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Synthesis and structure of silylene complexes of silacyclobutanes *

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Abstract

Reactions of 1.1-dichloro-2-neopentyl-3-vinyl-1-silacyclobutane (1a, b) with carbonyl metallates $[\{M(CO)_n\}_m]^{2-}$ (M = Fe, m = 1, n = 4; M = Cr, m = 1, n = 5; M = W, m = 2, n = 5) in THF/HMPA lead to novel compounds $[(CO)_nMSiC_{10}H_{18}] \cdot$ HMPA (M = Fe, n = 4; M = Cr, W, n = 5). ¹H, ¹³C and ²⁹Si NMR spectroscopic studies in solution support the formation of four diastereomeric pairs of enantiomers. The X-ray structure analyses of the crystals show folded 1-metallated 1-silacyclobutane units in which the HMPA ligand increases the coordination number of Si to 3 + 1. Crystals of $[(CO)_5CrSiC_{10}H_{18}] \cdot$ HMPA (2) and of $[(CO)_5WSiC_{10}H_{18}] \cdot$ HMPA (3) (corresponding values in brackets) are isotypic: $P2_1/n$ (No. 14); a = 1084(1)/[1099(1)], b = 1927(1)/[1937(1)], c = 1342.1(8)/[1342(1)] pm, $\beta = 97.11(7)/[97.18(7)]^\circ$, Z = 4. In both crystals enantiomeric [15,25,35]/[1R,2R,3R] pairs are present. In orthorhombic crystals of $[(CO)_4FeSiC_{10}H_{18}] \cdot$ HMPA (4) ($P2_12_12_1$ (No. 19), a = 896.4(5), b = 1693(1), c = 1753(1) pm, Z = 4) only the [15,25,35]-isomer is detected.

Keywords: Silacyclobutanes; Silylene complexes; Chromium; Tungsten; Iron; Silanes

1. Introduction

Although the synthesis and characterisation of monosilacyclobutanes has been a subject of intensive research work for many years [1], an increase in interest in four-membered Si–C ring systems can be noticed to this very day, which is strongly supported by current reports [2]. Studies of the pyrolysis of monosilacyclobutanes yielding silaethenes in the gas phase have been extensively published [3] and a lot of work is still done on the generation of new silene intermediates and the studies of their reactivity [4]. Thermolyses of four-membered ring systems lead to polymeric compounds [5]. The ring-opening polymerisation reaction takes place even at room temperature in the presence of a transition metal catalyst (H_2PtCl_6) [6]. The first step obviously

proceeds via the insertion of a metal fragment into the Si-C bond of the silacyclobutane, which has been demonstrated for iron [7] and platinum complexes [1]. The detailed studies of Tanaka confirm the high reactivity of silacyclobutanes towards transition metal compounds in general [2]. These results are in good agreement with the easily performed ring-opening reaction by Brønstedt and Lewis acids or bases [8]. In contrast, investigations on 1,1-dichloro-2-neopentyl-3-vinyl-1silacyclobutanes, which are easily accessible by a facile one-step synthesis, showed no ring-opening polymerisation when thermolysed, but an intramolecular isomerisation to silacyclohexenes [9]. In addition, initial studies confirm a remarkable stability towards hexachloroplatinic acid [10] and transition metal fragments; this is in good agreement with the outstanding stability of 1,1-dichloro-4-neopentyl-2,3-diorgano-1-silacyclobutenes [11]. In this paper we present the syntheses and comparative structural studies of three HMPA-stabilised silylene complexes prepared from the above-mentioned silacyclobutanes.

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 $^{^{*}}$ Dedicated to Professor Dr. H. Schumann on the occasion of his 60th birthday.

¹ Fenske–Hall calculations.

2. Results and discussion

2.1. Syntheses of silylene complexes of 2-neopentyl-3vinyl-1-silacyclobutanes with different metal fragments

According to Scheme 1, anti/syn stereoisomeric 1,1-dichloro-2-neopentyl-3-vinyl-1-silacyclobutanes are synthesized by the [2+2] cycloaddition reaction of dichloroneopentylsilene, $Cl_2Si=CHCH_2^{t}Bu$ and 1.3-butadiene as described previously [9]; the preliminary formation of silene results from the reaction of vinyl-trichlorosilane and Li^tBu in a non-polar solvent [10].

A promising synthetic route to silvlene complexes is the very effective salt elimination which occurs on reacting carbonylate dianions with diorganodichlorosilanes in the presence of the donor solvent HMPA [12]. This method allows both the use of mono- and di-nuclear metallate dianions; the presence of the HMPA donor increases the solubility of the different metallate dianions in THF allowing the formation of ion-pairs [13]. As shown in Scheme 2, the reaction of a stereoisomeric mixture of **1a/1b** and carbonyl metallates $[{M(CO)}_n]_m]^{2-}$ (M = Fe, m = 1, n = 4; M = Cr, m = 1, n = 5; M = W, m = 2, n = 5) in a solvent mixture of THF/HMPA leads to the formation of the donor-stabilised complexes [M]SiC₁₀H₁₈ · HMPA.

The introduction of the HMPA ligand into the coordination sphere of the silicon atom principally causes the formation of four diastereomeric pairs of enantiomers which were clearly detected by spectroscopic means (Scheme 3).

2.2. Spectroscopic characterisation of the silylene complexes of 2, 3 and 4

Proton, ¹³C and ²⁹Si NMR spectroscopic studies of the product mixtures in solution indicate the formation of up to four diastereomeric pairs of enantiomers for each silylene complex. According to the intensity distribution of the ¹H NMR signals, the four diastereomers



K ₂ [Cr(CO) ₅]	<u>1a/1b</u>	[Cr]-SiC ₁₀ H ₁₈ ·HMPA (2)
K ₂ [W ₂ (CO) ₁₀]	THF/HMPA -80°C≁rt	[W]-SiC ₁₀ H ₁₈ ·HMPA (<u>3</u>)
Na ₂ [Fe(CO) ₄]	-2MCI	[Fe]-SiC ₁₀ H ₁₈ ·HMPA (4)

(2): $[Cr] = Cr(CO)_5;$ (3): $[W] = W(CO)_5;$ (4): $[Fe] = Fe(CO)_4.$

Scheme 2.

are formed in ratios of approximately 1:0.65:0.37(2a/2b/2c), 1:0.83:0.15:0.07 (3a/3b/3c/3d) and 1:0.63:0.36:0.14 (4a/4b/4c/4d); isomer 2d, if present, was not detectable by NMR spectroscopy.

The ²⁹Si NMR spectroscopic investigations confirm the coordination of a HMPA donor to the silicon centre for all complexes; line splitting of the signals into doublets is detected for every diastereomer. The ²⁹Si NMR chemical shifts are in the characteristic range between 70 and 115 ppm which is in good agreement with literature data for other HMPA-stabilised Cr, W and Fe silvlene complexes containing alkyl groups at the silicon atoms [14]. The ²⁹Si NMR spectra of 2a/2cand 4a/4c, selectively prepared by the reaction of pure anti-(1a) with the carbonyl metallates [according to Scheme 2, see Experimental details), exhibit two doublets at 96.25 $[{}^{2}J({}^{31}P{}^{29}Si) = 34.2 \text{ Hz}]$ and 114.89 ppm $[^{2}J(^{31}P^{29}Si) = 30.7 \text{ Hz}]$ for the chromium complex and at 99.47 $[{}^{2}J({}^{31}P{}^{29}Si) = 26.6 \text{ Hz}]$ and 91.76 ppm $[^{2}J(^{31}P^{29}Si) = 30.5$ Hz] for the corresponding iron compound. Spectra of 2b and 4b show doublets at 91.96 $[{}^{2}J({}^{31}P{}^{29}Si) = 32.1 \text{ Hz}]$ and 99.28 ppm $[{}^{2}J({}^{31}P{}^{29}Si) =$ 26.7 Hz]. The tungsten complex 3a/3b from anti/syn-(1a/1b) displays an upfield chemical shift typical for the heavier homologous metal at 70.52 $[{}^{2}J({}^{31}P{}^{29}Si) =$ 31.8 Hz] and 68.36 ppm $[{}^{2}J({}^{31}P{}^{29}Si) = 28.9$ Hz].

Two signals at 218.38 and 218.26 ppm occur in the carbonyl region of the ¹³C NMR spectra for the diastereomeric pairs of 4a/4c. The diastereomers of complexes 2 and 3 are indicated by two different groups of carbonyl signals in the ranges 224–229 and 203–206 ppm.

The IR spectra of **2** and **3** in THF exhibit three carbonyl stretching bands as expected for an idealisec C_{4v} symmetry; on this basis the bands at 2027 (w) 1908 (sh,w) and 1900 (vs) cm⁻¹ for **2** and 2043 (w)



[M]: Cr(CO)₅ (2); W(CO)₅ (3); Fe(CO)₄ (4). Scheme 3.

1914 (sh,w) and 1907 (vs) cm⁻¹ for **3** can be assigned to A'₁, A''₁ and E modes, respectively. The carbonyl stretching region of the IR spectrum of **4** in THF shows transmission maxima at 2011 (m), 1928 (w) and 1889 (s) cm⁻¹ which are consistent with a typical axial coordination of the silylene ligand (C_{3y}) .

2.3. Crystal structures of $[(CO)_5 CrSiC_{10}H_{18}] \cdot HMPA$ (2), $[(CO)_5WSiC_{10}H_{18}] \cdot HMPA$ (3) and $[(CO)_4FeSi-C_{10}H_{18}] \cdot HMPA$ (4)

Both complexes $[(CO)_5 CrSiC_{10}H_{18}] \cdot HMPA$ (2) and $[(CO)_5 WSiC_{10}H_{18}] \cdot HMPA$ (3) were isolated as almost

colourless isotypic crystals and are best described as in the monoclinic space group $P2_1/n$ (No. 14). Molecules of (1S,2S,3S)-2-neopentyl-3-vinyl-1-silacyclobutane-1diyl-1-chromium(0)pentacarbonyl hexamethylphosphorotriamide (2) and of (1S,2S,3S)-2-neopentyl-3-vinyl-1-silacyclobutane-1-diyl-1-tungsten(0)pentacarbonyl hexamethylphosphorotriamide (3) (Figs. 1, 2) are present in the crystals as well as their corresponding enantiomers due to the centres of inversion in the monoclinic space group $P2_1/n$. Metal fragments in 2 and 3 have an undistorted octahedral coordination and come close to a local C_{4v} symmetry. One coordination site is occupied by the silacyclobutane unit.

Crystal data for 2 and 3 and experimental parameters

Crystal size (mm) $0.45 \times 0.70 \times 0.50$ $0.35 \times 0.50 \times 0.60$ Crystal size (mm) $0.45 \times 0.70 \times 0.50$ $0.35 \times 0.50 \times 0.60$ Crystal size (mm) $megular prisms$ monoclinic. $2/m$ Space group $P2_1/n$ (No. 14) $a = 1099(1)$ $b = 1027(1)$ $b = 1937(1)$ $b = 1937(1)$ $c = 1342.1(8)$ $c = 1342(1)$ $b = 97.1(7)$ $\beta = 97.1(7)$ $\beta = 97.18(7)$ $p = 1.284$ Calculated density ($g c m^{-1}$) $p = 1.284$ $p = -1.569$ Number of units $Z = 4$ STOE, STADI4 Temperature (K) $T = 185(2)$ $T = 185(2)$ Radiation, $A(pm)$ $MK \alpha$, 71.069 , graphite monochromator Scan made $\omega/2.20$ $\omega/2.04$ Scan mage (f) $3.72 < 20 < 45.00$ $3.72 < 20 < 43.24$ Range of indices $h = 0/14$ $0/19$ $k = 0/20$ $\omega/20$ $\omega/20$ Scan mode $-0.44 \ 1$ $-42 \ 2$ Cobserved ($I > 2\sigma_i$) 2410 2826 R_{int} 0.0434 $-44 \ 1$ Absorption correction $-24 \ 1$ $-44 \ 1$	Formula unit	[(CO) ₅ CrSiC ₁₀ H ₁₈] · HMPA	. (2)	$[(CO)_{5}WSiC_{10}H_{18}] \cdot HMPA(3)$
Crystal system Laue group monoclinic. 2/m tregular prisms Crystal system Laue group $P2_1/n (No. 14)$ $a = 1099(1)$ b = 1927(1) $b = 1937(1)$ $c = 1342.1(8)$ $c = 1342(1)c = 1342.1(8)$ $c = 1342(1)$ $b = 1937(1)c = 1342.1(8)$ $c = 1342(1)c = 1342.1(8)$ $c = 1342(1)c = 1342.1(8)$ $c = 1342(1)c = 1342.1(8)$ $c = 1342(1)Cell volume (106 pm3) V_{12} = 2781.94 V_{12} = 2834.61Calculated density (g \ cm^{-3}) p = 1.284 p = 1.569Number of units Z = 4 Z = 4Temperature (K) T = 185(2) T = 185(2)Radiation, A (pm) Mo Ka, \alpha, 71.069, graphine monochromatorScan mode a/260Scan mode a/260Scan mode a/260Scan mode a/260Scan mode a/260Scan mode a/260 a/260Scan mode a/260Scan a/260Scan a/260Scan a/260Scan a/260Scan a/260Scan a/260Scan a/260Scan a/260Scan$	Crystal size (mm)	$0.45 \times 0.70 \times 0.50$		$0.35 \times 0.50 \times 0.60$
Crystal system. Laue group monoclinic. $2/m$ Space group $P2_1/n$ (No. 14) Cell parameters (pm), (*) $a = 1084(1)$ $b = 1937(1)$ $c = 1342.1(8)$ $c = 1342.1(7)$ $\beta = 971(8)$ $c = 1342.1(8)$ $c = 1342.1(7)$ $\beta = 971(8)$ Cell volume (10 ⁶ pm ³) $V_{ez} = 278.94$ $V_{ez} = 283.461$ Calculated density (g cm ⁻³) $p = 1.234$ $p = 1.569$ Number of units $Z = 4$ $Z = 4$ Scan made $\omega/20$ Stall Scan made (*) $3.72 < 2.60 < 43.24$ $r = 185(2)$ Radiation, A (pm) $Mo K a, 71.069$, graphite monochromator $\omega/2.0$ Scan range (*) $3.72 < 2.60 < 43.24$ Range of indices $k: 0/20$ $k: 0/19$ $k: 0/20$ $k: 0/19$ It ovid (1 $\geq 2\sigma_1$) 2410 2826 R_{11} Number of refl. 3434 3152 $3.22 < 2.0 < 43.24$ Astorytion correction ψ scan -4.41 -4.22 -3.22 -3.22 -3.22 -3.22 -3.22 -3.22 -3.22 -3.22 -3.22 -3.22 -3.22	Crystal shape		irregular prisms	
Space group $P2_1/n$ (No. 14) $P=1/n$ (No. 14) Cell parameters (pm), (°) $a = 1084(1)$ $b = 1937(1)$ $b = 1937(1)$ $c = 1342(18)$ $c = 1342(1)$ $\beta = 97.18(7)$ $\beta = 97.18(7)$ Cell volume (10 ⁶ pm ³) $V_{tz} = 2781.94$ $\gamma = 1.569$ Number of units $Z = 4$ $Z = 4$ Diffractometer STOE, STADI4 Temperature (K) $T = 185(2)$ $T = 185(2)$ Radiation, A (pm) Mo K $\alpha, 71.069$, graphite monochromator Scan mode $\omega/26$ Scan range (°) $3.72 < 26 < 45.00$ $3.72 < 26 < 43.24$ Range of indices $h = 11/10$ $h = -11/4$ $h = 0/14$ $l = 0/13$ $0/14$ Number of refl. 2410 2826 Absorption correction ψ -scan Reflections $-4 + 2$ $f or C and O$ Difference Fourier synthesis (SHELNA-23) $f or C and O$ Difference Fourier synthesis (SHELNA-23) $f or C and O$ Calculated in idealised positions, not refined $h = -1/\sigma^2 (F_c^2) + (A \cdot P)^2 + B \cdot P;$ where $P = 1/3(F_{com}^2 + 2F_c^2)$ <	Crystal system. Laue group		monoclinic. $2/m$	
	Space group		$P2_{1}/n$ (No. 14)	
$ \begin{array}{cccc} b = 1927(1) & b = 1937(1) \\ c = 1342.1(8) & c = 1342(1) \\ \beta = 97.11(7) & \beta = 97.18(7) \\ Cell volume (10^{6} pm^{3}) & V_{EZ} = 2781.94 & V_{EZ} = 283.61 \\ Calculated density (g cm^{-1}) & p = 1.284 & p = 1.569 \\ Number of units & Z = 4 & Z = 4 \\ \hline & Z = 4$	Cell parameters (pm), (°)	a = 1084(1)		a = 1099(1)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		b = 1927(1)		b = 1937(1)
$ \begin{array}{c} \beta = 97.11(7) & \beta = 97.18(7) \\ Cell volume (10^6 \ pm^3) & V_{EZ} = 278.194 & V_{EZ} = 233.461 \\ \rho = 1.569 \\ Number of units & Z = 4 & Z = 4 \\ \end{array} $ $ \begin{array}{c} STOE, STADI4 \\ T = 185(2) & T = 185(2) \\ Mo K a, 71.069, graphite monochromator \\ Scan mode & \omega/269 \\ Scan range (*) & 3.72 < 26 < 45.00 & k: 0/19 \\ k: 0/20 & k: 0/19 \\ k: 0/14 & k: 0/19 \\ k: 0/20 & k: 0/19 \\ k: 0/14 & k: 0/10 \\ Observed (1 > 2\pi) & 0.013 \\ Observed (1 > 2\pi) & 0.012 \\ Observed (1 > 2\pi) & 0.001 \\ Obse$		c = 1342.1(8)		c = 1342(1)
Cell volume (10 ⁶ pm ³) $V_{\rm EZ} = 2781.94$ $V_{\rm EZ} = 2334.61$ Calculated density (g cm ⁻¹) $p = 1.284$ $p = 1.569$ Number of units $Z = 4$ $Z = 4$ Diffractometer STOE, STADI4 $T = 185(2)$ Radiation, λ (pm) $Mo K \alpha, 71.069, graphite monochormator \omega/2.09 Scan range (°) 3.72 < 2.0 < 45.00 3.72 < 2.0 < 43.24 Range of indices h: - 11/10 h: - 11/18 \omega/2.09 k: 0/19 h: 0/19 Number of refl. 3434 3152 Observed (I > 2\sigma_i) 2410 2826 R_{mit} 0.0434 -44.1 Absorption correction \psi-scan Reflections -44.2 -3.22 Initial coordinates: for P, Si, Cr and Mo Difference Fourier syntheses (SteLtAt-93) for I H Difference Fourier syntheses (SteLtAt-93) International Tables for X-ray Crystallography. Kluwer Academic Publishers, Dordrecht. The Netherlands, 1992, Vol. C. Full matrix least squares (SteLtAt-93) for P, Si Cr and Mo International Tables for X-ray Crystallography. Kluwer Academic Publishers, Dordrecht. The Netherlands, 1992, Vol. C. $		$\beta = 97.11(7)$		$\beta = 97.18(7)$
Calculated density (g cm ⁻¹) $\rho = 1.284$ $\rho = 1.569$ Number of units $Z = 4$ $Z = 4$ Diffractometer STOE, STADI4 Temperature (K) $T = 185(2)$ $K = 185(2)$ Radiation, A (pm) $\omega/20$ Scan range (°) $3.72 < 20 < 45.00$ $3.72 < 20 < 43.24$ Range of indices $h^ 11/10$ $h^ 11/8$ Range of indices $h^ 11/10$ $h^ 11/8$ Number of refl. 3434 3152 Observed ($I > 2\sigma_i$) 2410 2826 Rain 0.0434 -4 4 1 Absorption correction $-4 4 1$ Reflections $-4 4 1$ Initial coordinates: $-4 2 2$ for P, Si, Cr and Mo Difference Fourier syntheses (SHELXL-93) for I and O Difference Fourier syntheses (SHELXL-93) calculated in idealised positions, not refined International Tables for X-ray Crystallography. Kluwer Academic Publishers, Dordretch. The Netherlands, 1992, Vol. C. Full matrix least squares (SHELXL-93) for H acultated in idealised positions, not refined $Hertantional Tables for X-ray Crystallography. Klawer Academic Publishers, Dordretch. The Neth$	Cell volume (10^6 pm^3)	$V_{\rm EZ} = 2781.94$		$V_{\rm EZ} = 2834.61$
Number of units $Z = 4$ $Z = 4$ Diffractometer STOE, STADI4 remperature (K) $T = 185(2)$ Mo K a , 71.069, graphic monochromator Radiation, λ (pm) $W \ge 20$ $W \ge 20$ Scan mode $w/20$ $w/20$ Scan range (°) $3.72 < 20 < 45.00$ $3.72 < 20 < 43.24$ Range of indices $k = 0/10$ $k = 0/19$ $k = 0/20$ $k = 0/19$ $k = 0/13$ Number of refl. 3434 3152 Observed $(I \ge 2\sigma_I)$ 2410 2826 R_{in} 0/44 3152 Absorption correction $\frac{-4 \cdot 41}{-4 \cdot 2}3 \cdot 2}3 \cdot 23 \cdot 22 \cdot 1 \cdot 110 + -$	Calculated density (g cm ⁻³)	$\rho = 1.284$		$\rho = 1.569$
Difference STOE, STADI4 Temperature (k) T = 185(2) Radiation, λ (pm) Mo K α, 71.069, graphite monochromator Scan range (°) 3.72 < 20 < 43.24	Number of units	Z = 4		Z = 4
Temperature (k) $T = 185(2)$ $T = 185(2)$ Radiation, λ (pm) Mo K α , 71.069, graphite monochromator Scan mode $\omega/2\theta$ Scan range (°) $3.72 < 2\theta < 43.24$ Range of indices $k: - 01/16$ $k: - 0/20$ $k: 0/19$ $k: 0/20$ $k: 0/13$ $k: 0/20$ $k: 0/13$ $k: 0/20$ $k: 0/13$ $k: 0/20$ $k: 2.2$	Diffractometer		STOE, STADI4	
Radiation, λ (pm) Mo K α , 71.069, graphite monochromator Scan made $\omega/20$ Scan range (°) 3.72 < 20 < 45.00 3.72 < 20 < 43.24 Range of indices $k: -11/10$ $k: -11/8$ Range of indices $k: 0/10$ $k: 0/19$ Number of refl. 3434 3152 Observed ($l > 2\sigma_l$) 2410 2826 R_{int} 0.0434 4 Absorption correction ψ -scan -4.41 Reflections -4.41 -4.22 -3.22 Initial coordinates: $0.1899/0.9524$ $11.899/0.9524$ for P, Si, Cr and Mo Direct methods (SHELXS-86) $0.1899/0.9524$ for T A Caluated in idealised positions, not refined -4.41 Atomic scattering factors (neutral atoms) International Tables for X-ray Crystallography, Kluwer Academic Publishers, Dordrecht, The Netherlands, 1992, Vol. C. Refinement on F^2 Full matrix least squares (SHELXL-9.3) $-11/3(F_{2,max}^2 + 2F_c^2)$ Weighting scheme $\omega = 1/\sigma^2(F_o^2) + (A \cdot P)^2 + B \cdot P;$ where $P = 1/3(F_{2,max}^2 + 2F_c^2)$ $M_{11}(M_{2,m})$ based on $F > 4\sigma_F$ 0.1153 (0.0784) 0.0578 (0.0525) $w = 1/\sigma^2(F_o^$	Temperature (K)	T = 185(2)		T = 185(2)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Radiation, λ (pm)	Μο Κ α	, 71.069, graphite m	onochromator
Scan range (°) $3.72 < 20 < 43.24$ Range of indices $h: -11/10$ $h: -11/8$ Range of indices $h: -11/10$ $h: -11/8$ Range of indices $h: -11/10$ $h: -11/8$ Reflections $0/13$ Observed $(I > 2\sigma_{r})$ 2410 2826 Reflections -441 Reflections -441 Reflections -441 Reflections -2441 Reflections -211 Transmission (min./max) $0.1899/0.9524$ Initial coordinates: $0.1899/0.9524$ for P, Si, Cr and Mo Direct methods (SHELXS-86) for C and O Difference Fourier synthese (SHELXL-93) for H calculated in idealised positions, not refined Atomic scattering factors (neutral atoms) <i>International Tables for X-ray Crystallography.</i> Kluwer Academic Publishers, Dordrecht. The Netherlands, 1992, Vol. C. Refinement on F^2 Full matrix least squares (SHELXL-93) Minimised function $\Sigma w(F_0^2 - F_c^2)$ weighting scheme 256 $B - 7.14$ $B - 21.25$ Variables 256 <	Scan mode		$\omega/2\Theta$	
Range of indices $h: -11/10$ $h: -11/8$ $k: 0/20$ $k: 0/19$ $k: 0/20$ $k: 0/19$ Number of refl. 3434 3434 3152 Observed $(I > 2\sigma_I)$ 2410 Absorption correction ψ -scan Reflections -441 Absorption correction -422 Reflections -422 -322 -211 Transmission (min./max) 0.1899/0.9524 Initial coordinates: $0.1899/0.9524$ for P, Si, Cr and Mo Direct methods (SHELXS-86) Difference Fourier syntheses (SHELXL-93) $0.1899/0.9524$ for H calculated in idealised positions, not refined Atomic scattering factors (neutral atoms) International Tables for X-ray Crystallography, Kluwer Academic Publishers, Dordrecht. The Netherlands, 1992, Vol. C. Full matrix least squares (SHELXL-93) Minimised function $\Sigma w(F_2^2 - F_1^2)$ $w = 1/\sigma^2 (F_0^2) + (A \cdot P)^2 + B \cdot P;$ where $P = 1/3 (F_{0amax} + 2F_c^2)$ $A = 0.1351$ $A = 0.1198$ $B = 7.14$ $B = 21.25$ $Variables$ 256 257 256 Wa_{2_0}	Scan range (°)	$3.72 < 2\Theta < 45.00$		$3.72 < 2\Theta < 43.24$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Range of indices	h: -11/10		h: -11/8
l: $0/14$ l: $0/13$ Number of refl.34343152Observed $(I > 2\sigma_i)$ 24102826 R_{int} 0.0434Absorption correction ψ -scanReflections $-4.4.1$ $-4.2.2$ $-3.2.2$ $-3.2.2$ $-2.1.1$ Transmission (min./max)0.1899/0.9524Initial coordinates: $0.1899/0.9524$ for P, Si, Cr and MoDirect methods (SHELXS-86)for Hcalculated in idealised positions, not refinedAtomic scattering factors (neutral atoms)International Tables for X-ray Crystallography, Kluwer Academic Publishers, Dordrecht. The Netherlands, 1992, Vol. C.Refinement on F^2 Full matrix least squares (SHELXL-93)Minimised function $\Sigma w(F_g^2 - F_c^2)$ $M = 0.1351$ Variables256 256 257 $R_{all}(R_{obs})$ based on $F > 4\sigma_F$ 0.1153 (0.0784) 0.000 0.012Residual electron density (10 ⁻⁶ pm ⁻³) (min./max) $-0.59/1.35$ $-0.59/1.35$ $-1.69/2.14$ Programs usedSHELXS-80 [15], SHELXL-93 [16], ORTEP [17]		k: 0/20		k: 0/19
Number of refl.34343152Observed $(I > 2\sigma_i)$ 24102826Observed $(I > 2\sigma_i)$ 24102826Absorption correction ψ -scanReflections $-4.4.1$ $-4.2.2$ $-3.2.2$ $-3.2.2$ $-2.1.1$ Transmission (min./max) $0.1899/0.9524$ Initial coordinates: $0.1899/0.9524$ for P, Si, Cr and MoDirect methods (SHELXS-86)for C and ODifference Fourier syntheses (SHELXL-93)for Hcalculated in idealised positions, not refinedAtomic scattering factors (neutral atoms)International Tables for X-ray Crystallography, Kluwer Academic Publishers, Dordrecht. The Netherlands, 1992, Vol. C.Refinement on F^2 Full matrix least squares (SHELXL-9.9)Weighting scheme $w = 1/\sigma^2(F_0^2) + (A \cdot P)^2 + B \cdot P;$ where $P = 1/3(F_{o,max}^2 + 2F_c^2)$ $A = 0.1351$ $A = 0.1198$ $B - 7.14$ $B - 21.25$ Variables256 257 256 $Nar_{14}(wR_{obs})$ $0.0578 (0.0525)$ $wR_{14}(wR_{obs})$ $0.0570 (1.152)$ 0.000 0.012 Residual electron density (10^{-6} pm ⁻³)(min./max.) $-0.59/1.35$ $-1.69/2.14$ Programs usedSHELXS-80 [15], SHELXL-93 [16], ORTEr [17]		<i>l</i> : 0/14		<i>l</i> : 0/13
Observed $(l > 2\sigma_1)$ 2410 2826 R_{int} 0.0434 Absorption correction -4 4 1 Reflections -4 4 1 -4 2 2 -3 2 2 -2 1 1 -2 1 1 Transmission (min./max) 0.1899/0.9524 Initial coordinates: 67 P, Si, Cr and Mo for P, Si, Cr and Mo Direct methods (SHELXL-93) for A calculated in idealised positions, not refined Atomic scattering factors (neutral atoms) International Tables for X-ray Crystallography, Kluwer Academic Publishers, Dordrecht. The Netherlands, 1992, Vol. C. Refinement on F^2 Full matrix least squares (SHELXL-93) Weighting scheme $\sum W(F_0^2 - F_c^2)$ $W = 1/\sigma^2(F_0^2) + (A \cdot P)^2 + B \cdot P$; where $P = 1/3(F_{0,max}^2 + 2F_c^2)$ $A = 0.1351$ $A = 0.1198$ $B - 7.14$ $B - 21.25$ Variables 256 $Z57$ 2302 (0.2058) $R_{all}(R_{obb})$ based on $F > 4\sigma_F$ 0.1153 (0.0784) 0.0578 (0.0525) $Northolds(0, 0, 0, 0, 0)$ 0.012 0.000 0.012 Residual electron density (10 ⁻⁶ pm ⁻³) (min./max.) $-0.59/1.35$ -1.6	Number of refl.	3434		3152
R_{int} 0.0434 Absorption correction ψ -scan Reflections -441 -422 -322 -321 -322 -211 -421 Transmission (min./max) $0.1899/0.9524$ Initial coordinates: $0.1899/0.9524$ for P, Si, Cr and Mo Direct methods (SHELXS-86) for A calculated in idealised positions, not refined Atomic scattering factors (neutral atoms) International Tables for X-ray Crystallography, Kluwer Academic Publishers, Dordrecht. The Netherlands, 1992, Vol. C. Full matrix least squares (SHELXL-93) Minimised function $\Sigmaw(F_o^2 - F_c^2)$ $A = 0.1198$ $B - 7.14$ $B - 21.25$ Variables 256 257 $R_{all}(w_{abs})$ based on $F > 4\sigma_F$ 0.1153 (0.0784) 0.0578 (0.0525) $wrag_u(wR_{2,w})$ 0.2302 (0.2058) 0.1510 (0.1460) GOF _{all} (GOF _{abs}) 1.057 (1.152) 0.975 (1.000) Shift/esd (mean) 0.000 0.012 Residual electron density (10 ⁻⁶ pm ⁻³) -0.59/1.35 -1.69/2.14 (min./max.) $-0.59/1.35$ -1.69/2.14 <td>Observed $(I > 2\sigma_i)$</td> <td>2410</td> <td></td> <td>2826</td>	Observed $(I > 2\sigma_i)$	2410		2826
Absorption correction ψ -scanReflections -441 -422 -322 -211 Transmission (min./max) $0.1899/0.9524$ Initial coordinates: for P, Si, Cr and Mo for C and ODirect methods (SHELXS-86)for Hcalculated in idealised positions, not refinedAtomic scattering factors (neutral atoms) <i>International Tables for X-ray Crystallography</i> , Kluwer Academic Publishers, Dordrecht. The Netherlands, 1992, Vol. C.Refinement on F^2 Full matrix least squares (SHELXI-93)Minimised function $\Sigma w(F_0^2 - F_c^2)$ $w = 1/\sigma^2(F_0^2) + (A \cdot P)^2 + B \cdot P;$ where $P = 1/3(F_{0,max}^2 + 2F_c^2)$ $A = 0.1351$ Wariables256 $P = 7.14$ $B - 21.25$ Variables256 $Q_{2302}(0.2058)$ 0.1510 (0.1460) $QOF_{all}(GOF_{obs})$ 1.057 (1.152) $QOP = 0.153$ 0.975 (1.000)Shift/esd (mean)0.000 $QOU0.012Residual electron density (10-6 pm-3)-0.59/1.35(min./max.)-0.59/1.35-1.69/2.14Programs usedSHELXS-86 [15], SHELXL-93 [16], ORTEP [17]$	R _{int}	0.0434		
Reflections $-4 4 1$ $-4 2 2$ $-3 2 2$ $-2 1 1$ Transmission (min./max)0.1899/0.9524Initial coordinates: for P, Si, Cr and Mo for C and ODirect methods (SHELXL-93)for Hcalculated in idealised positions, not refinedAtomic scattering factors (neutral atoms)International Tables for X-ray Crystallography, Kluwer Academic Publishers, Dordrecht. The Netherlands, 1992, Vol. C.Refinement on F^2 Full matrix least squares (SHELXL-93)Minimised function $\Sigma w(F_o^2 - F_c^2)$ $w = 1/\sigma^2(F_o^2) + (A \cdot P)^2 + B \cdot P;$ where $P = 1/3(F_{o,max}^2 + 2F_c^2)$ $A = 0.1351$ Variables256Variables256 $OF_{R_{11}}(R_{obs})$ based on $F > 4\sigma_F$ $O.1510$ 0.0578 $OO_{2302}(0.2058)$ 0.1510 $OO_{11}(GOF_{obs})$ $1.057(1.152)$ $OO_{21}(GOF_{obs})$ 0.000 $OO(0)$ 0.012 Residual electron density (10^{-6} pm ⁻³)(min./max.) $-0.59/1.35$ $-1.69/2.14$ Programs usedSHELXS-86 [15], SHELXL-93 [16], ORTEP [17]	Absorption correction			ψ -scan
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Reflections			-441
$\begin{array}{cccc} & & & & & & & & & & & & & & & & & $				-422
$\begin{array}{cccc} & -211 \\ 0.1899/0.9524 \\ \hline \\ 1nitial coordinates: \\ for P, Si, Cr and Mo \\ for C and O \\ for H \\ Atomic scattering factors (neutral atoms) \\ Minimised function \\ Weighting scheme \\ \hline \\ Weighting scheme \\ \hline \\ Variables \\ Vari$				-322
Transmission (min./max) $0.1899/0.9524$ Initial coordinates: for P, Si, Cr and Mo for C and ODirect methods (SHELXS-86)for P, Si, Cr and Mo for HDifference Fourier syntheses (SHELXL-93) calculated in idealised positions, not refinedAtomic scattering factors (neutral atoms)International Tables for X-ray Crystallography, Kluwer Academic Publishers, Dordrecht. The Netherlands, 1992, Vol. C.Refinement on F^2 Full matrix least squares (SHELXL-93) $\Sigmaw(F_o^2 - F_c^2)$ $w = 1/\sigma^2(F_o^2) + (A \cdot P)^2 + B \cdot P;$ where $P = 1/3(F_{o,max}^2 + 2F_c^2)$ $A = 0.1198$ $B - 7.14$ Variables256Variables256 $QO_{11}(GOF_{obs})$ 0.153 (0.0784) $QO_{21}(GOF_{abs})$ 0.2302 (0.2058) $O.1150$ (0.1460) $O.000$ $OOO0$ 0.012Residual electron density (10^{-6} pm ⁻³) (min./max.) $-0.59/1.35$ $Programs used$ $-0.59/1.35$				-211
Initial coordinates: for P, Si, Cr and Mo for C and ODirect methods (SHELXS-86)Atomic scattering factors (neutral atoms)Difference Fourier syntheses (SHELXL-93) calculated in idealised positions, not refinedAtomic scattering factors (neutral atoms)International Tables for X-ray Crystallography, Kluwer Academic Publishers, Dordrecht. The Netherlands, 1992, Vol. C.Refinement on F^2 Full matrix least squares (SHELXL-93) $\Sigma w(F_o^2 - F_c^2)$ $w = 1/\sigma^2(F_o^2) + (A \cdot P)^2 + B \cdot P$; where $P = 1/3(F_{0,max}^2 + 2F_c^2)$ $A = 0.1351$ $B = 7.14$ $B - 21.25$ Variables256Variables256 $R_{all}(R_{obs})$ based on $F > 4\sigma_F$ 0.1153 (0.0784)0.2302 (0.2058)0.1510 (0.1460)GOF _{all} (GOF _{obs})1.057 (1.152)0.975 (1.000)0.012Shift/esd (mean)0.0000.0000.012Residual electron density (10 ⁻⁶ pm ⁻³) (min./max.)-0.59/1.35Programs usedSHELXS-86 [15], SHELXL-93 [16], ORTEP [17]	Transmission (min./max)			0.1899/0.9524
for P, Si, Cr and Mo for C and O for HDirect methods (SHELXS-86)Atomic scattering factors (neutral atoms)Difference Fourier syntheses (SHELXL-93) calculated in idealised positions, not refinedAtomic scattering factors (neutral atoms)International Tables for X-ray Crystallography, Kluwer Academic Publishers, Dordrecht. The Netherlands, 1992, Vol. C.Refinement on F^2 Full matrix least squares (SHELXL-93) $X = 1/\sigma^2(F_o^2) + (A \cdot P)^2 + B \cdot P$; where $P = 1/3(F_{0,max}^2 + 2F_c^2)$ $A = 0.1351$ $B = 7.14$ Weighting scheme $\Sigma w(F_o^2 - F_c^2)$ $w = 1/\sigma^2(F_o^2) + (A \cdot P)^2 + B \cdot P$; where $P = 1/3(F_{0,max}^2 + 2F_c^2)$ $A = 0.1198$ $B = 7.14$ Variables256 $S_{all}(R_{obs})$ based on $F > 4\sigma_F$ 0.1153 (0.0784) $0.0578 (0.0525)$ $wR_{2all} (wR_{2b})$ 0.2302 (0.2058) $0.1510 (0.1460)$ GOF _{all} (GOF _{obs})0.000Shift/esd (mean)0.000 0.000 0.012Residual electron density (10 ⁻⁶ pm ⁻³) (min./max.)-0.59/1.35 $-0.59/1.35$ $-1.69/2.14$	Initial coordinates:			
for C and O for HDifference Fourier syntheses (SHELXL-93) calculated in idealised positions, not refinedAtomic scattering factors (neutral atoms)International Tables for X-ray Crystallography, Kluwer Academic Publishers, Dordrecht. The Netherlands, 1992, Vol. C.Refinement on F^2 Full matrix least squares (SHELXL-93) Weighting schemeWeighting scheme $\Sigma w(F_o^2 - F_c^2)$ $w = 1/\sigma^2(F_o^2) + (A \cdot P)^2 + B \cdot P$; where $P = 1/3(F_{o,max}^2 + 2F_c^2)$ $A = 0.1198$ $B - 7.14$ Variables256Variables256 $Q_{all}(R_{obs})$ based on $F > 4\sigma_F$ $0.1153(0.0784)$ $0.0578(0.0525)$ $0.2302(0.2058)$ 0.000 0.012 Residual electron density (10^{-6} pm ⁻³)(min./max.) $-0.59/1.35$ Programs used $-1.69/2.14$	for P, Si, Cr and Mo	Direct methods (SHELXS-86)		
for Hcalculated in idealised positions, not refinedAtomic scattering factors (neutral atoms)International Tables for X-ray Crystallography, Kluwer Academic Publishers, Dordrecht. The Netherlands, 1992, Vol. C.Refinement on F^2 Full matrix least squares (SHELXL-93)Minimised function $\Sigma w (F_o^2 - F_c^2)$ $w = 1/\sigma^2 (F_o^2) + (A \cdot P)^2 + B \cdot P;$ where $P = 1/3(F_{o,max}^2 + 2F_c^2)$ $A = 0.1198$ $B - 7.14$ Variables256Variables256 $R_{all}(R_{obs})$ based on $F > 4\sigma_F$ 0.1153 (0.0784) $OOF_{all}(GOF_{obs})$ 1.057 (1.152) $OOP_{all}(GOF_{obs})$ 0.000Shift/esd (mean)0.000Residual electron density (10 ⁻⁶ pm ⁻³)(min./max.) $-0.59/1.35$ Programs used $-1.69/2.14$	for C and O	Difference Fourier syntheses (SHELXL-93)		
Atomic scattering factors (neutral atoms)International Tables for X-ray Crystallography, Kluwer Academic Publishers, Dordrecht. The Netherlands, 1992, Vol. C.Refinement on F^2 Full matrix least squares (SHELXL-93)Minimised function $\Sigma w(F_o^2 - F_c^2)$ $w = 1/\sigma^2(F_o^2) + (A \cdot P)^2 + B \cdot P$; where $P = 1/3(F_{o,max}^2 + 2F_c^2)$ $A = 0.1198$ $B - 7.14$ Variables 256 Variables 256 $R_{all}(R_{obs})$ based on $F > 4\sigma_F$ $0.1153 (0.0784)$ $OGF_{all}(GOF_{obs})$ $0.2302 (0.2058)$ $OII = 2000$ 0.012 Residual electron density (10^{-6} pm ⁻³)(min./max.) $-0.59/1.35$ Programs used $SHELXS-86 [15], SHELXL-93 [16], ORTEP [17]$	for H	calculated in idealised p	positions, not refined	
Kluwer Academic Publishers, Dordrecht. The Netherlands, 1992, Vol. C.Refinement on F^2 Kluwer Academic Publishers, Dordrecht. The Netherlands, 1992, Vol. C.Minimised function $\Sigma w(F_o^2 - F_c^2)$ Weighting scheme $\Sigma w(F_o^2 - F_c^2)$ Wariables $B = 7.14$ $B = 7.14$ $B = 21.25$ Variables 256 $R_{all}(R_{obs})$ based on $F > 4\sigma_F$ $0.1153 (0.0784)$ $OS78 (0.0525)$ $0.0578 (0.0525)$ $W_{2_{all}}(wR_{2_{obs}})$ $0.2302 (0.2058)$ $OI153 (0.0784)$ $0.975 (1.160)$ $OO00$ 0.012 Residual electron density $(10^{-6} \text{ pm}^{-3})$ $-0.59/1.35$ (min./max.) $-0.59/1.35$ $-1.69/2.14$ Programs usedSHELXS-86 [15], SHELXL-93 [16], ORTEP [17]	Atomic scattering factors (neutral atoms)	International Tables for	r X-ray Crystallogra	phy,
Refinement on F^2 Full matrix least squares (SHELXL-93) Minimised function $\Sigma w(F_o^2 - F_c^2)$ Weighting scheme $w = 1/\sigma^2(F_o^2) + (A \cdot P)^2 + B \cdot P$; where $P = 1/3(F_{o,max}^2 + 2F_c^2)$ $A = 0.1351$ $A = 0.1198$ $B - 7.14$ $B - 21.25$ Variables 256 $R_{all}(R_{obs})$ based on $F > 4\sigma_F$ 0.1153 (0.0784) $0.2302 (0.2058)$ 0.1510 (0.1460) $GOF_{all}(GOF_{obs})$ 1.057 (1.152) 0.975 (1.000) Shift/esd (mean) 0.000 0.012 Residual electron density (10 ⁻⁶ pm ⁻³) $-0.59/1.35$ $-1.69/2.14$ Programs used SHELXS-86 [15], SHELXL-93 [16], ORTEP [17]	2	Kluwer Academic Publ	ishers, Dordrecht. Th	ne Netherlands, 1992, Vol. C.
Minimised function $\sum w(F_o^2 - F_c^2)$ $w = 1/\sigma^2 (F_o^2) + (A \cdot P)^2 + B \cdot P$; where $P = 1/3(F_{0,max}^2 + 2F_c^2)$ $A = 0.1351$ $B - 21.25$ Variables 256 257 $R_{all}(R_{obs})$ based on $F > 4\sigma_F$ $0.1153 (0.0784)$ $0.2302 (0.2058)$ $0.0578 (0.0525)$ $0.1510 (0.1460)$ $0.0975 (1.000)$ GOF _{all} (GOF _{obs}) $1.057 (1.152)$ 0.000 $0.975 (1.000)$ $0.012Shift/esd (mean)0.0000.012Residual electron density (10^{-6} \text{ pm}^{-3})(min./max.)-0.59/1.35-1.69/2.14$	Refinement on F^2	Full matrix least square	s (SHELXL-93)	
Weighting scheme $w = 1/\sigma^2 (F_0^2) + (A \cdot P)^2 + B \cdot P$; where $P = 1/3 (F_{0,max}^2 + 2F_c^2)$ $A = 0.1351$ $A = 0.1198$ $B = 7.14$ $B - 21.25$ Variables 256 257 257 $R_{all}(R_{obs})$ based on $F > 4\sigma_F$ $0.1153 (0.0784)$ $0.0578 (0.0525)$ $0.2302 (0.2058)$ $0.1510 (0.1460)$ $GOF_{all} (GOF_{obs})$ $1.057 (1.152)$ OOD 0.012 Residual electron density $(10^{-6} \text{ pm}^{-3})$ (min./max.) $-0.59/1.35$ Programs used $SHELXS-86 [15], SHELXL-93 [16], ORTEP [17]$	Minimised function	$\sum w(F_{o}^{2}-F_{c}^{2})$. 2	
$A = 0.1351$ $A = 0.1198$ $B = 7.14$ $B = 21.25$ Variables256 $R_{all}(R_{obs})$ based on $F > 4\sigma_F$ $0.1153 (0.0784)$ $0.0578 (0.0525)$ $0.2302 (0.2058)$ $WR_{2_{all}} (WR_{2_{obs}})$ $0.2302 (0.2058)$ $OF_{all} (GOF_{obs})$ $1.057 (1.152)$ OOO $0.975 (1.000)$ Shift/esd (mean) 0.000 0.000 0.012 Residual electron density $(10^{-6} \text{ pm}^{-3})$ (min./max.) $-0.59/1.35$ Programs used $SHELXS-86 [15], SHELXL-93 [16], ORTEP [17]$	Weighting scheme	$w = 1/\sigma^2(F_o^2) + (A \cdot)$	$(P)^2 + B \cdot P$; where D	$P = 1/3(F_{o,max}^2 + 2F_c^2)$
$B = 7.14$ $B = 21.25$ Variables 256 257 $R_{all}(R_{obs})$ based on $F > 4\sigma_F$ 0.1153 (0.0784) 0.0578 (0.0525) $wR_{2_{all}}(wR_{2_{obs}})$ 0.2302 (0.2058) 0.1510 (0.1460) $GOF_{all}(GOF_{obs})$ 1.057 (1.152) 0.975 (1.000) Shift/esd (mean) 0.000 0.012 Residual electron density (10^{-6} pm ⁻³) $-0.59/1.35$ $-1.69/2.14$ Programs used SHELXS-86 [15], SHELXL-93 [16], ORTEP [17]		A = 0.1351		A = 0.1198
Variables 256 257 $R_{all}(R_{obs})$ based on $F > 4\sigma_F$ 0.1153 (0.0784) 0.0578 (0.0525) $wR_{2_{all}}(wR_{2_{obs}})$ 0.2302 (0.2058) 0.1510 (0.1460) $GOF_{all}(GOF_{obs})$ 1.057 (1.152) 0.975 (1.000) Shift/esd (mean) 0.000 0.012 Residual electron density (10 ⁻⁶ pm ⁻³) -0.59/1.35 -1.69/2.14 Programs used SHELXS-86 [15], SHELXL-93 [16], ORTEP [17]		B = 7.14		B = 21.25
$R_{all}(R_{obs})$ based on $F > 4\sigma_F$ 0.1153 (0.0784) 0.0578 (0.0525) $wR_{2_{all}}(wR_{2_{obs}})$ 0.2302 (0.2058) 0.1510 (0.1460) $GOF_{all}(GOF_{obs})$ 1.057 (1.152) 0.975 (1.000) Shift/esd (mean) 0.000 0.012 Residual electron density (10 ⁻⁶ pm ⁻³) -0.59/1.35 -1.69/2.14 Programs used SHELXS-86 [15], SHELXL-93 [16], ORTEP [17]	Variables	256		257
$wR_{2_{all}}(wR_{2_{obs}})$ 0.2302 (0.2058) 0.1510 (0.1460) $GOF_{all}(GOF_{obs})$ 1.057 (1.152) 0.975 (1.000) Shift/esd (mean) 0.000 0.012 Residual electron density (10 ⁻⁶ pm ⁻³) -0.59/1.35 -1.69/2.14 Programs used SHELXS-86 [15], SHELXL-93 [16], ORTEP [17]	$R_{\rm all}(R_{\rm obs})$ based on $F > 4\sigma_{\rm F}$	0.1153 (0.0784)		0.0578 (0.0525)
GOF_{all} (GOF_{obs}) 1.057 (1.152) 0.975 (1.000) Shift/esd (mean) 0.000 0.012 Residual electron density (10^{-6} pm ⁻³) -0.59/1.35 -1.69/2.14 Programs used SHELXS-86 [15], SHELXL-93 [16], ORTEP [17]	$wR_{2_{all}}(wR_{2_{obs}})$	0.2302 (0.2058)		0.1510 (0.1460)
Shift/esd (mean) 0.000 0.012 Residual electron density (10 ⁻⁶ pm ⁻³) -0.59/1.35 -1.69/2.14 Programs used SHELXS-86 [15], SHELXL-93 [16], ORTEP [17]	GOF _{all} (GOF _{obs})	1.057 (1.152)		0.975 (1.000)
Kesidual electron density (10^{-6} pm ⁻³) (min./max.) $-0.59/1.35$ Programs used $-1.69/2.14$ SHELXS-86 [15], SHELXL-93 [16], ORTEP [17]	Shift/esd (mean)	0.000		0.012
(min./max.) -0.59/1.35 -1.69/2.14 Programs used SHELXS-86 [15], SHELXL-93 [16], OR TEP [17]	Residual electron density $(10^{-6} \text{ pm}^{-3})$	0.70.41.07		
Programs used SHELXS-86 [15], SHELXL-93 [16], ORTEP [17]	(min./max.)	-0.59/1.35	[]	-1.69/2.14
	Programs used	SHELXS-86 [15], SHELXL-93 [16], ORTEP [17]		



Fig. 1. ORTEP drawing (30% probability) of 2 and selected bond lengths (pm): Cr-Si, 241.2(3); Si-O6, 173.7(6); Si-C6, 189.3(8); Si-C8, 193.5(10).

The fractional coordinates and equivalent isotropic thermal parameters for 2 are listed in Table 3 and the corresponding bond lengths and angles are given in

Table 2

Table 4. The related data for **3** and **4** are listed in Tables 5 and 6, and in Tables 7 and 8, respectively. From these data, it will be seen that all Cr–C(carbonyl) and W–C(carbonyl) bond lengths should be considered essentially equal within error limits, the range being 185.9(8)-189.5(8) pm and 200.3(12)-205.0(13) pm, respectively. Furthermore there is no obvious difference in the carbonyl C–O distances [113.8(9)–115.3(8) pm in **2** and 112.9(14)–115.3(13) pm in **3**] caused by the silicon coordination to the metal centres.

The pentacarbonylchromium(0) and pentacarbonyltungsten(0) units are attached to the silicon atoms of folded silacyclobutane rings with metal-silicon distances of 241.2(3) pm in **2** and 256.2(3) pm in **3**, respectively.

In contrast to 2 and 3, red crystals of $[(CO)_4FeSiC_{10}-H_{18}] \cdot HMPA$ (4) (Fig. 3) contain only the 1S, 2S, 3R-diastereomer of 2-neopentyl-3-vinyl-1-silacyclobutane-1-diyl-1-iron(0)tetracarbonyl hexamethylphosphorotri-

Crystal data for 4	
Formula unit	$[(CO)_4 FeC_{10}H_{18}] \cdot HMPA (4)$
Crystal size (mm)	$0.40 \times 0.30 \times 0.50$
Crystal shape	inegular prism
Crystal system, Laue group	orthorhombic, 222
Space group	$P2_{1}2_{1}2_{1}$ (No. 19)
Cell parameters (pm)	a = 896.4(5)
	b = 1693.4(10)
	c = 1753.4(10)
Cell volume (10^6 pm^3)	$V_{\rm EZ} = 2662(3)$
Calculated density $(g \text{ cm}^{-3})$	$\rho = 1.281$
Number of units	Z = 4
Diffractometer	STOE, STAD14
Temperature (K)	T = 188(2)
Radiation, λ (pm)	Mo K α , 71.069, graphite monochromator
Scan mode	$\omega/2\Theta$
Scan range (°)	$3.34 < 2\Theta < 45.00$
Range of indices	h: 0/9
	k: 0/18
	<i>l</i> : 0/18
Number of refl.	2004
Observed $(I > 2\sigma_i)$	1597
Initial coordinates:	
for P, Si and Fe	Patterson synthesis (SHELXS-86)
for C and O	Difference Fourier syntheses (SHELXL-93)
for H	calculated in idealised positions, not refined
Atomic scattering factors (neutral atoms)	International Tables for X-ray-Crystallography,
2	Kluwer Academic Publishers, Dordrecht, The Netherlands, 1992, Vol. C.
Refinement on F^2	Full matrix least squares (SHELXL-93)
Minimised function	$\sum w(F_0^2 - F_c^2)$
Weighting scheme	$w = 1/\sigma(F_0^2) + (A \cdot P)^2 + B \cdot P$: where $P = 1/3(F_{0,max}^2 + 2F_c^2)$
	A = 0.0439
	B = 2.1201
Variables	243
$R_{\rm all}(R_{\rm obs})$ based on $F > 4\sigma_{\rm F}$	0.0668 (0.0432)
$WR_{2_{all}}(WR_{2_{obs}})$	0.099 (0.0918)
$GOF_{all}(GOF_{obs})$	1.062 (1.122)
Shift/esd (mean) Desidual electron density $(10^{-6} \text{ mm}^{-3})$	0.000
(is (is)	0.20 /0.22
(min./max.)	-0.29/0.32
Programs used	SHELXS-86 [10], SHELXL-93 [10], ORTEP [17]



Fig. 2. ORTEP drawing (30% probability) of **3** and selected bond lengths (pm): W-Si, 256.2(3); Si-O6, 174.0(8); Si-C6, 188.4(11); Si-C8, 195.8(14).

amide because of the lack of centres of inversion in the non-centrosymmetric space group $P2_12_12_1$ (No. 19). The coordination at the iron atom is best described as

trigonal bipyramidal, with the silicon atom attached to an axial coordination site and the carbonyl ligands occupying the other axial and the three equatorial positions. The geometry at iron very closely resembles a local C_{3v} symmetry. The variations of the distances of the carbonyl-carbon atoms to the iron centre [Fe-C(carbonyl): 174.3(8)-177.6(9) pm] and the carbonoxygen distances [C(carbonyl)-O: 115.7(8)-118.6(8) pm] all lie within a narrow range. A small distortion of the trigonal bipyramidal structure is probably due to the coordination of silicon trans to the carbonyl group C4-O4 such that all the equatorial carbonyl ligands are bent towards the silacyclobutanediyl moiety [Si-Fe- C_{eq} 84.5(2)-84.9(2)°]. The iron-silicon bond distance of 228.4(2) pm is close to that found for similar donorstabilised silvlene complexes with tetracarbonyl iron fragments (227.7(1) pm [18] and 228.0(1), 227.8(1) pm [14]). The metal-silicon bonds are in the range of M-Si single bonds as it was observed for similar donor-stabilised silylene complexes previously reported in the literature (and citations therein), e.g., Cr-Si, 240.9(1)pm [18]; Fe-Si, 228.0(1)pm [19], and do not indicate a multiple-bond character. As in the case of complexes 1

Table 3 Fractional coordinates and equivalent isotropic thermal parameters (*) for 2

Atom	x	у	z	U_{eq} a
Crl	0.60805(10)	0.40762(6)	-0.36780(8)	0.0282(4)(*)
C1	0.7253(7)	0.4165(4)	-0.2518(6)	0.040(2)(*)
O1	0.7937(5)	0.4235(3)	-0.1809(4)	0.062(2)(*)
C2	0.6813(7)	0.3255(4)	-0.4069(5)	0.039(2)(*)
O2	0.7260(6)	0.2759(3)	-0.4340(5)	0.070(2)(*)
C3	0.4780(7)	0.3897(4)	-0.4702(6)	0.037(2)(*)
03	0.4013(6)	0.3768(3)	-0.5333(5)	0.058(2)(*)
C4	0.5236(7)	0.4872(4)	-0.3283(5)	0.035(2)(*)
04	0.4750(6)	0.5355(3)	-0.3033(4)	0.056(2)(*)
C5	0.6998(7)	0.4590(4)	- 0.4499(5)	0.034(2)(*)
05	0.7568(5)	0.4893(3)	-0.5024(4)	0.0521(15)(*)
Si	0.4874(2)	0.34241(11)	-0.26071(14)	0.0334(6)(*)
C6	0.5228(9)	0.3422(5)	-0.1190(6)	0.056(3)(*)
C7	0.4203(8)	0.3977(6)	-0.1185(6)	0.062(3)(*)
C71	0.3608(12)	0.3998(7)	-0.0233(10)	0.099(4)
C72	0.3473(16)	0.4474(10)	0.0294(15)	0.150(7)
C8	0.3343(9)	0.3777(6)	-0.2198(7)	0.070(3)(*)
C81	0.2208(10)	0.3378(7)	-0.2112(8)	0.083(3)(*)
C82	0.1203(8)	0.3432(6)	-0.3030(7)	0.071(3)(*)
C83	0.1672(9)	0.3103(5)	-0.3936(7)	0.066(3)
C84	0.0536(12)	0.4091(6)	-0.3326(10)	0.101(4)
C85	0.0196(13)	0.2905(7)	-0.2710(11)	0.109(5)
Р	0.4705(2)	0.17877(10)	-0.29328(14)	0.0382(6)(*)
06	0.4603(5)	0.2569(3)	- 0.2979(4)	0.0519(15)(*)
N1	0.5905(8)	0.1579(4)	-0.2191(6)	0.069(2)(*)
C11	0.6048(12)	0.0900(6)	-0.1705(10)	0.095(4)
C12	0.7059(10)	0.2012(6)	-0.2067(8)	0.080(3)
N2	0.4737(7)	0.1535(4)	-0.4074(5)	0.054(2)(*)
C21	0.4360(10)	0.1950(5)	-0.4963(8)	0.074(3)
C22	0.5065(14)	0.0823(7)	-0.4293(11)	0.116(5)
N3	0.3528(8)	0.1416(4)	-0.2541(6)	0.070(2)(*)
C31	0.2504(13)	0.1085(7)	-0.3197(11)	0.106(4)
C32	0.3268(13)	0.1467(7)	- 0.1536(11)	0.111(5)

^a Equivalent isotropic U defined as one-third of the trace of the orthogonalised U_{ii} tensor.

Table 4 Bond lengths (pm) and angles (°) in 2

Done to guio (p		/ =	
(a) Pentacarbon	ylchromium frag	ment:	
Cr1—C5	185.9(8)	C5-Crl-C2	90.4(3)
Cr1—C4	189.5(8)	C5—Cr1—C3	94.1(3)
Cri—C3	187.5(8)	C5—Crl—C4	92.7(3)
Cr1—C2	187.4(8)	C5-Cr1-C1	94.9(3)
Cr1—C1	189.2(9)	C3—Cr1—C1	170.9(3)
C1-01	113.9(9)	C3-Cr1-C4	90.5(3)
C2—O2	115.1(9)	C2—Cr1—C3	86.9(3)
C3-03	113.8(9)	C2-Cr1-C1	92.4(3)
C4—O4	114.0(9)	C2—Cr1—C4	176.1(3)
C5—O5	115.3(8)	C5-Cr1-Si	179.2(2)
	. ,		
		Ol-Cl-Crl	177.8(7)
		O2—C2—Cr1	177.9(7)
		O3—C3—Cr1	177.5(7)
		04—C4—Cr1	178.5(6)
		05-C5-Cr1	178.2(6)
Cr1—Si	241 2(3)	C4-CrI-Si	86 5(2)
	211.2(0)	$C_3 - C_1 - S_1$	85 8(2)
		C^2 — $Cr1$ —Si	90.4(2)
		$C_2 = C_{r1} = C_4$	1761(3)
		C1 Cr1 Si	85 1(2)
		CI = CI = CI	85.1(2)
		01-01-04	09.7(3)
(h) Cyclosilane	tivl fraament		
Si-06	173 7(6)	06—Si—C6	1070(3)
SiC6	189 3(8)	06—Si—C8	107.0(3)
Si_C8	193 5(10)	06-Si-Cr1	1141(2)
$Si \cdots C7$	2377(8)	C6_Si_C8	77.9(4)
C6C7	1543(13)	C6 SiCt1	122 8(3)
C7_C8	159.8(12)	C6 - C7 - C8	122.8(3)
C7 - C71	150(2)	CR Si Cri	100.0(7) 122.2(4)
C_{1}	130(2)	C_{0}	86.9(5)
$C_{1} = C_{12}$	110(2) 1467(13)	C71 C7 C6	1141(0)
C_{81}	140.7(13)	C71 - C7 - C8	1176(8)
$C_{81} = C_{82}$	149(2)	C_{1}^{-} C_{2}^{-} C_{3}^{-} C_{3}^{-}	120 0(16)
$C_{02} - C_{04}$	147(2)	$C_{12} = C_{1} = C_{1}$	1179(9)
$C_{02} - C_{03}$	151.4(15)	$C_{01} = C_{0} = C_{1}$	117.0(0)
02-003	155(2)	$C_{1} = C_{0} = S_{1}$	84.0(5)
		$C^{2} = C^{2} = C^{2}$	1147(0)
		$C_{0} = C_{01} = C_{02}$	114.7(9)
		C84 - C82 - C83	1228(10)
		$C_{04} = C_{02} = C_{01}$	122.8(10)
		$C_{03} - C_{02} - C_{01}$	109.7(8)
		$C_{04} - C_{02} - C_{03}$	100.9(9)
		$C_{03} - C_{02} - C_{03}$	105.0(9)
		$C_{01} = C_{02} = C_{03}$	100.4(9)
		0-01-02	114.7(9)
(c) HMPA Baca	d		
(c) Amr A ugan P 06	4 1510(6)	06PN1	100 1(4)
P-00	151.0(0)	O_{0} P N2	109.1(4)
r IN I D N2	150.0(0)	OU - r - INS NI D N2	113.0(4)
P-N3	100.7(8)	NI - P - NS	107.7(3)
r - NZ	101.2(7) 146 4(14)	$V_0 - r - N_2$	103.8(3)
	140.4(14)	N1 - F - N2	114.0(4)
$\frac{1}{2} = \frac{1}{2}$	149.3(13)	r = r = r = r = r	100.7(4)
N2 - C21	143.2(12)	r	137.7(4)
$N_2 = C_2^2$	143.0(13)	CII = NI = CI2	114.1(8)
N3-C31	14/(2)	CII—NI—P	122.0(8)
N3-C32	141(2)	C12 - N1 - P	122.5(7)
		C_{21} N_{2} C_{22}	113.8(8)
		C_{21} N_{2} P	123.3(0)
		C22—N2—P	120.7(7)
		C_{22} N2 D	112.0(10)
		C32-N3-P	122.8(8)
		Col-No-P	124.3(8)

Table 5 Fractional coordinates and equivalent thermal parameters (*) for 3

Atom	x	у	z	U _{eq} ^a
W	0.60988(3)	0.40676(2)	-0.36747(3)	0.0285(3)(*)
C1	0.7317(11)	0.4168(6)	-0.2443(10)	0.040(3)(*)
O1	0.8005(9)	0.4236(5)	-0.1728(7)	0.070(3)(*)
C2	0.6886(11)	0.3191(7)	-0.4096(9)	0.049(3)(*)
O2	0.7343(10)	0.2712(5)	-0.4350(8)	0.077(3)(*)
C3	0.4750(12)	0.3876(6)	- 0.4797(9)	0.041(3)(*)
O3	0.3973(9)	0.3753(5)	-0.5412(7)	0.070(3)(*)
C4	0.5217(10)	0.4934(6)	- 0.3257(8)	0.040(3)(*)
04	0.4712(8)	0.5404(5)	- 0.3021(6)	0.056(2)(*)
C5	0.7063(10)	0.4623(6)	- 0.4562(8)	0.039(3)(*)
O5	0.7631(8)	0.4940(5)	- 0.5066(7)	0.063(2)(*)
C6	0.5139(13)	0.3433(7)	-0.1122(8)	0.060(4)(*)
C7	0.4163(14)	0.3999(8)	-0.1143(9)	0.056(4)(*)
C71	0.3569(18)	0.4046(9)	-0.0244(14)	0.088(5)
C72	0.3459(26)	0.4568(16)	0.0240(22)	0.161(11)
C8	0.3294(12)	0.3802(9)	-0.2150(10)	0.064(4)(*)
C81	0.2196(13)	0.3399(9)	-0.2041(12)	0.077(4)(*)
C82	0.1209(12)	0.3391(9)	-0.2941(11)	0.074(4)(*)
C83	0.1670(14)	0.3078(8)	-0.3856(11)	0.074(4)
C84	0.0560(19)	0.4068(8)	-0.3242(15)	0.092(6)
C85	0.0228(19)	0.2855(11)	-0.2638(15)	0.109(6)
Р	0.4693(3)	0.1780(2)	-0.2878(2)	0.0443(8)(*)
O6	0.4478(8)	0.2549(4)	- 0.2867(6)	0.056(2)(*)
N1	0.3513(16)	0.1377(7)	-0.2527(10)	0.074(5)(*)
C11	0.2553(23)	0.1012(11)	-0.3229(18)	0.121(7)
C12	0.3155(21)	0.1411(12)	-0.1598(15)	0.118(7)
N2	0.4724(11)	0.1566(6)	-0.4009(8)	0.066(3)(*)
C21	0.4321(15)	0.1956(8)	-0.4868(11)	0.082(5)
C22	0.5105(34)	0.0864(15)	- 0.4244(26)	0.179(13)
N3	0.5887(15)	0.1596(6)	- 0.2166(10)	0.073(5)(*)
C31	0.6969(17)	0.2027(10)	- 0.2034(14)	0.101(6)
C32	0.5928(24)	0.0925(10)	- 0.1617(18)	0.123(8)

^a Equivalent isotropic U defined as one-third of the trace of the orthogonalised U_{ij} tensor.

and 2, the silicon atom is tetracoordinated with a distortion from the ideal tetrahedral geometry due to ring strain in the four-membered ring.

The fourth coordination gap at silicon is filled by an oxygen atom of a HMPA ligand. The silicon-oxygen distances in **2**, **3** and **4** are seemingly independent of the nature of the coordinated metal atom and equal in length within the accuracy attained: 173.7(6) pm in **2**, 174.0(8) pm in **3** and 173.4(7) pm in **4**. However, in all three cases they are undoubtedly longer than an Si-O single bond (see, for example, $(CO)_4Fe=Si(O'Bu)_2$. HMPA: the Si-O'Bu single bond distances are 161.0(8) and 163.6(4) pm [20]). Thus a donor-acceptor interaction links the HMPA molecule and the silicon atom. Consequently silicon exhibits a 3 + 1 coordination in all three molecules.

The coordination at silicon is strongly distorted tetrahedral, the bond angles ranging from 77.9(4)° (C6–Si– C8) to 122.8(3)° (C8–Si–Cr) in **2**, from 77.8(6)° (C6– Si–C8) to 122.2(4)° (C6–Si–W) in **3** and from 78.1(3)° (C6–Si–C8) to 124.6(3)° in (C₆–Si–Fe) **4**. All other angles are close to tetrahedral except for M–Si–O which are larger (i) to compensate for the small angle

Table 6 Bond lengths (pm) and angles (°) in 3

0 1	<u> </u>		
(a) Pentacarbon	yltungsten fragr	nent	
WC5	200.3(12)	C5—WC2	90.5(4)
WC4	205.0(13)	C5—W—C3	92.8(4)
WC3	201.2(14)	C5—W—C4	91.5(4)
WC2	201.8(13)	C5-W-C1	95.2(5)
WC1	200.3(13)	C3—W—C2	86.3(5)
C101	115.2(14)	C3—W—C4	91.5(4)
C2	112.9(14)	C1 - W - C4	89.1(4)
C303	113.6(14)	C1—WC2	92.7(4)
C4	113.2(13)	C1 - W - C3	172.0(4)
C505	115 3(13)	$C^2 - W - C^4$	177 2(4)
05-05	115.5(15)	02 11 04	177.2(1)
		01-C1-W	178 7(9)
		$0^{2}-C^{2}-W$	1780(11)
		03 - C3 - W	177.8(10)
		$O_4 C_4 W$	178 6(0)
		$O_4 = C_4 = W$	170.0(9)
W C:	2562(2)	$C_5 W S$	177.2(10)
w 31	230.2(3)	C_{3} W S_{1}	177.3(3)
		C4 - w - 51	80.1(3)
		$C_3 = W = C_5$	00.0(3)
		C3—wC5	92.8(4)
		C2-W-Si	92.0(4)
		C1 - W - S1	85.3(4)
(1) .			
(b) Cyclo-silane	diyl fragment		
Si-06	174.0(8)	06SiC6	107.2(5)
Si—C6	188.4(11)	06—Si—C8	106.7(6)
Si—C8	195.8(14)	C6SiC8	77.8(6)
$Si \cdot \cdot \cdot C7$	237.5(12)	06SiW	115.8(3)
C6C7	153(2)	C6—Si—W	122.2(4)
C7—C71	147(2)	C8—Si—W	120.7(5)
C7—C8	160(2)	C7—C6—Si	87.5(8)
C71C72	120(3)	C71—C7—C6	114.3(13)
C8C81	146(2)	C71—C7—C8	116.3(13)
C81—C82	152(2)	C6—C7—C8	100.8(10)
C82C83	151(2)	C72—C71—C7	124.8(22)
C82—C84	152(2)	C81—C8—C7	117.1(12)
C82—C85	159(2)	C81C8Si	123.6(12)
		C7—C8—Si	83.1(8)
		C8—C81—C82	116.2(13)
		C83—C82—C81	111.8(11)
		C83—C82—C84	108.9(13)
		C81-C82-C84	117.7(15)
		C83—C82—C85	104.7(14)
		C81—C82—C85	104.1(13)
		C84—C82—C85	108.7(13)
(c) HMPA ligan	d		
P06	150.9(9)	O6—P—N3	109.9(6)
P—N3	156.5(13)	O6—P—N2	106.9(5)
P-N2	157.7(10)	N3—P—N2	114.2(7)
P-N1	163.3(14)	06—P—N1	109.8(7)
N1 - C12	136(2)	N3-P-N1	110 5(9)
NI-C11	150(3)	N2—P—N1	105,4(7)
N2_C21	130(3) 140(2)	P_06_Si	156.0(6)
N2	147(3)	C12 = N1 = C11	109 8(17)
N3_C31	145(2)	C12 = N1 = P	125 1(14)
N3C32	149(2)	C12 = N1 = P	122 4(17)
1.5 - 0.52	1 T/(2)	$C_{21} = N_{2} = C_{22}$	127.7(12) 1130(17)
		$C_{21} = N_2 = C_{22}$	127 3(10)
		$C_{21} = N_2 = r$	110 /(15)
		$C_{22} - n_2 - r$	1170(15)
		$C_{21} = N_2 = C_{22}$	11/.7(13)
		C_{21} M_{3} P	123.9(11)
		C32—N3—P	118.2(14)

within the silacyclobutanes and (ii) to avoid steric interactions between the bulky $M(CO)_n$ (M = Cr, W: n = 5; M = Fe: n = 4) and HMPA moieties on silicon. The silacyclobutane units are folded with the interplanar angles amounting to $145.4(7)^{\circ}$ (2), $146(1)^{\circ}$ (3) and $157.5(6)^{\circ}$ (4) with respect to the Si-C7 axes (Fig. 4). The silicon-carbon bond lengths range from 188.4(11) to 195.8(14) pm. Within the silacyclobutane ring, both Si-C distances are in the range of Si-C single bonds; however, the carbon C8 atoms in 2 and 3 which are connected to the neopentyl substituents have longer bonds to silicon than the carbon C6 atoms, possibly resulting from steric interactions with the HMPA donor. All other C-C bonds show no special features and are in the normal range expected for unsaturated and saturated hydrocarbons in the solid state.

The puckering of the four-membered ring in 4 is quite different from that in 2 and 3 because the silacyclobutanediyl unit is folded towards the iron atom, while in 2 and 3 the folding is towards the HMPA ligand. This reduces the steric interaction of the neopentyl group at C8 and the HMPA molecule in 4, and may explain the equality of both Si-C bond distances. This may also be the reason for the smaller interplanar angle $[157.5(6)^{\circ}]$ compared to the chromium and tungsten complexes (see above).

Despite the different ring structures in the $Fe(CO)_4$ silacyclo*butane* (folded, this work) and the corresponding silacyclo*butene* complexes (5, 6; planar, [11]), the coordination geometries at the silicon centres are almost the same in both types of compounds (see Scheme 4).

The slightly different Si–C bond lengths are probably due to steric effects; this is supported by the fact that those in **4** are equal within the accuracy attained, while the analogous bonds in **2**, **3**, **5** and **6** differ by 4.2, 7.4, 2.3 and 3.9 pm [11]. Furthermore, the Si–C distances in **2**, **3** and **4** are intermediate between the ion contact sum for Si⁴⁺–C^{4–} (179 pm) [21] and the sum of the covalent radii (194 pm) [22]; they are in the same order of magnitude as observed, for example, in the crystal structures of spiro-silacycluses [23].

2.4. Molecular orbital calculations

As typical for the series of silylene complexes described in this paper, the chromium compound 2 was investigated using the Fenske-Hall molecular orbital method [24]. Basis functions were generated by the numerical $X\alpha$ atomic orbital program of Herman and Skillman [25] used in conjunction with the $X\alpha$ -to-Slater basis program of Bursten and Fenske [26]. For simplification, the substituents at the silacyclobutane unit and the dimethylamino groups of the HMPA ligand were replaced by hydrogen atoms; nevertheless the donor influence of the ligand was preserved.

Two fragments of the molecule can be identified as relevant to the metal-silicon bond, viz. the $Cr(CO)_{5}$ unit and \dot{Si} -CH₂-CH₂- \dot{CH}_2 · OPH₃, and their frontier orbitals as well as their bonding were investigated. The three frontier molecular orbitals of the chromium moiety can be used for bonding to silicon. Two occupied orbitals form the degenerate HOMOs with π character, while the unoccupied orbital, the LUMO, exhibits σ properties. In order to evaluate the nature of the M-Si bond, the frontier orbitals as well as the bonding of the silicon fragment in the model compound have to be compared with a donor free silylene. Both, HOMO and LUMO of dimethylsilylene $(CH_3)_2$ Si: are energetically in a region where they are able to interact with the chromium frontier orbitals. As the HOMO has σ and the LUMO π character, one σ - and one π -bonding interaction can be established between the silicon and the chromium atom. This is demonstrated by the molecular orbital diagram of $(CO)_5Cr=SiMe_2$ expressing two main interactions, namely a σ - and a π -bond. The bonding molecular orbital for the σ -bond has a contribution of 37% from the Si p, and 10% from the Si s orbital, as well as 17% from the Cr d_z^2 and 10% from

Table 7 Fractional coordinates and equivalent thermal parameters (*) for 4

the chromium p_z orbital. In the π -bonding MO the main contributions derive from the Cr d_{xz} and the Si p_x orbital (43% and 20%, respectively). The two highest molecular orbitals are metal-centred (HOMO 60% d_{yz} and SHOMO 54% d_{xy}) whereas the LUMO is the π^* orbital of the Cr–Si bond (19% Cr d_{xz} and 64% Si p_x). There is a significant π overlap between Cr and Si. The π interaction is basically back-donation from chromium to silicon, resulting in the involvement of the carbonyl *trans* to the silylene ligand. This is expressed in the smaller population value of the carbon p_x orbital and in a slight decrease in the charge on the carbon atom compared to the other carbonyl carbon atoms.

In contrast, the silacyclobutanediyl ligand has only one orbital of σ symmetry (HOMO) available to interact with the chromium. The orbitals with π symmetry are rather high in energy. The main bonding therefore is a σ -bonding interaction (19% Cr d_z², 30% Si p_z and a minor contribution from the Si s orbital). The three highest occupied orbitals in the complex are metal-based and have all main contributions from the Cr d_{xy}, d_{xz} and d_{yz} orbitals. There is no major π interaction as in the case of the dimethylsilylene complex.

Atom	r	v		1/ a
	0.00717(11)	9	0.10.440(5)	
Fe	0.06717(11)	0.87939(5)	0.19449(5)	0.0321(3)(1)
CI	-0.0825(10)	0.9461(4)	0.2019(4)	0.043(2)(-)
01	-0.1829(7)	0.9897(3)	0.2091(3)	0.071(2)(*)
C2	0.0576(9)	0.7962(5)	0.1361(4)	0.046(2)(*)
O2	0.0533(7)	0.7398(4)	0.0961(3)	0.069(2)(*)
C3	0.2007(9)	0.8844(4)	0.2678(4)	0.044(2)(*)
O3	0.2887(6)	0.8893(3)	0.3158(3)	0.065(2)(*)
C4	0.1761(10)	0.9375(5)	0.1311(5)	0.048(2)(*)
04	0.2509(8)	0.9745(4)	0.0898(4)	0.076(2)(*)
Si	- 0.0654(2)	0.80507(10)	0.27948(9)	0.0307(4)(*)
C6	0.0185(9)	0.7294(5)	0.3455(4)	0.046(2)(*)
C7	-0.0823(10)	0.7593(4)	0.4108(4)	0.048(2)(*)
C71	- 0.2039(10)	0.7074(5)	0.4256(5)	0.057(2)
C72	-0.2375(11)	0.6727(5)	0.4919(5)	0.066(3)
C8	-0.1275(8)	0.8419(4)	0.3754(4)	0.039(2)(*)
C81	- 0.2727(8)	0.8827(5)	0.3952(4)	0.042(2)(*)
C82	-0.2693(9)	0.9471(4)	0.4576(4)	0.043(2)(*)
C83	-0.4250(11)	0.9779(5)	0.4694(5)	0.069(3)
C84	-0.1737(12)	1.0155(6)	0.4292(5)	0.083(4)
C85	-0.2052(11)	0.9157(5)	0.5310(5)	0.070(3)
Р	-0.3257(2)	0.70783(10)	0.19618(10)	0.0320(4)(*)
O5	-0.2261(5)	0.7647(3)	0.2406(3)	0.0370(12)(*)
N1	-0.4178(7)	0.7591(3)	0.1350(3)	0.0413(15)(*)
CH	-0.5653(10)	0.7345(5)	0.1075(5)	0.064(3)
C12	-0.3553(10)	0.8260(5)	0.0939(5)	0.061(3)
N2	-0.4375(7)	0.6661(3)	0.2549(3)	0.038(2)(*)
C21	- 0.5349(10)	0.7148(5)	0.3027(5)	0.069(3)
C22	-0.4793(11)	0.5828(5)	0.2558(6)	0.071(3)
N3	-0.2291(7)	0.6400(3)	0.1547(3)	0.038(2)(*)
C31	-0.1195(9)	0.5940(4)	0.1988(5)	0.057(2)
C32	-0.2334(9)	0.6209(5)	0.0738(4)	0.055(2)

^a Equivalent isotropic U defined as one-third of the trace of the orthogonalised U_{ij} tensor.

2.5. Summary

Reactions of the stereoisomeric silacyclobutanes 1a/1b (Scheme 1) with carbonyl metallates of

Table	8
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Bond lengths (p	m) and angles	(°) in 4	
(a) Tetracarbon	yliron fragment		
Fe—C2	174.8(8)	C3—Fe—Cl	115.7(3)
Fe—C3	175.8(8)	C3—Fe—C4	93.2(4)
Fe—C1	175.9(9)	C2—Fe—C3	120.1(4)
Fe—C4	177.6(9)	C2-Fe-C1	121.7(4)
C1-01	117.0(9)	C2—Fe—C4	96.2(3)
C2—O2	118.6(8)	01C1Fe	177.9(6)
C3	115.7(8)	O2-C2-Fe	179.0(7)
C4—04	117.0(9)	03-C3-Fe	178.6(7)
		04C4Fe	178 2(8)
		0. 0. 10	1,0.2(0)
		C1—Fe—C4	96.3(3)
		C2-Fe-Si	84.9(2)
Fe—Si	228.4(2)	C3—Fe—Si	84.5(2)
		C1-Fe-Si	84.8(2)
		C4-Fe-Si	177.7(3)
(b) Cyclo-silane	diyl fragment		
Si—O5	173.4(5)	05—Si—C8	103.7(3)
Si—C8	187.8(7)	05SiC6	107.8(3)
Si—C6	188.4(7)	C8—Si—C6	78.1(3)
$Si \cdots C7$	243.4(7)	O5—Si—Fe	113.1(2)
C6—C7	154.4(10)	C8—Si—Fe	123.7(3)
C7—C71	142.4(11)	C6Si-Fe	124.6(3)
C71—C72	133.7(11)	05-Si-C7	101.2(3)
C7—C8	158.3(10)	Si-C6-C7	89.9(5)
C8—C81	151.4(9)	C6C7C8	98.6(5)
C81—C82	154.5(10)	C6C7C71	112.3(7)
C82—C83	150.4(12)	C7C71C72	127.0(9)
C82—C85	150.6(11)	C7Si	88.9(4)
C82C84	152.5(11)	C7C8C81	122.2(7)
		C71—C7—C8	114.9(7)
		C81—C8—Si	127.7(5)
		C8-C81-C82	117.9(6)
		C83-C82-C85	111.0(7)
		C83 - C82 - C84	107 6(7)
		C85 - C82 - C84	109 5(7)
		C83C82C81	108.9(7)
		C85 - C82 - C81	111 4(6)
		C84 - C82 - C81	108 4(6)
		002 001	1001 ((0)
(c) HMPA ligar	nd		
P05	152.7(5)	O5—P—N2	108.5(3)
P—N2	160.1(6)	O5P-N1	107.4(3)
P—N1	160.9(6)	N2—P—N1	110.2(3)
P—N3	161.2(6)	O5PN3	111.4(3)
N1	145.4(9)	N2PN3	108.2(3)
N1-C11	146.7(10)	N1-P-N3	111.0(3)
N2—C22	145.9(9)	P—O5—Si	159.2(3)
N2C21	146.5(9)	C12—N1—C11	114.0(6)
N3—C32	145.5(9)	C12—N1—P	123.6(5)
N3—C31	147.3(9)	C11—N1—P	121.9(5)
		C22—N2C21	112.7(7)
		C22N2P	126.4(6)
		C21—N2—P	119.5(5)
		C32—N3—C31	114.3(6)
		C32—N3—P	125.7(5)
		C31—N3—P	119.9(5)



Fig. 3. ORTEP drawing (30% probability) of **4** and selected bond lengths (pm): Fe-Si, 228.4(2); Si-O5, 173.4(5); Si-C6, 188.4(7); Si-C8, 187.8(7).

chromium, iron and tungsten yield a mixture of the corresponding diastereomeric complexes 2-4. The crystalline products have been characterized by X-ray structure determination. In the case of the crystals of com-



Fig. 4. ORTEP view (30% probability) of the silacyclobutane units in (a) 2, (b) 3 and (c) 4 all along the Si-C7 axis.



pound 4, the absolute structure of the specimen investigated is fixed because it was possible to distinguish between the enantiomorphic forms of the crystal during the refinement. The molecules found in the crystals of 2 and 3 are pairs of enantiomers. X-Ray structure investigations of other crystal specimens did not show any anti complexes 2a, 2c, 3a, 3c, 4a or 4c (neopenty) group anti to the vinyl group). In order to obtain the pure *anti* complexes, the reactions of **1a** with carbonyl metallates of chromium, iron and tungsten were carried out and gave the isomeric complexes 2a, 2c, 3a, 3c, 4a and 4c (see Scheme 3) exclusively, which are also present in the product mixture obtained from 1a/1b. These control experiments with 1a confirmed that no ring-opening in the course of the reaction of the metallates with 1a/1b occurred. The X-ray structure determinations prove that the metal-silicon distances in all three silvlene complexes are in the range of M-Si single bonds. This fits well with the first Fenske-Hall calculations, confirming that the major bonding interaction has mainly σ character.

3. Experimental details

All manipulations were performed under an atmosphere of dry argon; air-sensitive materials were handled by standard Schlenk techniques. All solvents were dried by distillation from NaK alloy/benzophenone ketyl (THF, Et_2O) or from CaH₂ (pentane) and stored over molecular sieves. Trichlorovinylsilane was distilled from K₂CO₃. The preparation of dipotassium pentacarbonylchromate and dipotassium decacarbonylditungstate from potassium–graphite (C₈K) laminate was performed according to the literature method [27].

¹H NMR, ¹³C NMR and ²⁹Si NMR spectra were recorded in C_6D_6 solution with a Bruker AM-300 NMR spectrometer; ¹H, ¹³C and ²⁹Si chemical shifts were measured using the solvent resonances or TMS as standard. IR spectra were recorded on a Bruker IFS-55 FT-IR spectrometer as solutions in 0.1-mm KBr cells. Mass spectra were recorded on a Hewlett Packard 599A instrument by EI ionisation at 70 eV. GC–MS spectra were obtained from samples passed through Chrompack CP9000 (10 m, 0.25 mm CP-Sil 5 CB column) using a Finnigan MAT ITD 800 as the mass-selective detector. Microanalyses were performed by the Micronalytische: Labor der Humboldt-Universität zu Berlin.

3.1. Syntheses

For the synthesis of 1a/1b see Ref. [9]. Nearly pure 1a and 1b could be separated from the mixture of both stereoisomers by spinning band column distillation (10⁶ Pa, boiling range: 18.6–22.4°C).

The syntheses of the silylene complexes 2, 3 and 4 were performed both from a mixture of *anti/syn* (1a/1b) and pure *anti*-(1a) (GC: 99.8%) and the different carbonylate dianions [according to Scheme 2]. The reaction of 1a with the carbonyl metallates yielded a mixture of 2a/2c, 3a/3c and 4a/4c, respectively.

3.1.1. 2-Neopentyl-3-vinyl-1-silacyclobutane-1-diyl-1chromium(0)pentacarbonyl hexamethylphosphorotriamide (2)

A suspension of $K_2Cr(CO)_5$ [made from C_8K laminate (3.65 g, 27.0 mmol K) and 2.97 g (13.5 mmol) of $Cr(CO)_6$] in 70 ml THF was cooled to $-78^{\circ}C$. After addition of 2.35 ml (13.5 mmol) of HMPA, 3.18 ml (13.5 mmol) of 1,1-dichloro-2-neopentyl-3-vinyl-silacyclobutane (1a/1b) was added to the solution. The reaction mixture was stirred and warmed to room temperature. Pentane (50 ml) was added to precipitate the KCl formed. After filtration from insoluble residues (graphite, KCl), the solvent was stripped off under vacuum and the residual yellow oil transferred to ε cooled $(-10^{\circ}C)$ chromatographic column. The product was eluted with THF as the fastest yellow fraction. THF was removed under vacuum and the product recrystallised from diethyl ether/pentane to give 3.91 g (7.27 mmol, 53.8%) of a white-yellow microcrystalline solid. Compound 2 can be crystallised from a saturated Et_2O solution at 0°C as white needles. Elemental analysis for C₂₁H₃₆CrN₃O₆PSi (M_r, 537.58): Calc.: C, 46.92; H, 6.75; Cr, 9.67; N, 7.82; O, 17.86; P, 5.76; Si, 5.22%. Found: C, 46.59; H, 6.69; N, 7.89%. MS (*m/e*, relative intensity): 537 (M⁺, 9.4); 453 (M⁺ – 3CO, 3.7); 425 $(M^+ - 4CO, 9.4); 397 (M^+ - 5CO, 44.9).$

Compound **2a**: ¹H NMR (C_6D_6) δ : 6.12–5.9 (m, 1H, $CH = CH_2$); 5.14–4.88 (m, 2H, $CH = CH_2$); 2.17 [d, 18H, ²J(³¹P¹³C) = 10.2 Hz, N(CH_3)₂]; 1.11 [s, 9H, $C(CH_3)_3$] ppm. ¹³C NMR (C_6D_6) δ : 228.47 (CO); 224.46 (CO); 144.87 ($CH = CH_2$); 110.74 ($CH = CH_2$); 43.73 (CH_2 ^tBu); 43.66 (Si*C*H); 39.35 (*C*H); 36.19 [d, ²J(³¹P¹³C) = 5.3 Hz, N(CH_3)₂]; 31.14 [$C(CH_3)_3$]; 29.80[$C(CH_3)_3$]; 28.61 (Si CH_2) ppm. ²⁹Si NMR (C_6D_6) δ : 96.25 [d, ²J(³¹P²⁹Si) = 34.2 Hz] ppm.

Compound **2b**: ¹H NMR (C_6D_6) δ : 6.12–5.9 (m, 1H, $CH = CH_2$); 5.14–4.88 (m, 2H, $CH = CH_2$); 2.19 [d, 18H, ²J(³¹P¹³C) = 10.0 Hz, N(CH_3)₂]; 1.06 [s, 9H, C(CH_3)₃] ppm. ¹³C NMR (C_6D_6) δ : 228.72 (CO); 224.71 (CO); 143.30 ($CH = CH_2$); 112.75 ($CH = CH_2$); 39.88 (CH₂^tBu); 38.91 (SiCH); 37.90 (CH); 36.28 [d, ² $J(^{31}P^{13}C) = 5.3$ Hz, N(CH₃)₂]; 31.54 [C(CH₃)₃]; 30.11 [C(CH₃)₃]; 29.05 (SiCH₂) ppm. ²⁹Si NMR (C₆D₆) δ : 91.96 [d, ³ $J(^{31}P^{29}Si) = 32.1$ Hz] ppm.

Compound **2c**: ¹H NMR (C_6D_6) δ : 6.12–5.9 (m, 1H, $CH = CH_2$); 5.14–4.88 (m, 2H, $CH = CH_2$); 2.18 [d, 18H, ²J(³¹P¹³C) = 9.9 Hz, N(CH_3)₂]; 1.15 (s, 9H, C(CH_3)₃)] ppm. ¹³C NMR (C_6D_6) δ : 228.21 (CO); 224.26 (CO); 145.62 ($CH = CH_2$); 109.55 ($CH = CH_2$); 49.97 (SiCH); 46.16 (CH_2 'Bu); 40.66 (CH); 36.39 [d, ²J(³¹P¹³C) = 5.4 Hz, N(CH_3)₂]; 31.37 [$C(CH_3)_3$]; 30.50 [$C(CH_3)_3$]; 29.16 (SiCH₂) ppm. ²⁹Si NMR (C_6D_6) δ : 114.89 [d, ²J(³¹P²⁹Si) = 30.7 Hz] ppm.

Compounds 2a-2c: IR (cm⁻¹, THF): 2027 (w); 1908 (sh, w); 1900 (vs).

3.1.2. 2-Neopentyl-3-vinyl-1-silacyclobutane-1-diyl-1tungsten(0)pentacarbonyl hexamethylphosphorotriamide (3)

To a suspension of $K_2[W_2(CO)_{10}]$ [made from 4.92 g (14.0 mmol) $W(CO)_6$ and 3.78 g (28.0 mmol) C_8K laminate] in 50 ml of THF was added 2.46 ml (14.0 mmol) of HMPA and 3.32 ml (14.0 mmol) of 1,1-dichloro-2-neopentyl-3-vinyl-silacyclobutane at -78°C. The reaction mixture was worked up as described for **2** to give 2.56 g (3.83 mmol, 27.3%) of a yellow solid. Elemental analysis for $C_{21}H_{36}N_3O_6PSiW$ (M_r 669.43): Calc.: C, 37.68; H, 5.42; N, 6.27; O, 14.34; P, 4.62; Si, 4.20; W, 27.47%. Found: C, 37.51; H, 5.48; N, 6.24%. MS (*m/e*, relative intensity): 669 (M⁺, 1.3); 585 (M⁺ - 3CO, 1.6); 557 (M⁺ - 4CO, 1.4); 529 (M⁺ - 5CO, 2.5).

Compound **3a**: ¹H NMR $(C_6D_6)\delta$: 6.17–5.98 $(CH=CH_2)$; 5.14–5.00 (m, 2H, CH= CH_2); 2.16 [d, 18H, ²J(³¹P¹³C) = 10.2 Hz, N(CH₃)₂]; 1.08 [s, 9H, C(CH₃)₃] ppm. ¹³C NMR $(C_6D_6)\delta$: 205.31 (CO); 203.25 (CO); 144.98 (CH=CH₂); 110.69 (CH= CH_2); 44.31 (CH₂⁻¹Bu); 42.89 (SiCH); 38.20 (CH); 36.22 [d, ²J(³¹P¹³C) = 5.3 Hz, N(CH₃)₂]; 31.19 [C(CH₃)₃]; 29.97 [C(CH₃)₃]; 28.99 (SiCH₂) ppm.²⁹Si NMR $(C_6D_6)\delta$: 70.52 [d, ²J(³¹P²⁹Si) = 31.8 Hz] ppm. Compound **3b**: ¹H NMR (C₆D₆)\delta: 6.17–5.98

Compound **3b**: ¹H NMR (C_6D_6) δ : 6.17–5.98 ($CH = CH_2$); 5.14–5.00 (m, 2H, $CH = CH_2$); 2.13 [d, 18H, ²J(³¹P¹³C) = 10.1 Hz, N(CH_3)₂]; 1.13 [s, 9H, C(CH_3)₃] ppm. ¹³C NMR (C_6D_6) δ : 205.81 (CO); 203.68 (CO); 143.54 ($CH = CH_2$); 112.57 ($CH = CH_2$); 40.07 (CH_2 ¹Bu); 39.02 (SiCH); 37.70 (CH); 36.27 [d, ²J(³¹P¹³C) = 5.6 Hz, N(CH_3)₂]; 31.44 [$C(CH_3$)₃]; 30.25 [$C(CH_3)_3$]; 29.04 (Si CH_2) ppm. ²⁹Si NMR (C_6D_6) δ : 68.36 [d, ²J(³¹P²⁹Si) = 28.9 Hz] ppm. Compound **3c**: ¹H NMR (C_6D_6) δ : 6.17–5.98 (m,

Compound **3c**: ¹H NMR (C_6D_6) δ : 6.17–5.98 (m, 1H, CH=CH₂); 5.14–5.00 (m, 2H, CH=CH₂); 2.14 [d, 18H, ²J(³¹P¹³C) = 7.3 Hz, N(CH₃)₂]; 1.20 [s, 9H, C(CH₃)₃] ppm. ¹³C NMR (C_6D_6) δ : 204.49 (CO); 203.38 (CO); 145.82 (CH=CH₂); 109.58 (CH=CH₂); 50.98 (SiCH); 45.99 (CH₂^tBu); 41.01 (CH); 36.55 [d, ${}^{2}J({}^{31}P^{13}C) = 5.2 \text{ Hz}, \text{ N}(CH_{3})_{2}]; 30.69 [C(CH_{3})_{3}];$ 29.16 (SiCH₂) ppm.

Compound **3d**: ¹H NMR (C_6D_6) δ : 6.17–5.98 (m, 1H, $CH = CH_2$); 5.14–5.00 (m, 2H, $CH = CH_2$); 1.10 [s, 9H, $C(CH_3)_3$] ppm. ¹³C NMR (C_6D_6) δ : 144.90 ($CH = CH_2$); 113.92 ($CH = CH_2$) ppm.

Compounds 3a-3d: IR (cm⁻¹, THF): 2043 (w); 1914 (sh, w); 1907 (vs).

3.1.3. 2-Neopentyl-3-vinyl-1-silacyclobutane-1-diyl-1iron(0)tetracarbonyl hexamethylphosphorotriamide (4)

To a suspension of 3.18 g (11.0 mmol) of $Na_2Fe(CO)_4 \cdot 1.5C_4H_8O_2$ (C₄H₈O₂: dioxan) in 50 ml of THF was added 1.91 ml (11.0 mmol) of HMPA and 2.61 ml (11.0 mmol) of 1a/1b at -78° C. The mixture was stirred and slowly allowed to warm to room temperature. After stirring overnight, 50 ml of pentane was added and the precipitated NaCl separated by filtration. The volatiles were removed under reduced pressure and the remaining dark red oil worked up by chromatography as described above. The compound was crystallised from diethyl ether to give red cubes (4.05 g, 7.9 mmol, 71.8%). Elemental analysis for $C_{20}H_{36}FeN_3O_5PSi$ (M_r 513.42): Calc.: C, 46.79; H, 7.07; Fe, 10.88; N, 8.18; O, 15.58; P, 6.03; Si, 5.47%. Found: C, 46.61; H, 6.93; N, 8.23%. MS (m/e, relative intensity): 513 (M^+ , 25.4); 485 (M^+ - CO, 8.8); 457 (M^+ - 2CO, 48.9); 429 (M^+ -3CO, 5.7; 401 (M⁺ -4CO, 100.0).

Compound 4a: ¹H NMR $(C_6D_6)\delta$: 6.04–5.90 (m, 1H, $CH = CH_2$); 5.07–4.89 (m, 2H, $CH = CH_2$); 2.27 [d, 18H, ² $J({}^{31}P^{13}C) = 10.3$ Hz, $N(CH_3)_2$]; 1.18 [s, 9H, $C(CH_3)_3$] ppm. ¹³C NMR $(C_6D_6)\delta$: 218.38 (CO); 144.75 $(CH = CH_2)$; 110.39 $(CH = CH_2)$; 47.35 (SiCH); 45.05 $(CH_2^{-1}Bu)$; 43.42 (CH); 36.78 [d, ² $J({}^{31}P^{13}C) =$ 4.9 Hz, $N(CH_3)_2$]; 31.18 $[C(CH_3)_3]$; 30.78 $(SiCH_2)$; 30.25 $[C(CH_3)_3]$ ppm. ²⁹Si NMR $(C_6D_6)\delta$: 99.47 [d, ² $J({}^{31}P^{29}Si) = 26.6$ Hz] ppm.

Compound **4b**: ¹H NMR $(C_6 D_6)\delta$: 6.09–5.94 (m, 1H, $CH = CH_2$); 5.11–4.90 (m, 2H, $CH = CH_2$); 2.24 [d, 18H, ² $J({}^{31}P^{13}C) = 12.7$ Hz, $N(CH_3)_2$]; 1.05 [s, 9H, $C(CH_3)_3$] ppm. ¹³C NMR $(C_6 D_6)\delta$: 218 (CO); 143.15 $(CH = CH_2)$; 113.56 (CH = CH_2); 43.43 (SiCH); 43.16 (CH); 40.88 (CH₂⁺Bu); 36.15 [d, ² $J({}^{31}P^{13}C) = 5.6$ Hz, $N(CH_3)_2$]; 31.92 [$C(CH_3)_3$]; 31.31 [SiCH₂]; 29.79 [$C(CH_3)_3$] ppm. ²⁹Si NMR $(C_6 D_6)\delta$: 99.28 [d, ² $J({}^{31}P^{29}Si) = 26.7$ Hz] ppm.

Compound 4c: ¹H NMR $(C_6D_6)\delta$: 6.04–5.90 (m, 1H, $CH = CH_2$); 5.07–4.89 (m, 2H, $CH = CH_2$); 2.21 [d, 18H, ² $J({}^{31}P^{13}C) = 9.7$ Hz, $N(CH_3)_2$]; 1.09 [s, 9H, $C(CH_3)_3$] ppm. ¹³C NMR $(C_6D_6)\delta$: 218.26 (CO); 144.91 ($CH = CH_2$); 110.96 ($CH = CH_2$); 44.46 ($CH_2{}^{1}Bu$); 41.92 (SiCH); 40.53 (CH); 36.64 [d, ² $J({}^{31}P^{13}C) = 5.1$ Hz, $N(CH_3)_2$]; 31.36 (SiCH₂); 31.02 [$C(CH_3)_3$]; 30.16 [$C(CH_3)_3$] ppm. ²⁹Si NMR (C_6D_6) δ : 91.76 [d, ² $J({}^{31}P^{29}Si) = 30.5$ Hz] ppm.

Compound **4d**: ¹H NMR $(C_6 D_6)\delta$: 6.04–5.90 (m,

1H, $CH = CH_2$); 5.07–4.89 (m, 2H, $CH = CH_2$); 2.22 [d, 18H, ${}^2J({}^{31}P^{13}C) = 11.1$ Hz, $N(CH_3)_2$]; 1.07 [s, 9H, $C(CH_3)_3$] ppm. ${}^{13}C$ NMR (C_6D_6) δ : 143.68 ($CH = CH_2$); 113.33 ($CH = CH_2$); 36.39 [d, ${}^2J({}^{31}P^{13}C) = 4.9$ Hz, $N(CH_3)_2$]; 30.08 [$C(CH_3)_3$] ppm.

Compounds 4a-4c IR (cm⁻¹, THF): 2011 (m); 1928 (w); 1889 (s).

Crystal structure investigations

Further details of the structure investigations are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftliche Information mbH, D-76344 Eggenstein Leopoldshafen 2, on quoting the depository number CSD-58972, the names of the authors and the journal citation, or from the author (N.A.).

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