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Decamethylpentasilacycloheptyne $\cdot$ $Mo_2(CO)_4(\eta^5\text{-}C_5H_5)_2$ and cycloheptyne $\cdot$ $Mo_2(CO)_4(\eta^5\text{-}C_5H_5)_2$[1]

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Abstract

A dimolybdenum derivative of decamethylpentasilacycloheptyne (**1**) was synthesized by direct reaction of the heptyne with $Mo_2(CO)_4(\eta^5\text{-}C_5H_5)_2$. **1** crystallized in the space group $P\bar{1}$, $a = 9.386(2)$, $b = 9.866(3)$, $c = 20.178(4)$ Å, $\alpha = 92.17(2)$, $\beta = 97.17(2)$, $\gamma = 115.71(2)°$. The acetylenic bond is lengthened from 1.213 Å in the free ligand to 1.359(4) Å and all the Si–Si bond lengths in **1** are significantly lengthened upon complexation. This is due to relaxation of the ring strain as evidenced by the Si–C–C bond angles in **1** of 132.7 and 140.9° compared to 159.2 and 162.6° in the uncomplexed ring. ^{29}Si-NMR data exhibit significant downfield chemical shifts upon complexation for the Si atoms adjacent to the triple bond, with moderate upfield shifts for the other Si atoms. The related cycloheptyne $\cdot$ $Mo_2(CO)_4(\eta^5\text{-}C_5H_5)_2$ (**2**) was synthesized by the reaction of cyclohepteno-1,2,3-selenadiazole with $Mo_2(CO)_4(\eta^5\text{-}C_5H_5)_2$. **2** crystallized in the space group $C2_1/c$, $a = 30.396(10)$, $b = 8.9093(3)$, $c = 16.156(4)$ Å, $\beta = 115.39(2)°$. The acetylenic bond in **2** is 1.345 Å, compared with a calculated value (ab initio 3-21 G*) of 1.190 Å for the free cycloheptyne. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Decamethylpentasilacycloheptyne; Cycloheptyne; Molybdenum; Carbonyl

1. Introduction

Recent studies have demonstrated the stability of small ring polysilylacetylenes [1,2]. The carbon analogues, for example cyclohexyne and cycloheptyne, are only isolable as stable species when complexed by transition metal centers. Thus, complexes based upon platinum[3], zirconium [4] and molybdenum [5] have been used to stabilize cyclohexyne and related small ring cycloalkynes. We now report the reaction between $Mo_2(CO)_4(\eta^5\text{-}C_5H_5)_2$, a useful platform for complexing small ring acetylenes [5], and decamethylpentasilacycloheptyne including the complete spectral and structural characterization of the product, $Me_{10}Si_5C_2 \cdot Mo_2(CO)_4(\eta^5\text{-}C_5H_5)_2$ (**1**). We also compare the structural characteristics of the complexed pentasilacycloheptyne in **1** with its carbon counterpart in cycloheptyne $\cdot$ $Mo_2(CO)_4(\eta^5\text{-}C_5H_5)_2$ (**2**), prepared from the reaction of cyclohepteno-1,2,3-selenadiazole with $Mo_2(CO)_4(\eta^5\text{-}C_5H_5)_2$.

2. Experimental section

All experiments were performed under an inert atmosphere in dry solvents. NMR data were collected on a Bruker NR-200 FTNMR instrument, IR data were obtained using a Perkin-Elmer 1600 FT-IR, analyses were performed by Galbraith Laboratories, Knoxville, TN.

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[1] Happy birthday Bruce from Ramesh and Keith.

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2.1. Synthesis of $Me_{10}Si_5C_2 \cdot Mo_2(CO)_4(\eta^5\text{-}C_5H_5)_2$ (1)

In a 50 ml flask 0.31 g of $(\eta^5\text{-}C_5H_5)_2Mo_2CO_6$ was dissolved in 10 ml of diglyme and the solution was heated to reflux for 2 h under an argon atmosphere. After this time period the solution contained $(\eta^5\text{-}C_5H_5)_2Mo_2CO_4$ a complex containing a Mo–Mo triple bond as evidenced by the gradual appearance of CO stretching frequencies at 1889 and 1854 cm^{-1}. The solution was cooled to room temperature (r.t.) and 0.2 g of $Me_{10}Si_5C_2$ was added in 1 ml of THF. The solution was stirred overnight and after removal of the solvents in vacuo the red/brown residue was extracted in 50 ml hexane. This solution was concentrated to 5 ml and placed upon a 2.5 × 15 cm silica gel column and the red band formed was eluted with hexane. After removal of the solvent the residue was recrystallized from CH_2Cl_2/hexane to yield 0.3 (60%) of **1**, m.p. 172–174°C. Analysis for $C_{26}H_{40}Mo_2O_4Si_5$ (748.91): Calc. (Found), C: 41.69 (41.20); H: 5.38 (5.12). ^{1}H-NMR: δ 0.52, 0.54, 0.73 (Me, 30H); 5.12(η^5-C_5H_5, 10H) ppm. ^{13}C-NMR: δ −4.78, −3.74, 2.54 (Me); 78.8 (acetylenic C); 88.8 (η^5-C_5H_5); 229.7 (CO) ppm. ^{29}Si-NMR: δ −4.24, −42.0, −44.5 ppm. IR (hexane) 1946, 1899, 1987, 1838 cm^{-1}.

2.2. Synthesis of cycloheptyne $\cdot Mo_2(CO)_4(\eta^5\text{-}C_5H_5)_2$ (2)

This was performed in an analogous manner to that reported for the cyclohexyne complex using cyclohepteno-1,2,3-selenadiazole as starting material [5,8]. A solution of 1.5 g (3.0 mmol) of $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_6$ in 15 ml diglyme was heated under reflux for 4 h. After cooling in ice, 300 mg (1.5 mmol) of cyclohepta-1,2,3-selenadiazole was added, and the solution was stirred at r.t. for 1 h, and then at 60°C for 6 h. After removing the solvent in vacuo, the residue was extracted with 3 × 10 ml CH_2Cl_2 and the product purified by column chromatography (SiO_2, 4 × 60 cm, −20°C). The cycloheptyne complex was eluted as a brown/purple band with hexane/dichloromethane (3:1) solvent mixture. After recrystallization from the same solvent mixture, 80 mg (10%) of the pure complex was isolated, m.p. 180°C (d). Analysis for $C_{21}H_{20}O_4Mo_2$ (528.27): Calc. (Found) C, 47.75 (47.37); H, 3.82 (3.79). ^{1}H-NMR: δ 5.5, (s, C_5H_5, 10H); 3.2, (t, α-H, 4H); 1.9–1.7 (m, β, γ-H, 6H) ppm. ^{13}C-NMR: δ 231 (CO), 91.9 (η^5-C_5H_5), 88.5 (acetylenic C), 38.8, 31.5, 29.9 (CH_2) ppm. IR (hexane) 1976, 1919, 1910, 1845 cm^{-1}.

2.3. X-ray structure determination for 1 and 2.

Unit cell parameters and standard deviations for both crystals were obtained by least-squares fit of 25 randomly selected reflections in the 2θ range of 15–30°. Intensity data were collected on a Siemens R3m/v

Table 1
Data collection and refinement details

	1	**2**
Empirical formula	$C_{26}H_{40}Mo_2O_4Si_5$	$C_{21}H_{20}O_4Mo_2$
Formula weight	748.9	528.3
Color; habit	Purple fragment	Violet fragment
Crystal size (mm)	0.16 × 0.20 × 0.20	0.10 × 0.20 × 0.30
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$ (no. 1)	$C2_1/c$ (no. 15)
Unit cell dimensions	$a = 9.386(2)$ Å, $\alpha = 92.17(2)°$	$a = 30.396(10)$ Å
	$b = 9.866(3)$ Å, $\beta = 97.72(2)°$	$b = 8.909(3)$ Å, $\beta = 115.39(2)°$
	$c = 20.178(4)$ Å, $\gamma = 115.71(2)°$	$c = 16.156(4)$ Å
Volume (Å^3)	1658.6(7)	3953(2)
Z	2	8
$D_{calc.}$ (g cm^{-3})	1.500	1.775
μ (mm^{-1})	0.943	1.261
F(000)	764	2096
Radiation	Graphite-monochromated Mo–K_α ($\lambda = 0.71073$ Å)	
2θ range (°)	$3.5 \leq 2\theta \leq 45.0$	$3.0 \leq 2\theta \leq 45.0$
Scan type	ω	$2\theta - \omega$
Scan speed (variable, ° min^{-1})	3.00–20.00	3.00–15.00
Scan range (°)	$1.40 + K_\alpha$ separation	$1.26 + K_\alpha$ separation
Standard reflections	Three measured every 100 reflections	
Index ranges	$0 \leq h \leq 10$ $-10 \leq k \leq 9$ $-21 \leq l \leq 21$	$-32 \leq h \leq 29$ $0 \leq k \leq 9$ $0 \leq l \leq 17$
Reflections collected	4312	3001
Independent reflections	4012 (R_{int} = 1.59%)	2579 (R_{int} = 1.87%)
Observed reflections ($F \geq 3\sigma(F)$)	3534	1906
Absorption correction	Semi empirical (Ψ-scans)	
Min/max transmission	0.6650/0.9897	
Refinement method	Full-matrix least-squares	
Quantity minimized	$\Sigma w(F_o - F_c)^2$	
Extinction coefficient, χ^a	0.00066(9)	
Hydrogen atoms	Riding model, fixed isotropic U	
Weighting scheme, w^{-1}	$\sigma^2(F) + 0.0007F^2$	$\sigma^2(F) + 0.0008F^2$
Number of parameters	335	244
Final R indices (obs. data)	$R = 0.0258$, $wR = 0.0353$	$R = 0.0549$, $wR = 0.0553$
R indices (all data)	$R = 0.0399$, $wR = 0.0416$	$R = 0.0792$, $wR = 0.0590$
GOF	1.03	1.13
Largest and mean shift/estimated S.D.	0.069, 0.016	0.111, 0.002
Data-to-parameter-ratio	10.5:1	7.8:1
Largest difference peak (e Å^{-3})	0.32	0.67
Largest difference hole (e Å^{-3})	−0.24	−0.54

[a] $F^* = F[1 + 0.002\chi F^2/\sin(2\theta)]^{-1/4}\chi$.

Table 2
Selected bond lengths (Å) and angles (°)[a]

1		2	
Bond lengths			
Mo1–Mo2	2.978(1)	Mo1–Mo2	2.972(1)
Mo1–C1	2.185(3)	Mo1–C1	2.142(9)
Mo1–C2	2.280(3)	Mo1–C2	2.236(8)
Mo2–C1	2.184(3)	Mo2–C1	2.26(1)
Mo2–C2	2.217(3)	Mo2–C2	2.170(9)
Si1–Si2	2.368(1)	C1–C2	1.34(1)
Si1–C2	1.870(3)	C1–C7	1.50(1)
Si2–Si3	2.361(1)	C2–C3	1.50(1)
Si3–Si4	2.351(1)	C3–C4	1.50(2)
Si4–Si5	2.360(1)	C4–C5	1.55(2)
Si5–C1	1.858(3)	C5–C6	1.50(2)
C1–C2	1.359(3)	C6–C7	1.52(2)
Bond angles			
Mo2–Mo1–C1	47.0(1)	Mo2–Mo1–C1	49.2(4)
Mo2–Mo1–C2	47.6(1)	Mo2–Mo1–C2	46.6(4)
C1–Mo1–C2	35.4(2)	C1–Mo1–C2	35.7(6)
Mo1–Mo2–C1	47.0(1)	Mo1–Mo2–C1	45.9(4)
Mo1–Mo2–C2	49.4(1)	Mo1–Mo2–C2	35.3(6)
C1–Mo2–C2	36.0(2)	C1–Mo2–C2	35.3(6)
Si2–Si1–C2	118.8(2)	Mo1–C1–Mo2	84.9(5)
Si1–Si2–Si3	123.79(9)	Mo1–C1–C2	76.0(9)
Si2–Si3–Si4	118.1(1)	Mo1–C1–C7	135.2(1)
Si3–Si4–Si5	113.00(9)	Mo2–C1–C2	68.7(9)
Si4–Si5–C1	116.8(2)	Mo2–C1–C7	133.8(1)
Mo1–C1–Mo2	86.0(2)	C2–C1–C7	132.1(1)
Mo1–C1–Si5	129.9(3)	Mo1–C2–Mo2	84.8(5)
Mo1–C1–C2	76.1(3)	Mo1–C2–C1	68.3(9)
Mo2–C1–Si5	135.8(3)	Mo1–C2–C3	137.5(1)
Mo2–C1–C2	73.3(3)	Mo2–C2–C1	76.0(9)
Si5–C1–C2	132.7(4)	Mo2–C2–C3	131.5(1)
Mo1–C1–Mo2	82.9(2)	C1–C2–C3	132.8(1)
Mo1–C2–Si1	135.2(2)	C2–C3–C4	111.4(1)
Mo1–C2–C1	68.5(3)	C3–C4–C5	115.8(2)
Mo2–C2–Si1	132.0(2)	C4–C5–C6	117.3(2)
Mo2–C2–C1	70.7(3)	C5–C6–C7	118.2(2)
Si1–C2–C1	140.9(4)	C1–C7–C6	112.6(1)

[a] Estimated standard deviations in parentheses.

single crystal diffractometer. Background counts were taken with stationary crystal and total background time to scan time ratio of 0.5. Intensity check reflections indicated no crystal decay. The structures were solved by direct methods and refined by anisotropic full matrix least squares for the non-hydrogen atoms. The data were corrected for Lorentz and polarization effects.

All calculations were performed on a Micro Vax II computer using the VMS version of the SHELEXTL-PLUS software package. All non-hydrogen atoms were placed at calculated positions with C–H bond distances of 0.96 Å and average isotropic thermal parameters of 0.08. No efforts were made to improve the *Rw* values by changing the weighting schemes.

Crystal data, data collection and least-squares details and other relevant crystallographic information are shown in Table 1, selected bond lengths and angles in Table 2 and atomic coordinates in Table 3.

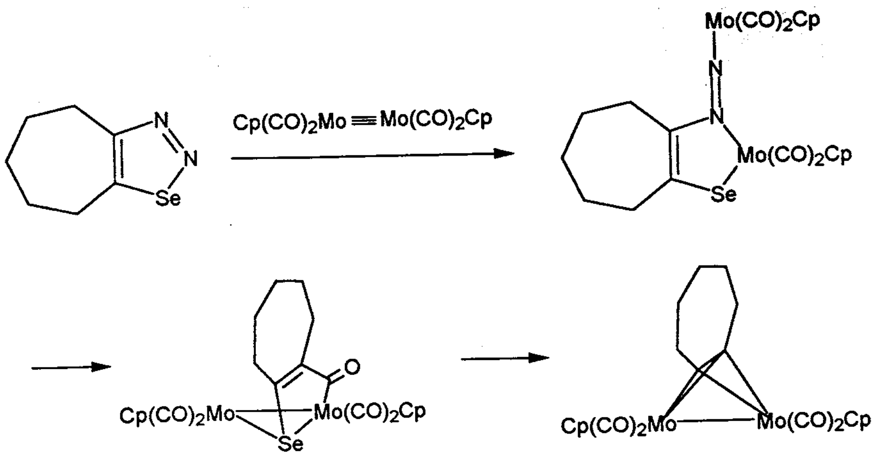
3. Results and discussion

The reaction between decamethylpentasilacycloheptyne and $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4$ was straightforward with no significant side products. All spectral properties are in accord with a simple complexation in which the two Mo atoms bridge the acetylenic bond. Previous studies on silylacetylene transition metal complexes illustrate that coordination produces a significant downfield shift in the ^{29}Si-NMR resonance of the atoms directly bonded to the triple bond [6,7]. Thus, values of $\Delta\delta$ (the difference in chemical shift between the complexed and uncomplexed ligand) vary from 10 ppm (singly coordinated as in $Me_3SiC_2SiMe_3 \cdot Fe(CO)_4$) to 20 ppm (doubly coordinated as in $Me_3SiC_2SiMe_3 \cdot Co_2(CO)_6$) have been reported. The parent pentasilacycloheptyne exhibits ^{29}Si

Table 3
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$)

Atom	*x*	*y*	*z*	*U*(eq)[a]
Mo(1)	642(1)	8653(1)	3573(1)	30(1)
Mo(2)	2270(1)	6668(1)	3808(1)	30(1)
Si(1)	−1613(1)	4665(1)	2624(1)	32(1)
Si(2)	−2729(1)	4696(1)	1503(1)	49(1)
Si(3)	−1771(2)	6828(2)	898(1)	54(1)
Si(4)	788(2)	8801(1)	1307(1)	49(1)
Si(5)	2329(1)	8082(1)	2110(1)	37(1)
O(1)	−507(4)	4020(3)	4321(2)	63(1)
O(2)	2932(4)	8666(3)	5140(2)	56(1)
O(3)	−2476(4)	7800(4)	2537(2)	64(2)
O(4)	−1670(4)	6771(3)	4533(2)	57(1)
C(1)	1554(4)	7532(3)	2908(2)	29(1)
C(2)	199(4)	6386(3)	3047(2)	27(1)
C(3)	−1031(5)	3068(4)	2595(2)	51(2)
C(4)	−3277(5)	4141(5)	3131(2)	52(2)
C(5)	−2654(9)	3100(6)	984(3)	101(4)
C(6)	−4917(6)	4134(7)	1501(3)	92(3)
C(7)	−1704(8)	6114(7)	24(3)	94(3)
C(8)	−3279(6)	7616(7)	794(3)	92(3)
C(9)	1978(7)	9241(7)	595(3)	84(3)
C(10)	574(7)	10566(5)	1536(3)	78(3)
C(11)	4451(5)	9639(5)	2269(3)	63(2)
C(12)	2292(6)	6374(5)	1645(2)	62(2)
C(13)	1785(5)	10720(4)	4388(2)	52(2)
C(14)	3031(5)	10851(4)	4015(3)	54(2)
C(15)	2569(6)	11058(4)	3354(3)	56(2)
C(16)	1065(6)	11062(4)	3313(2)	55(2)
C(17)	593(6)	10880(4)	3945(2)	54(2)
C(18)	4494(5)	6864(6)	3316(3)	60(2)
C(19)	5070(5)	7574(5)	3981(3)	67(2)
C(20)	4445(6)	6428(6)	4405(3)	66(3)
C(21)	3502(5)	5076(5)	4013(3)	57(2)
C(22)	3517(5)	5328(5)	3346(3)	58(2)
C(23)	480(5)	5048(4)	4130(2)	41(2)
C(24)	2563(5)	7986(4)	4613(2)	41(2)
C(25)	−1329(5)	8078(4)	2913(2)	39(2)
C(26)	−819(5)	7407(4)	4172(2)	38(2)

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



2

Scheme 1.

resonances at −38.2, −34.3 and −33.3 ppm [1] whereas the coordinated ligand exhibits resonances at −4.24, −42.0, −44.5 ppm. Thus a very large shift for the Si_α atom contrasts both the Si_β and Si_γ atoms which exhibit smaller low field shifts, similar to published data [6].

The reaction sequence of cyclohepteno-1,2,3-selenadiazole and $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4$ is indicated below. The intermediate complexes are isolable, however, **2** can be synthesized in a one-pot reaction, provided that a 100% molar excess of $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4$ is used [9] (Scheme 1).

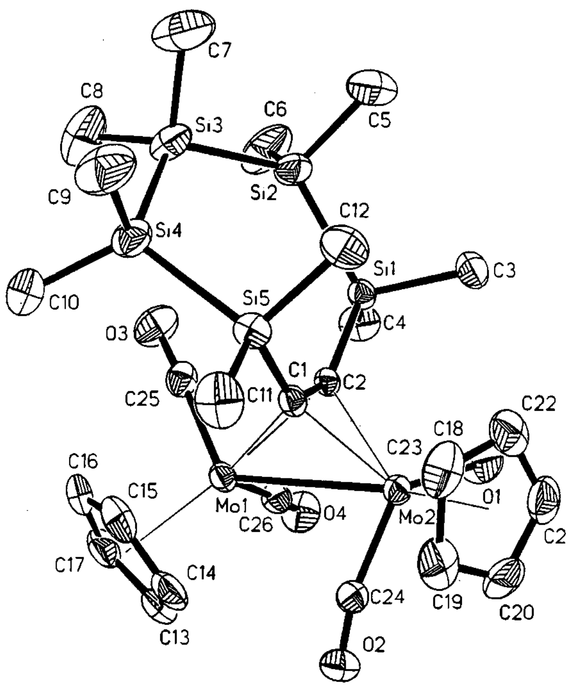


Fig. 1. Structure of $Me_{10}Si_5C_2 \cdot Mo_2(CO)_4(\eta^5\text{-}C_5H_5)_2$ (**1**). Hydrogen atoms are omitted for clarity. Thermal elipsoids represent 40% probabilities.

We have compared the structure of **1** (Fig. 1) with pentasilacycloheptyne [1] using the atomic coordinates retrieved from the Cambridge crystallographic data base. The uncomplexed ligand exhibits a typical envelope structure with the acetylenic C atoms and each of the neighbouring pair of Si atoms coplanar (mean deviation from planarity for these six atoms is 0.34 Å). Upon complexation to the bimetallic Mo–Mo substrate all bond lengths and bond angles in the ring expand except C(1)–C(2)–Si(5) and C(2)–C(1)–Si(1) which contract from 159.2 and 162.6° in the uncomplexed ring to 132.7 and 140.9°, respectively, in the molybdenum complex. This effect, also observed in similar complexes produces a puckered conformation in the ring as illustrated in Fig. 2. A similar puckering was observed for

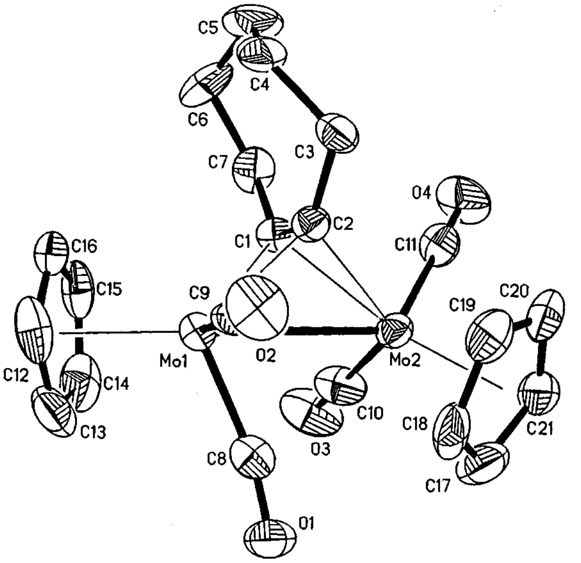


Fig. 2. Structure of $C_7H_{10} \cdot Mo_2(CO)_4(\eta^5\text{-}C_5H_5)_2$ (**2**). Hydrogen atoms are omitted for clarity. Thermal elipsoids represent 50% probabilities.

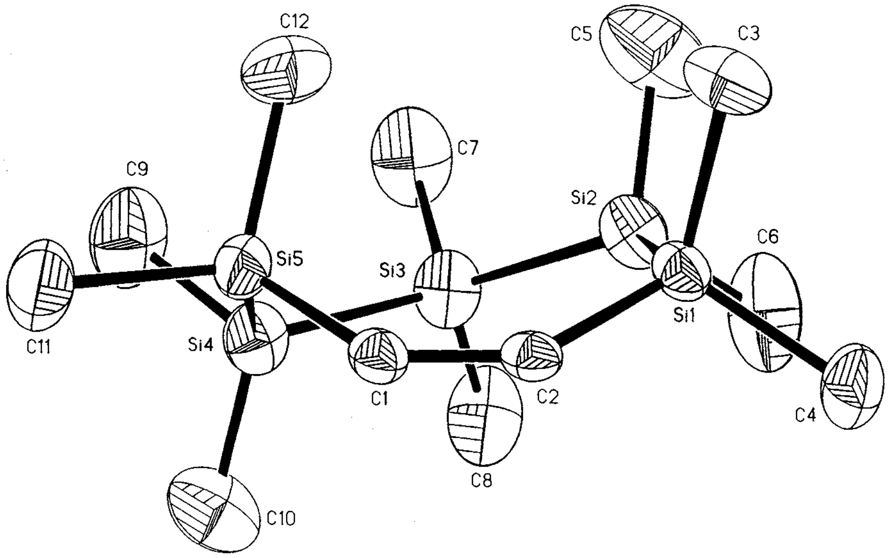


Fig. 3. Geometry of the ligand in **1**.

the non-silicon-containing cycloheptyne·(η^5-C_5H_5)$_2$ Mo_2CO_4 (**2**, with bond angles at the alkyne bond at 132.2 and 132.9°); however, the equivalent atoms Si(3) and C(5) point in opposite directions, Fig. 3.

The length of the acetylenic C≡C bond in **1** was determined to be 1.359(4) Å, significantly longer than in the non-coordinated ligand, 1.213 Å. In the cycloheptyne·(η^5-C_5H_5)$_2Mo_2CO_4$ complex **2**, the corresponding bond length is 1.345(13) Å compared with a calculated value of 1.190 Å in the free cycloalkyne (ab initio calculation at the 3-12 G* level, using the Spartan computational package). These values are indicative for reduction of the C≡C bond to a C=C bond upon coordination to the two Mo atoms due to a release of steric strain within the ring upon formally changing the hybridization of the two ring C atoms from sp^3 to sp^2. This is also in agreement with related non-silicon containing cyclic acetylene complexes of the (η^5-C_5H_5)$_2Mo_2CO_4$ group. For example, the related C–C bond length in the cyclohexyne complex is 1.35(1) Å [5]. Single metal coordination results in shorter, more acetylenic bonds with bond lengths centered around 1.29(1) Å [3,4]. The various Si–Si bonds (Si(1)–Si(2) 2.368(2), Si(2)–Si(3) 2.361(2), Si(3)–Si(4) 2.350(2) and Si(4)–Si(5) 2.360(2) Å) all significantly longer than their uncomplexed counterparts which are reported as 2.342, 2.354, 2.341 and 2.353 Å, respectively.

Acknowledgements

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[9] The details concerning the preparation and isolation of the intermediate complexes will be the subject of a forthcoming article.