# Transition-metal-substituted acylphosphanes and phosphaalkenes. 18. P-metalated iminophosphiranes by isocyanide addition to a metallophosphaalkene. X-ray structure determination of [cyclic](.eta.5-C5Me5)(CO)2FePC(SiMe3)2C:NPh

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# Transition-Metal-Substituted Acylphosphanes and Phosphaalkenes. 18.[1] P-Metalated Iminophosphiranes by Isocyanide Addition to a Metallophosphaalkene. X-ray Structure Determination of $(\eta^5\text{-}C_5Me_5)(CO)_2Fe\overline{PC(SiMe_3)_2C}{=}NPh$

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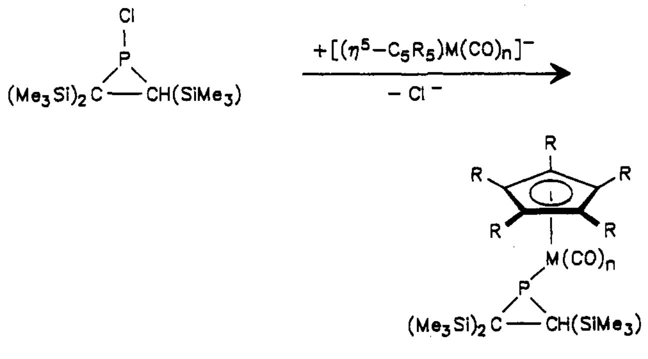
The reaction of $(\eta^5\text{-}C_5Me_5)(CO)_2FeP{=}C(SiMe_3)_2$ (**1**) with the isocyanides arylNC (**2**: aryl = Ph (**a**), 2-$MeC_6H_4$ (**b**), 2,6-$Me_2C_6H_3$ (**c**)) in benzene at 20 °C afforded the transition-metal-functionalized iminophosphiranes **3a–c** as red crystalline solids. The novel compounds were characterized by elemental analyses and spectroscopic methods (IR, $^1H$, $^{13}C$, and $^{31}P$ NMR, and mass spectroscopy). The molecular structure of the iminophosphirane $(\eta^5\text{-}C_5Me_5)(CO)_2Fe\overline{PC(SiMe_3)_2C}{=}NPh$ (**3a**) was established by a complete single-crystal diffraction study (space group, *C*2/*c*; *Z* = 8, *a* = 27.214(4) Å, *b* = 15.146(2) Å, *c* = 15.854(2) Å, *β* = 114.350(10)°).

## Introduction

Three-membered rings containing heavy p-block elements are of continuing interest for theoretical and preparative chemists.[2,3] The first phosphirane was discovered in 1963, when sodium derivatives of $PH_3$ and $RPH_2$ were allowed to react with 1,2-dichloroalkanes in liquid ammonia.[4] Meanwhile, several synthetic routes to this ring system are known. They include approaches starting with P and $C_2$ as well as PC and C building blocks.[3] In addition, cyclization processes of functionalized PCC or CPC units proved to be useful for this target.[3]

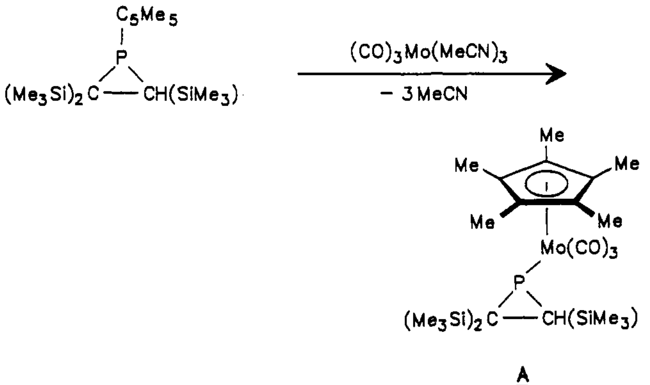
The first P-metalated phosphiranes were recently obtained by the reaction of a *P*-chlorophosphirane with carbonylmetalates. Alternatively, the insertion of a metal complex fragment into the reactive P–C bond of a $\eta^1$-$C_5Me_5$-substituted phosphirane was also successful.[5]

During the course of our chemical studies on metallodiphosphenes and metallophosphaalkenes we attempted the conversion of the latter to metallophosphiranes by means of sulfur ylides.[6] This method, however, which was highly successful in the chemistry of diphosphenes,[7] failed with phosphaalkenes. Instead of the expected three-membered ring **B**, we obtained $\eta^3$-phosphaallyl complexes such as **C**.[6]



**A**

M = Fe, R = H, Me, n = 2; M = Mo, R = Me, n = 3



**A**

The preparation of metalated iminodiphosphiranes from metallodiphosphenes and isocyanides[8,9] which parallels the synthesis of an iminodisilirane from a disilene and *o*-xylyl isocyanide,[10] prompted us to employ the metallophosphaalkene $(\eta^5\text{-}C_5Me_5)(CO)_2FeP{=}C(SiMe_3)_2$ in the reaction with a number of aryl isocyanides.

## Experimental Section

**General Information.** Standard inert-atmosphere techniques were used for the manipulation of all reagents and reaction products. Infrared spectra were recorded on a Mattson Polaris

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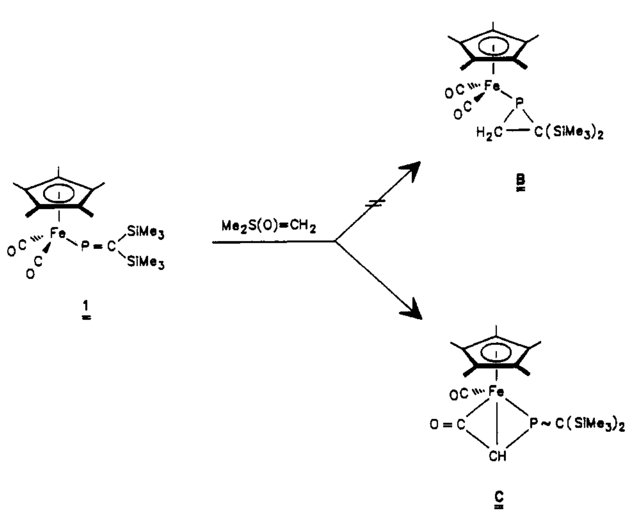

(FT/IR)/Atari 1040 STF. The $^1H$, $^{13}C$, and $^{31}P$ NMR spectra were taken in $C_6D_6$ solution at 22 °C on Bruker AC 100 ($^1H$, 100.131 MHz; $^{13}C$, 25.180 MHz; $^{31}P$, 40.539 MHz) and Bruker AM 300 ($^1H$, 300.1 MHz; $^{13}C$, 75.5 MHz; $^{31}P$, 121.7 MHz) spectrometers. Spectral standards were $SiMe_4$ ($^1H$, $^{13}C$) and 85% $H_3PO_4$ ($^{31}P$). Elemental analyses were obtained from the Microanalytical Laboratory DORNIS and KOLBE, Mülheim, Germany.

**Materials.** $(\eta^5\text{-}C_5Me_5)(CO)_2FeP{=}C(SiMe_3)_2$[11] and the isocyanides[12] were prepared as described in the literature. All solvents were rigorously dried with an appropriate drying agent and distilled before use.

**Preparation of Compounds. $(\eta^5\text{-}C_5Me_5)(CO)_2Fe\overline{PC(SiMe_3)_2C}{=}NPh$ (3a).** To a solution of 0.64 g (1.47 mmol) of $(\eta^5\text{-}C_5Me_5)(CO)_2FeP{=}C(SiMe_3)_2$ (1) in 30 mL of benzene was added 0.15 g (1.47 mmol) of phenyl isocyanide at 20 °C, and the mixture was stirred for 2 h. The course of the reaction was monitored by $^{31}P$ NMR spectroscopy. Solvent and volatiles were removed in vacuo, and the dark red residue was extracted with 40 mL of pentane. The filtered extract was concentrated to ca. 10 mL and stored at −40 °C for 3 days. The mother liquor was decanted from orange-red crystalline **3a**, and the product was dried in vacuo; yield 0.44 g (56%). IR (KBr, $cm^{-1}$): 2951 w, 2900 w, 1995 s [$\nu(CO)$], 1933 s [$\nu(CO)$], 1630 w, 1590 m, 1437 w, 1383 w, 1246 m [$\delta(Si(CH_3)_3)$], 1043 m, 841 s [$\rho(Si(CH_3)_3)$], 696 w, 639 w, 581 s. $^1H$ NMR ($\delta$): 0.45 [d, $^4J_{PH} = 2.2$ Hz, 9H, $Si(CH_3)_3$]; 0.55 [s, 9H, $Si(CH_3)_3$]; 1.25 [s, 15H, $C_5Me_5$]; 6.95 s, 6.99 s, 7.35 s, 7.40 s [phenyl H]. $^{13}C\{^1H\}$ NMR ($\delta$): 1.43 [s, $Si(CH_3)_3$]; 1.44 [d, $^3J_{PC} = 12.1$ Hz, $Si(CH_3)_3$]; 8.56 [d, $^3J_{PC} = 9.3$ Hz, $C_5(CH_3)_5$]; 96.26] d, $^2J_{PC} = 1.5$ Hz, $C_5(CH_3)_5$]; 122.41 s, 122.45 s, 123.40 s [C phenyl]; 155.11 [d, $^3J_{PC} = 2.4$ Hz, *i*-C phenyl]; 186.92 [d, $^1J_{PC} = 85.9$ Hz, C═N]; 216.40 [d, $^2J_{PC} = 3.4$ Hz, CO]; 217.24 [d, $^2J_{PC} = 2.7$ Hz, CO]. $^{31}P\{^1H\}$ NMR ($\delta$): −34.2. Anal. Calcd for $C_{26}H_{38}FeNO_2PSi_2$ (mol wt 539.6): C, 57.87; H, 7.09; N, 2.59. Found: C, 54.48; H, 6.75; N, 2.81.

**$(\eta^5\text{-}C_5Me_5)(CO)_2Fe\overline{PC(SiMe_3)_2C}{=}N(2\text{-}MeC_6H_4)$ (3b).** Orange-red crystalline **3b** was analogously synthesized from 0.80 g (1.83 mmol) of **1** and 0.22 g (1.83 mmol) of 2-methylphenyl isocyanide in 30 mL of benzene; yield 0.68 g (67%). IR (KBr, $cm^{-1}$): 2955 w, 2911 w, 1994 vs [$\nu(CO)$], 1946 vs [$\nu(CO)$], 1588 w, 1574 w, 1481 w, 1379 w, 1243 m [$\delta(Si(CH_3)_3)$], 1030 m, 840 s [$\rho(Si(CH_3)_3)$], 757 w, 637 w, 580 m. $^1H$ NMR ($\delta$): 0.45 [d, $^4J_{PH} = 2.2$ Hz, 9H, $Si(CH_3)_3$]; 0.55 [s, 9H, $Si(CH_3)_3$]; 1.26 [d, $^4J_{PH} = 0.6$ Hz, 15 H, $C_5(CH_3)_5$]; 2.60 [s, 3H, $CH_3C_6H_4$]; 7.03 s, 7.07 s, 7.10 s, 7.20 s [aryl H]. $^{13}C\{^1H\}$ NMR ($\delta$): 1.32 [s, $Si(CH_3)_3$]; 1.36 [d, $^3J_{PC} = 11.8$ Hz, $Si(CH_3)_3$]; 8.63 [d, $^3J_{PC} = 8.6$ Hz, $C_5(CH_3)_5$]; 18.45 [s, $2\text{-}(CH_3)C_6H_4$]; 96.25 [d, $^2J_{PC} = 1.8$ Hz, $C_5(CH_3)_5$]; 118.70 s, 118.73 s, 123.74 s, 132.93 s [C aryl]; 153.06 [d, $^3J_{PC} = 1.9$ Hz, *i*-C aryl]; 185.62 [d, $^1J_{PC} = 85.7$ Hz, C═N]; 216.22 [d, $^2J_{PC} = 3.0$ Hz, CO]; 217.22 [d, $^2J_{PC} = 2.0$ Hz, CO]. $^{31}P\{^1H\}$ NMR ($\delta$): −36.2. Anal. Calcd for $C_{27}H_{40}FeNO_2PSi_2$ (mol wt 553.6): C, 58.58; H, 7.28; N, 2.53. Found: C, 58.45; H, 7.04; N, 2.58.

**$(\eta^5\text{-}C_5Me_5)(CO)_2Fe\overline{PC(SiMe_3)_2C}{=}N(2,6\text{-}Me_2C_6H_3)$ (3c).** Orange-red crystalline **3c** was prepared as described before from 0.92 g (2.11 mmol) of **1** and 0.28 g (2.11 mmol) of 2,6-dimethylphenyl isocyanide in 35 mL of benzene; yield 0.83 g (69%). IR (KBr, $cm^{-1}$): 2956 w, 2920 w, 1989 s [$\nu(CO)$], 1948 s [$\nu(CO)$], 1744 w, 1623 w, 1584 w, 1381 m, 1244 m [$\delta(Si(CH_3)_3)$], 1015 m, 836 s [$\rho(Si(CH_3)_3)$], 759 m, 645 w, 582 m. $^1H$ NMR ($\delta$): 0.47 [d, $^4J_{PH} = 1.1$ Hz, 9H, $Si(CH_3)_3$]; 0.57 [s, 9H, $Si(CH_3)_3$]; 1.22 [s, 15H, $C_5(CH_3)_5$]; 2.54 [S, 6H, $2,6(CH_3)_2C_6H_3$]; 7.01 s, 7.06 s [aryl H]. $^{13}C\{^1H\}$ NMR ($\delta$): 1.71 [d, $^3J_{PC} = 10.8$ Hz, $Si(CH_3)_3$]; 1.78 [s, $Si(CH_3)_3$]; 8.59 [d, $^3J_{PC} = 9.0$ Hz, $C_5(CH_3)_5$]; 20.44 [s, $(CH_3)_2C_6H_3$]; 20.65 [s, $(CH_3)_2C_6H_3$]; 96.47 [d, $^2J_{PC} = 1.5$ Hz, $C_5(CH_3)_5$]; 97.90 [s, C aryl]; 122.63 [s, C aryl]; 152.60 [d, $^3J_{PC} = 2.3$ Hz, *i*-C aryl]; 184.70 (d, $^1J_{PC} = 89.1$ Hz, C═N]; 216.47 [d, $^2J_{PC} = 3.5$ Hz, CO]; 216.80 [d, $^2J_{PC} = 2.9$ Hz, CO]. $^{31}P\{^1H\}$ NMR ($\delta$): −28.7. Anal. Calcd for $C_{28}H_{42}FeNO_2PSi_2$ (mol wt 567.6): C, 59.25; H, 7.46; N, 2.47. Found: C, 58.71; H, 7.41; N, 2.65.

**X-ray Structure Determination of $(\eta^5\text{-}C_5Me_5)(CO)_2Fe\overline{PC(SiMe_3)_2C}{=}NPh$ (3a).** Crystals of **3a** were grown from *n*-pentane at −40 °C. An irregularly shaped crystal of the approximate dimensions 0.25 × 0.25 × 0.30 $mm^3$ was coated with a layer of hydrocarbon oil, attached to a glass fiber, cooled to 163 K for data collection, and mounted on a Siemens $P2_1$ four-circle diffractometer (Mo K$\alpha$ radiation, graphite monochromator). The cell dimensions were determined by refinement of the setting angles of 30 reflections ($5° \leq 2\theta \leq 20°$): $a = 27.214(4)$ Å, $b = 15.146(2)$ Å, $c = 15.854(2)$ Å, $\beta = 114.350(10)°$, $V = 5953.2(15)$ $Å^3$. The space group was established to be $C2/c$ ($Z = 8$, $D_{calc} = 1.204$ g $cm^{-3}$, $\mu = 6.58$ $cm^{-1}$), with $\omega$-scan data collection of 5237 independent intensities ($3° \leq 2\theta \leq 50°$), 2654 of which were treated as observed ($F_o \geq 4.0\sigma(F)$). The structure was solved by direct methods, successive difference Fourier maps, and full-matrix least-squares cycles. The crystallographic program applied was Siemens SHELXTL PLUS (VMS), using intrinsic scattering factors. All non-hydrogen atoms were given anisotropic displacement parameters; all the hydrogen atoms were fixed at calculated positions with an isotropic $U$ value of 0.08 $Å^2$.

The $R$ values, based on the final model refined with 298 parameters, were $R = \sum[(|F_o| - |F_c|)/\sum(|F_o|)] = 0.065$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)]^{1/2} = 0.045$, where $w^{-1} = \sigma^2(F)$. The maximum residual electron density was 0.71 e/$Å^3$.

## Results and Discussion

Diphosphenes[8,9] and a disilene[10] are effectively converted into iminodiphosphiranes and iminodisiliranes, respectively, by isocyanides. We have extended this synthetic approach to the phosphorus–carbon double bond in a transition-metal-functionalized phosphaalkene (metallophosphaalkene).

The iron compound **1** smoothly reacts with equimolar amounts of the aryl isocyanides **2a–c** in benzene at ambient temperature to give the orange-red crystalline iminophosphiranes **3a–c** in 56–69% yield. In contrast to the situation with diphosphenes,[8] the employment of an excess of the isocyanides does not lead to the incorporation of a second molecule into **3a–c** to give bis(imino)phosphetanes.

The course of the reaction is conveniently monitored by $^{31}P$ NMR spectroscopy. The low-field singlet of the starting material is replaced by a singlet in the characteristic high-field region for strained three-membered rings. The compounds **3a–c** are isolated by fractional crytallization from *n*-pentane. The diamagnetic products are air- and moisture-sensitive. They can be stored under a nitrogen atmosphere at room temperature without significant decomposition.

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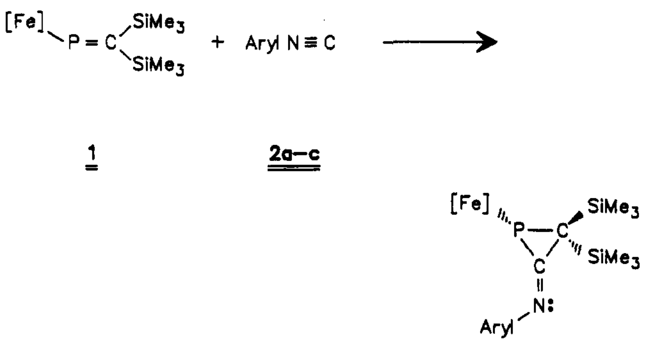


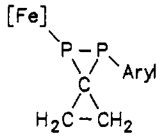
1

2a–c

3a–c

| 2, 3 | Aryl |
|---|---|
| a | $C_6H_5$ |
| b | $2-CH_3C_6H_4$ |
| c | $2,6-(CH_3)_2C_6H_3$ |

The P-metallophosphiranes 3 were initially characterized by elemental analyses and spectroscopic methods. The $^{31}P\{^1H\}$NMR spectra of 3a–c display singlets at high field (3a, $\delta$ −34.2; 3b, $\delta$ −36.2; 3c, $\delta$ −28.7) which are diagnostic for three-membered strained phosphorus ring compounds.[13,14] The metalated P atom in the metallodiphosphirane fragment of 4 is observed at $\delta$ −37.95.[7]



[Fe] = $(\eta^5-C_5Me_5)(CO)_2Fe$,

Aryl = $2,4,6-tBu_3C_6H_2$

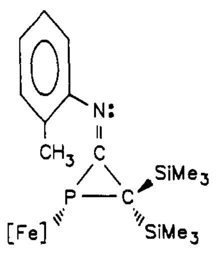
4

Due to the presence of a chiral center at the phosphorus atom the two trimethylsilyl groups are diastereotopic. In the $^1$H NMR spectra their protons give rise to a doublet and a singlet at $\delta$ 0.45 (d, $^4J_{PH}$ = 2.2 Hz) and 0.55 (s) for 3a as well as 3b and $\delta$ 0.47 (d, $^4J_{PH}$ = 1.1 Hz) and 0.57 (s) for 3c.

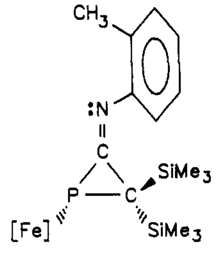
The doublet is assigned to the silyl group which is cis-oriented with respect to the lone pair of the phosphorus atom. For the *o*-methyl group of the aryl substituent of 3b one singlet is observed at $\delta$ 2.60.

In 3c only one singlet at $\delta$ 2.54 for the two *o*-methyl groups is registered. Due to chirality these groups should be chemically and magnetically different and thus be discriminated by NMR. Obviously they are isochronous by accident. The $^1$H NMR spectra of 3a–c do not change markedly at −80 °C.

The $^{13}C\{^1H\}$ NMR spectrum of 3c (20 °C) shows the expected two discrete resonances for the carbon atoms of the *o*-methyl groups at $\delta$ 20.4 and 20.7. In the low-field region of the $^{13}C\{^1H\}$ NMR spectra of 3a–c a doublet at $\delta$ 184.7–186.9 ($^1J_{PC}$ = 85.7–89.1 Hz) is assigned to the carbon atom of the imino function. The chemical shifts as well as the absolute values of the $^1J_{PC}$ couplings compare well with the respective data in iminodiphosphiranes such as 5 ($^{13}$C: $\delta$ 180.0 dd, $^1J_{PC}$ = −90.0, $^1J_{PC}$ = −57.6 Hz).[15] The resonance for the tetracoordinate ring carbon atoms in 3a–c could not be detected in the $^{13}C\{^1H\}$ NMR spectra.



A



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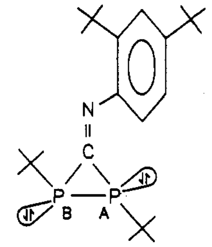


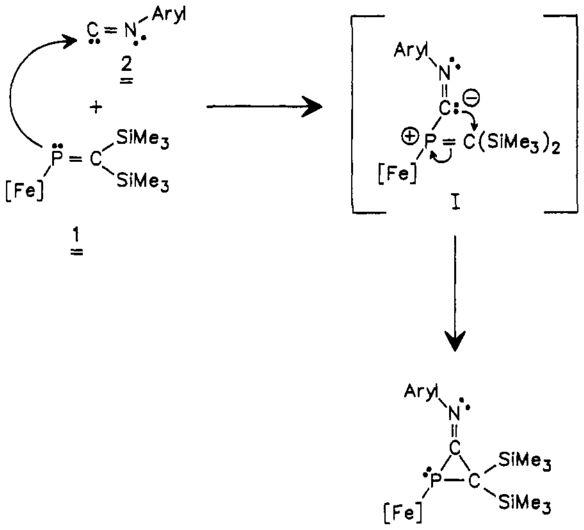
5

The magnetically different carbonyl ligands at the iron atom in 3a–c were observed as two doublets in the narrow range of $\delta$ 216.2–217.2 with $^2J_{PC}$ = 2.0–3.5 Hz.

The observation of only one set of signals in the $^1$H, $^{13}$C, and $^{31}$P NMR spectra for 3a–c is consistent with either the presence of only one isomer (A or B) or a rapid inversion at the sp$^2$-hybridized nitrogen. As shown below for 3a, the isomer corresponding to A is present in the crystal.

In the IR spectra of the complexes the carbonyl stretching vibrations give rise to two intense bands at 1989–1995 and 1933–1948 cm$^{-1}$. In 1 two carbonyl stretches at 1980 and 1935 cm$^{-1}$ [11] are registered, which implies that the phosphaalkenyl ligand in the latter transfers more electron density to the metal than the three-membered ring ligand in 3a–c.

It is conceivable that the formation of the iminophosphiranes is initiated by the electrophilic attack of the highly nucleophilic phosphorus at the carbene-like carbon atom of the isocyanide. The attack of the negatively polarized C atom of the isocyanide fragment at the positively polarized C atom of the phosphaalkene fragment in the intermediate I leads to the final products.



3

**X-ray Structure Analysis of 3a.** An X-ray structure analysis was desirable to unambiguously determine the

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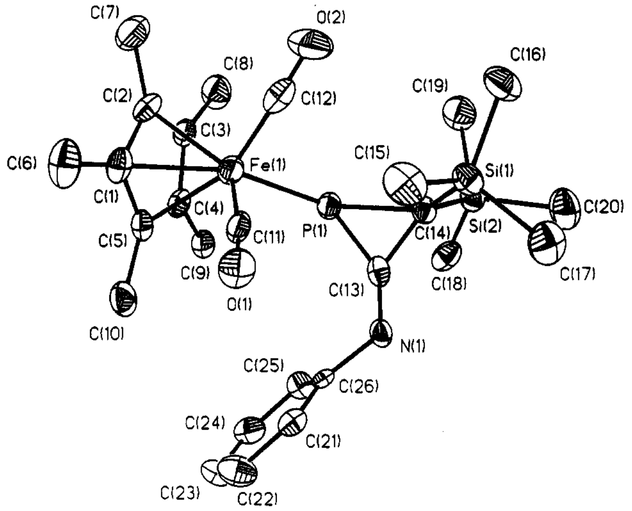

**Figure 1.** Molecular structure of **3a** in the crystal (ORTEP; ellipsoids at the 50% probability level; hydrogen atoms omitted for clarity).

**Table I. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$)**

| | *x* | *y* | *z* | *U*(eq)[a] |
|---|---|---|---|---|
| Fe(1) | 1367(1) | 647(1) | 1958(1) | 29(1) |
| Si(1) | 739(1) | 3475(1) | 1540(1) | 35(1) |
| Si(2) | 1136(1) | 3343(1) | −119(1) | 32(1) |
| P(1) | 1498(1) | 1768(1) | 1114(1) | 28(1) |
| N(1) | 2111(2) | 3153(3) | 2452(4) | 25(2) |
| O(1) | 1756(2) | 1555(3) | 3735(3) | 44(3) |
| O(2) | 228(2) | 1087(4) | 1211(4) | 72(3) |
| C(1) | 1579(3) | −584(5) | 2617(5) | 32(3) |
| C(2) | 1180(3) | −698(5) | 1709(5) | 29(3) |
| C(3) | 1381(3) | −384(4) | 1082(5) | 27(3) |
| C(4) | 1926(3) | −104(4) | 1594(5) | 29(3) |
| C(5) | 2039(3) | −192(4) | 2541(5) | 29(3) |
| C(6) | 1553(3) | −902(5) | 3497(5) | 51(4) |
| C(7) | 647(3) | −1141(5) | 1468(5) | 51(4) |
| C(8) | 1098(3) | −429(5) | 30(4) | 46(4) |
| C(9) | 2315(3) | 184(4) | 1191(4) | 34(3) |
| C(10) | 2570(3) | 17(4) | 3325(5) | 43(4) |
| C(11) | 1590(3) | 1238(4) | 3007(5) | 32(4) |
| C(13) | 1755(3) | 2772(4) | 1750(5) | 24(3) |
| C(14) | 1207(3) | 2981(4) | 1071(4) | 25(3) |
| C(15) | 784(3) | 2975(5) | 2649(5) | 51(4) |
| C(16) | 30(3) | 3394(5) | 655(5) | 51(4) |
| C(17) | 931(3) | 4660(4) | 1836(5) | 51(4) |
| C(18) | 1787(3) | 3225(4) | −243(4) | 39(3) |
| C(19) | 599(3) | 2681(5) | −1028(4) | 50(4) |
| C(20) | 950(3) | 4536(4) | −354(5) | 55(4) |
| C(21) | 2812(3) | 2684(4) | 3911(5) | 36(4) |
| C(22) | 3302(3) | 2290(5) | 4415(5) | 51(4) |
| C(23) | 3591(3) | 1901(5) | 3965(6) | 50(4) |
| C(24) | 3385(3) | 1931(5) | 3006(6) | 45(4) |
| C(25) | 2895(3) | 2316(4) | 2506(5) | 33(3) |
| C(26) | 2602(3) | 2696(4) | 2950(5) | 29(3) |

[a] Equivalent isotropic *U*, defined as one-third of the trace of the orthogonalized $U_{ij}$ tensor.

**Table II. Selected Bond Lengths (Å) and Bond Angles (deg) for 3a**

| | | | |
|---|---|---|---|
| Fe(1)–P(1) | 2.279(2) | Fe(1)–C(1) | 2.098(7) |
| Fe(1)–C(2) | 2.097(7) | Fe(1)–C(3) | 2.101(7) |
| Fe(1)–C(4) | 2.159(8) | Fe(1)–C(5) | 2.103(7) |
| Fe(1)–C(11) | 1.762(7) | Fe(1)–C(12) | 1.754(9) |
| Si(1)–C(14) | 1.875(8) | P(1)–C(14) | 1.990(7) |
| Si(2)–C(14) | 1.897(7) | N(1)–C(26) | 1.421(8) |
| P(1)–C(13) | 1.799(7) | O(2)–C(12) | 1.152(10) |
| N(1)–C(13) | 1.273(7) | O(1)–C(11) | 1.156(9) |
| C(13)–C(14) | 1.469(8) | | |
| C(14)–Si(1)–C(15) | 114.8(3) | P(1)–Fe(1)–C(11) | 95.7(3) |
| Fe(1)–P(1)–C(13) | 114.8(3) | P(1)–Fe(1)–C(12) | 88.9(3) |
| C(13)–P(1)–C(14) | 45.3(3) | C(11)–Fe(1)–C(12) | 98.4(4) |
| Fe(1)–C(11)–O(1) | 173.8(6) | Fe(1)–P(1)–C(14) | 123.6(3) |
| P(1)–C(13)–N(1) | 148.5(5) | C(13)–N(1)–C(26) | 117.9(6) |

stereochemistry of the iminophosphiranes. Single crystals of **3a** are grown from *n*-pentane at −40 °C. The results of the structural determinations are shown in Figure 1. Positional parameters for the complex are given in Table I, and selected distances and angles are presented in Table II. The analysis confirms the presence of an iminophosphirane system linked to the metal by an Fe–P single bond (2.279(2) Å), which compares well with the corresponding bond length in 1 (2.26 Å).[11] Usually Fe–P bond distances in low-valent carbonyliron complexes fall in the range 2.11–2.37 Å.[16] The organophosphorus ligand could be regarded as one leg in a distorted three-legged piano-stool arrangement. The three angles the ligands form with the metal center are P(1)–Fe–C(11) = 95.7(3)°, C(11)–Fe–C(12) = 98.4(4)°, and P(1)–Fe–C(12) = 88.9(3)°. Two legs of the piano stool are represented by terminal, nearly linear, carbonyl groups.

The most interesting feature of **3a** is the geometry of the phosphirane ring. In the $PC_2$ triangle the P–C distances (P(1)–C(14) = 1.990(7) Å, P(1)–C(13) = 1.799(7) Å) are expectedly longer than the C–C distance (1.469(8) Å). The shorter P–C distance resembles those in **4** (1.799(5), 1.824(5) Å), whereas the longer one exceeds the standard value of a P–C single bond (ca. 1.85 Å)[17] markedly. Similarly long endocyclic P–C bonds (1.931(12)–1.967(12) Å) are reported for the 1,2-diphosphetane $PhCH_2P(PhCH_2)PC(Ph)(OSiMe_3)C(Ph)OSiMe_3$.[18] The endocyclic angle at the trigonal-planar ring carbon atom C(13) of 74.3(4)° is very acute as compared to the standard value of 120°. Also, the endocyclic angle at phosphorus (45.3(3)°) is compressed. In the spiro compound **4** such angles are determined to 52.0(2) and 53.0(2)°.[7] The endocyclic angle at C(14) (60.5(3)°) is close to the ideal valence angle in cyclopropane. The exocyclic angles at phosphorus Fe(1)–P(1)–C(14) = 123.6(3)° and Fe(1)–P(1)–C(13) = 114.8(3)° are significantly different, the more obtuse of which presumably results from steric interactions between the iron complex fragment and the cis-located silyl group. The difference in the exocyclic angles at C(14) (Si(1)–C(14)–P(1) = 132.8(4)° and Si(2)–C(14)–P(1) = 100.2(4)°) supports this view.

The C═N distance of the imino group (1.273(7) Å) and the bond angle C(13)–N–C(26) (117.9(6)°) are not unusual. The phenyl substituent at the N atom is directed toward the phosphorus atom with a nearly perpendicular orientation with respect to the plane of the $PC_2$ triangle.

Presumably because of steric repulsions between the complex iron fragment and the phenyl ring the angle P(1)–C(13)–N(1) (148.5(5)°) clearly exceeds the exocyclic angle N(1)–C(13)–C(14) (136.1(6)°).

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