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Coordination Chemistry of Perhalogenated Cyclopentadienes and Alkynes. 8.[1] Pentakis(dimethylsilyl)cymantrene†

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Summary: Starting from $[\eta^5\text{-}C_5Br_5]Mn(CO)_3$, the first π-complex of a cyclopentadienyl ligand with five silyl substituents, $[\eta^5\text{-}C_5(SiMe_2H)_5]Mn(CO)_3$, was prepared by a series of halogen-lithium exchange reactions, followed by silylation with $SiMe_2HCl$. The crystal structure determination of this compound shows a highly symmetrical "paddle wheel" orientation of the five silyl groups around the cyclopentadienyl ring.

Introduction

Polysilylated cyclopentadienyl ligands have been of interest over the past decade. Increasing the number of silyl substituents is believed to enhance the solubility in nonpolar solvents and the volatility of the compounds and to increase their kinetic stability. Thus, a series of stable π-cyclopentadienyl complexes of main-group elements and lanthanides or actinides with the $[C_5(SiMe_3)_3H_2]$ ligand could be obtained.[2] However, attempts to introduce more than three $SiMe_3$ groups into the cyclopentadienyl system thus far have been unsuccessful.[3] We report here the first π-complex containing a 5-fold silylated cyclopentadienyl ligand.

Results and Discussion

We showed recently that starting from $[(C_5Cl_4Br)Mn(CO)_3]$ (1), the consecutive introduction of five SMe groups into the cyclopentadienyl ligand can be achieved by repeated alternate reaction with *n*-butyllithium and dimethyl disulfide.[4] When other electrophiles are used, multiple substitution in 1 works only when electrophiles containing donor atoms such as S, Se, or P are used. However, in the case of the related $[(C_5Br_5)Mn(CO)_3]$ (2)[5] all the bromine atoms can be substituted stepwise by the $SiMe_2H$ group (Scheme I).

Double lithiations can be performed for each of the compounds 2–5. Thus, 7 can be prepared in three steps from 2 in an overall yield of about 60%. All derivatives $[C_5Br_{5-n}(SiMe_2H)_n]Mn(CO)_3$ with $n = 1\text{–}5$ are air-stable, crystalline powders, that are very soluble in hexane and can be obtained in good to excellent yields. Their ^1H NMR spectra show the minimum number of signals that can be expected from symmetry considerations. This means obviously that in all compounds, even in the sterically crowded 6 and 7, a rapid rotation of the silyl group around the ring–silicon bond must occur.

Comparable sterically congested systems such as $Cr(CO)_3[C_6(SiMe_2H)_6]$,[6] $[C_5(^iPr)_5]CoCp^+$,[7] and $[C_5(^iPr)_5]Mo(CO)_3Me$[8] show strongly temperature-dependent NMR spectra with internal rotation barriers ranging from 56 to 72 kJ/mol. Cooling a toluene solution of 7 results in broadening of the ^1H NMR doublet for the methyl groups until one broad resonance is observed at −80 °C. Going down to −90 °C, which is the lowest reasonable temperature achievable in this solvent, results in two broad signals without any fine structure. This leads to an approximate $\Delta G^{\ddagger}$ value of 40 kJ/mol. In comparison to the abovementioned compounds, this is a much lower value which means the steric hindrance is here not as great as might have been expected.

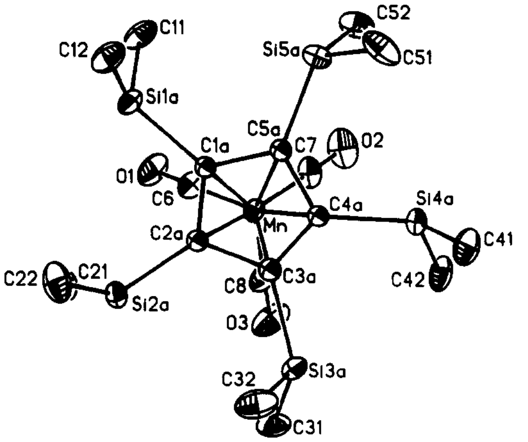

Figure 1. Molecular structure of 7 (thermal ellipsoids on the 20% probability level; the picture shows the higher populated A form). Averaged bond lengths (Å): Mn–(C1A–C5A) 2.17 (1); C–C 1.46 (1); C_{ring}–Si 1.87 (1); Si–C_{Me} 1.88 (1).

Figure 1 shows the solid state structure of 7.[9] All $SiMe_2H$ groups show the same "paddle wheel" orientation with the Si–H bond lying in the plane of the cyclopentadienyl ring. Compound 7 is therefore chiral. Interestingly, there is an obvious disorder in the silicon positions, which also can be resolved for the ring carbon atoms but not for the methyl groups. The site occupancy factors can be refined to values of 0.74:0.26, which means that both enantiomers are distributed statistically over the four symmetry-equivalent positions of the unit cell and not in special pairs, as would be demanded by crystallographic symmetry. Similar observations have been reported for

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† Dedicated to Prof. Wolfgang Beck on the occasion of his 60th birthday.

(1) Part 7: Sünkel, K. *Chem. Ber.* **1991**, *124*, 2449.

(2) For a review, see: Jutzi, P. *J. Organomet. Chem.* **1990**, *400*, 1, and literature cited therein.

(3) The synthesis of $C_6(SiMe_3)_6$ was reported in a short communication: Miftakhof, M. S.; Tolstikov, G. A.; Lomailina, S. I. *Zh. Obshch. Khim.* **1976**, *46*, 2754; *Chem. Abstr.* **1977**, *86*, 121430z.

(4) Sünkel, K.; Motz, D. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 934.

(5) Nefedov, V. A. *Zh. Org. Khim.* **1973**, *9*, 719. Herrmann, W. A., Huber, M. *J. Organomet. Chem.* **1977**, *140*, 55.

(6) Schuster, I. I.; Weissensteiner, W.; Mislow, K. *J. Am. Chem. Soc.* **1986**, *108*, 6661.

(7) Gloaguen, B.; Astruc, D. *J. Am. Chem. Soc.* **1990**, *112*, 4607.

(8) Sitzmann, H. *Chem. Ber.* **1990**, *123*, 2311.

(9) In the first difference Fourier synthesis after the whole molecule had been identified, five maxima of electron density were found in a distance of about 1 Å from each of the Si atoms in the plane of the cyclopentadienyl ring. Refinement of these positions as site B for the silicon atoms lead to relative site occupancy factors of 3:1 for A:B, but no new positions for the corresponding five ring C atoms could be located. However, the appearance of the corresponding thermal ellipsoids indicated that there were two carbon positions as well. By fixing the sof's of the found carbon sites to 0.5 and the isotropic thermal parameters to 0.02 Å^2, a new difference Fourier synthesis could localize the B site for the ring carbons as well. Isotropic refinement of the C and Si positions with the restriction of common thermal parameters for each A–B pair yielded a final sof of 0.74 for site A. No B sites for the methyl carbons could be localized; nor could any hydrogen positions. Thus, only one methyl carbon site was used in refinement and hydrogens were omitted at all.

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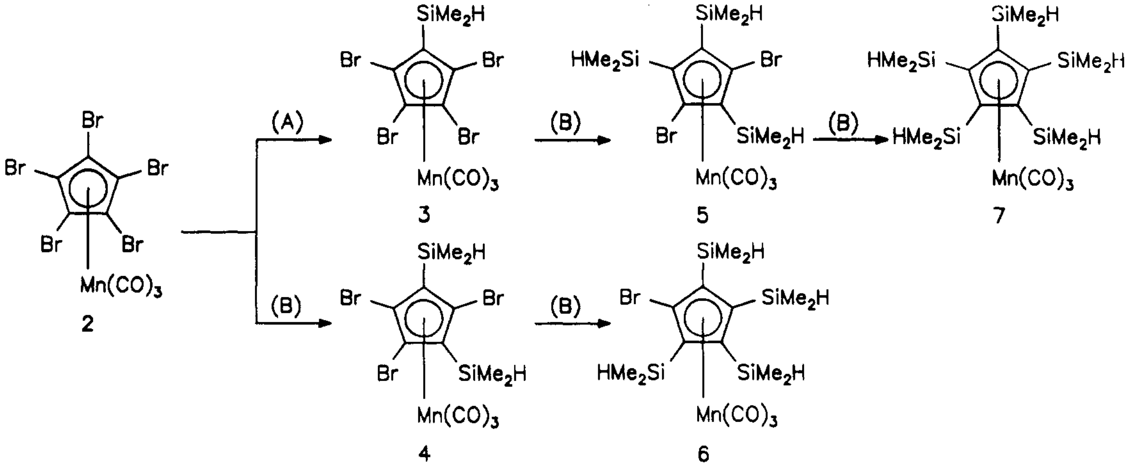
Scheme I[a]



[a] (A) (1) 1.1 equiv of *n*-BuLi; (2) 1 equiv of $SiMe_2HCl$. (B) (1) 2 equiv of *n*-BuLi; (2) 2 equiv of $SiMe_2HCl$.

Table I. Crystallographic Data for 7

Crystal Parameters			
formula	$C_{18}H_{35}MnO_3Si_5$	*Z*	4
space group	$Pna2_1$	cryst dimens, mm	0.50 × 0.50 × 0.15
cryst syst	orthorhombic	cryst color	yellow
a, Å	19.329 (13)	*D*(calc), g/cm³	1.119
b, Å	10.693 (6)	μ(Mo Kα), cm^{-1}	6.91
c, Å	13.200 (3)	temp, °C	18
V, Å³	2728 (3)		
Data Collection			
diffractometer	Nicolet R3	rflns collcd	3955
monochromator	graphite	indpt rflns	2670
		R(merg), %	3.98
scan technique	ω–2θ	indpt rflns obsd $F_o \geq 4\sigma(F_o)$	2308
radiation	Mo Kα		
λ, Å	0.71073	data collcd	$\pm h,\pm k,\pm l$
2θ range, deg	2–20 20–50		$+h,+k,+l$
std rflns	2 std/98 rflns		
Refinement			
program	SHELXTL PLUS 4.11/V		
abs corr	empirical (ψ scan)		
min/max transm	0.388/0.502		
R, %	5.3	R_w, %	6.54
$\Delta_{max}(\rho)$, e Å^{-3}	0.71	$w^{-1} = \sigma^2(F_o) + 0.0005(F_o)^2$	

Table II. Positional (×10⁴) and Equivalent Isotropic Thermal Parameters (Å² × 10³)

	x	*y*	*z*	*U*(eq)
Mn	1432 (1)	928 (1)	0	43 (1)
C(1A)	1625 (5)	509 (8)	1581 (8)	37 (2)
C(2A)	1279 (5)	1707 (8)	1498 (8)	39 (2)
C(3A)	602 (5)	1478 (11)	1023 (10)	40 (2)
C(4A)	541 (5)	181 (7)	785 (8)	36 (2)
C(5A)	1164 (5)	−454 (10)	1157 (9)	42 (2)
Si(1A)	2486 (1)	255 (3)	2182 (3)	53 (1)
Si(2A)	1570 (2)	3265 (3)	1966 (3)	53 (1)
Si(3A)	−149 (2)	2613 (3)	962 (3)	64 (1)
Si(4A)	−173 (1)	−648 (3)	101 (3)	53 (1)
Si(5A)	1314 (2)	−2178 (2)	1280 (3)	57 (1)
C(1B)	1564 (15)	57 (26)	1512 (22)	37 (2)
C(2B)	1453 (15)	1415 (27)	1602 (22)	39 (2)
C(3B)	740 (18)	1661 (32)	1094 (29)	40 (2)
C(4B)	475 (14)	601 (26)	807 (23)	36 (2)
C(5B)	958 (16)	−454 (28)	980 (24)	42 (2)
Si(1B)	2308 (4)	−780 (8)	2077 (7)	56 (3)
Si(2B)	2033 (4)	2604 (7)	2176 (7)	53 (3)
Si(3B)	294 (5)	3240 (7)	1284 (7)	59 (3)
Si(4B)	−387 (4)	293 (9)	154 (9)	64 (3)
Si(5B)	819 (5)	−2165 (7)	766 (7)	55 (3)
C(11)	3123 (4)	−725 (9)	1423 (8)	84 (4)
C(12)	2382 (5)	−356 (9)	3495 (7)	77 (3)
C(21)	2349 (5)	3926 (7)	1375 (8)	74 (3)
C(22)	1631 (6)	3266 (9)	3391 (7)	87 (4)
C(31)	−74 (5)	4006 (8)	67 (10)	95 (4)
C(32)	−366 (5)	3126 (9)	2287 (8)	104 (4)
C(41)	−938 (4)	−882 (8)	944 (9)	87 (4)
C(42)	−395 (5)	42 (9)	−1159 (7)	85 (4)
C(51)	563 (6)	−2903 (7)	1962 (9)	95 (4)
C(52)	1523 (5)	−3035 (7)	71 (9)	89 (4)
C(6)	2313 (4)	1287 (7)	−234 (6)	59 (3)
O(1)	2886 (3)	1528 (6)	−409 (6)	96 (3)
C(7)	1438 (5)	−164 (9)	−998 (6)	67 (3)
O(2)	1456 (4)	−852 (7)	−1667 (6)	110 (3)
C(8)	1191 (4)	2094 (8)	−900 (7)	66 (3)
O(3)	1040 (3)	2822 (7)	−1489 (6)	108 (3)

the benzene derivatives $C_6(CHR_2)_6$ (R = Cl, Me)[10] and very recently, for the $[C_5{}^iPr_5]$ radical.[11] The C_5 ring in **7** shows no deviation from planarity. Two silicon atoms in 1,3 position are shifted out of this plane by 30 pm away from the manganese atom, while the silicon atom in between is situated 12 pm on the proximal side of the ring. Thus the steric interaction between the silyl groups becomes minimized.

7 contains not only a 5-fold silylated cyclopentadienyl ring but also five Si–H groups that might be used for further functionalization. Complexes with the $[C_5H_4(SiMe_2H)]$ ligand have been used in the hydrosilylation of alkynes[12] as well as of metal carbonyls.[13] Use of compounds **3–7** in such reactions should result in a variety of interesting, novel polyfunctionalized cyclopentadienyl complexes. Compound **7** can be expected to be a key intermediate in the synthesis of persilylated cyclopentadienyl ligands.

Experimental Section

All reactions were carried out under nitrogen with standard Schlenk tube techniques. Solvents were dried according to standard procedures and saturated with nitrogen. For the

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[10] Siegel, J.; Gutierrez, A.; Schweizer, W. B.; Ermer, O.; Mislow, K. *J. Am. Chem. Soc.* **1986**, *108*, 1569. Kahr, B.; Biali, S. E.; Schaefer, W.; Buda, A. B.; Mislow, K. *J. Org. Chem.* **1987**, *52*, 3713.

[11] Sitzmann, H.; Boese, R. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 971.

[12] Drössmar-Wolf, M. *Gmelin Handbook of* Inorganic *Chemistry*, 8th ed.; Organoiron Compounds Part A, Ferrocene 9; Springer-Verlag: Berlin, 1989; p 305.

[13] E.g.: Colomer, E.; Corriu, R. J. P.; Pleixats, R. *J. Organomet. Chem.* **1990**, *381*, C1.

Table III. Important Distances (Å) and Angles (deg) in 7

C(1A)–C(5A)	1.472 (14)	C(1A)–C(2A)	1.449 (12)	C(2A)–C(3A)	1.472 (14)
C(3A)–C(4A)	1.426 (14)	C(4A)–C(5A)	1.467 (14)	C(1A)–Si(1a)	1.864 (10)
C(2A)–Si(2A)	1.864 (9)	C(3A)–Si(3A)	1.894 (11)	C(4A)–Si(4A)	1.872 (10)
C(5A)–Si(5A)	1.873 (11)				
C(2A)–C(1A)–C(5A)	108.0 (8)	C(1A)–C(2A)–C(3A)	107.2 (8)		
C(2A)–C(3A)–C(4A)	109.2 (9)	C(3A)–C(4A)–C(5A)	108.0 (9)		
C(4A)–C(5A)–C(1A)	107.5 (8)				

chromatographic separations Kieselgel 60 from Merck was used. 2 was prepared from $Mn(CO)_5Br$ and $C_5Br_4N_2$ according to a literature procedure.[5] *n*-Butyllithium was purchased as a 1.6 M solution in hexane from Aldrich. $SiMe_2HCl$ (Fluka) was distilled from CaH_2 under nitrogen. For details of the crystal structure determination, see Table I. Positional and thermal parameters of all atoms are included in Table II; important distances and angles are in Table III.

Preparation of 3. With continuous stirring, 1.04 mL of BuLi solution (1.66 mmol) was added to a solution of 1.0 g of 2 (1.67 mmol) in 20 mL of Et_2O at −76 °C. After 30 min, 0.18 mL of $SiMe_2HCl$ (1.67 mmol) was added, and then the temperature was gradually raised to ambient temperature during 14 h. After evaporation of the solvent in vacuo, the residue was extracted with hexane, the extracts were evaporated, and the residue was chromatographed on silica gel (2.5 cm × 10 cm, eluent hexane). Recrystallization of the eluate yielded 0.87 g of analytically pure product (91%), mp 100–102 °C. ^1H NMR (270 MHz, C_6D_6) δ = 0.215 (d, $^3J(H,H)$ = 3.9 Hz, 6 H, $SiCH_3$), 4.548 (sept, $^3J(H,H)$ = 3.9 Hz, 1 H, SiH). ^{13}C NMR (68 MHz, C_6D_6) δ = −2.7 ($SiCH_3$), 80.6, 90.2, 94.9 (π-C_5R_5), 222.4 (MnCO). IR (Nujol) ν [cm^{-1}] = 2169 w (Si–H), 2039 vs, 1969 vs (MnC–O). $C_{10}H_7Br_4MnO_3Si$ (577.80) (calcd/found) C 20.79/21.02, H 1.22/1.30.

Preparation of 4. A solution of 0.50 g of 2 (0.84 mmol) in 10 mL of Et_2O was treated with 1.05 mL of BuLi solution (1.68 mmol) at −76 °C with continuous stirring. After 35 min, 0.18 mL of $SiMe_2HCl$ (1.67 mmol) was added. The temperature was raised to 20 °C during the course of 14 h. Further workup was performed as described for 3, yield 0.45 g (92%), mp 96–98 °C). ^1H NMR (270 MHz, C_6D_6) δ 0.279 (d, $^3J(H,H)$ 3.9 Hz, 6 H, $SiCH_3$), 0.312 (d, $^3J(H,H)$ = 4.0 Hz, 6 H, $SiCH_3$), 4.697 (sept, $^3J(H,H)$ = 3.9 Hz, 2 H, SiH). ^{13}C NMR (100 MHz, C_6D_6) δ = −3.11, −2.43 ($SiCH_3$), 86.14, 97.15, 101.92 (π-C_5R_5), 223.0 (Mn–CO). IR (hexane) ν [cm^{-1}] = 2169 w (Si–H), 2035 vs, 1966 vs (MnC–O). $C_{12}H_{14}Br_3MnO_3Si_2$ (557.05); C, 25.87/26.36; H, 2.53/2.61.

Preparation of 5. In a manner similar to the synthesis of 4, compound 5 is obtained from 3 by double lithiation: A solution of 0.58 g of 3 (1.00 mmol) in 10 mL of Et_2O was treated with 1.25 mL of BuLi solution (2.00 mmol) at −76 °C. After 30 min, 0.22 mL of $SiMe_2HCl$ (2.01 mmol) was added. After workup, 0.42 g of 5 was obtained (78%), mp 62.5 °C, ^1H NMR (400 MHz, C_6D_6) δ = 0.250 (d, $^3J(H,H)$ = 3.7 Hz, 6 H, $SiCH_3$), 0.368 (d, $^3J(H,H)$ = 3.9 Hz, 6 H, $SiCH_3$), 0.415 (d, $^3J(H,H)$ = 4.2 Hz, 6 H, $SiCH_3$), 4.723 (sept, $^3J(H,H)$ = 3.9 Hz, 2 H, SiH), 4.806 (sept, $^3J(H,H)$ = 3.9 Hz, 1 H, SiH). ^{13}C NMR (100 MHz, C_6D_6) δ = −1.74, −2.55, −2.78 ($SiCH_3$), 89.57, 94.20, 105.62 (π-C_5R_5), 223.6 (Mn–CO). IR (hexane) ν [cm^{-1}] = 2166 w (Si–H), 2030 vs, 1960 vs, 1955 vs (MnC–O). $C_{14}H_{21}Br_2MnO_3Si_3$ (536.30): C, 31.35/31.16; H, 3.95/4.10.

Preparation of 6. Starting from 4, 6 was prepared by double lithiation: 0.40 g of 4 (0.72 mmol), dissolved in 10 mL of Et_2O, was treated with 0.90 mL of BuLi solution (1.44 mmol) at −76 °C. After addition of 0.16 mL of $SiMe_2HCl$ (1.44 mmol) and the usual workup procedure, 0.29 g of 6 was isolated (78%), mp 101–103 °C. ^1H NMR (270 MHz, C_6D_6) δ = 0.319 (d, $^3J(H,H)$ = 3.9 Hz, 6 H, $SiCH_3$), 0.327 (d, $^3J(H,H)$ = 3.9 Hz, 6 H, $SiCH_3$), 0.402 (d, $^3J(H,H)$ = 3.9 Hz, 6 H, $SiCH_3$), 0.502 (d, $^3J(H,H)$ = 3.9 Hz 6 H, $SiCH_3$), 4.562 (m, 2 H, SiH), 4.676 (m, 2 H, SiH). ^{13}C NMR (100 MHz, C_6D_6) δ = −0.89, −1.15, −1.30, −2.37 ($SiCH_3$), 96.91, 106.41, 110.93 (π-C_5R_5), 224.3 (Mn–CO). IR (hexane) ν [cm^{-1}] = 2162 w (Si–H), 2023 vs, 1952 vs, 1945 vs (MnC–O). $C_{16}H_{28}BrMnO_3Si_4$ (515.55): C, 37.27/36.98; H, 5.47/5.61.

Preparation of 7. To a solution of 1.79 g of 5 (3.33 mmol) in 20 mL of Et_2O, 4.58 mL of BuLi solution (7.33 mmol) was added at −76 °C. After stirring for 45 min, 0.80 mL of $SiMe_2HCl$ (7.33 mmol) was added and the temperature was raised to 20 °C during the course of 14 h. After the usual workup procedure, a yield of 1.40 g of light yellow crystals were obtained (85%), mp 121–123 °C. ^1H NMR (400 MHz, 25 °C, C_6D_6) δ = 0.437 (d, $^3J(H,H)$ = 3.9 Hz, 30 H, $SiCH_3$), 4.539 (sept, $^3J(H,H)$ = 3.9 Hz, 5 H, SiH). ^{13}C NMR (68 MHz, C_6D_6) δ = −0.73 ($SiCH_3$), 109.32 (π-C_5R_5), 225.0 (Mn–CO). Low-temperature ^1H NMR (90 MHz, toluene-d_8): coalescence of the doublet at 0.45 ppm is observed at −80 °C, at −90 °C two broad signals with a distance of approximately 27 Hz can be seen. IR (hexane) ν [cm^{-1}] = 2157 w (Si–H), 2017 vs, 1940 vs (MnC–O). $C_{18}H_{35}MnO_3Si_5$ (494.80): C, 43.69/43.33; H, 7.13/6.98.

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Supplementary Material Available: Tables of atomic coordinates, bond lengths, bond angles and anisotropic displacement coefficients (8 pages). Ordering information is given on any current masthead page.

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