

Synthesis of (fluorosilyl) phosphido iron and nickel complexes and ferrosilyl-substituted (fluorosilyl) phosphanes and evidence for the formation of a metallo phosphasilene of the type $[M]-P=SiR_2$

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Received 11 March 1996; accepted 29 April 1996

Abstract

A way to the first transition-metal-substituted (fluorosilyl)phosphanes ($R_2Si(F)P(H)-M$) and a *P*-ferrio phosphasilene ($R_2Si=P-M$) is reported. The bulkily substituted metal phosphido complexes $[Is_2Si(F)P(H)-M]$ **1a–c** ($M = (C_5H_5)Fe(CO)_2$, $(C_5Me_5)Fe(CO)_2$, $(C_5Me_5)Ni(PPH_3)$; $Is = 2,4,6$ -triisopropylphenyl) were prepared in good yields (68–76%) by salt condensation reactions of the corresponding (fluorosilyl)phosphanide **2** with metal bromides. They were characterized by means of NMR and IR spectroscopy and, with the exception of **1a**, by X-ray structure analyses. They do not react with RLi bases ($R = ^nBu$, tBu , N^iPr_2) to give the desired *P*-lithium phosphanide precursors **3a–c**; instead, nucleophilic M–P bond cleavage was observed. Thus, thermolabile $[Is_2Si(F)P(Li(thf)_3)-Fe(CO)_2(C_5H_5)]$ **3a** was prepared via the tin/lithium exchange reaction starting from $[Is_2Si(F)P(SnMe_3)-Fe(CO)_2(C_5H_5)]$ **6a** and nBuLi in THF. Thermolysis of **3a** in hexane affords, upon LiF elimination, $[Is_2Si=P-Fe(CO)_2(C_5H_5)]$ **7**. Although **3a** and **7** could not be isolated, their structures were unambiguously proven by characteristic ^{31}P and ^{29}Si NMR data and the composition of **7** was established by high resolution mass spectrometry. Furthermore, the ferrosilyl phosphanes $[Is_2Si(F)P(H)-SiMe(R)Fe(CO)_2(C_5H_5)]$ **8a** ($R = Me$) and **8b** ($R = ^tBu$) were prepared and the crystal structure of **8b** was elucidated. These compounds and their *P*- $SnMe_3$ derivatives could not be transformed into phosphasilene derivatives.

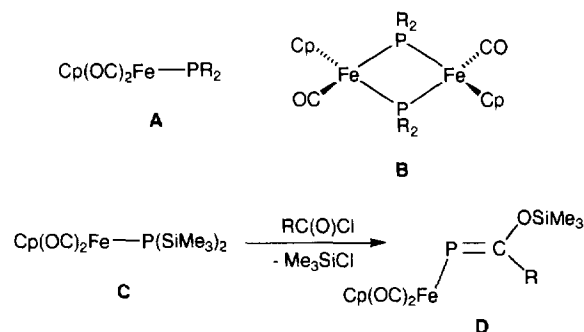
Keywords: Metal phosphides; Multiple bonds; Silicon–phosphorus compounds; Tin–phosphorus compounds

1. Introduction

There is considerable interest in developing metal phosphido complexes as templates for the synthesis of functionalized cyclic phosphorus–carbon ligands [1] and low-valent phosphorus metal compounds [2] (see also Ref. [3]). Phosphido complexes of the type $CpFe(CO)_2PR_2$ **A** ($R = alkyl$) usually dimerize, under loss of CO, to form μ_2-PR_2 bridged complexes **B** [4] (Scheme 1). However, electron poor phosphanyl groups such as $(CF_3)_2P$ and Ph_2P [5] and sterically demanding substituents at phosphorus favor form **A**. The latter has been observed for the functionalized and bulkily substituted bis(trimethylsilyl)phosphido iron complex **C** [6], which does not undergo dimerization and is a versatile starting material for *P*-metallo phosphalkenes **D** [3] due to the high reactivity of the Si–P bond (Scheme 1).

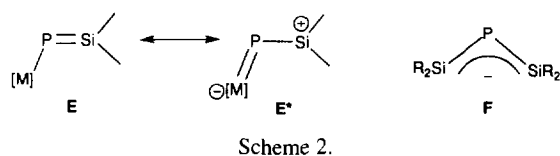
While the chemistry of metallo phosphalkene com-

plexes is nowadays well developed, an analogous metallo phosphasilene **E** is hitherto unknown. Metastable silylidenephosphanes ($Si=P$, phosphasilenes) have been synthesized [7,8], i.e. via LiF elimination from corresponding lithium (fluorosilyl)phosphanides [8], and are versatile building blocks for the preparation of electronically unusual silicon–phosphorus heterocycles [8]. However, the low-coordinate silicon of the $Si=P$ bond



Scheme 1.

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needs steric protection by bulky aryl and alkyl substituents. It is expected that, compared with **D** and phosphasilenes, *P*-metallo-phosphasilenes of the type $R_2Si=P[M]$ **E** ($R = \text{Aryl, Alkyl, Silyl}$), bearing a 17 valence electron transition metal complex fragment $[M]$, are much more reactive toward unsaturated organic compounds and organometallic reagents due to a contribution of the polar form **E*** to the electronic ground state (Scheme 2).

The same is the case for the as yet unknown silaphosphaallyl transition metal complexes. There is only one reported example of a silaphosphaallyl compound. The structure of a 1,3-diphospha-2-silaallyl lithium complex has been established by X-ray structure analysis [9]. In this context, the stabilization of a 1,3-disila-2-phosphaallyl anion **F** would be desirable (Scheme 2), since most of the π -electron density is localized in the 1,3 positions at silicon and not at the electronegative phosphorus center.

Here we report on the synthesis and structures of (fluorosilyl)phosphido iron and nickel complexes, having the bulky 2,4,6-triisopropylphenyl (Is) substituent at silicon, which were converted into corresponding *P*-metallo phosphasilenes. Furthermore, the preparation and characterization of ferrosilyl (fluorosilyl)phosphanes is presented, which, however, could not be transformed into a phosphasilene or 1,3-disila-2-phosphaallyl iron complex.

2. Experimental details

2.1. General procedures

All manipulations with reagents, syntheses and spectroscopic measurements were carried out under anaerobic conditions in a nitrogen atmosphere. Solvents were purified by conventional methods and stored under a nitrogen atmosphere. The starting compounds $Is_2Si(F)PHLi$ [10], $[(C_5H_5)Fe(CO)_2Br]$ [11], $[(C_5Me_5)Fe(CO)_2Br]$ [12], $[(C_5Me_5)Ni(PPh_3)Br]$ [13], $[(C_5H_5)Fe(CO)_2(SiMe_2Cl)]$ and $[(C_5H_5)Fe(CO)_2(SiMe^tBuCl)]$ [14] were prepared according to the literature.

2.2. Physical measurements

1H NMR (90 MHz, 200 MHz), ^{31}P NMR (36 MHz, 81 MHz), ^{19}F NMR (89 MHz), and ^{29}Si NMR spectra

(37 MHz) were recorded on a Jeol-FX90Q and/or Bruker AC200 spectrometer. Chemical shifts (δ) are given relative to external standards (1H , ^{29}Si : $SiMe_4$; ^{31}P : 85% aq. H_3PO_4 ; ^{19}F : $CFCl_3$). IR spectra were recorded on a Perkin–Elmer spectrometer, and mass spectra on a Finnigan MAT 8230. All isolated compounds gave C, H analyses consistent with their formulas.

2.3. Syntheses of $[(C_5H_5)Fe(CO)_2-PH-Si(F)Is_2]$ **1a**, $[(C_5Me_5)Fe(CO)_2-PH-Si(F)Is_2]$ **1b**, and $[(C_5Me_5)Ni(PPh_3)-PH-Si(F)Is_2]$ **1c**

1a. A slurry of 1.18 g (4.6 mmol) $[(C_5H_5)Fe(CO)_2Br]$ in 30 ml THF was treated with a solution of 4.6 mmol **2** in 20 ml THF at $-20^\circ C$. The reaction mixture was stirred for 10 h at room temperature, and subsequently the solvent was evaporated off in vacuo (10^{-2} Torr). The red-brown residue was taken up in 30 ml toluene, filtered through a GIII frit, and the solvent was evaporated off. The solid residue was recrystallized in hexane at room temperature. Yield: 2.3 g (3.5 mmol, 76%), red-brown crystals. Fp. $115^\circ C$. 1H NMR (C_6D_6): δ 7.17 (s, 4H, arom. H), 4.16 (s, 5H, C_5H_5), 3.85 (br, 4H, *o*- $CHMe_2$), 2.79 (m, 2H, *p*- $CHMe_2$), 1.21 (d, 24H, *o*- $CHMe_2$), 1.18 (d, 12H, *p*- $CHMe_2$). ^{31}P NMR (C_6D_6): δ -214.9 (d, $^1J(P,H) = 168$ Hz). ^{19}F NMR (C_6D_6): δ -131.0 (s). IR (CH_2Cl_2 , cm^{-1}): $\nu(CO)$ 2061, 2017, 2056, 2012. MS (m/z , %): 662 (M^+ , 32), 634 ($(M-CO)^+$, 46), 606 ($(M-2CO)^+$, 80), 454 (Is_2SiFH^+ , 100). Anal. Found: C, 67.02; H, 8.13. $C_{37}H_{52}FFeO_2PSi$ (662.73). Calc.: C, 67.06; H, 7.91%.

1b. Similar to the procedure for the synthesis of **1a**, starting from 1.12 g (3.43 mmol) $[(C_5Me_5)Fe(CO)_2Br]$ and 3.43 mmol **2**. Yield: 1.75 g (2.4 mmol, 70%), red-brown solid. Fp. $154^\circ C$. 1H NMR (C_6D_6): δ 7.10 (s, 4H, arom. H), 3.91 (br, 4H, *o*- $CHMe_2$), 2.80 (m, 2H, *p*- $CHMe_2$), 1.31 (s, 15H, C_5Me_5), 1.11 (d, 36H, $CHMe_2$). ^{31}P NMR (C_6D_6): δ 172.0 (dd, $^1J(P,H) = 154$ Hz, $^2J(P,F) = 15$ Hz). ^{19}F NMR (C_6D_6): δ -128.6 (d, $^2J(F,P) = 15$ Hz). IR (CH_2Cl_2 , cm^{-1}): $\nu(CO)$ 2003, 1959. MS (FAB, m/z , %): 732 (M^+ , 100), 704 ($(M-CO)^+$, 16), 676 ($(M-2CO)^+$, 22), 453 (Is_2SiF^+ , 30). Anal. Found: C, 68.34; H, 8.61. $C_{42}H_{62}FFeO_2PSi$ (732.86). Calc.: C, 68.82; H, 8.52%.

1c. Similar to the procedure for the synthesis of **1a**, starting from 1.82 g (3.40 mmol) $[(C_5Me_5)Ni(PPh_3)Br]$ and 3.40 mmol **2**. Yield: 2.20 g (2.34 mmol, 68.8%), red-brown solid. Fp. $135^\circ C$. 1H NMR (C_6D_6): δ 7.55 (dd, 6H, *o*-H), 7.10 (s, 4H, arom. H), 6.93 (dd, 3H, *p*-H), 6.79 (dt, 6H, *m*-H), 3.8–4.4 (br, 4H, *o*- $CHMe_2$), 2.80 (m, 2H, *p*- $CHMe_2$), 1.58 (s, 15H, C_5Me_5), 1.26 (d, 12H, *p*- $CHMe_2$), 1.22 (d, 24H, *o*- $CHMe_2$). ^{31}P NMR (C_6D_6): δ 46.9 (s, PPh_3), -125.7 (d, $^1J(P,H) = 190$ Hz). ^{19}F NMR (C_6D_6): δ -141 (s). ^{29}Si NMR

(C₆D₆): δ 27.2 (ddd, $^1J(\text{Si},\text{F}) = 323$ Hz, $^1J(\text{Si},\text{P}) = 81.6$ Hz, $^3J(\text{Si},\text{P}) = 6.7$ Hz). MS (EI, m/z , %): 679 ((M - PPh₃ - 1)⁺, 40), 454 (Is₂SiFH⁺, 43), 262 (PPh₃⁺, 100). Anal. Found: C, 73.45; H, 8.34. C₅₈H₇₇FNiP₂Si (941.97). Calc.: C, 73.95; H, 8.24%.

2.4. Syntheses of Is₂Si(F)PHSnMe₃, **4**, Is₂Si(F)-P[Li(thf)₃]SnMe₃, **5**, and [(C₅H₅)Fe(CO)₂-P(SnMe₃)-Si(F)Is₂] **6a**

4. A solution of 0.62 g (3.1 mmol) Me₃SnCl in 20 ml THF was treated with 3 mmol of **2** in 10 ml THF at -40 °C. The mixture was warmed up to room temperature within 6 h and subsequently the solvent was removed in vacuo (10⁻² Torr). The residue was taken up in 20 ml hexane, LiCl was removed upon filtration, and the solvent was evaporated off to give **4** as a colorless oil. Yield: 1.30 g (1.98 mmol, 66%). ¹H NMR (C₆D₆): δ 7.10 (s, 4H, arom. H), 3.75 (m, 4H, *o*-CHMe₂), 2.90 (m, 2H, *p*-CHMe₂), 1.25 (m, 36H, CHMe₂), 0.55 (s, 9H, SnMe₃). ³¹P NMR (C₆D₆): δ -236.0 (dd, $^1J(\text{P},\text{H}) = 176$ Hz, $^2J(\text{P},\text{F}) = 31$ Hz, $^1J(\text{P},^{119}\text{Sn}) = 557$ Hz). ¹⁹F NMR (C₆D₆): δ -121.0 (d, $^2J(\text{F},\text{P}) = 31$ Hz). MS (EI, m/z , %): 650 (M⁺, 10), 635 ((M - Me)⁺, 5), 486 ((Is₂Si(F)PH₂)⁺, 20), 453 (Is₂SiF⁺, 100).

5. A solution of 2.47 g (3.81 mmol) **4** in 20 ml THF was treated with an equimolar amount of LiNⁱPr₂ in 10 ml THF at -78 °C. The yellow solution was stirred for 1 h at this temperature, and subsequently warmed up to room temperature. The solvent was evaporated off and the residue was recrystallized from a small amount of hexane. Yield: 2.76 g (3.16 mmol, 83%), colorless crystals. ¹H NMR (C₆D₆): δ 7.15 (s, 4H, arom. H), 4.60 (br, 4H, *o*-CHMe₂), 3.5 (m, 12H, THF), 2.70 (m, 2H, *p*-CHMe₂), 1.31 (m, 12H, THF), 1.28 (m, 36H, CHMe₂), 0.59 (s, 9H, SnMe₃). ³¹P NMR (C₆D₆): δ -284.0 (d, $^2J(\text{P},\text{F}) = 35$ Hz, $^1J(\text{P},^{119}\text{Sn}) = 1048$ Hz). ¹⁹F NMR (C₆D₆): δ -111.3 (d, $^2J(\text{F},\text{P}) = 35$ Hz). ²⁹Si NMR (C₆D₆): δ 25.6 (dd, $^1J(\text{Si},\text{F}) = 287$ Hz, $^1J(\text{Si},\text{P}) = 115$ Hz). Anal. Found: C, 61.44; H, 9.00. C₄₅H₇₉FLiO₃PSiSn. Calc.: C, 62.00; H, 9.06%.

6a. To a slurry of 1.27 g (4.94 mmol) [(C₅H₅)Fe(CO)₂Br] in 60 ml hexane was added a solution of **5** in 20 ml THF within 30 min at -78 °C. The mixture was warmed up to room temperature within 8 h, and subsequently the solvent was removed in vacuo (10⁻² Torr). The residue was taken up in 30 ml hexane and filtered through a GIII frit. The clear red solution was concentrated to 10 ml, whereby the product was crystallized at room temperature. Yield: 2.56 g (3.06 mmol, 62%), deep red crystals. Fp. 201 °C (dec.). ¹H NMR (C₆D₆): δ 7.20 (s, 4H, arom. H), 4.40 (s, 5H, C₅H₅), 4.11 (br, 4H, *o*-CHMe₂), 2.93 (m, 2H, *p*-CHMe₂), 1.32 (m, 36H, CHMe₂), 0.32 (s, 9H, SnMe₃). ³¹P NMR (C₆D₆): δ -247.1 (br, $^1J(\text{P},^{119}\text{Sn}) = 1050$ Hz). ¹⁹F NMR (C₆D₆): δ -123.0 (s). ²⁹Si NMR (C₆D₆): δ 26.6 (dd,

$^1J(\text{Si},\text{F}) = 345$ Hz, $^1J(\text{Si},\text{P}) = 95$ Hz). IR (CH₂Cl₂, cm⁻¹): $\nu(\text{CO})$ 2022, 1981, 2012, 2005, 1968, 1961. MS (EI, m/z , %): 826 (M⁺, 8), 798 ((M - CO)⁺, 8), 661 ((M - SnMe₃)⁺, 5), 605 (100). Anal. Found: C, 57.73; H, 7.21. C₄₀H₆₀FFeO₂PSiSn (825.48). Calc.: C, 58.20; H, 7.32%.

2.5. Formation of [(C₅H₅)Fe(CO)₂-P[Li(thf)_nSi(F)Is₂] **3a** and [(C₅H₅)Fe(CO)₂-P=SiIs₂] **7**

3a. A solution of 0.76 g (0.92 mmol) **6a** in 20 ml THF was treated with 0.92 mmol ⁿBuLi (2.5 M solution in hexane) at -78 °C. The solution was stirred for 1 h at this temperature and subsequently warmed up to room temperature within 8 h. The ³¹P NMR spectrum of the brown solution shows formation of **3a** to 50% (δ (³¹P) = -378 (s), δ (¹⁹F) = -138). Upon hydrolysis of the mixture at -30 °C, **3a** was completely converted into **1a** (³¹P NMR).

7. The solution containing 50% of **3a** was evaporated to dryness and the residue was taken up in 20 ml hexane and heated at 50 °C. The clear red solution contained **7** to ca. 45% (³¹P NMR). ³¹P NMR: δ 57 (s, $^1J(\text{P},\text{Si}) = 163$ Hz). ²⁹Si NMR: δ 201 (d, $^1J(\text{Si},\text{P}) = 163$ Hz). High resolution MS, calc. for C₃₇H₅₁FeO₂PSi: 642.2731; found: 642.2726.

2.6. Synthesis of [(C₅H₅)Fe(CO)₂(SiMe₂)PH-Si(F)Is₂] **8a** and (C₅Me₅)Fe(CO)₂(SiMe^tBu)-PH-Si(F)Is₂] **8b**

8a. A solution of 2.12 g (4.5 mmol) [(C₅H₅)Fe(CO)₂(SiMe₂Cl)] in 40 ml THF at -78 °C was treated with a solution of 4.5 mmol **2** in THF at -78 °C. After stirring for 1 h the mixture was allowed to warm up to room temperature. The solvent was removed in vacuo (10⁻² Torr) and the residue was taken up in 20 ml hexane, and the solid was filtered. Removal of hexane yielded a red-brown oil. Yield: 2.10 g (2.79 mmol, 62%). ¹H NMR (C₆D₆): δ 7.10 (s, 4H, arom. H), 4.31 (s, 5H, C₅H₅), 3.71 (br, 4H, *o*-CHMe₂), 2.75 (m, 2H, *p*-CHMe₂), 1.1–1.4 (m, 42H, CHMe₂ and SiMe₂). ³¹P NMR (C₆D₆): δ -181.1 (d, $^1J(\text{P},\text{H}) = 198$ Hz). ¹⁹F NMR (C₆D₆): δ -128.5 (s). ²⁹Si NMR (C₆D₆): δ 50.2 (d, SiMe₂, $^1J(\text{Si},\text{P}) = 60$ Hz), 13.5 (dd, SiF, $^1J(\text{Si},\text{F}) = 341$ Hz, $^1J(\text{Si},\text{P}) = 50$ Hz). IR (CH₂Cl₂, cm⁻¹): $\nu(\text{CO})$ 2005, 1955. MS (EI, m/z , %): 720 (M⁺, 10), 664((M - 2CO)⁺, 34), 542 ((Is₂Si(F)PHSiMe₂ - 1)⁺, 43), 453 (Is₂SiF⁺, 100). Anal. Found: C, 64.77; H, 8.23. C₃₉H₅₈FFeO₂PSi₂ (720.86). Calc.: C, 64.98; H, 8.11%.

8b. Similar to the procedure for the synthesis of **8a**, starting from 1.44 g (4.5 mmol) [(C₅H₅)Fe(CO)₂(SiMe^tBuCl)] and 4.5 mmol **2**. Recrystallization from hexane at room temperature gave a yellow solid. Yield: 1.20 g (1.62 mmol, 36%). Fp. 234 °C (dec.). ¹H NMR (C₆D₆): δ 7.10 (s, 4H, arom. H), 4.51 (s, 5H, C₅H₅), 3.85 (br, 4H, *o*-CHMe₂), 2.80 (m, 2H, *p*-CHMe₂),

1.0–1.3 (m, 48H, CHMe_2 and $\text{SiMe}'\text{Bu}$). ^{31}P NMR (C_6D_6): $\delta -184.2$ (d, $^1J(\text{P,H}) = 205$ Hz). ^{19}F NMR (C_6D_6): $\delta -126.3$ (s). ^{29}Si NMR (C_6D_6): $\delta 56.2$ (d, $\text{SiMe}'\text{Bu}$, $^1J(\text{Si,P}) = 61$ Hz), 12.5 (dd, SiF , $^1J(\text{Si,F}) = 340$ Hz, $^1J(\text{Si,P}) = 53$ Hz). IR (CH_2Cl_2 , cm^{-1}): $\nu(\text{CO})$ 2003, 1953. MS (EI, m/z , %): 762 (M^+ , 3), 706 ($(\text{M} - 2\text{CO})^+$, 24), 585 ($(\text{Is}_2\text{Si}(\text{F})\text{PHSiMe}'\text{Bu} - 1)^+$, 43), 453 (Is_2SiF^+ , 100). Anal. Found: C, 65.89; H, 8.38. $\text{C}_{42}\text{H}_{64}\text{FFeO}_2\text{PSi}_2$ (762.94). Calc.: C, 66.12; H, 8.45%.

2.7. Formation of $[(\text{C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{SiMe}_2)\text{P} - [\text{SnMe}_3]\text{Si}(\text{F})\text{Is}_2]$ **10** and $[(\text{C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{SiMe}_2)\text{P} - [\text{Li}(\text{thf})_n]\text{Si}(\text{F})\text{Is}_2]$ **9a**

10. A solution of 4 mmol **5** in 10 ml THF was treated with a solution of 1.08 g (4 mmol) $[(\text{C}_5\text{H}_5)\text{Fe}(\text{CO})_2 - (\text{SiMe}_2\text{Cl})]$ in 40 ml THF at -78°C . The red solution was allowed to warm up to room temperature within 8 h. After removal of the solvent in vacuo (10^{-2} Torr) the residue was taken up in 30 ml hexane, and the solution was filtered through a GIII frit. Evaporation of hexane afforded a brown oil which contained ca. 30% **10** as shown by ^{31}P NMR and high resolution MS. ^{31}P NMR: $\delta -216.3$ (s, $^1J(\text{P},^{119}\text{Sn}) = 1056$ Hz). High resolution MS, calc. for $\text{C}_{42}\text{H}_{66}\text{FFeO}_2\text{PSi}_2^{118}\text{Sn}$: 880.6086; found: 880.6057. Major product (ca. 70%) of this reac-

tion was **8a** which was identified by its characteristic ^{31}P NMR data.

9a. The reaction mixture containing 30% **10** was treated with 1.4 mmol $^n\text{BuLi}$ (2.5 M solution in hexane) at -78°C . After 2 h at this temperature **10** was completely converted into **9a** as shown by ^{31}P NMR spectroscopy. However, none of the products could be isolated. **9a** was characterized by ^{31}P NMR spectroscopy ($\delta(^{31}\text{P}) = -326.5$ (s)) and by derivatization reaction upon hydrolysis of the mixture; the latter process afforded **8a** (^{31}P NMR) and, as yet, unidentified products.

2.8. X-ray crystal structure analyses of **1b**, **1c** and **8b**

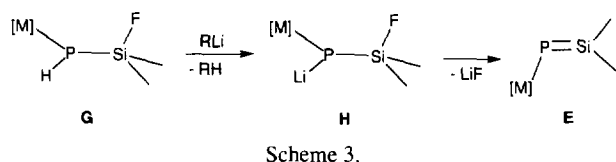
Details of data collection and refinement are given in Table 1. Intensity data for **1b** were collected on a Siemens–Stoe AED2, for **1c**, **8b** on a Syntex R3 diffractometer (Mo $\text{K}\alpha$ radiation, $\lambda = 0.7107$ Å, ω -scan) and corrected for absorption (ψ -scans). The structures were solved by direct methods (SHELXS 86) and refined by using full-matrix least squares techniques based on F^2 with all measured reflections (SHELXL 93) [15] with anisotropic temperature factors for all non-hydrogen atoms. Hydrogen atoms were included in calculated positions or treated as part of a rigid group (CH_3). Only common isotropic temperature factors were refined. Only the hydrogen atoms at phosphorus were

Table 1
Crystallographic data for **1b**, **1c** and **8b**

	1b	1c	8b
Formula	$\text{C}_{42}\text{H}_{62}\text{O}_2\text{FFePSi}$	$\text{C}_{58}\text{H}_{77}\text{FNiP}_2\text{Si}$	$\text{C}_{42}\text{H}_{64}\text{O}_2\text{FFePSi}_2$
Fw	732.8	941.9	762.9
Crystal size (mm^3)	$0.15 \times 0.6 \times 0.7$	$0.4 \times 0.5 \times 0.7$	$0.3 \times 0.4 \times 0.4$
a (Å)	17.729(12)	14.565(4)	10.158(2)
b (Å)	10.979(8)	14.647(4)	10.590(2)
c (Å)	22.260(15)	14.786(4)	21.386(4)
α (deg)	90	70.52(2)	102.95(2)
β (deg)	97.04(5)	67.94(2)	90.55(2)
γ (deg)	90	74.15(2)	99.52(2)
Crystal system	monoclinic	triclinic	triclinic
Space group	$P2_1/a$	$P\bar{1}$	$P\bar{1}$
Volume (Å^3)	4300	2716	2209
Z	4	2	2
Temperature ($^\circ\text{C}$)	ambient	-100	ambient
D_{calc} (g cm^{-3})	1.13	1.15	1.15
Absorption coefficient μ (cm^{-1})	4.5	4.8	4.7
No. of measured reflections	5620	8532	7349
No. of unique reflections	5620	8532	6925
No. of observed reflections	2751	6791	5003
No. of parameters	520	595	471
θ max (deg)	22.5	24	24
h, k, l index range	$-19/+18, 0/+11, 0/+23$	$0/+16, -15/+16, -15/+16$	$0/+11, -12/+11, -24/+24$
$R1^a$	0.059	0.038	0.056
$wR2^b$	0.191	0.092	0.123

^a $R1 = (\sum(|F_o| - |F_c|) / \sum|F_o|)$ for observed reflections.

^b $wR2 = \{\sum[w(F_o^2 - F_c^2)^2] / \sum(wF_o^2)\}^{1/2}$ for all measured reflections.



located in difference Fourier maps and refined isotropically. The (C_5Me_5) -ring in **1b** is disordered and was refined by two sets of atoms (site occupation 0.66/0.34).

3. Results and discussion

3.1. Synthesis of the (fluorosilyl)phosphido complexes **1a–c**

Our approach to *P*-metallo phosphasilenes **E** is analogous to that for metastable silyl-substituted phosphasilenes [8], starting from *P*-metal (fluorosilyl)phosphanes **G** with lithiation on phosphorus thereof to form **H** and subsequent LiF elimination (Scheme 3).

Therefore, appropriately substituted (fluorosilyl)phosphanes **1**, that is compounds of type **G**, were synthesized first. The synthesis of the new iron and nickel complexes **1a–c** was achieved in a manner analogous to the procedure for lithium (fluorosilyl)silylphosphanides [8] (Scheme 4). Reaction of the bulkily substituted lithium (fluorosilyl)phosphanide **2** with the iron bromides and the nickel bromide affords the desired phosphido complexes **1a–c** in 68–76% yields.

The compounds form reddish brown crystals which are readily soluble in non-polar solvents such as hexane. The ^{31}P NMR and IR spectroscopic characterization of the complexes revealed some interesting features. Owing to the obviously higher group electronegativity of the metal complex fragments, the ^{31}P nuclei are significantly less shielded (**1a**: $\delta = -214.9$; **1b**: $\delta = -172.0$; **1c**: $\delta = -125.7$, 46.5 (PPh₃)) compared with related (fluorosilyl)silyl, germyl and stannyphosphanes (δ range: -220 to 240) [8,16]. Clearly, steric effects are responsible for the large difference between the $\delta(^{31}P)$ values of **1a,b**, whereas the rather strong deshielding of the phosphorus in **1c** may indicate a stronger metal phosphido-phosphorus π donation and a higher *s*-contribution in the phosphido-phosphorus valence orbitals. This is supported by a larger $^1J(P,H)$ coupling constant (190 Hz) in comparison with the values for **1a** (168 Hz)

and **1b** (154 Hz). The ^{31}P NMR chemical shifts of **1c** are also very different compared with the values of the related complex $[(C_5H_5)Ni(PPh_3)P(SiMe_3)_2]$ ($\delta = -269$, 35 (PPh₃)) [17]. Interestingly, the IR spectrum of **1a** in CH_2Cl_2 (Table 2) shows four absorptions for the CO stretching vibrations, due to the presence of a rotational isomer, whereas **1b** gives two bands as expected for local C_s symmetry of the metal complex fragments. The wavenumbers are significantly blue shifted compared with the values of related complexes (see Table 2).

The phosphino ligand in **1a,b** unequivocally increases the strength of the $C\equiv O$ triple bond, owing to its favorable donor/acceptor ability.

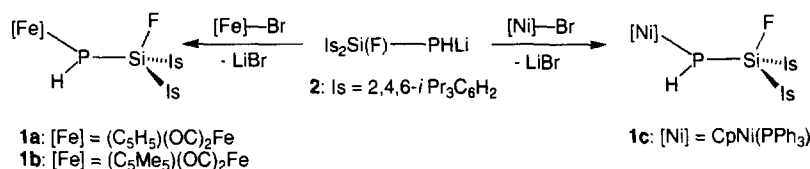
3.2. Crystal structures of **1b,c**

The structures of **1b** (Fig. 1) and **1c** (Fig. 2) were established by X-ray crystal structure analyses in order to determine the coordination geometry around the phosphido-P atoms. The P atoms are pyramidally coordinated, with the sum of bonding angles being 306.3° (**1b**) and 321.4° (**1c**). Therefore, a π donor interaction between the P atom and the metal centers seems negligible. This situation is probably different in solution, since the inversion barrier at phosphorus may be as little as in disilylphosphanes (10 – 15 kcal mol⁻¹) [19].

The Fe–P distance in **1b** of 2.323(2) Å is very similar to the value observed in related iron phosphido complexes [18], i.e. $[(C_5Me_5)Fe(CO)_2PPh_2]$ with 2.323(4) Å [18]. The Ni1–P2 distance of 2.215(1) Å is, as expected, significantly longer than the value for the Ni1–P1 bond (2.146(1) Å). Similar relationships have been observed in a disilylphosphino (bisphosphine) nickel(I) complex [20]. The respective P–Si and Si–F distances and the angles around the silicon atom in **1b,c** (Tables 3 and 4) are very similar and lie in the expected range of other (fluorosilyl)phosphanes [8,16] and fluorosilanes [21].

3.3. Attempts to lithiate phosphorus in **1a–c**

It appears that the reaction of **1a–c** with ⁿBuLi, ^tBuLi and lithium diisopropylamide does not yield the desired *P*-lithium phosphanides **3a–c** (Scheme 5). Surprisingly, instead of deprotonation on phosphorus, the metal–P bond is cleaved by nucleophilic attack even at low temperature ($-78^\circ C$), whereby **2** and probably the



Scheme 4.

Table 2
CO stretching vibrations of **1a,b** and related complexes

$[(C_5Me_5)Fe(CO)_2-PR^1R^2]$	Wavenumber (cm ⁻¹)	Ref.
$R_1 = R_2 = ^iBu$	1980, 1930	[18]
$R_1 = ^iBu, R_2 = SiMe_3$	1987, 1940	[18]
$R_1 = R_2 = SiMe_3$	1990, 1945	[18]
$R_1 = R_2 = Ph$	2000, 1953	[18]
1a	2061, 2056,	this work
	2017, 2012	
1b	2003, 1959	this work

respective metal alkyl and amido complexes have been formed. The latter, however, could not be isolated. The formation of **2** is proven by its characteristic ³¹P, ²⁹Si and ¹⁹F NMR data. Clearly, this reactivity is due to the high electrophilicity of the metal centers. Owing to the lack of lithiation on phosphorus, we have attempted the preparation of the *P*-trimethylstannyl analogs of **1a–c**, that is compounds of type **6**, starting from **5** via **4** (Scheme 5). A subsequent tin/lithium exchange reaction provided the desired lithium phosphanides **3a–c**. However, it turned out that merely **6a** is accessible for steric reasons.

3.4. Synthesis of the *P*-trimethylstannyl-substituted (fluorosilyl)phosphido complex **6a**

Reaction of the lithium phosphanide **2** with Me₃SnCl affords the stannylated phosphane **4** in 66% yield, which has been isolated in the form of a colorless oil. Its ³¹P NMR spectrum shows a doublet of doublets at $\delta = -236.0$ (¹*J*(P,H) = 176 Hz, ²*J*(P,F) = 31 Hz) with ^{119/117}Sn satellites (¹*J*(P, ¹¹⁹Sn) = 557 Hz). These NMR data are in the expected range for stannylphosphanes

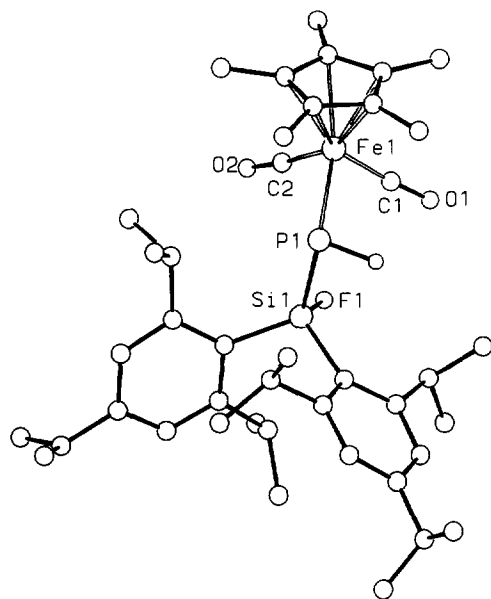


Fig. 1. Solid-state structure of **1b**. H atoms (with exception of P–H) are omitted for clarity.

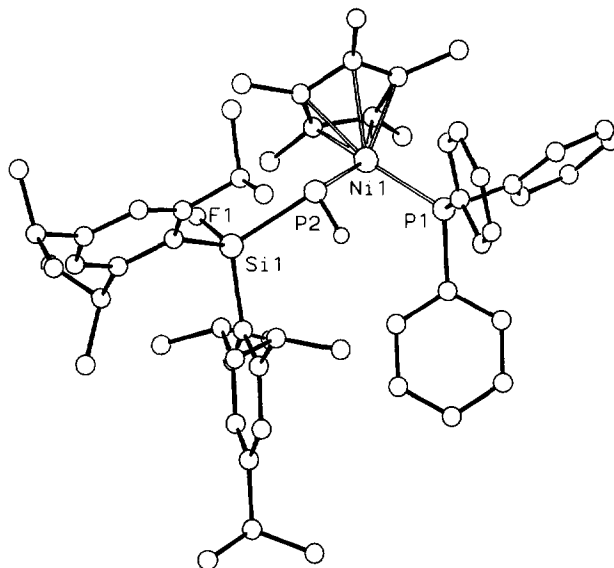


Fig. 2. Solid-state structure of **1c**. H atoms (with exception of P–H) are omitted for clarity.

[22]. Subsequent lithiation on phosphorus with lithium diisopropylamide in THF as solvent at -78°C gave rise to the lithium (fluorosilyl)stannylphosphanide **5**, which was isolated in 83% yield in the form of a colorless solid. Its ³¹P NMR spectrum shows a doublet at $\delta = -284.0$ (²*J*(P,F) = 35 Hz) with a much larger ¹¹⁹Sn coupling constant of 1048 Hz than that observed for **4** due to its higher polarity. Treatment of **4** with other strong bases such as ⁿBuLi and ^tBuLi, however, does not result in the formation of **5**. Instead, a tin/lithium exchange reaction occurs, leading to **2** and Me₃SnBu.

A crystal structure analysis of **5** revealed that the tetrahedrally coordinated lithium center is bonded to phosphorus and three donor molecules of THF. The P atom is pyramidally coordinated with a sum of bonding angles of 340.7° . However, owing to poor crystal quality and disorder of the methyl groups at tin and the THF molecules, a discussion of bonding parameters is meaningless.

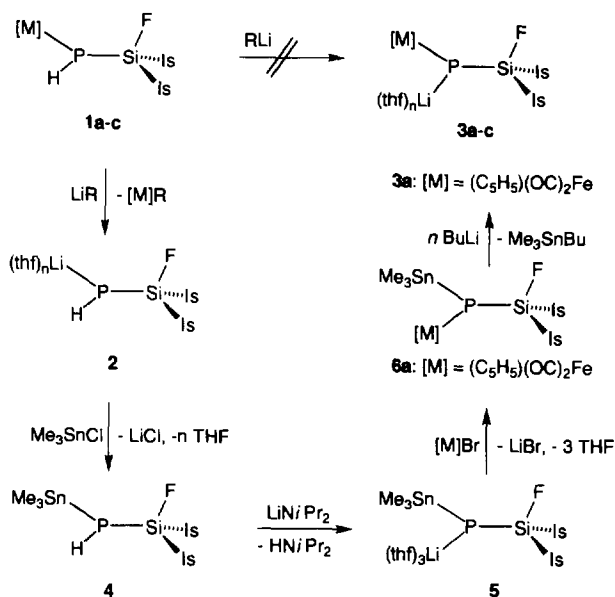
Table 3
Selected bond lengths (Å) and angles (deg) for **1b**

Fe(1)–C(1)	1.736(9)
Fe(1)–C(2)	1.747(9)
Fe(1)–P(1)	2.323(2)
P(1)–Si(1)	2.248(3)
P(1)–H(1)	1.40(4)
Si(1)–F(1)	1.619(3)
C(1)–Fe(1)–C(2)	94.7(4)
C(1)–Fe(1)–P(1)	88.5(3)
C(2)–Fe(1)–P(1)	93.7(3)
Si(1)–P(1)–Fe(1)	115.32(10)
Si(1)–P(1)–H(1)	89.0(20)
Fe(1)–P(1)–H(1)	103.0(20)

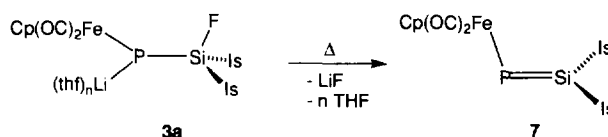
Table 4
Selected bond lengths (Å) and angles (deg) for **1c**

Ni(1)–P(1)	2.1456(10)
Ni(1)–P(2)	2.2148(10)
P(2)–Si(1)	2.2599(10)
P(2)–H(1)	1.28(3)
Si(1)–F(1)	1.614(2)
P(1)–Ni(1)–P(2)	92.97(4)
Ni(1)–P(2)–Si(1)	121.76(4)
Ni(1)–P(2)–H(1)	109.5(12)
Si(1)–P(2)–H(1)	90.4(12)

The formation of the desired ferrio (fluorosilyl)stanlylphosphane **6a** succeeds in 62% yields by reaction of **5** with $[(C_5H_5)Fe(CO)_2Br]$. Its ^{31}P NMR spectrum (25 °C) shows a broadened signal at $\delta = -247.0$ ($h_{1/2} = 85$ Hz) with ^{119}Sn satellites ($^1J = 1050$ Hz), indicating a less shielded ^{31}P nucleus than that observed in **5**. The IR spectrum exhibits two absorptions at 2022 and 1981 cm^{-1} for the CO vibrations, corresponding to local C_s symmetry; additionally, four less-intense bands at 2012, 2005, 1968 and 1961 cm^{-1} , which are attributed to rotational isomers, were observed. The wavenumbers signify the larger σ donor character of the phosphido ligand compared with **1a**. A preliminary X-ray structure analysis of poor quality crystals of **6a** revealed that the P atom has flattened pyramidal coordination (sum of bonding angles of 324°) and the Fe–P distance (2.362(8) Å) is significantly longer than that observed for **1a** (2.323(4) Å); this clearly reflects the steric crowding at phosphorus.



Scheme 5.



Scheme 6.

3.5. Tin / lithium exchange reaction of **6a** and thermolysis of **3a**

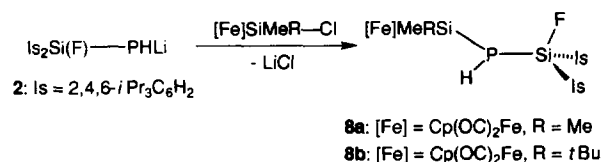
The reaction of **6a** with nBuLi in THF at $-78^\circ C$ gave rise to the lithium ferriophosphanide **3a** which cannot be directly prepared by lithiation of **1a** (Scheme 5). Owing to its thermal instability, **3a** has merely been characterized by its ^{31}P NMR spectrum, showing a singlet at $\delta = -378.2$; this value is within the characteristic region for dimetallated silylphosphanes [23]. Furthermore, the constitution of **3a** has been indirectly proven by hydrolysis which gave rise to **1a** in quantitative yields ($\delta(^{31}P) = -214.9$; $^1J(P,H) = 168$ Hz).

Heating **3a** in hexane at $50^\circ C$ led, under LiF elimination, to a deep red solution, which contained ca. 45% of the ferrio phosphasilene **7** and other, as yet, unidentified products (Scheme 6). Although **7** could not be isolated, its composition was confirmed by high resolution mass spectrometry; **7** decomposes if heated above $60^\circ C$.

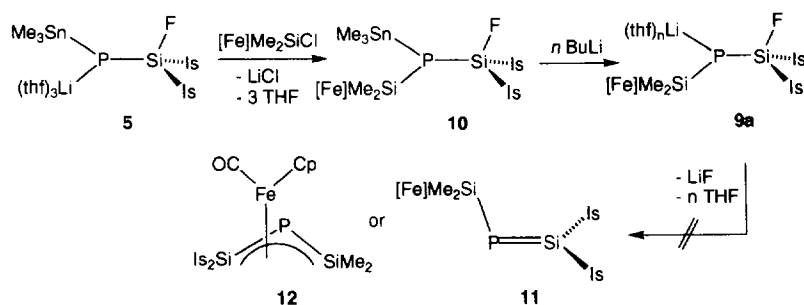
The presence of an Si=P bond in **7** is proven by its ^{31}P and ^{29}Si NMR data: the ^{31}P NMR spectrum exhibits a singlet at $\delta = 57$ with ^{29}Si satellites ($^1J(P,Si) = 163$ Hz), whereas the ^{29}Si NMR spectrum shows a doublet, as expected, at very low field ($\delta = 201$, identical $^1J(Si,P)$ coupling constant). Although similar values have been observed in the ^{29}Si NMR spectra for electronically related phosphasilenes having a σ donor substituent at phosphorus, i.e. silyl- and germyl-substituted phosphasilenes [8], the ^{31}P chemical shift reflects rather strong deshielding, which indicates a P(lone pair)–Fe π back-bonding interaction.

3.6. Synthesis of the ferriosilyl (fluorosilyl)phosphanes **8a,b**

Our attempts to synthesize a ferriosilyl-substituted phosphasilene and/or a 1,3-disila-2-phosphaallyl iron complex, starting from the novel ferriosilyl (fluorosilyl)phosphanes **8a,b**, have not yet been successful (Schemes 7 and 8). The latter compounds were prepared



Scheme 7.



Scheme 8.

by reaction of **2** with $[(C_5H_5)_2Fe(CO)_2SiMe(R)Cl]$ ($R = Me, ^tBu$) (Scheme 7) and were characterized by NMR and IR spectroscopy.

Interestingly, the ^{31}P NMR resonance signals of **8a,b** ($\delta = -181.1$ (**8a**), -184.2 (**8b**)) are shifted down-field compared with **1a** ($\delta = -214.9$), indicating the lower σ donor ability of the ferrosilyl groups. This is consistent with the observed wavenumbers for the CO stretching modes in the IR spectra. The two resonances (**8a**: 1955, 2005 cm^{-1} ; **8b**: 2005, 2049 cm^{-1}) are significantly blue shifted compared with **1a** (2017, 2061 cm^{-1}).

3.7. Crystal structure of **8b**

The constitution of **8b** was also elucidated by an X-ray structure analysis (Fig. 3, Table 5). The phosphorus atom is pyramidally coordinated with a sum of bonding angles of 297.6° . The Si–P distances are significantly different and represent values in the upper range of Si–P single bonds [24]. The longer Si1–P1 distance of 2.297(1) Å compared with the Si2–P1 value of 2.264(1) Å is attributed to Fe(d)/Si1–P1 (σ^*) hyperconjugation. The Fe–Si distance of 2.346(1) Å lies

within the range of values observed for other silyl iron complexes (2.22–2.49 Å) [25].

3.8. Formation of *P*-lithium ferrosilyl (fluorosilyl)phosphane **9a** via tin/lithium exchange

Direct lithiation of **8a,b** with RLi ($R = ^nBu, ^tBu, N^iPr_2$) does not afford the corresponding lithium phosphonides **9** as is seen for **1a–c**. Therefore, we have synthesized the *P*-stannylated analog of **8a**, that is compound **10**, which was transformed into **9a** via the tin/lithium exchange reaction (Scheme 8).

However, the reaction of **5** with the respective ferrosilyl chloride affords **10** in only 30% yields (^{31}P NMR) and **8a** as major product (ca. 70%, ^{31}P NMR). The unexpected formation of **8a** is attributed to kinetically favored tin/lithium exchange followed by proton abstraction from neighboring molecules. Although **10** could not be isolated, it was unambiguously characterized by ^{31}P NMR ($\delta = -216.3$, $^1J(P, ^{119}Sn) = 1056$ Hz) and high resolution mass spectrometry.

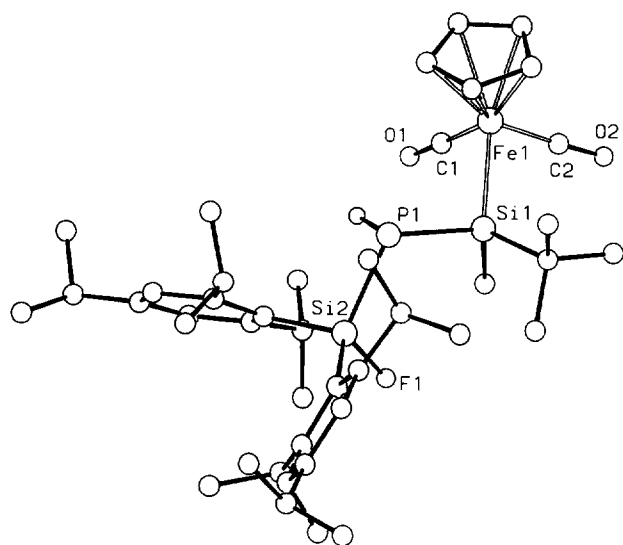


Fig. 3. Solid state structure of **8b**. H atoms (with exception of P–H) are omitted for clarity.

Table 5
Selected bond lengths (Å) and angles (deg) for **8b**

Fe(1)–C(1)	1.734(5)
Fe(1)–C(2)	1.738(5)
Fe(1)–Si(1)	2.3457(12)
P(1)–Si(2)	2.264(2)
P(1)–Si(1)	2.2965(14)
P(1)–H(1)	1.29(4)
Si(1)–C(8)	1.880(4)
Si(1)–C(9)	1.919(4)
Si(2)–F(1)	1.607(2)
C(1)–Fe(1)–C(2)	93.3(2)
C(1)–Fe(1)–Si(1)	85.27(14)
C(2)–Fe(1)–Si(1)	85.98(13)
Si(2)–P(1)–Si(1)	112.82(6)
Si(2)–P(1)–H(1)	91.0(20)
Si(1)–P(1)–H(1)	93.0(20)
C(8)–Si(1)–C(9)	106.0(2)
C(8)–Si(1)–P(1)	110.97(13)
C(9)–Si(1)–P(1)	107.80(13)
C(8)–Si(1)–Fe(1)	111.23(14)
C(9)–Si(1)–Fe(1)	116.67(13)
P(1)–Si(1)–Fe(1)	104.19(5)

It appears that the product mixture of **8a** and **10** reacts with ⁿBuLi in THF at –78 °C, leading to **9a** (ca. 30%, ³¹P NMR) in addition to several, as yet, unidentified products. The formation of **9a** was proven by the ³¹P NMR spectrum of the reaction mixture, which shows a singlet at very high field ($\delta = -326.5$) characteristic for lithium disilylphosphanides. This signal disappeared after hydrolysis of the reaction mixture and the doublet signal of **8a** appeared in the ³¹P NMR spectrum. Thermolysis of the reaction mixture containing **9a** in toluene at 50 °C has not provided NMR spectroscopic evidence for the formation of **11** or **12**, although complete LiF elimination from **9a** was observed (¹⁹F NMR).

4. Supplementary material available

Listings of atomic coordinates, isotropic thermal parameter and all bond distances and angles of **1b,c** and **8b** are available from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76012 Eggenstein-Leopoldshafen by quoting the deposition numbers CSD-405403 (**1b**), CSD-405402 (**1c**), and CSD-405401 (**8b**).

Acknowledgements

We thank the Deutsche Forschungsgemeinschaft (SFB 247) and the Fonds der Chemischen Industrie for financial support.

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