

Iron(III) chloride (0.22 g, 1.36 mmol) was added to a stirred solution of Li(L') (**1b**) (1.7 g, 4.03 mmol) in thf (30 cm<sup>3</sup>) at -78 °C. The mixture was allowed to warm to room temperature and was



Scheme 3.

**Table 2**  
Mass spectral data (EI, 70 eV) on **3–9**<sup>a</sup>

Compound	<i>m/e</i> (relative intensity, %), and assignment
[Fe(L) <sub>2</sub> ] ( <b>3</b> )	772(100), [M] <sup>+</sup> ; 699(17), [M-SiMe <sub>3</sub> ] <sup>+</sup> ; 487(16), [Fe(L)SiMe <sub>3</sub> ] <sup>+</sup> ; 413(88), [Fe(L)-1] <sup>+</sup>
Co(L) <sub>2</sub> ( <b>4</b> )	775(22), [M] <sup>+</sup> ; 760(2), [M-Me] <sup>+</sup> ; 702(2), [M-SiMe <sub>3</sub> ] <sup>+</sup> ; 675(8), [M-CHSiMe <sub>3</sub> -Me+1] <sup>+</sup>
[ZrCl <sub>3</sub> (L)] ( <b>5</b> )	555(4), [M] <sup>+</sup> ; 540(31), [M-Me] <sup>+</sup> ; 518(14), [M-Cl] <sup>+</sup> ; 464(54), [M-Ph-Me+1] <sup>+</sup>
[Fe(L) <sub>3</sub> ] ( <b>6</b> )	772(15), [M-L] <sup>+</sup> ; 442(21), [M-L-2Ph-2SiMe <sub>3</sub> -2Me] <sup>+</sup> ; 428(50), [M-L-2Ph-SiMe <sub>3</sub> -NSiMe <sub>3</sub> -2Me] <sup>+</sup> ; 344(42), [HL-Me] <sup>+</sup>
[Fe(L) <sub>2</sub> ] ( <b>7</b> )	886(34), [M] <sup>+</sup> ; 814(12), [M-NEt <sub>2</sub> ] <sup>+</sup> ; 470(85), [FeL-1] <sup>+</sup> ; 401(61), [HL-Me] <sup>+</sup>
[Co(L) <sub>2</sub> ] ( <b>8</b> )	889(6), [M] <sup>+</sup> ; 818(3), [M-NEt <sub>2</sub> +1] <sup>+</sup> ; 690(3), [M-2Ph-3Me] <sup>+</sup> ; 616(7), [M-2SiMe <sub>2</sub> NEt <sub>2</sub> -CH] <sup>+</sup>
[Co(L') <sub>2</sub> ] ( <b>9</b> )	981(19), [M] <sup>+</sup> ; 967(43), [M-Me+1] <sup>+</sup> ; 879(19), [M-NSiMe <sub>3</sub> -Me] <sup>+</sup> ; 792(18), [M-2NSiMe <sub>3</sub> -Me] <sup>+</sup>

<sup>a</sup> [M]<sup>+</sup> represents the parent molecular ion; only the four highest *m/e* peaks are listed.

**Table 3**  
Selected crystallographic data for **3**

Formula	C <sub>38</sub> H <sub>58</sub> FeN <sub>2</sub> P <sub>2</sub> Si <sub>4</sub>
<i>M</i>	773.01
Crystal system	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i> (No. 14)
<i>a</i> (Å)	12.935(2)
<i>b</i> (Å)	18.013(9)
<i>c</i> (Å)	19.781(5)
$\beta$ (°)	106.28(2)
<i>V</i> (Å <sup>3</sup> )	4424(3)
<i>Z</i>	4
Absorption coefficient (mm <sup>-1</sup> )	0.55
Unique reflections, <i>R</i> <sub>int</sub>	7775, 0.019
Reflections with <i>I</i> > 2σ( <i>I</i> ) <i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub>	5083
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	0.060, 0.138
<i>R</i> indices (all data)	0.103, 0.162

then stirred for ca. 12 h. Volatiles were removed from the red-brown solution *in vacuo*. The residue was extracted with pentane. The filtered extract was concentrated *in vacuo* to ca. 2 cm<sup>3</sup>, which after 12 h at room temperature yielded yellow crystals of **7** (0.94 g, 79%), mp. 151–153 °C,  $\mu_{\text{eff}}$  6.0 $\mu_{\text{B}}$  (C<sub>44</sub>H<sub>72</sub>FeN<sub>4</sub>P<sub>2</sub>Si<sub>4</sub> requires C, 59.6; H, 8.18; N, 6.31. Found: C, 58.7; H, 8.20; N, 6.21%).

### 3.7. Preparation of [Co{CH(SiMe<sub>2</sub>NEt<sub>2</sub>)P(Ph)<sub>2</sub>NSiMe<sub>3</sub>}<sub>2</sub>] (**8**)

Using a similar procedure to that described for **7**, treatment of cobalt(II) chloride (0.15 g, 1.15 mmol) with **1b** (1.0 g, 2.37 mmol) afforded deep blue crystals of **8** (0.84 g, 80%), mp. 146–149 °C,  $\mu_{\text{eff}}$  5.9 $\mu_{\text{B}}$  (C<sub>44</sub>H<sub>72</sub>CoN<sub>4</sub>P<sub>2</sub>Si<sub>4</sub> requires C, 59.4; H, 8.15; N, 6.29. Found: C, 61.2; H, 8.55; N, 5.56%).

### 3.8. Preparation of [Co{N(SiMe<sub>3</sub>)C(Ph)C(H)P(Ph)<sub>2</sub>NSiMe<sub>3</sub>}<sub>2</sub>] (**9**)

Cobalt(II) chloride (0.11 g, 0.85 mmol) was added to a solution of Li(L), prepared from the reaction of the lithium salt **1a** (0.65 g, 1.78 mmol) and benzonitrile (0.18 cm<sup>3</sup>, 1.77 mmol) in thf (30 cm<sup>3</sup>), at –78 °C. The stirred mixture was set aside for ca. 12 h, whereafter the volatiles were removed *in vacuo*. The residue was extracted with hexane. The filtered extract was concentrated to ca. 2 cm<sup>3</sup>; which, after 12 h at room temperature, yielded dark blue crystals of **9** (0.51 g, 61%), mp. 150–154 °C,  $\mu_{\text{eff}}$  5.8 $\mu_{\text{B}}$  (C<sub>52</sub>H<sub>68</sub>CoN<sub>4</sub>P<sub>2</sub>Si<sub>4</sub> requires C, 63.6; H, 6.98; N, 5.70. Found: C, 62.4; H, 7.28; N, 5.43%).

### 3.9. Mass spectra of **3–9**

The four highest *m/e* peaks of the EI mass spectra for each of compounds **3–9**, with assignments, are listed in Table 2.

### 3.10. X-ray crystallographic study

Diffraction data were collected at 293(2) K on an Enraf–Nonius CAD4 diffractometer using monochromated Mo K $\alpha$  radiation

( $\lambda = 0.71069$  Å). Crystals were mounted under an inert atmosphere into a capillary which was then sealed. All non-hydrogen atoms were anisotropic; H's were included in riding mode with  $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$  or  $1.5 U_{\text{eq}}(\text{C})$  for methyl groups. The structure was refined on all *F*<sup>2</sup> using SHELXL-97 [19]. Further details are in Table 3.

### Acknowledgements

We thank the Chinese Government and the British Council for financial support for Z.-X.W., and Dr. A.V. Protchenko for useful discussion.

### Appendix A. Supplementary material

CCDC 696887 contains the supplementary crystallographic data for complex **3**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

### References

- [1] K. Izod, *Coord. Chem. Rev.* 227 (2002) 153.
- [2] C. Freund, N. Barros, H. Gornitzka, B. Martin-Vaca, L. Maron, D. Bourissou, *Organometallics* 25 (2006) 4927. and references therein.
- [3] M. Said, M. Thornton-Pett, M. Bochmann, *J. Chem. Soc., Dalton Trans.* (2001) 2844.
- [4] S.A. Ahmed, M.S. Hill, P.B. Hitchcock, *Organometallics* 25 (2006) 394. and references therein.
- [5] (a) T.K. Panda, A. Zulus, M.T. Gamer, P.W. Roesky, *Organometallics* 24 (2005) 2197;  
(b) M. Rastätter, A. Zulus, P.W. Roesky, *Chem. Eur. J.* 13 (2007) 3606;  
(c) M.T. Gamer, P.W. Roesky, I. Palard, M. Le Hellaye, S.M. Guillaume, *Organometallics* 26 (2007) 651.
- [6] (a) D.J. Evans, M.S. Hill, P.B. Hitchcock, *Dalton Trans.* (2003) 570;  
(b) M.S. Hill, P.B. Hitchcock, *J. Organomet. Chem.* 689 (2004) 3163.
- [7] S. Al-Benna, M.J. Sarsfield, M. Thornton-Pett, D.L. Ormsby, P.J. Maddox, P. Brès, M. Bochmann, *J. Chem. Soc., Dalton Trans.* (2000) 4247.
- [8] C. Bibal, M. Pink, Y.D. Smurnyy, J. Tomaszewski, K.G. Caulton, *J. Am. Chem. Soc.* 126 (2004) 2312.
- [9] J. Barluenga, F. López, F. Palacios, *J. Chem. Res. S* 211 (1985) 2541. *M* (1985) 2541.
- [10] A. Murso, D. Stalke, *Eur. J. Inorg. Chem.* (2004) 4272.
- [11] Z.-X. Wang, L. Wang, *Chem. Commun.* (2007) 2423.
- [12] K. Itoh, M. Okamura, Y. Ishii, *J. Organomet. Chem.* 65 (1974) 327.
- [13] P.B. Hitchcock, M.F. Lappert, P.G.H. Uiterweerd, Z.-X. Wang, *J. Chem. Soc., Dalton Trans.* (1999) 3413.
- [14] P.B. Hitchcock, M.F. Lappert, Z.-X. Wang, *J. Chem. Soc., Dalton Trans.* (1997) 1953.
- [15] A. Panda, M. Spender, R.J. Wright, M.M. Olmstead, P. Klavins, P.P. Power, *Inorg. Chem.* 41 (2002) 3909.
- [16] P.B. Hitchcock, M.F. Lappert, R. Sablong, J.R. Severn, *J. Organomet. Chem.* 693 (2009). manuscript in preparation.
- [17] A.G. Avent, P.B. Hitchcock, M.F. Lappert, R. Sablong, J.R. Severn, *Organometallics* 23 (2004) 2591.
- [18] (a) R. Appel, I. Ruppert, *Z. Anorg. Allg. Chem.* 406 (1974) 131;  
(b) M.J. Sarsfield, M. Said, L.A. Gerrard, M. Thornton-Pett, M. Bochmann, *J. Chem. Soc., Dalton Trans.* (2001) 822.
- [19] G.M. Sheldrick, SHELXL-97, Program for the Crystal Structure Refinement, Universität Göttingen, 1997.