

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 $[(CO)_nMSiC_{10}H_{18}] \cdot HMPA$ ($M = Fe$, $n = 4$; $M = Cr$, $n = 5$). 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 $[1S,2S,3S]/[1R,2R,3R]$ pairs are present. In orthorhombic crystals of $[(CO)_4FeSiC_{10}H_{18}] \cdot HMPA$ (**4**) ($P2_12_1$ (No. 19), $a = 896.4(5)$, $b = 1693(1)$, $c = 1753(1)$ pm, $Z = 4$) only the $[1S,2S,3S]$ -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 Brønsted and Lewis acids or bases [8]. In contrast, investigations on 1,1-dichloro-2-neopentyl-3-vinyl-1-silacyclobutanes, 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-3-vinyl-1-silacyclobutanes with different metal fragments

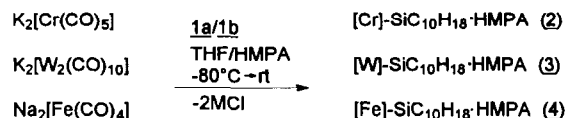
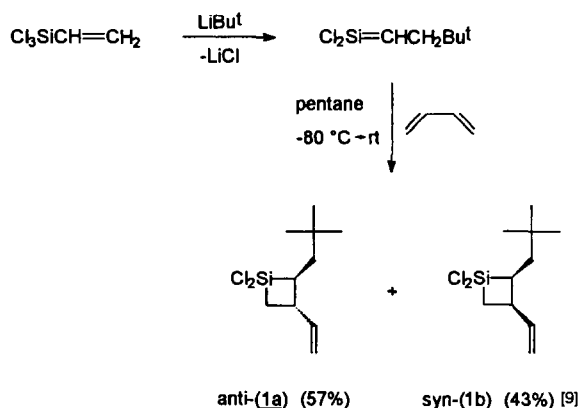
According to Scheme 1, *anti/syn* stereoisomeric 1,1-dichloro-2-neopentyl-3-vinyl-1-silacyclobutanes are synthesized by the [2 + 2] cycloaddition reaction of dichloroneopentylsilene, $\text{Cl}_2\text{Si}=\text{CHCH}_2^t\text{Bu}$ and 1,3-butadiene as described previously [9]; the preliminary formation of silene results from the reaction of vinyl-trichlorosilane and Li^tBu in a non-polar solvent [10].

A promising synthetic route to silylene 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 $[\{\text{M}(\text{CO})_n\}_m]^{2-}$ ($\text{M} = \text{Fe}$, $m = 1$, $n = 4$; $\text{M} = \text{Cr}$, $m = 1$, $n = 5$; $\text{M} = \text{W}$, $m = 2$, $n = 5$) in a solvent mixture of THF/HMPA leads to the formation of the donor-stabilised complexes $[\text{M}]\text{SiC}_{10}\text{H}_{18} \cdot \text{HMPA}$.

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, ^{13}C and ^{29}Si 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



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

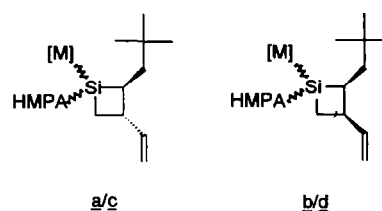
Scheme 2.

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 ^{29}Si 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 ^{29}Si 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 silylene complexes containing alkyl groups at the silicon atoms [14]. The ^{29}Si NMR spectra of **2a/2c** and **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 [$^2J(^{31}\text{P}^{29}\text{Si}) = 34.2$ Hz] and 114.89 ppm [$^2J(^{31}\text{P}^{29}\text{Si}) = 30.7$ Hz] for the chromium complex and at 99.47 [$^2J(^{31}\text{P}^{29}\text{Si}) = 26.6$ Hz] and 91.76 ppm [$^2J(^{31}\text{P}^{29}\text{Si}) = 30.5$ Hz] for the corresponding iron compound. Spectra of **2b** and **4b** show doublets at 91.96 [$^2J(^{31}\text{P}^{29}\text{Si}) = 32.1$ Hz] and 99.28 ppm [$^2J(^{31}\text{P}^{29}\text{Si}) = 26.7$ 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 [$^2J(^{31}\text{P}^{29}\text{Si}) = 31.8$ Hz] and 68.36 ppm [$^2J(^{31}\text{P}^{29}\text{Si}) = 28.9$ Hz].

Two signals at 218.38 and 218.26 ppm occur in the carbonyl region of the ^{13}C 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 idealised C_{4v} symmetry; on this basis the bands at 2027 (w) 1908 (sh,w) and 1900 (vs) cm^{-1} for **2** and 2043 (w)



$[\text{M}] = \text{Cr}(\text{CO})_5$ (2); $\text{W}(\text{CO})_5$ (3); $\text{Fe}(\text{CO})_4$ (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_{3v}).

2.3. Crystal structures of $[(\text{CO})_5\text{CrSiC}_{10}\text{H}_{18}] \cdot \text{HMPA}$ (**2**), $[(\text{CO})_5\text{WSiC}_{10}\text{H}_{18}] \cdot \text{HMPA}$ (**3**) and $[(\text{CO})_4\text{FeSiC}_{10}\text{H}_{18}] \cdot \text{HMPA}$ (**4**)

Both complexes $[(\text{CO})_5\text{CrSiC}_{10}\text{H}_{18}] \cdot \text{HMPA}$ (**2**) and $[(\text{CO})_5\text{WSiC}_{10}\text{H}_{18}] \cdot \text{HMPA}$ (**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 (1*S*,2*S*,3*S*)-2-neopentyl-3-vinyl-1-silacyclobutane-1-diyl-1-chromium(0)pentacarbonyl hexamethylphosphorotriamide (**2**) and of (1*S*,2*S*,3*S*)-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.

Table 1
Crystal data for **2** and **3** and experimental parameters

Formula unit	$[(\text{CO})_5\text{CrSiC}_{10}\text{H}_{18}] \cdot \text{HMPA}$ (2)	$[(\text{CO})_5\text{WSiC}_{10}\text{H}_{18}] \cdot \text{HMPA}$ (3)
Crystal size (mm)	$0.45 \times 0.70 \times 0.50$	$0.35 \times 0.50 \times 0.60$
Crystal shape	irregular prisms	
Crystal system. Laue group	monoclinic. $2/m$	
Space group	$P2_1/n$ (No. 14)	
Cell parameters (pm), ($^\circ$)	$a = 1084(1)$ $b = 1927(1)$ $c = 1342.1(8)$ $\beta = 97.11(7)$	$a = 1099(1)$ $b = 1937(1)$ $c = 1342(1)$ $\beta = 97.18(7)$
Cell volume (10^6 pm^3)	$V_{\text{EZ}} = 2781.94$	$V_{\text{EZ}} = 2834.61$
Calculated density (g cm^{-3})	$\rho = 1.284$	$\rho = 1.569$
Number of units	$Z = 4$	$Z = 4$
Diffractometer	STOE, STAD14	
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 ($^\circ$)	$3.72 < 2\theta < 45.00$	$3.72 < 2\theta < 43.24$
Range of indices	$h: -11/10$ $k: 0/20$ $l: 0/14$	$h: -11/8$ $k: 0/19$ $l: 0/13$
Number of refl.	3434	3152
Observed ($I > 2\sigma$)	2410	2826
R_{int}	0.0434	
Absorption correction		ψ -scan
Reflections		-4 4 1 -4 2 2 -3 2 2 -2 1 1 0.1899/0.9524
Transmission (min./max)		
Initial coordinates:	Direct methods (SHELXS-86)	
for P, Si, Cr and Mo	Difference Fourier syntheses (SHELXL-93)	
for C and O	calculated in idealised positions, not refined	
for H	<i>International Tables for X-ray Crystallography</i> ,	
Atomic scattering factors (neutral atoms)	Kluwer Academic Publishers, Dordrecht. The Netherlands, 1992, Vol. C.	
Refinement on F^2	Full matrix least squares (SHELXL-93)	
Minimised function	$\sum w(F_o^2 - F_c^2)$	
Weighting scheme	$w = 1/\sigma^2(F_o^2) + (A \cdot P)^2 + B \cdot P$; where $P = 1/3(F_{o,\text{max}}^2 + 2F_c^2)$	
Variables	$A = 0.1351$	$A = 0.1198$
R_{all} (R_{obs}) based on $F > 4\sigma_F$	$B = 7.14$	$B = 21.25$
wR_2 (wR_2^{obs})	256	257
GOF $_{\text{all}}$ (GOF $_{\text{obs}}$)	0.1153 (0.0784)	0.0578 (0.0525)
Shift/esd (mean)	0.2302 (0.2058)	0.1510 (0.1460)
Residual electron density (10^{-6} pm^{-3})	1.057 (1.152)	0.975 (1.000)
(min./max.)	0.000	0.012
Programs used	-0.59/1.35	-1.69/2.14
	SHELXS-86 [15], SHELXL-93 [16], ORTEP [17]	

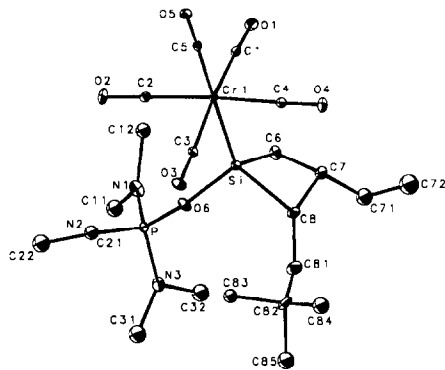


Fig. 1. ORTEP drawing (30% probability) of **2** and selected bond lengths (pm): Cr–Si, 241.2(3); Si–O6, 173.7(6); Si–C6, 189.3(8); Si–C8, 193.5(10).

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 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 $[(\text{CO})_4\text{FeSiC}_{10}\text{H}_{18}] \cdot \text{HMPA}$ (**4**) (Fig. 3) contain only the 1*S*,2*S*,3*R*-diastereomer of 2-neopentyl-3-vinyl-1-silacyclobutane-1-diyl-1-iron(0)tetracarbonyl hexamethylphosphorotri-

Table 2
Crystal data for **4**

Formula unit	$[(\text{CO})_4\text{FeC}_{10}\text{H}_{18}] \cdot \text{HMPA}$ (4)
Crystal size (mm)	0.40 × 0.30 × 0.50
Crystal shape	irregular prism
Crystal system, Laue group	orthorhombic, 222
Space group	$P2_12_12_1$ (No. 19)
Cell parameters (pm)	$a = 896.4(5)$ $b = 1693.4(10)$ $c = 1753.4(10)$
Cell volume (10^6 pm^3)	$V_{\text{EZ}} = 2662(3)$
Calculated density (g cm^{-3})	$\rho = 1.281$
Number of units	$Z = 4$
Diffractometer	STOE, STADI4
Temperature (K)	$T = 188(2)$
Radiation, λ (pm)	Mo K α , 71.069, graphite monochromator
Scan mode	$\omega/2\theta$
Scan range ($^\circ$)	$3.34 < 2\theta < 45.00$
Range of indices	$h: 0/9$ $k: 0/18$ $l: 0/18$
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)	<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	$\sum w(F_o^2 - F_c^2)$
Weighting scheme	$w = 1/\sigma(F_o^2) + (A \cdot P)^2 + B \cdot P$: where $P = 1/3(F_{o,\text{max}}^2 + 2F_c^2)$ $A = 0.0439$ $B = 2.1201$
Variables	243
R_{all} (R_{obs}) based on $F > 4\sigma_F$	0.0668 (0.0432)
$wR_{2,\text{all}}$ ($wR_{2,\text{obs}}$)	0.099 (0.0918)
GOF _{all} (GOF _{obs})	1.062 (1.122)
Shift/esd (mean)	0.000
Residual electron density (10^{-6} pm^{-3})	
(min./max.)	–0.29/0.32
Programs used	SHELXS-86 [15], SHELXL-93 [16], ORTEP [17]

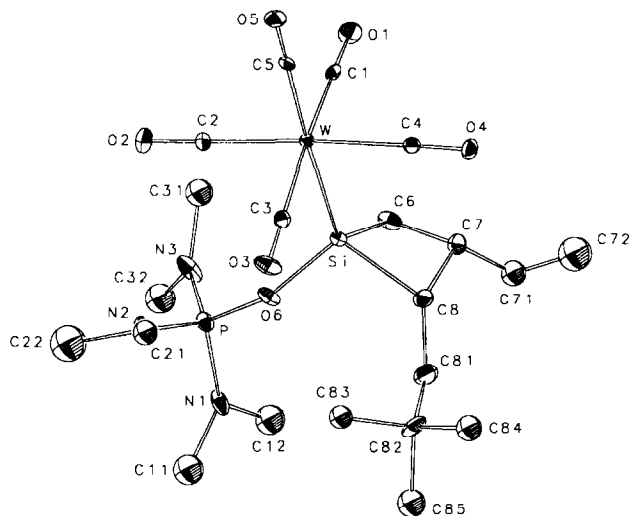


Fig. 2. ORTEP drawing (30% probability) of **3** and selected bond lengths (pm): W–Si, 256.2(3); Si–O6, 174.0(8); Si–C6, 188.4(11); Si–C8, 195.8(14).

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 carbon–oxygen 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 silacyclobutenediyl moiety [Si–Fe–C_{eq}: 84.5(2)–84.9(2)^o]. The iron–silicon bond distance of 228.4(2) pm is close to that found for similar donor-stabilised silylene 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 (^o) for **2**

Atom	x	y	z	U_{eq}^a
Cr1	0.60805(10)	0.40762(6)	–0.36780(8)	0.0282(4)(^o)
C1	0.7253(7)	0.4165(4)	–0.2518(6)	0.040(2)(^o)
O1	0.7937(5)	0.4235(3)	–0.1809(4)	0.062(2)(^o)
C2	0.6813(7)	0.3255(4)	–0.4069(5)	0.039(2)(^o)
O2	0.7260(6)	0.2759(3)	–0.4340(5)	0.070(2)(^o)
C3	0.4780(7)	0.3897(4)	–0.4702(6)	0.037(2)(^o)
O3	0.4013(6)	0.3768(3)	–0.5333(5)	0.058(2)(^o)
C4	0.5236(7)	0.4872(4)	–0.3283(5)	0.035(2)(^o)
O4	0.4750(6)	0.5355(3)	–0.3033(4)	0.056(2)(^o)
C5	0.6998(7)	0.4590(4)	–0.4499(5)	0.034(2)(^o)
O5	0.7568(5)	0.4893(3)	–0.5024(4)	0.0521(15)(^o)
Si	0.4874(2)	0.34241(11)	–0.26071(14)	0.0334(6)(^o)
C6	0.5228(9)	0.3422(5)	–0.1190(6)	0.056(3)(^o)
C7	0.4203(8)	0.3977(6)	–0.1185(6)	0.062(3)(^o)
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)(^o)
C81	0.2208(10)	0.3378(7)	–0.2112(8)	0.083(3)(^o)
C82	0.1203(8)	0.3432(6)	–0.3030(7)	0.071(3)(^o)
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)
P	0.4705(2)	0.17877(10)	–0.29328(14)	0.0382(6)(^o)
O6	0.4603(5)	0.2569(3)	–0.2979(4)	0.0519(15)(^o)
N1	0.5905(8)	0.1579(4)	–0.2191(6)	0.069(2)(^o)
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)(^o)
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)(^o)
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_{ij} tensor.

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

(a) <i>Pentacarbonyltungsten fragment</i>			
W—C5	200.3(12)	C5—W—C2	90.5(4)
W—C4	205.0(13)	C5—W—C3	92.8(4)
W—C3	201.2(14)	C5—W—C4	91.5(4)
W—C2	201.8(13)	C5—W—C1	95.2(5)
W—C1	200.3(13)	C3—W—C2	86.3(5)
C1—O1	115.2(14)	C3—W—C4	91.5(4)
C2—O2	112.9(14)	C1—W—C4	89.1(4)
C3—O3	113.6(14)	C1—W—C2	92.7(4)
C4—O4	113.2(13)	C1—W—C3	172.0(4)
C5—O5	115.3(13)	C2—W—C4	177.2(4)
		O1—C1—W	178.7(9)
		O2—C2—W	178.0(11)
		O3—C3—W	177.8(10)
		O4—C4—W	178.6(9)
		O5—C5—W	179.2(10)
W—Si	256.2(3)	C5—W—Si	177.5(3)
		C4—W—Si	86.1(3)
		C3—W—Si	86.8(3)
		C3—W—C5	92.8(4)
		C2—W—Si	92.0(4)
		C1—W—Si	85.3(4)
(b) <i>Cyclo-silanediyyl fragment</i>			
Si—O6	174.0(8)	O6—Si—C6	107.2(5)
Si—C6	188.4(11)	O6—Si—C8	106.7(6)
Si—C8	195.8(14)	C6—Si—C8	77.8(6)
Si...C7	237.5(12)	O6—Si—W	115.8(3)
C6—C7	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)
C71—C72	120(3)	C71—C7—C6	114.3(13)
C8—C81	146(2)	C71—C7—C8	116.3(13)
C81—C82	152(2)	C6—C7—C8	100.8(10)
C82—C83	151(2)	C72—C71—C7	124.8(22)
C82—C84	152(2)	C81—C8—C7	117.1(12)
C82—C85	159(2)	C81—C8—Si	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) <i>HMPA ligand</i>			
P—O6	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)	O6—P—N1	109.8(7)
N1—C12	136(2)	N3—P—N1	110.5(9)
N1—C11	150(3)	N2—P—N1	105.4(7)
N2—C21	140(2)	P—O6—Si	156.0(6)
N2—C22	147(3)	C12—N1—C11	109.8(17)
N3—C31	145(2)	C12—N1—P	125.1(14)
N3—C32	149(2)	C11—N1—P	124.4(12)
		C21—N2—C22	113.0(17)
		C21—N2—P	127.3(10)
		C22—N2—P	119.4(15)
		C31—N3—C32	117.9(15)
		C31—N3—P	123.9(11)
		C32—N3—P	118.2(14)

within the silacyclobutanes and (ii) to avoid steric interactions between the bulky $M(\text{CO})_n$ ($M = \text{Cr}, \text{W}; n = 5$; $M = \text{Fe}; n = 4$) 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 $\text{Fe}(\text{CO})_4$ -silacyclobutane (folded, this work) and the corresponding silacyclobutene 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 $\text{Si}^{4+}\text{—C}^{4-}$ (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 $\text{Cr}(\text{CO})_5$ unit and $\text{Si}-\text{CH}_2-\text{CH}_2-\text{CH}_2 \cdot \text{OPH}_3$, 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 $(\text{CH}_3)_2\text{Si}$: 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 $(\text{CO})_5\text{Cr}=\text{SiMe}_2$ 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_z and 10% from the Si s orbital, as well as 17% from the Cr d_z^2 and 10% from

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_z^2 , 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.

Table 7
Fractional coordinates and equivalent thermal parameters ($^\circ$) for 4

Atom	x	y	z	U_{eq}^a
Fe	0.06717(11)	0.87939(5)	0.19449(5)	0.0321(3)($^\circ$)
C1	-0.0825(10)	0.9461(4)	0.2019(4)	0.043(2)($^\circ$)
O1	-0.1829(7)	0.9897(3)	0.2091(3)	0.071(2)($^\circ$)
C2	0.0576(9)	0.7962(5)	0.1361(4)	0.046(2)($^\circ$)
O2	0.0533(7)	0.7398(4)	0.0961(3)	0.069(2)($^\circ$)
C3	0.2007(9)	0.8844(4)	0.2678(4)	0.044(2)($^\circ$)
O3	0.2887(6)	0.8893(3)	0.3158(3)	0.065(2)($^\circ$)
C4	0.1761(10)	0.9375(5)	0.1311(5)	0.048(2)($^\circ$)
O4	0.2509(8)	0.9745(4)	0.0898(4)	0.076(2)($^\circ$)
Si	-0.0654(2)	0.80507(10)	0.27948(9)	0.0307(4)($^\circ$)
C6	0.0185(9)	0.7294(5)	0.3455(4)	0.046(2)($^\circ$)
C7	-0.0823(10)	0.7593(4)	0.4108(4)	0.048(2)($^\circ$)
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)($^\circ$)
C81	-0.2727(8)	0.8827(5)	0.3952(4)	0.042(2)($^\circ$)
C82	-0.2693(9)	0.9471(4)	0.4576(4)	0.043(2)($^\circ$)
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)
P	-0.3257(2)	0.70783(10)	0.19618(10)	0.0320(4)($^\circ$)
O5	-0.2261(5)	0.7647(3)	0.2406(3)	0.0370(12)($^\circ$)
N1	-0.4178(7)	0.7591(3)	0.1350(3)	0.0413(15)($^\circ$)
C11	-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)($^\circ$)
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)($^\circ$)
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
Bond lengths (pm) and angles (°) in **4**

(a) Tetracarbonyliron fragment

Fe—C2	174.8(8)	C3—Fe—C1	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—O1	117.0(9)	C2—Fe—C4	96.2(3)
C2—O2	118.6(8)	O1—C1—Fe	177.9(6)
C3—O3	115.7(8)	O2—C2—Fe	179.0(7)
C4—O4	117.0(9)	O3—C3—Fe	178.6(7)
		O4—C4—Fe	178.2(8)

		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-silanedeyl fragment

Si—O5	173.4(5)	O5—Si—C8	103.7(3)
Si—C8	187.8(7)	O5—Si—C6	107.8(3)
Si—C6	188.4(7)	C8—Si—C6	78.1(3)
Si...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)	C6—Si—Fe	124.6(3)
C71—C72	133.7(11)	O5—Si—C7	101.2(3)
C7—C8	158.3(10)	Si—C6—C7	89.9(5)
C8—C81	151.4(9)	C6—C7—C8	98.6(5)
C81—C82	154.5(10)	C6—C7—C71	112.3(7)
C82—C83	150.4(12)	C7—C71—C72	127.0(9)
C82—C85	150.6(11)	C7—C8—Si	88.9(4)
C82—C84	152.5(11)	C7—C8—C81	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)
		C83—C82—C81	108.9(7)
		C85—C82—C81	111.4(6)
		C84—C82—C81	108.4(6)

(c) HMPA ligand

P—O5	152.7(5)	O5—P—N2	108.5(3)
P—N2	160.1(6)	O5—P—N1	107.4(3)
P—N1	160.9(6)	N2—P—N1	110.2(3)
P—N3	161.2(6)	O5—P—N3	111.4(3)
N1—C12	145.4(9)	N2—P—N3	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)
N2—C21	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—N2—C21	112.7(7)
		C22—N2—P	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)

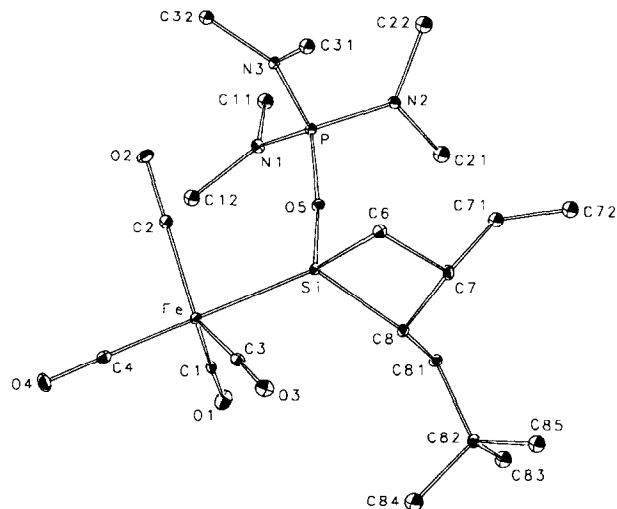


Fig. 3. ORTEP drawing (30% probability) of **4** and selected bond lengths (pm): Fe—Si, 228.4(2); Si—O5, 173.4(5); Si—C6, 188.4(7); Si—C8, 187.8(7).

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-

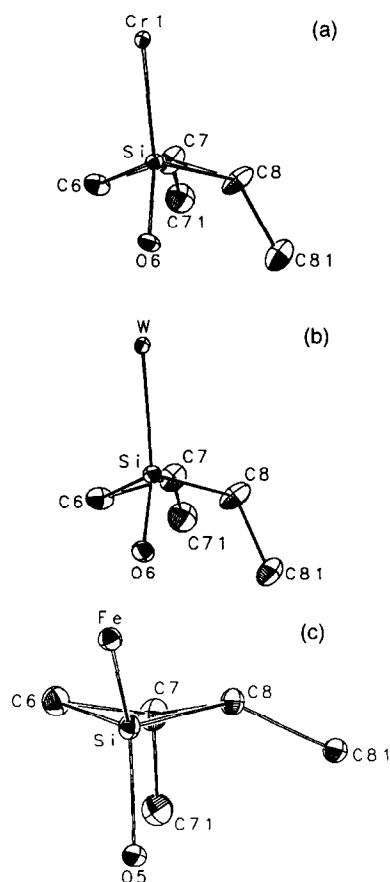
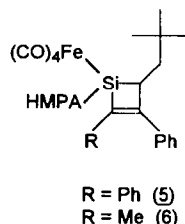


Fig. 4. ORTEP view (30% probability) of the silacyclobutane units in (a) **2**, (b) **3** and (c) **4** all along the Si—C7 axis.



Scheme 4.

compound **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** (neopentyl 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 silylene 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, Et₂O) 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 C₆D₆ 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-chromium(0)pentacarbonyl hexamethylphosphorotriamide (**2**)

A suspension of K₂Cr(CO)₅ [made from C₈K 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°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 a cooled (–10°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 Et₂O 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 (C₆D₆) δ: 6.12–5.9 (m, 1H, CH=CH₂); 5.14–4.88 (m, 2H, CH=CH₂); 2.17 [d, 18H, ²J(³¹P¹³C) = 10.2 Hz, N(CH₃)₂]; 1.11 [s, 9H, C(CH₃)₃] ppm. ¹³C NMR (C₆D₆) δ: 228.47 (CO); 224.46 (CO); 144.87 (CH=CH₂); 110.74 (CH=CH₂); 43.73 (CH₂Bu); 43.66 (SiCH); 39.35 (CH); 36.19 [d, ²J(³¹P¹³C) = 5.3 Hz, N(CH₃)₂]; 31.14 [C(CH₃)₃]; 29.80 [C(CH₃)₃]; 28.61 (SiCH₂) ppm. ²⁹Si NMR (C₆D₆) δ: 96.25 [d, ²J(³¹P²⁹Si) = 34.2 Hz] ppm.

Compound **2b**: ¹H NMR (C₆D₆) δ: 6.12–5.9 (m, 1H, CH=CH₂); 5.14–4.88 (m, 2H, CH=CH₂); 2.19 [d, 18H, ²J(³¹P¹³C) = 10.0 Hz, N(CH₃)₂]; 1.06 [s, 9H, C(CH₃)₃] ppm. ¹³C NMR (C₆D₆) δ: 228.72 (CO); 224.71 (CO); 143.30 (CH=CH₂); 112.75 (CH=CH₂);

39.88 (CH₂¹Bu); 38.91 (SiCH); 37.90 (CH); 36.28 [d, ²J(³¹P¹³C) = 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, ²J(³¹P²⁹Si) = 32.1 Hz] ppm.

Compound **2c**: ¹H NMR (C₆D₆) δ: 6.12–5.9 (m, 1H, CH=CH₂); 5.14–4.88 (m, 2H, CH=CH₂); 2.18 [d, 18H, ²J(³¹P¹³C) = 9.9 Hz, N(CH₃)₂]; 1.15 (s, 9H, C(CH₃)₃) ppm. ¹³C NMR (C₆D₆) δ: 228.21 (CO); 224.26 (CO); 145.62 (CH=CH₂); 109.55 (CH=CH₂); 49.97 (SiCH); 46.16 (CH₂¹Bu); 40.66 (CH); 36.39 [d, ²J(³¹P¹³C) = 5.4 Hz, N(CH₃)₂]; 31.37 [C(CH₃)₃]; 30.50 [C(CH₃)₃]; 29.16 (SiCH₂) ppm. ²⁹Si NMR (C₆D₆) 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-1-tungsten(0)pentacarbonyl hexamethylphosphorotriamide (3)

To a suspension of K₂[W₅(CO)₁₀] [made from 4.92 g (14.0 mmol) W(CO)₆ and 3.78 g (28.0 mmol) C₈K 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 C₂₁H₃₆N₃O₆PSiW (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 (C₆D₆) δ: 6.17–5.98 (CH=CH₂); 5.14–5.00 (m, 2H, CH=CH₂); 2.16 [d, 18H, ²J(³¹P¹³C) = 10.2 Hz, N(CH₃)₂]; 1.08 [s, 9H, C(CH₃)₃] ppm. ¹³C NMR (C₆D₆) δ: 205.31 (CO); 203.25 (CO); 144.98 (CH=CH₂); 110.69 (CH=CH₂); 44.31 (CH₂¹Bu); 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 (C₆D₆) δ: 70.52 [d, ²J(³¹P²⁹Si) = 31.8 Hz] ppm.

Compound **3b**: ¹H NMR (C₆D₆) δ: 6.17–5.98 (CH=CH₂); 5.14–5.00 (m, 2H, CH=CH₂); 2.13 [d, 18H, ²J(³¹P¹³C) = 10.1 Hz, N(CH₃)₂]; 1.13 [s, 9H, C(CH₃)₃] ppm. ¹³C NMR (C₆D₆) δ: 205.81 (CO); 203.68 (CO); 143.54 (CH=CH₂); 112.57 (CH=CH₂); 40.07 (CH₂¹Bu); 39.02 (SiCH); 37.70 (CH); 36.27 [d, ²J(³¹P¹³C) = 5.6 Hz, N(CH₃)₂]; 31.44 [C(CH₃)₃]; 30.25 [C(CH₃)₃]; 29.04 (SiCH₂) ppm. ²⁹Si NMR (C₆D₆) δ: 68.36 [d, ²J(³¹P²⁹Si) = 28.9 Hz] ppm.

Compound **3c**: ¹H NMR (C₆D₆) 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 (C₆D₆) δ: 204.49 (CO); 203.38 (CO); 145.82 (CH=CH₂); 109.58 (CH=CH₂); 50.98 (SiCH); 45.99 (CH₂¹Bu); 41.01 (CH); 36.55 [d,

²J(³¹P¹³C) = 5.2 Hz, N(CH₃)₂]; 30.69 [C(CH₃)₃]; 29.16 (SiCH₂) ppm.

Compound **3d**: ¹H NMR (C₆D₆) δ: 6.17–5.98 (m, 1H, CH=CH₂); 5.14–5.00 (m, 2H, CH=CH₂); 1.10 [s, 9H, C(CH₃)₃] ppm. ¹³C NMR (C₆D₆) δ: 144.90 (CH=CH₂); 113.92 (CH=CH₂) 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-1-iron(0)tetracarbonyl hexamethylphosphorotriamide (4)

To a suspension of 3.18 g (11.0 mmol) of Na₂Fe(CO)₄ · 1.5C₄H₈O₂ (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 C₂₀H₃₆FeN₃O₅PSi (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 (C₆D₆) δ: 6.04–5.90 (m, 1H, CH=CH₂); 5.07–4.89 (m, 2H, CH=CH₂); 2.27 [d, 18H, ²J(³¹P¹³C) = 10.3 Hz, N(CH₃)₂]; 1.18 [s, 9H, C(CH₃)₃] ppm. ¹³C NMR (C₆D₆) δ: 218.38 (CO); 144.75 (CH=CH₂); 110.39 (CH=CH₂); 47.35 (SiCH); 45.05 (CH₂¹Bu); 43.42 (CH); 36.78 [d, ²J(³¹P¹³C) = 4.9 Hz, N(CH₃)₂]; 31.18 [C(CH₃)₃]; 30.78 (SiCH₂); 30.25 [C(CH₃)₃] ppm. ²⁹Si NMR (C₆D₆) δ: 99.47 [d, ²J(³¹P²⁹Si) = 26.6 Hz] ppm.

Compound **4b**: ¹H NMR (C₆D₆) δ: 6.09–5.94 (m, 1H, CH=CH₂); 5.11–4.90 (m, 2H, CH=CH₂); 2.24 [d, 18H, ²J(³¹P¹³C) = 12.7 Hz, N(CH₃)₂]; 1.05 [s, 9H, C(CH₃)₃] ppm. ¹³C NMR (C₆D₆) δ: 218 (CO); 143.15 (CH=CH₂); 113.56 (CH=CH₂); 43.43 (SiCH); 43.16 (CH); 40.88 (CH₂¹Bu); 36.15 [d, ²J(³¹P¹³C) = 5.6 Hz, N(CH₃)₂]; 31.92 [C(CH₃)₃]; 31.31 [SiCH₂]; 29.79 [C(CH₃)₃] ppm. ²⁹Si NMR (C₆D₆) δ: 99.28 [d, ²J(³¹P²⁹Si) = 26.7 Hz] ppm.

Compound **4c**: ¹H NMR (C₆D₆) δ: 6.04–5.90 (m, 1H, CH=CH₂); 5.07–4.89 (m, 2H, CH=CH₂); 2.21 [d, 18H, ²J(³¹P¹³C) = 9.7 Hz, N(CH₃)₂]; 1.09 [s, 9H, C(CH₃)₃] ppm. ¹³C NMR (C₆D₆) δ: 218.26 (CO); 144.91 (CH=CH₂); 110.96 (CH=CH₂); 44.46 (CH₂¹Bu); 41.92 (SiCH); 40.53 (CH); 36.64 [d, ²J(³¹P¹³C) = 5.1 Hz, N(CH₃)₂]; 31.36 (SiCH₂); 31.02 [C(CH₃)₃]; 30.16 [C(CH₃)₃] ppm. ²⁹Si NMR (C₆D₆) δ: 91.76 [d, ²J(³¹P²⁹Si) = 30.5 Hz] ppm.

Compound **4d**: ¹H NMR (C₆D₆) δ: 6.04–5.90 (m,

1H, CH=CH₂); 5.07–4.89 (m, 2H, CH=CH₂); 2.22 [d, 18H, ²J(³¹P¹³C) = 11.1 Hz, N(CH₃)₂]; 1.07 [s, 9H, C(CH₃)₃] ppm. ¹³C NMR (C₆D₆)δ: 143.68 (CH=CH₂); 113.33 (CH=CH₂); 36.39 [d, ²J(³¹P¹³C) = 4.9 Hz, N(CH₃)₂]; 30.08 [C(CH₃)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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