

Coordination Chemistry of Perhalogenated Cyclopentadienes and Alkynes, XXXII [1]. Hydrolysis of Cymantrenyl-chlorosilanes $[\text{C}_5\text{X}_{5-n}(\text{SiMe}_2\text{Cl})_n]\text{Mn}(\text{CO})_3$ ($n \geq 3$) and Formation of Cyclopentadienyl-annelated 1,2,5-Oxadisiloles

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Dedicated to Professor Hubert Schmidbaur on the occasion of his 80th birthday

When cymantrenyl-chlorosilanes $[\text{C}_5\text{X}_{5-n}(\text{SiMe}_2\text{Cl})_n]\text{Mn}(\text{CO})_3$ ($\text{X} = \text{H}$: $n = 4$; $\text{X} = \text{Br}$: $n = 3 - 5$; **1a–d**) come in contact with moist solvents, hydrolysis of two vicinal SiMe_2Cl groups occurs with condensation to give 1,2,5-oxadisiloles. With $n = 3$, only one oxadisilole ring is formed, while with $n = 4$ or 5 the formation of one and/or two oxadisiloles is observed. Similar reactions occur, when **1a–d** are treated with MeMgCl or MeOH . The molecular structures of two products, $[\text{C}_5\text{Br}_2(\text{SiMe}_2\text{Cl})(\text{Si}_2\text{Me}_4\text{O})]\text{Mn}(\text{CO})_3$ and $[\text{C}_5(\text{SiMe}_2\text{OMe})(\text{Si}_2\text{Me}_4\text{O})_2]\text{Mn}(\text{CO})_3$, are reported.

Key words: Cymantrene, Chlorosilanes, Oxadisilole, Crystal Structure Determination

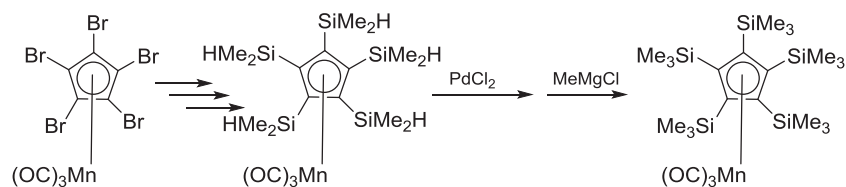
Introduction

Chlorosilanes are arguably the most versatile reagents for the preparation of organosilicon compounds [2]. For example, they can be used for an easy build-up of silicon-carbon [3] and silicon-oxygen bonds, which can be used for the protection of oxygen-containing functional groups in organic synthesis [4], as well as for the modification of surface OH groups in materials chemistry [5], and last, but not least, the production of silicones and other silicon-containing polymers [6]. Their high affinity for hydroxyl groups makes them very prone to hydrolysis reactions, and thus strictly inert reaction conditions are usually necessary in order to obtain pure products. In metallocene chemistry, mainly chlorosilane derivatives of ferrocene [7–9] and Cp_2MX_2 ($M = \text{Ti}, \text{Zr}, \text{Hf}$) [10, 11] have been reported, and the ease of the hydrolysis of the Si–Cl bond has been noted. When we started a project directed towards coordination compounds of the pentakis(trimethylsilyl)cyclopentadienyl ligand $[\text{C}_5(\text{SiMe}_3)_5]$ several years ago, [12], [13] we chose the synthetic pathway summarized in Scheme 1.

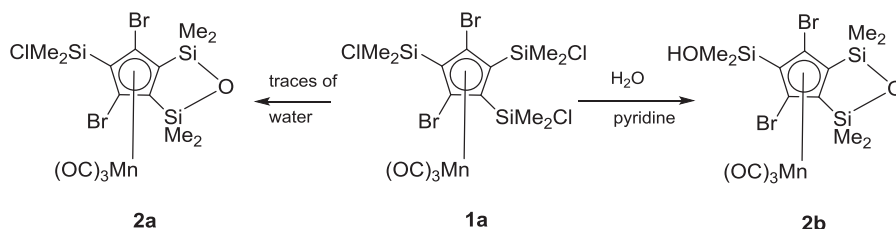
It turned out that the intermediate chlorosilanes $[\text{C}_5\text{X}_{5-n}(\text{SiMe}_2\text{Cl})_n]\text{Mn}(\text{CO})_3$ could not be isolated in pure form and had to be generated *in situ*. The analytical data of the isolated chlorosilanes suggested a loss of chlorine and formation of some kind of siloxanes. We now have decided to have a closer look at these hydrolysis reactions and to isolate and characterize the products.

Results and Discussion

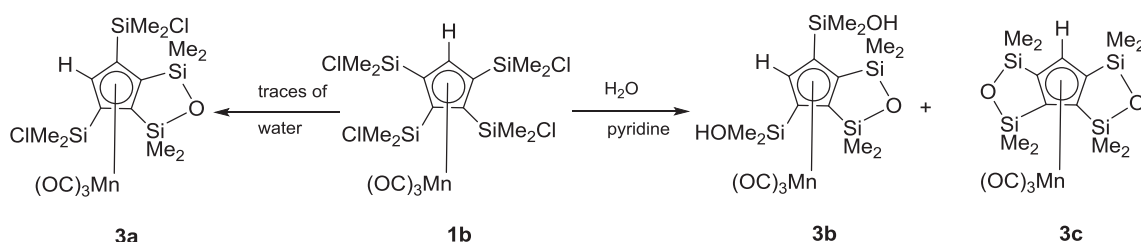
When a pentane solution of $[\text{C}_5\text{Br}_2(\text{SiMe}_2\text{Cl})_3]\text{Mn}(\text{CO})_3$ (**1a**) is allowed to stand for several days at -20°C , yellow crystalline needles precipitate, which are suitable for a crystal structure determination. These crystals turned out to be the oxadisilole complex $[\text{C}_5\text{Br}_2(\text{SiMe}_2\text{Cl})(\text{Si}_2\text{Me}_4\text{O})]\text{Mn}(\text{CO})_3$ (**2a**). The NMR spectra of solutions of these crystals in C_6D_6 , however, showed the presence of another species, probably of the silanol **2b**. A ferrocenyl oxadisilole was reported as a product of the oxidative decomposition of $\text{CpFe}(\text{C}_5\text{H}_3(\text{SiMe}_2\text{C}_5\text{H}_4\text{SiMe}_2))$ and characterized by ^1H and ^{13}C NMR spectroscopy [14]. Com-



Scheme 1.



Scheme 2.



Scheme 3.

pound **2b** could be prepared in a pure form, when an ethereal solution of **1a** was treated with water in the presence of a few drops of pyridine (Scheme 2).

The NMR spectra of freshly prepared solutions of $[\text{C}_5\text{H}(\text{SiMe}_2\text{Cl})_4]\text{Mn}(\text{CO})_3$ (**1b**) always show varying amounts of another species to which we assign the constitution $[\text{C}_5\text{H}(\text{SiMe}_2\text{Cl})_2(\text{Si}_2\text{Me}_4\text{O})]\text{Mn}(\text{CO})_3$ (**3a**). Deliberate addition of water to ethereal solutions of **1b** in the presence of a few drops of pyridine yields a mixture of several compounds, from which the mono-oxadisilole $[\text{C}_5\text{H}(\text{SiMe}_2\text{OH})_2(\text{Si}_2\text{Me}_4\text{O})]\text{Mn}(\text{CO})_3$ (**3b**) and the bis-oxadisilole $[\text{C}_5\text{H}(\text{Si}_2\text{Me}_4\text{O})_2]\text{Mn}(\text{CO})_3$ (**3c**) could be identified by mass spectrometry (Scheme 3).

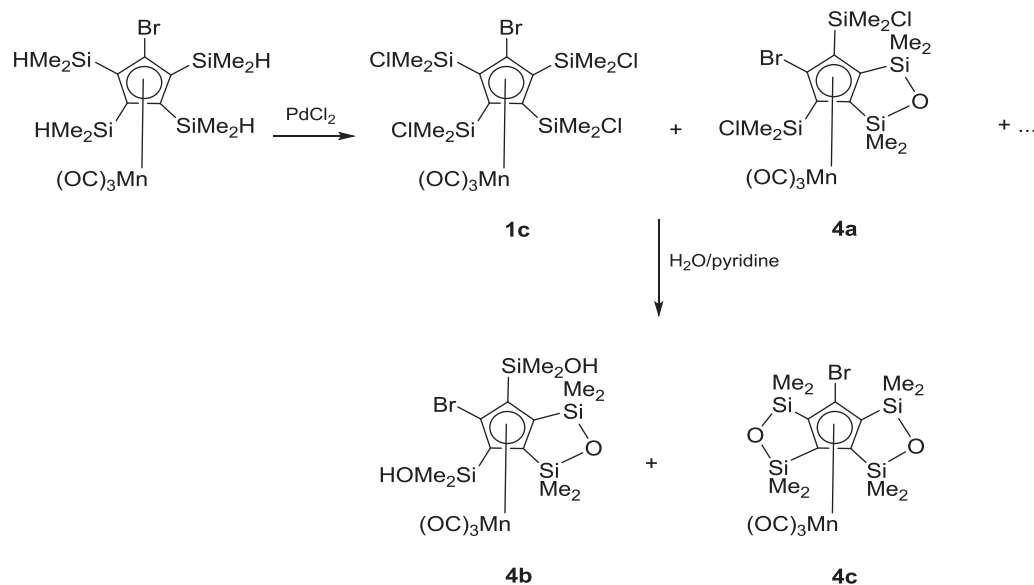
Presumably the main product (*ca.* 65% of the mixture) **3b** is formed by further hydrolysis of **3a**, while **3c** is an alternative hydrolysis product of **1b**.

The chlorination of $[\text{C}_5\text{Br}(\text{SiMe}_2\text{H})_4]\text{Mn}(\text{CO})_3$ with PdCl_2 always leads to a complex product mixture. The presence of several singlet signals and a septet in the region $\delta = 4.0\text{--}5.0$ ppm indicates incomplete chlorination of the Si–H function as well as desilyla-

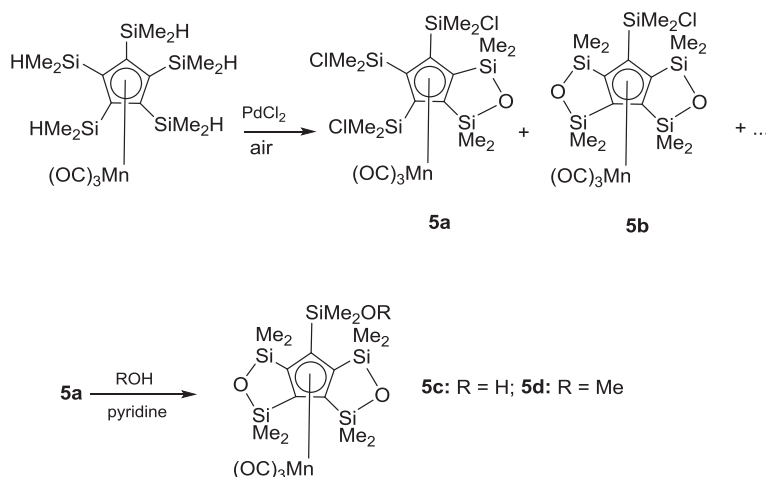
tion, most likely induced by the HCl formed during chlorination. However, the main products of the reaction are the desired $[\text{C}_5\text{Br}(\text{SiMe}_2\text{Cl})_4]\text{Mn}(\text{CO})_3$ (**1c**) and a product which we believe is the bromo-analog of mono-oxadisilole **3a**, namely $[\text{C}_5\text{Br}(\text{SiMe}_2\text{Cl})_2(\text{Si}_2\text{Me}_4\text{O})]\text{Mn}(\text{CO})_3$ (**4a**). Controlled hydrolysis of this mixture by addition of water in the presence of pyridine yields a product mixture with the bis-oxadisilole $[\text{C}_5\text{Br}(\text{Si}_2\text{Me}_4\text{O})_2]\text{Mn}(\text{CO})_3$ (**4c**) as the main product. The mono-oxadisilole $[\text{C}_5\text{Br}(\text{SiMe}_2\text{OH})_2(\text{Si}_2\text{Me}_4\text{O})]\text{Mn}(\text{CO})_3$ (**4b**) is the only other product that could be identified by mass spectrometry and NMR spectroscopy (Scheme 4).

Indirect proof of the suggested structure **4b** comes from an unexpected product of the attempted synthesis of $[\text{C}_5\text{Br}(\text{SiMe}_3)_4]\text{Mn}(\text{CO})_3$ *via* methylation of the original chlorination mixture with MeMgCl . The crystals that could be isolated after product purification turned out to be the mono-oxadisilole $[\text{C}_5\text{Br}(\text{SiMe}_3)_2(\text{Si}_2\text{Me}_4\text{O})]\text{Mn}(\text{CO})_3$ (**4d**) [15].

The chlorination of $[\text{C}_5(\text{SiMe}_2\text{H})_5]\text{Mn}(\text{CO})_3$ with PdCl_2 under rigorous exclusion of moisture and



Scheme 4.



Scheme 5.

air, followed by reaction with MeMgCl gives a complex product mixture, from which the desired $[\text{C}_5(\text{SiMe}_3)_5]\text{Mn}(\text{CO})_3$ could only be identified by HRMS [12]. Although this is an indication that the pentakis-chlorosilane $[\text{C}_5(\text{SiMe}_2\text{Cl})_5]\text{Mn}(\text{CO})_3$ (**1d**) had been formed, all attempts to isolate this compound met with failure. Instead, only the mono-oxadisilole $[\text{C}_5(\text{SiMe}_2\text{Cl})_3(\text{Si}_2\text{Me}_4\text{O})]\text{Mn}(\text{CO})_3$ (**5a**) could be isolated. When the chlorination was performed in air, the reaction yielded,

besides **5a**, also the bis-oxadisilole $[\text{C}_5(\text{SiMe}_2\text{Cl})(\text{Si}_2\text{Me}_4\text{O})_2]\text{Mn}(\text{CO})_3$ (**5b**). Deliberate addition of water to an ethereal solution of **5a** in the presence of pyridine leads to the formation of the silanol-bis-oxadisilole $[\text{C}_5(\text{SiMe}_2\text{OH})(\text{Si}_2\text{Me}_4\text{O})_2]\text{Mn}(\text{CO})_3$ (**5c**) (Scheme 5).

Indirect proof of the proposed structure of **5c** comes from the methanolysis of a mixture of **5a/b**. The crystals formed after recrystallization turned out to be $[\text{C}_5(\text{SiMe}_2\text{OMe})(\text{Si}_2\text{Me}_4\text{O})_2]\text{Mn}(\text{CO})_3$ (**5d**) [16].

Table 1. ^1H NMR data of compounds **2**–**5**.

Comp.	δ (SiCH_3)	Other signals (assignment)
2a	0.776, 0.445, 0.143	–
2b	0.501, 0.485, 0.193	1.946 (1H, Si–OH)
3a	0.594, 0.436, 0.364, 0.351	5.276 (1H, Cp–H)
3b	0.670, 0.372, 0.223, 0.138	5.119 (1H, Cp–H), 1.162 (2H, Si–OH)
3c	0.491, 0.461, 0.194, 0.156	4.522 (1H, Cp–H)
4a	0.900, 0.766, 0.672, 0.594	–
4b	0.659, 0.464, 0.284, 0.211	1.135 (2H, Si–OH)
4c	0.582, 0.399, 0.253, 0.163	–
5a	0.738, 0.710, 0.652, 0.438	–
5b	0.652, 0.473, 0.457, 0.362, 0.182	–
5c	0.649, 0.506, 0.336, 0.216, 0.195	1.357 (1H, Si–OH)

Table 2. ^{13}C NMR data of compounds **2**–**5**.

Comp.	δ (SiCH_3)	δ (C_5R_5)	δ (Mn–CO)
2a	4.8, 1.1, 1.0	104.7, 94.3, 87.0	222.6
2b	2.5, 1.2, 1.1	103.9, 96.7, 93.0	223.9
3a	3.6, 3.3, 2.7	114.8, 111.0, 91.1	224.0
3b	2.6, 2.4, 2.1, 2.0	114.1, 106.3, 94.2	225.4
3c	2.9, 2.2, 2.1, 1.1	109.0, 107.7, 94.7	225.3
4a	8.4, 8.2, 6.2, 0.4	108.0, 105.0, 96.2	222.7
4c	2.9, 1.9, 1.2, 1.0	109.5, 107.8, 96.8	224.7
5a	7.6, 7.5, 7.1, 5.4, 3.2	119.7, 112.4, 102.4	223.5
5b	8.7, 3.0, 2.9, 2.8, 1.8	117.9, 111.8, 97.7	225.0
5c	2.9, 2.80, 2.77, 2.6, 1.8	116.8, 110.9, 102.4	225.5

All new compounds were characterized by their ^1H and ^{13}C NMR spectra (Tables 1 and 2).

The chemical shifts in the ^1H and ^{13}C NMR spectra are more influenced by the substitution pattern of the cyclopentadienyl ring – Br_2Si_3 vs. HSi_4 vs. BrSi_4 vs. Si_5 – than by the particular substituents at silicon. Thus no assignment of the oxadisilole unit can be made from the chemical shifts alone. In the IR spectra absorptions at *ca.* 1250 cm^{-1} might be associated with the Si–O–Si linkage of a cyclic disiloxane [17], but IR data of such substances for comparison are scarce in the literature.

The silanols **2b**, **3b** and **5c** are characterized by weak but sharp $\nu(\text{OH})$ absorptions at 3660, 3646 and 3686 cm^{-1} , respectively, resulting from isolated SiOH groups, and medium intensity broad absorptions at *ca.* $3400\text{--}3410\text{ cm}^{-1}$ indicating hydrogen bonds.

Molecular structures of **2a** and **5d**

In the structure of **2a** (Fig. 1) the cyclopentadienyl ring ($\sigma_{\text{pln}} = 0.011$)¹ and the oxadisilole ring ($\sigma_{\text{pln}} =$

¹The σ_{pln} parameter as defined in the program PLATON, implemented in WINGX.

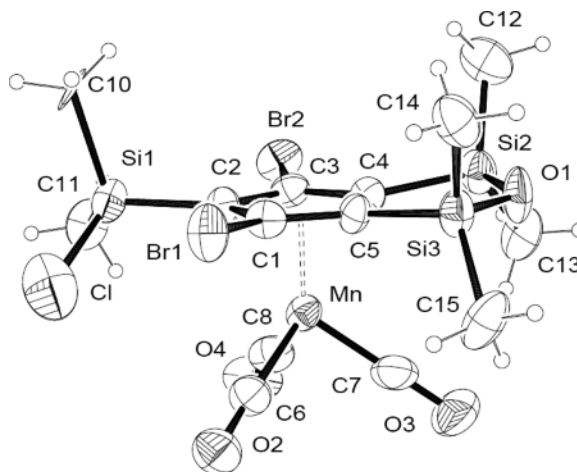


Fig. 1. ORTEP-III view of the molecular structure of $[\text{C}_5\text{Br}_2(\text{SiMe}_2\text{Cl})(\text{Si}_2\text{Me}_4\text{O})]\text{Mn}(\text{CO})_3$ (**2a**) in the crystal. Displacement ellipsoids are drawn at the 30% probability level, H atoms as spheres with arbitrary radii.

0.073) are nearly coplanar (interplanar angle 4.7°), and the oxadisilole unit is slightly twisted along Si2–O1. The Si–O–Si angle has a value of $122.2(5)^\circ$, and the corresponding Si–O bonds measure $1.648(9)$ and $1.640(8)\text{ \AA}$. All five substituents of the cyclopentadienyl ring are situated on the distal side relative to the manganese atom. The strange displacement ellipsoid of carbon atom C10 together with the relatively large B_{iso} value of the chlorine atom Cl might be either the consequence of a positional disorder between these two atoms, or, alternatively, a co-crystallized molecule of the silanol **2b**, with the OH group on one of these positions. However, the quality of the data set did not allow a resolution of this problem.

In the structure of **5d**, the cyclopentadienyl ring ($\sigma_{\text{pln}} = 0.004$) and the two oxadisilole rings ($\sigma_{\text{pln}}(\text{Si1–O4–Si2–C5–C4}) = 0.063$ and $\sigma_{\text{pln}} = 0.071$) are nearly coplanar with interplanar angles of 4.6 and 3.3° . Both oxadisilole units are slightly twisted along Si2–O4 and Si3–O5, respectively. The disiloxane angles Si1–O4–Si2 and Si3–O5–Si4 amount to $120.3(2)^\circ$ and $120.4(2)^\circ$, respectively, and are thus *ca.* 2° smaller than in **2a**. The Si–O bond lengths within the rings measure $1.645\text{--}1.656(5)\text{ \AA}$ and $1.658(5)\text{ \AA}$ for the Si–OMe bond and are thus slightly longer than in **2a**. All silicon atoms reside on the distal side of the cyclopentadienyl ring.

The structure of one $\text{Mo}(\text{CO})_3$ complex of a cyclopentadienyl-annulated oxadisilole has been mentioned

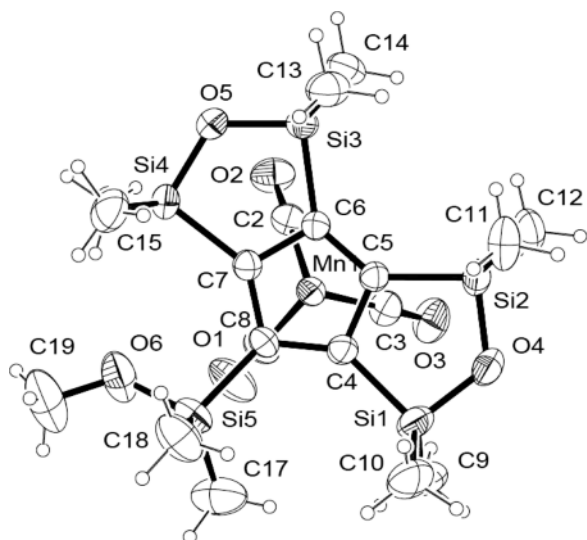


Fig. 2. ORTEP-III view of the molecular structure of $[C_5(SiMe_2OMe)(Si_2Me_4O)_2]Mn(CO)_3$ (**5d**) in the crystal. Displacement ellipsoids are drawn at the 30% probability level, H atoms as spheres with arbitrary radii.

in the literature, however, no structural parameters have been given [18]. A few crystal structure determinations of benzene-annelated oxadisiloles have been reported, the most interesting of them being the benzotrioxadisilole $[C_6(Si_2Me_4O)_3]$ [19]. Here the four rings are nearly coplanar, with Si–O bond lengths ranging from 1.641 to 1.647 Å and Si–O–Si angles between 117.3 and 117.7°. Thus the Si–O bonds have more or less identical values as are found in our compounds, but the angles are significantly smaller, which certainly is a consequence of the shorter Si–Si distances in the six-membered rings compared to those in our five-membered rings. For comparison, in the less strained disiloxane-bridged ferrocenophane $[Fe(C_5H_4SiMe_2O-SiMe_2C_5H_4)]$ the Si–O bonds measure 1.630–1.637 Å with an Si–O–Si angle of 143.6° [20], while the dinuclear strain-free $FcSiMe_2O-SiMe_2Fc$ moiety contains a close to linear Si–O–Si unit (159.9°) and even shorter Si–O bonds (*ca.* 1.62 Å) [21].

Experimental Section

All reactions were performed under dry nitrogen using standard Schlenk tube techniques. The Schlenk tubes were carefully flame-dried under dynamic vacuum and cooled to ambient temperature under dry nitrogen. The solvents were dried with standard procedures and saturated with nitrogen. The $PdCl_2$ (Degussa) used for the chlorinations was heated

in vacuo at 80 °C for 3–4 d immediately before use. Silica gel (“Kieselgel 60”, Merck) was heated several hours *in vacuo* at 400 °C. After cooling to r. t. freshly distilled Et_2O and $SiMe_3Cl$ were added and the mixture stirred for several days. The solvent and unreacted $SiMe_3Cl$ were evaporated *in vacuo*, and the obtained “silanized silica gel” was dried for several hours *in vacuo* at r. t. The cymantrenyl-hydrosilanes $[C_5X_{5-n}(SiMe_2H)_n]Mn(CO)_3$ were prepared as described by us earlier [22].

Dibromo-1,2,4-tris(chlorodimethylsilyl)-cyclopentadienyl-tricarbonyl manganese, $[C_5Br_2(SiMe_2Cl)_3]Mn(CO)_3$ (**1a**), and formation of its hydrolysis products $[C_5Br_2(SiMe_2Cl)(Si_2Me_4O)]Mn(CO)_3$ (**2a**) and $[C_5Br_2(SiMe_2OH)(Si_2Me_4O)]Mn(CO)_3$ (**2b**)

A solution of $[C_5Br_2(SiMe_2H)_3]Mn(CO)_3$ (1.650 g, 3.08 mmol) in dry benzene (5 mL) is treated with dry $PdCl_2$ (2.026 g, 11.43 mmol). The mixture turns black immediately and is stirred for 15 h at r. t. Then the solvent is evaporated *in vacuo* and the residue extracted several times with 10 mL portions of dry pentane. The combined extracts are evaporated to dryness, leaving **1a** (1.951 g, ~2.99 mmol, 97%) as a yellow oil. – IR (film): $\nu(CO) = 2028$ vs, 1953 vs, cm^{-1} . – 1H NMR (270 MHz, C_6D_6): $\delta = 0.73$ (s, 6H), 0.72 (s, 6H), 0.67 ppm (s, 6H). – ^{13}C NMR (68 MHz, C_6D_6): $\delta = 222.3$ (CO), 105.0, 94.9, 88.1 (C_5R_5), 7.1, 7.0, 5.8 ppm ($SiCH_3$).

1.0 g of the yellow oil is dissolved in 10 mL pentane, and this solution is kept in a freezer at –20 °C for several days. Yellow needle-like crystals of $[C_5Br_2(SiMe_2Cl)(Si_2Me_4O)]Mn(CO)_3$ (**2a**) are formed (395 mg, 40%), which are suitable for an X-ray crystal structure determination. – IR (nujol mull): $\nu(CO) = 2030$ vs, 1954 vs, cm^{-1} . NMR data see Tables 1 and 2.

550 mg of the yellow oil is dissolved in Et_2O (10 mL) and treated with water (1.0 mL, 55.5 mmol) and ten drops of pyridine. A colorless precipitate is formed immediately. Stirring is continued for one hour, and the solvent is evaporated *in vacuo*. The residue is extracted with two 10 mL portions of pentane, and the combined extracts are stirred with addition of dry Na_2SO_4 overnight. The suspension is filtered and the filtrate evaporated to dryness and dried *in vacuo*. $[C_5Br_2(SiMe_2OH)(Si_2Me_4O)]Mn(CO)_3$, **2b**, is obtained as a yellow powder (255 mg, 0.45 mmol, 52%). – IR (nujol mull): $\nu(OH) \approx 3660$ w, 3400 br, cm^{-1} , $\nu(CO) = 2029$ vs, 1952 vs, cm^{-1} . – $C_{14}H_{19}Br_2MnO_5Si_3 \cdot 0.25 C_5H_{12}$ (581.06): calcd. C 31.52, H 3.82; found C 31.53, H 3.87.

[C_5H(SiMe_2Cl)_4]Mn(CO)_3 (**1b**), and formation of its hydrolysis products $[C_5H(SiMe_2Cl)_2(Si_2Me_4O)]Mn(CO)_3$ (**3a**), $[C_5H(SiMe_2OH)_2(Si_2Me_4O)]Mn(CO)_3$ (**3b**) and $[C_5H(Si_2Me_4O)_2]Mn(CO)_3$ (**3c**)

A solution of $[C_5H(SiMe_2H)_4]Mn(CO)_3$ (1.988 g, 4.55 mmol) in dry benzene (10 mL) is treated with dry

PdCl₂ (4.840 g, 27.29 mmol) which results in the immediate formation of a black suspension with considerable heat evolution. After stirring for three days at r. t., the solvent is evaporated *in vacuo*. The residue is extracted with three 5 mL portions of dry *n*-hexane. The combined extracts are filtered and evaporated to dryness, leaving a yellow oil (2.312 g). According to the NMR spectra the oil consists of varying amounts, from 1 : 1 to 1 : 2, of **1b** and **3a**. – NMR data of **1b**: ¹H NMR (270 MHz, C₆D₆): δ = 6.11 (s, 1H, C₅H), 0.72/0.71 (2s, 12H, SiCH₃), 0.66 (s, 6H, SiCH₃), 0.62 ppm (s, 6H, SiCH₃). – ¹³C NMR (68 MHz, C₆D₆): δ = 223.2 (CO), 112.4, 107.4, 96.3 (C₅R₅), 7.4, 7.1, 6.4, 6.2 ppm (SiCH₃).

A solution of the yellow oil (385 mg, *ca.* 0.67 mmol) in Et₂O (5 mL) is treated with water (0.50 mL, 28 mmol) and 20 drops of pyridine, and the mixture is stirred for 2 h. The solvent is removed *in vacuo* and the residue taken up in 20 mL pentane and filtered through a small column filled with silanized silica gel. Evaporation of the eluate yields a yellow powder, which according to its NMR data consists of a 10 : 1 mixture of **3b** and **3c**. – MS ((+)-DEI): *m/z* = 482 (**3b**, [M]⁺, 8%), 464 (**3c**, [M]⁺, 7%), 454 (**3b**, [M–CO]⁺, 6%), 408 (**3c**, [M–2CO]⁺, 8%), 398 (**3b**, [M–3CO]⁺, 100%), 380 (**3c**, [M–3CO]⁺, 97%).

Careful recrystallization of the powder yields **3b** as yellow microcrystals (220 mg, 0.45 mmol, 68%). – IR (Nujol): ν(OH) = 3646 w, 3410 m, br, cm^{–1}; ν(CO) = 2018 vs, 1939 vs, cm^{–1}. – C₁₆H₂₇MnSi₄O₆·0.25 C₅H₁₂ (500.58): calcd. C 41.39, H 6.04; found C 41.25, H 5.86.

[C₅Br(SiMe₂Cl)₄]Mn(CO)₃ (**1c**), and formation of its hydrolysis products [C₅Br(SiMe₂Cl)₂(Si₂Me₄O)]Mn(CO)₃ (**4a**), [C₅Br(SiMe₂OH)₂(Si₂Me₄O)]Mn(CO)₃ (**4b**) and [C₅Br(Si₂Me₄O)₂]Mn(CO)₃ (**4c**)

A solution of [C₅Br(SiMe₂H)₄]Mn(CO)₃ (3.000 g, 5.82 mmol) in dry benzene (10 mL) is treated with dry PdCl₂ (6.115 g, 34.49 mmol) which results in the immediate formation of a black suspension with considerable heat evolution. After stirring for five days at r. t., the solvent is evaporated *in vacuo*. The residue is extracted with three 5 mL portions of dry *n*-hexane. The combined extracts are filtered and evaporated to dryness, leaving a yellow solid (3.480 g). According to the NMR spectra it contains the desired **1c** and its first hydrolysis product **4a**, together with several unidentified compounds. – NMR data of **1c**: ¹H NMR (270 MHz, C₆D₆): δ = 0.933 (s, 6H, SiCH₃), 0.813 (br, 12H, SiCH₃), 0.772 ppm (s, 6H, SiCH₃). – ¹³C NMR (68 MHz, C₆D₆): δ = 222.3 (CO), 109.8, 109.1, 98.1 (C₅R₅), 10.5, 7.9, 7.6 ppm (SiCH₃).

A solution of the yellow solid (220 mg, *ca.* 0.3 mmol) in Et₂O (5 mL) is treated with water (0.50 mL, 27.8 mmol) and 15 drops of pyridine, and the mixture is stirred for 200 min. The solvent is removed *in vacuo* and the residue taken up

in 20 mL pentane and filtered through a small column filled with silanized silica gel. Evaporation of the eluate yields a yellow powder, which contains according to the NMR data the bis-oxadisilole **4c** as the main component together with the bis-silanol **4b** and other unidentified by-products. – MS ((+)-DEI): *m/z* = 560/562 (**4b**, [M]⁺, 1%), 542/544 (**4c**, [M]⁺, 4%), 476/478 (**4b**, [M–3CO]⁺, 17%), 458/460 (**4c**, [M–3CO]⁺, 100%).

A few yellow crystals that precipitate from the C₆D₆ solution are identified as pure **4c**. – IR (Nujol): ν(CO) = 2023 vs, 1984 vs, cm^{–1}. – C₁₆H₂₄BrMnO₅Si₄ (543.37): calcd. C 35.33, H 4.45; found C 34.36, H 4.63.

Formation of [C₅Br(SiMe₃)₂(Si₂Me₄O)]Mn(CO)₃ (**4d**)

A fraction (366 mg, ~0.56 mmol) of the product mixture obtained in the chlorination of [C₅Br(SiMe₂H)₄]Mn(CO)₃ is dissolved in dry Et₂O (10 mL) and treated with a 3 M THF solution of MeMgCl (0.75 mL, 2.25 mmol). Stirring at r. t. is continued for 15 h. The solvents are evaporated *in vacuo*, and the residue is taken up in pentane (10 mL), hydrolyzed by addition of a few drops of water and filtered through silica gel. Leaving the filtrate for several days in a freezer at –20 °C produces a few crystalline needles, which are suitable for a crystal structure determination. – IR (nujol): ν(CO) = 2020 vs, 1947 vs, 1940 vs, cm^{–1}. – ¹H NMR (270 MHz, C₆D₆): δ = 0.58 (s, 18H, SiMe₃), 0.33 (s, 6H, SiMe₂), 0.26 ppm (s, 6H, SiMe₂). – ¹³C NMR (68 MHz, C₆D₆): δ = 224.7 (CO), 112.5, 111.6, 94.2 (C₅R₅), 2.9/2.8 (Si₂Me₄O), 1.0 ppm (SiMe₃). – C₁₈H₃₀BrMnO₄Si (557.66): calcd. C 38.77, H 5.42; found C 38.54, H 5.28. – Crystal structure data: orthorhombic, *Pnma*; *a* = 13.989(4), *b* = 19.488(6), *c* = 9.882(3) Å, *Z* = 4; 3530 reflections collected, 1046 observed (*I* > 2 σ(*I*)); 136 parameters refined; *R*1 = 0.0492; residual electron density +0.38/–0.40 [15].

[C₅(SiMe₂Cl)₃(Si₂Me₄O)]Mn(CO)₃ (**5a**),
[C₅(SiMe₂Cl)(Si₂Me₄O)₂]Mn(CO)₃ (**5b**),
[C₅(SiMe₂OH)(Si₂Me₄O)₂]Mn(CO)₃ (**5c**), and
[C₅(SiMe₂OMe)(Si₂Me₄O)₂]Mn(CO)₃ (**5d**)

(a) Under argon atmosphere, a solution of [C₅(SiMe₂H)₅]Mn(CO)₃ (1.515 g, 3.06 mmol) in dry benzene (10 mL) is treated with dry PdCl₂ (3.802 g, 21.44 mmol) which results in the immediate formation of a black suspension with considerable heat evolution. After stirring for three days at r. t. the solvent is evaporated *in vacuo*. The residue is extracted with three 5 mL portions of dry *n*-hexane. The combined extracts are filtered and evaporated to dryness, leaving **5a** as a yellow microcrystalline solid (1.670 g, 3.00 mmol, 98%). – IR (CCl₄): ν(CO) = 2024 vs, 1953 vs, 1944 vs, cm^{–1}.

(b) A solution of [C₅(SiMe₂H)₅]Mn(CO)₃ (200 mg, 0.40 mmol) in benzene (5 mL) is treated in air with PdCl₂

(502 mg, 2.83 mmol), and the mixture is stirred for 15 h. Evaporation of the solvent, extraction of the residue with pentane, filtration through silanized silica gel, and evaporation of the eluate *in vacuo* yield a yellow oil (245 mg), which according to the NMR spectra contains a mixture of **5a** and **5b**.

- (c) A solution of **5a** (294 mg, *ca.* 0.53 mmol) in Et₂O (5 mL) is treated with water (0.50 mL, 27.8 mmol) and 20 drops of pyridine, and the mixture is stirred for 4 h. The solvent is removed *in vacuo* and the residue taken up in 20 mL pentane and filtered through a small column filled with silanized silica gel. Evaporation of the eluate yields **5c** as a yellow-orange powder (240 mg, 0.44 mmol, 83 %). – IR: (nujol): $\nu(\text{CO}) = 2015$ vs, 1936 vs; $\nu(\text{OH}) = 3686$ w, 3410 m, br, cm^{-1} . – MS ((+)-DEI): $m/z(\%) = 538$ (4) [M]⁺, 454 (100) [M–3CO]⁺. – C₁₈H₃₁MnO₆Si₅ (538.61): calcd. C 40.10, H 5.80; found C 40.71, H 5.57.
- (d) A solution of **5a** (294 mg, *ca.* 0.53 mmol) in Et₂O (5 mL) is treated with methanol (0.11 mL, 2.71 mmol) and 20 drops of pyridine, and the mixture is stirred for 1 h. The solvent is removed *in vacuo* and the residue taken up in 20 mL pentane and filtered through a small column filled with silanized silica gel. Evaporation of the eluate to about 5 mL and leaving the solution for several days in a freezer at –20 °C yields **5d** as faint-yellow platelets that are suitable for a crystal structure determination. – IR: (nujol): $\nu(\text{CO}) = 2016$ vs, 1937 vs, cm^{-1} . – ¹H NMR (270 MHz, C₆D₆): $\delta = 3.137$ (s, 3H, OCH₃), 0.654, 0.511, 0.321, 0.226, 0.206 ppm (5 × s, 30H, SiMe₂); ¹³C NMR (100 MHz, C₆D₆): $\delta = 225.4$ (CO), 117.5, 110.8, 100.3 (C₅R₅), 49.6 (OCH₃), 2.9, 2.7, 2.3, 1.8, 0.1 ppm (SiMe₂). – C₁₉H₃₃MnO₆Si₅ (552.84): calcd. C 41.26, H 6.02; found C 41.26, H 6.41.

X-Ray structure determinations

A yellow needle of **2a** was mounted with epoxy glue to the top of a glass fiber. The structure determination was performed on a Syntex R3 diffractometer. A yellow platelet of **5d** was fixed in a glass capillary. The structure determination was performed on a Nonius CAD4 diffractometer. Data were collected in ω -scan technique, using

Table 3. Crystal structure data for **2a** and **5d**.

Compound	2a	5d
Empirical formula	C ₁₄ H ₁₈ Br ₂ ClMnO ₄ Si ₃	C ₁₉ H ₃₃ MnO ₆ Si
<i>M_r</i>	584.76	552.84
Crystal size, mm ³	0.70 × 0.20 × 0.08	0.53 × 0.47 × 0.20
Crystal system	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>C</i> 2/ <i>c</i>
<i>a</i> , Å	10.981(3)	21.257(6)
<i>b</i> , Å	14.184(6)	15.012(4)
<i>c</i> , Å	15.268(4)	21.484(6)
β , deg	105.455(18)	120.56(2)
<i>V</i> , Å ³	2292.2(13)	5903.4(28)
<i>Z</i>	4	8
<i>D</i> _{calcd.} , g cm ^{–3}	1.70	1.24
μ (MoK α), cm ^{–1}	43.5	6.8
<i>F</i> (000), <i>e</i>	1152	2320
<i>hkl</i> range	–3 ≤ <i>h</i> ≤ 11 0 ≤ <i>k</i> ≤ 15 –16 ≤ <i>l</i> ≤ 16	–23 ≤ <i>h</i> ≤ 20 0 ≤ <i>k</i> ≤ 16 0 ≤ <i>l</i> ≤ 23
Refl. measured	4251	4233
Refl. unique/ <i>R</i> _{int}	3027/0.0793	4103/0.0102
Param. refined	232	291
<i>R</i> 1 (<i>F</i>)/ <i>wR</i> 2 (<i>F</i> ²) (all refls.)	0.1427/0.1806	0.0520/0.1239
GoF (<i>F</i> ²)	1.013	1.075
$\Delta\rho_{\text{fin}}$ (max/min), <i>e</i> Å ^{–3}	0.47/–0.70	0.45/–0.25

MoK α radiation with a graphite monochromator. The structure solution and refinement were performed using the SHELXS/L programs [23, 24], and the evaluation of the geometric parameters was carried out with the program PLATON as implemented in WINGX [25–28]. Numerical details of the structure determinations are summarized in Table 3.

CCDC 1017523 and 200857 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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