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Synthesis and structure of iron silylene complexes of silacyclobut-2-enes[†]

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Summary – The corresponding tetracarbonyl iron silylene complexes (**3** and **4**) have been synthesized by reaction of two different 1,1-dichloro-4-neopentyl-2,3-diorgano-1-silacyclobut-2-enes (**1** and **2**) with $Na_2Fe(CO)_4$. The metal compounds **3** and **4** have been structurally characterized by X-ray crystallography.

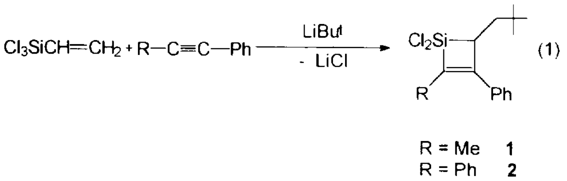
silacyclobutenes / silylene-complexes

Introduction and background

Reactivity studies on silacyclobutenes have been very difficult in the past because of the lack of a simple preparative route to these substances and no procedure for the preparation of silicon-functionalized silacyclobutenes was known in the literature. After elucidation of a synthetic pathway to generate 1,1-dichloro-4-neopentyl-2,3-diorgano-1-silacyclobut-2-enes [1], studies on their chemical reactivity can now be easily accomplished. These compounds have an exceptional chemical and thermal stability [2] and thus show properties that are not "typical" for silacyclobutenes. This is confirmed by the synthesis of silylene complexes which have been prepared from dichloro-substituted silacyclobutene precursors and which are presented in this paper.

Results

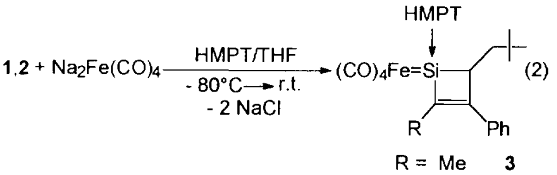
The silacyclobutenes **1** and **2** are synthesized by addition of $LiBu^t$ to trichlorovinylsilane in the presence of diorgano-substituted alkynes [1] [equation (1)].



R = Me **1**
R = Ph **2**

1,1-Dichloroneopentylsilene ($Cl_2Si{=}CHCH_2Bu^t$), which is formed *in situ* as a reactive intermediate from trichlorovinylsilane/$LiBu^t$, cannot be detected spectroscopically and reacts spontaneously with alkynes to give the silacyclobutenes **1** and **2**, which can be isolated in good yields (60 or 80%, respectively) [1].

Reaction of **1** and **2** with $Na_2Fe(CO)_4$ in a solvent mixture of HMPT/THF leads to formation of the two complexes **3** and **4** [equation (2)].



R = Me **3**
R = Ph **4**

In this reaction HMPT increases the solubility of $Na_2Fe(CO)_4$ in THF and acts as a stabilizing donor substituent for the electrophilic silicon atom in the resulting complex compounds [3]. According to redox processes, dark-red $H[Fe_3(CO)_{11}]$ is formed as a byproduct via a side reaction which is not mentioned in equation (2) [4].

Complexes **3** and **4** were purified by column chromatography on silica gel; recrystallization from a THF/toluene/pentane mixture yields cream microcrystalline solids. Solutions of **3** and **4** contain mixtures of two diastereomers *E*/*Z* because the HMPT donor

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[†] Dedicated to Professor Dr R Calas on the occasion of his 80th birthday.

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can coordinate to the silicon center *E* or *Z* relative to the neopentyl group. This has been confirmed by NMR spectroscopic measurements of dissolved **3** and **4** [5]. In the ^{29}Si NMR spectra of the complexes **3** and **4**, coordination of HMPT donor molecules leads to a line splitting into doublets at 76.58 ($^2J_{SiP}$ = 36.4 Hz) for *E*-**3** and 77.90 ($^2J_{SiP}$ = 47.0 Hz) for *Z*-**3**, or at 72.03 ($^2J_{SiP}$ = 32.3 Hz) for *E*-**4** and 76.25 ($^2J_{SiP}$ = 29.4 Hz) for *Z*-**4**. In comparison with $(OC)_4Fe{=}SiMe_2{\bullet}HMPT$ (δ ^{29}Si 92.6 ppm [5]) the ^{29}Si resonances of **3** and **4** are shifted to higher field. This can be explained with a stronger shielding of the silicon atoms by the more electron-rich silacyclobutene rings.

In contrast to this, the ^{1}H and ^{13}C resonances of the silacyclobutene ligands in **3** and **4** are shifted to lower field compared with the shifts of the starting compounds **1** and **2**. This is also due to the electron deficiency at the silicon center in the complex.

Two signals each for both the axial and the equatorial CO ligands are found in the carbonyl region of the ^{13}C NMR spectrum of **4** (δ 218.00 and 218.02 for *E*-**4**; 218.08 and 218.10 for *Z*-**4**). This indicates a local trigonal bipyramidal structure at the iron atom. An exact assignment of the sets of NMR signals to the respective diastereomers was possible due to the selective crystallization of the *E* isomers. IR spectra of dissolved **3** and **4** show three absorptions (two A1 and one E) in the carbonyl region for *E*/*Z*-**3** (2 011, 1 929, 1 989 cm^{-1}) and *E*/*Z*-**4** (2 040, 1 931, 1 904 cm^{-1}), which are typical for $M(CO)_4$ fragments of C_{3v} symmetry and indicate the axial configuration of the silicon ligands in the iron-centered trigonal bipyramids. Structures of *E*/*Z*-**3** (*E*-**3** : fig 1, tables I, II) and *E*/*Z*-**4** (*E*-**4** : fig 2, tables I, III) are comparable in the solid state as well as in solution. Interestingly only one diastereomer selectively crystallizes from solutions of the two silylene complexes, which is confirmed by the results of the X-ray structural analysis for *E*-**3** and *E*-**4**.

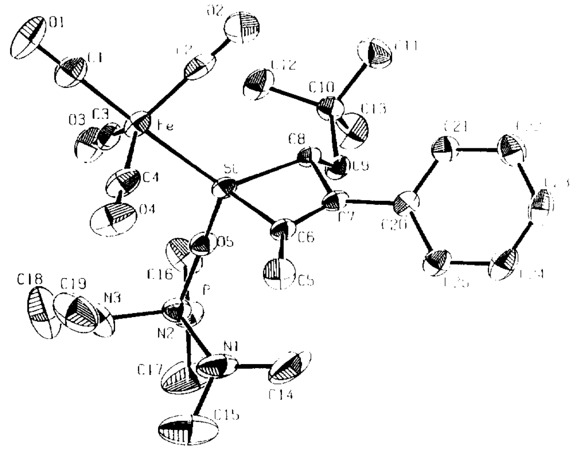

Fig 1. Ortep plot of *E*-**3** (50% probability, hydrogen atoms omitted).

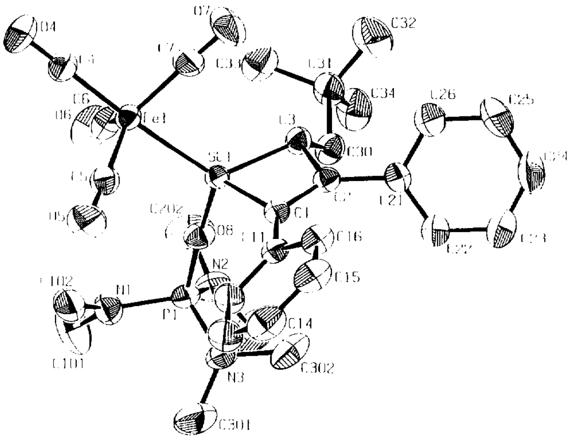

Fig 2. Ortep plot of *E*-**4** (30% probability, hydrogen atoms omitted).

Table I. Selected bond lengths (pm) and angles (°) of *E*-**3** and *E*-**4**.

compound *E*-**3**		compound *E*-**4**	
Fe-Si	227.7(1)	Fe-Si	227.2(1)
Fe-C(1)	178.5(3)	Fe-C(4)	176.8(6)
Fe-C(2)	173.3(3)	Fe-C(7)	175.3(6)
Fe-C(3)	176.4(3)	Fe-C(6)	176.3(6)
Fe-C(4)	177.4(3)	Fe-C(5)	174.2(6)
P-O(5)	152.0(2)	P-O(8)	151.4(3)
P-N(1)	161.6(3)	P-N(2)	162.4(4)
P-N(2)	160.9(3)	P-N(3)	161.2(4)
P-N(3)	161.7(3)	P-N(1)	160.0(4)
Si-O(5)	172.8(2)	Si-O(8)	171.7(3)
Si-C(6)	186.5(3)	Si-C(1)	187.9(4)
Si-C(8)	190.4(3)	Si-C(3)	190.2(4)
C(5)-C(6)	150.4(4)	C(1)-C(11)	147.2(5)
C(6)-C(7)	134.5(4)	C(1)-C(2)	134.8(5)
C(7)-C(8)	154.4(4)	C(2)-C(3)	153.3(6)
C(7)-C(20)	147.4(4)	C(2)-C(21)	147.9(5)
C(8)-C(9)	153.1(4)	C(3)-C(30)	152.3(7)
Fe-Si-O(5)	113.7(1)	Fe-Si-O(8)	112.6(1)
Fe-Si-C(6)	125.5(1)	Fe-Si-C(1)	125.4(1)
Fe-Si-C(8)	124.1(1)	Fe-Si-C(3)	123.1(1)
O(5)-Si-C(6)	106.0(1)	O(8)-Si-C(1)	107.3(1)
O(5)-Si-C(8)	104.3(1)	O(8)-Si-C(3)	106.3(2)
C(6)-Si-C(8)	76.7(1)	C(1)-Si-C(3)	76.4(2)
Si-C(6)-C(5)	138.1(2)	Si-C(1)-C(11)	137.9(3)
Si-C(6)-C(7)	91.3(2)	Si-C(1)-C(2)	90.7(3)
C(5)-C(6)-C(7)	130.4(3)	C(11)-C(1)-C(2)	131.0(4)
C(6)-C(7)-C(8)	107.9(2)	C(1)-C(2)-C(3)	108.4(3)
C(6)-C(7)-C(20)	130.2(2)	C(1)-C(2)-C(21)	130.5(4)
C(8)-C(7)-C(20)	121.8(2)	C(3)-C(2)-C(21)	121.1(3)
Si-C(8)-C(7)	84.1(2)	Si-C(3)-C(2)	84.5(2)
Si-C(8)-C(9)	122.8(2)	Si-C(3)-C(30)	124.9(3)
C(7)-C(8)-C(9)	116.2(2)	C(2)-C(3)-C(30)	117.7(4)

The $Fe(CO)_4$ fragments in the crystal show local C_{3v} symmetry; the silylene ligands occupy one axial position in the trigonal bipyramidal ligand sphere due to their stronger σ donor and weaker π acceptor properties compared with the carbonyl ligands.

The iron-silicon bond lengths (227.7(1) pm for *E*-**3** and 227.2(1) pm for *E*-**4**) are in the same range as in the known complexes $(OC)_4Fe{=}SiMe_2{\bullet}HMPT$ (228.0(1) pm [5]) and $(OC)_4Fe{=}Si(SBu^t)_2{\bullet}HMPT$ (227.8(1) pm [5]).

The distorted tetrahedral ligand sphere of the silicon centers is completed by the HMPT donors which are coordinated *via* the oxygen atoms. The silicon-oxygen distances are significantly longer (172.8(2) pm for *E*-**3** and 171.7(3) pm for *E*-**4**) than covalent Si-O bonds in compounds such as $(OC)_4Fe{=}Si(OBu^t)_2{\bullet}HMPT$ (161.0(3) and 163.6(4) pm [6]), which is due to their donor contact character.

The central, visibly distorted four-membered Si-C rings are nearly planar. The bond lengths and angles are mainly influenced by the predominant steric impact of the substituents at the ring backbone and the short endocyclic carbon-carbon double bond. Values of the endocyclic bond angles at the silicon atom are 76.7(1)° (*E*-**3**) and 76.4(3)° (*Z*-**4**), which is analogous to most of the known silacyclobutenes [7].

The formation of the iron silylene complexes **3** and **4** characterizes the high chemical stability of the silacyclobutene backbone against ring-opening reactions. This surprising result is in contrast to monosilacyclobutanes [8] and disilacyclobutenes [9, 10] which react with transition metal fragments under insertion into the Si-C bond of the ring skeleton. Further experiments and theoretical calculations on the unusual stability of the SiC four-membered ring systems are in progress.

Experimental section

All manipulations were carried out under an atmosphere of purified nitrogen. The solvents were dried and degassed by the usual methods.

*(2-Methyl-4-neopentyl-3-phenyl-1-silylenacyclobut-2-ene)-tetracarbonyliron(0) • HMPT E/Z-***3**

Compound **1** (0.76 g, 2.54 mmol) and 0.5 g (2.54 mmol) HMPT in 10 mL THF were added dropwise to a cooled suspension of 0.88 g (2.54 mmol) $Na_2Fe(CO)_4{\bullet}1.5$ dioxane in 70 mL THF. The cream suspension was allowed to warm up to rt over 10 h and turned into a deep-red solution. Pentane (50 mL) was added to precipitate the NaCl formed. The supernatant solution was filtered and the volatiles were condensed off. The residual red oil was chromatographed at −10°C on silica gel. The product was eluted with THF and was recrystallized from pentane/toluene/THF to give a cream solid (1.05 g, 1.83 mmol, 72%).

- *E*-**3**

^1H NMR (C_6D_6, 270 MHz, 20°C) : δ 1.34 (s, 9H, $C(CH_3)_3$), 1.62 (m, 2H, CH_2), 2.12-2.22 (s, 3H, CH_3), 2.14 (d, 18H, $(N(CH_3)_2)_3$ $^3J_{HP}$ = 10.7 Hz), 3.38 (m, 1H, CH), 7.22 (m, 5H, C_6H_5).

^{13}C NMR (C_6D_6, 67.8 MHz, 20°C) : δ 14.00 (CH_3), 29.98 ($C(\mathit{C}H_3)_3$), 30.55 ($\mathit{C}(CH_3)_3$), 36.50 (d, $(N(CH_3)_2)_3$, $^3J_{CP}$ = 5.5 Hz), 39.53 (CH_2), 41.05 (CH), 127.75, 128.98 (*C*H Ph), 137.83 (C_q Ph), 151.23 (^2C), 153.05 (^3C), 216.52 (CO_{eq}), 216.77 (CO_{ax}).

^{29}Si NMR (C_6D_6, 54.4 MHz, 20°C) : δ 76.58 (d, $^2J_{SiP}$ = 36.4 Hz).

- *Z*-**3**

^1H NMR (C_6D_6, 270 MHz, 20°C) : δ 1.34 (s, 9H, $C(CH_3)_3$, 2.20 (d, 18H, $(N(CH_3)_2)_3$, $^3J_{HP}$ = 10.3 Hz); all other resonances identical; ratio of integral values *E*-**3**/*Z*-**3** = 45:55.

^{13}C NMR (C_6D_6, 67.8 MHz, 20°C) : δ 15.10 (CH_3), 30.02 ($C(\mathit{C}H_3)_3$), 31.23 ($\mathit{C}(CH_3)_3$), 36.95 (d, $(N(CH_3)_2)_3$, $^3J_{CP}$ = 5.1 Hz), 39.80 (CH_2), 41.28 (CH), 127.75, 128.98 (*C*H Ph), 137.89 (C_q Ph), 151.56 (^2C), 153.09 (^3C), 217.28 (CO_{eq}), 217.47 (CO_{ax}).

^{29}Si NMR (C_6D_6, 54.4 MHz, 20°C) : δ 77.90 (d, $^2J_{SiP}$ = 47.0 Hz).

- *E/Z*-**3**

IR (THF) : ν(CO) 2 011 (m), 1 929 (s), 1 889 (vs) cm^{-1}.

MS (CI, C_4H_8) : *m/z* 576 (M^+ + 1, 60%), 539 (5), 477 (5), 359 (100), 180 (25).

Anal calc for $C_{25}H_{38}FeN_3O_5PSi$: C, 52.18 ; H, 6.66 ; N, 7.30 ; Si, 4,88. Found : C, 51.84 ; H, 6.34 ; N, 6.83 ; Si, 4.37.

*(4-Neopentyl-2,3-diphenyl-1-silylenacyclobut-2-ene)-tetracarbonyliron(0) • HMPT E/Z-***4**

The reaction was carried out analogously to *E/Z*-**3** (yield 65%).

- *E*-**4**

^1H NMR (d_8-toluene, 270 MHz, 20°C) : δ 1.00 (s, 9H, $C(CH_3)_3$), 1.43 (m, 2H, CH_2), 2.25 (d, 18H, $(N(CH_3)_2)_3$, $^3J_{HP}$ = 10.3 Hz), 3.16 (m, 1H, CH), 7.24 (m, 10H, C_6H_5).

^{13}C NMR (C_6D_6, 67.8 MHz, 20°C) : δ 30.02 ($C(\mathit{C}H_3)_3$), 31.09 ($\mathit{C}(CH_3)_3$), 36.40 (d, $(N(CH_3)_2)_3$, $^3J_{CP}$ = 5.0 Hz), 38.96 (CH_2), 39.98 (CH), 127.71, 128.41, 128.44, 128.60, 128.68, 129.42 (*C*H Ph), 137.48, 139.05 (C_q Ph), 152.57 (^2C), 153.35 (^3C), 218.00 (CO_{eq}), 218.02 (CO_{ax}).

^{29}Si NMR (d_8-toluene, 54.4 MHz, 20°C) : δ 72.03 (d, $^2J_{SiP}$ = 32.3 Hz).

- *Z*-**4**

^1H NMR (d_8-toluene, 270 MHz, 20°C) : δ 1.03 (s, 9H, $C(CH_3)_3$), 2.08 (d, 18H, $(N(CH_3)_2)_3$, $^3J_{HP}$ = 10.3 Hz); all other resonances identical; ratio of integral values *E*-**4**/*Z*-**4** = 35:65.

^{13}C NMR (d_8-toluene, 67.8 MHz, 20°C) : δ 30.20 ($C(\mathit{C}H_3)_3$), 31.31 ($\mathit{C}(CH_3)_3$), 36.77 (d, $(N(CH_3)_2)_3$, $^3J_{CP}$ = 5.5 Hz), 39.94 (CH_2), 41.58 (CH), 127.71, 128.41, 128.44, 128.60, 128.68, 129.42 (CH Ph), 137.74, 139.36 (C_q Ph), 153.25 (^2C), 153.94 (^3C), 218.08 (CO_{eq}), 218.10 (CO_{ax}).

^{29}Si NMR (d_8-toluene, 54.4 MHz, 20°C) : δ 76.25 (d, $^2J_{SiP}$ = 29.4 Hz).

- *E/Z*-**4**

IR (THF) : ν(CO) 2 040 (m), 1 931 (s), 1 904 (vs) cm^{-1}.

MS (CI, C_4H_8) : *m/z* 638 (M^+ + 1, 70%), 610 (8), 582 (15), 526 (9), 471 (9), 415 (6), 359 (10), 315 (7), 180 (100), 135 (10).

Anal calc for $C_{30}H_{40}FeN_3O_5PSi$; C, 56.52 ; H, 6.32 ; N, 6.59 ; Si, 4.41. Found : C, 55.30 ; H, 6.46 ; N, 6.60 ; Si 4.30.

Crystallographic data for $C_{25}H_{38}N_3FeO_5SiP$*; compound E-***3**

M_r = 575.5, orthorhombic, *Pbca* (No 61), a = 1 741.6(2), b = 1 877.5(4), c = 1 847.1(4) pm, $V = 6\,040 \cdot 10^6$ pm^3, Z = 8, ρ_{calcd} = 1.266 g cm^{-3}, $F000$ = 432, μ = 6.2 cm^{-1}. Data were collected on an Enraf-Nonius CAD-4 diffractometer with graphite monochromator, MoKα (λ = 71.073 pm), $\Theta/2\Theta$-scans, $1.0° < \Theta < 25.0°$. During data collection no decay was observed, no absorption correction, and no correction for extinction effects were applied. From 5 928 collected data points 1 298 were rejected (systematic absences; negative intensities). After merging all 4 608 unique data ($I > 0$) were used in the final refinement. The structure was solved with direct methods, and refined by full-matrix least-squares calculations, with anisotropic thermal parameters for all non-hydrogens. All hydrogen atoms were calculated at ideal positions, included in the refinements but not refined. Refinement was concluded with $R = 0.054$ and $wR = 0.036$, $w = 1/\sigma^2(F_o)$. All software and the sources of the scattering factors are contained in the STRUX-V [11] system using the programs MULTAN 11/82, ORTEP II, PLATON-92″, PLUTON-92″, SCHAKAL, and SDP. Positional parameters are listed in table II.

Table II. Atomic coordinates and isotropic thermal parameters for *E*-**3**.

Atom	x/a	y/b	z/c	U_{eq} [Å^2]
Fe	0.08290(2)	0.14341(2)	0.17721(2)	0.0286(1)
P	0.15741(5)	0.34692(4)	0.28856(5)	0.0305(3)
Si	0.13557(4)	0.18076(4)	0.28346(5)	0.0233(2)
O(1)	0.0176(1)	0.0912(1)	0.0410(1)	0.0652(9)
O(2)	0.0554(1)	0.0126(1)	0.2576(1)	0.0629(9)
O(3)	−0.0213(1)	0.2640(1)	0.1967(1)	0.0429(8)
O(4)	0.2361(1)	0.1625(1)	0.1156(1)	0.0608(9)
O(5)	0.1276(1)	0.2714(1)	0.2977(1)	0.0288(7)
N(1)	0.2454(1)	0.3511(1)	0.3160(2)	0.0549(10)
N(2)	0.1014(1)	0.3956(1)	0.3370(1)	0.0353(9)
N(3)	0.1573(2)	0.3726(1)	0.2050(1)	0.0469(10)
C(1)	0.0424(2)	0.1123(2)	0.0942(2)	0.0410(11)
C(2)	0.0664(2)	0.0655(2)	0.2251(2)	0.0394(11)
C(3)	0.0197(2)	0.2159(2)	0.1889(1)	0.0318(10)
C(4)	0.1759(2)	0.1558(2)	0.1403(1)	0.0400(11)
C(5)	0.3137(2)	0.1528(2)	0.2916(1)	0.0421(10)
C(6)	0.2321(1)	0.1549(1)	0.3183(1)	0.0253(9)
C(7)	0.2012(1)	0.1298(1)	0.3800(2)	0.0243(9)
C(8)	0.1133(1)	0.1396(2)	0.3753(1)	0.0244(9)
C(9)	0.0759(2)	0.1814(2)	0.4370(1)	0.0278(9)
C(10)	−0.0118(2)	0.1679(2)	0.4463(2)	0.0277(9)
C(11)	−0.0264(2)	0.0936(2)	0.4739(2)	0.0510(12)
C(12)	−0.0537(2)	0.1784(2)	0.3740(2)	0.0420(10)
C(13)	−0.0426(2)	0.2215(2)	0.5009(2)	0.0478(14)
C(14)	0.2637(2)	0.3246(2)	0.3877(2)	0.0850(16)
C(15)	0.3038(2)	0.3996(2)	0.2858(3)	0.0943(18)
C(16)	0.0196(2)	0.3791(2)	0.3474(2)	0.0487(12)
C(17)	0.1244(2)	0.4660(2)	0.3619(3)	0.0867(18)
C(18)	0.0982(3)	0.4180(2)	0.1737(2)	0.0857(17)
C(19)	0.1993(3)	0.3319(2)	0.1494(2)	0.0747(16)
C(20)	0.2377(2)	0.0935(2)	0.4418(1)	0.0250(9)
C(21)	0.2028(2)	0.0353(2)	0.4743(2)	0.0311(10)
C(22)	0.2376(2)	−0.0012(2)	0.5307(2)	0.0401(11)
C(23)	0.3085(2)	0.0218(2)	0.5565(2)	0.0417(11)
C(24)	0.3430(2)	0.0803(2)	0.5257(2)	0.0412(11)
C(25)	0.3089(2)	0.1159(2)	0.4693(2)	0.0331(10)

U_{eq} = 1/3 of the trace of the orthogonalized U_{ij} tensor.

Crystallographic data for $C_{30}H_{40}N_3FeO_5SiP$*; compound E*-**4**

$M_r = 637.6$, monoclinic, $P2_1/n$ (No 14), $a = 1\,845.6(2)$, $b = 979.7(1)$, $c = 1\,897.0(1)$ pm, $\beta = 91.50(1)°$, $V = 3\,429 \cdot 10^6$ pm^3, $Z = 4$, $\rho_{calcd} = 1.235$ g cm^{-3}, $F000 = 1\,344$, $\mu = 5.6$ cm^{-1}. Data were collected on an Enraf-Nonius CAD-4 diffractometer with graphite monochromator, Mo$K\alpha$ ($\lambda = 71.073$ pm), $\Theta/2\Theta$-scans, $1.0° < \Theta < 25.0°$. During data collection no decay was observed, no absorption correction, and no correction for extinction effects were applied. From 4 128 collected data points 5 were rejected (systematic absences). After merging ($R_{int} = 0.016$) all 4 013 unique data ($I > 0.0$) were used in the final refinement. The structure was solved with direct methods, and refined by full-matrix least-squares calculations, with anisotropic thermal parameters for all non-hydrogens. All hydrogen atoms were found and refined with isotropic thermal parameters. Refinement was concluded with $R1 = 0.052$ and $wR2 = 0.136$, $w = 1/\sigma^2(F_o^2)$. All software and the sources of the scattering factors are contained in the STRUX-V [11] system using the programs PLATON-92″, PLUTON-92″, SCHAKAL, SHELXL-86, and SHELXL-93. Positional parameters are listed in table III.

Table III. Atomic coordinates and isotropic thermal parameters for *E*-**4**.

Atom	x/a	y/b	z/c	U_{eq} [Å^2]
Fe	0.34863(3)	0.98628(6)	0.44602(3)	0.0511(2)
P	0.34284(7)	0.58551(12)	0.31605(6)	0.0534(4)
Si	0.27280(6)	0.86230(11)	0.37477(5)	0.0434(3)
O(4)	0.4379(3)	1.1594(5)	0.5381(2)	0.121(2)
O(5)	0.4261(2)	1.0654(5)	0.3209(2)	0.102(2)
O(6)	0.3902(3)	0.7286(5)	0.5117(2)	0.107(2)
O(7)	0.2142(2)	1.1209(5)	0.4809(3)	0.142(3)
O(8)	0.3095(2)	0.7085(3)	0.3510(2)	0.060(1)
N(1)	0.4288(2)	0.5871(5)	0.3292(2)	0.073(2)
N(2)	0.3103(3)	0.4482(4)	0.3512(2)	0.076(2)
N(3)	0.3231(2)	0.5894(5)	0.2328(2)	0.073(2)
C(1)	0.2208(2)	0.9300(4)	0.2958(2)	0.047(1)
C(2)	0.1577(2)	0.8924(4)	0.3243(2)	0.050(1)
C(3)	0.1745(2)	0.8269(5)	0.3963(2)	0.055(1)
C(4)	0.4029(3)	1.0899(6)	0.5025(3)	0.074(2)
C(5)	0.3940(3)	1.0313(5)	0.3701(3)	0.065(2)
C(6)	0.3730(3)	0.8299(6)	0.4861(3)	0.071(2)
C(7)	0.2675(3)	1.0679(6)	0.4672(3)	0.082(2)
C(11)	0.2356(2)	1.0088(4)	0.2317(2)	0.051(1)
C(12)	0.2994(3)	0.9908(5)	0.1974(2)	0.068(2)
C(13)	0.3162(3)	1.0643(7)	0.1380(3)	0.086(2)
C(14)	0.2691(4)	1.1615(6)	0.1132(3)	0.090(2)
C(15)	0.2052(4)	1.1824(5)	0.1460(3)	0.080(2)
C(16)	0.1879(3)	1.1070(5)	0.2048(3)	0.066(2)
C(21)	0.0822(2)	0.9076(5)	0.2973(2)	0.058(2)
C(22)	0.0595(3)	0.8623(7)	0.2328(3)	0.094(3)
C(23)	−0.0107(4)	0.8725(9)	0.2084(4)	0.123(4)
C(24)	−0.0601(4)	0.9307(9)	0.2488(5)	0.113(3)
C(25)	−0.0412(4)	0.9752(9)	0.3151(5)	0.132(4)
C(26)	0.0299(3)	0.9623(7)	0.3397(4)	0.099(3)
C(30)	0.1430(3)	0.6860(5)	0.4102(3)	0.068(2)
C(31)	0.1247(3)	0.6550(6)	0.4869(3)	0.077(2)
C(32)	0.0619(4)	0.7416(8)	0.5105(4)	0.117(3)
C(33)	0.1897(3)	0.6818(7)	0.5353(3)	0.094(3)
C(34)	0.1037(4)	0.5070(6)	0.4913(4)	0.104(3)
C(101)	0.4711(4)	0.4684(9)	0.3484(5)	0.147(4)
C(102)	0.4694(3)	0.7114(7)	0.3174(3)	0.098(3)
C(201)	0.2791(4)	0.3360(6)	0.3126(4)	0.114(3)
C(202)	0.3162(4)	0.4308(6)	0.4274(3)	0.107(3)
C(301)	0.3719(5)	0.5397(10)	0.1817(4)	0.151(5)
C(302)	0.2501(4)	0.6152(6)	0.2069(3)	0.101(3)

U_{eq} = 1/3 of the trace of the orthogonalized U_{ij} tensor.

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