ELSEVIER

www.elsevier.nl/locate/jorganchem

Journal of Organometallic Chemistry 590 (1999) 129–137

Journal of Organo metallic Chemistry

Ferrocenylethenylsilatranes and a cymantrenylsilatrane

Bjørn Pedersen [a], Gabriele Wagner [a,1], Rudolf Herrmann [a,*], Wolfgang Scherer [b], Klaus Meerholz [c], Elmar Schmälzlin [c], Christoph Bräuchle [c]

[a] *Institut für Organische Chemie und Biochemie der Technischen Universität München, Lichtenbergstrasse 4, D-85747 Garching, Germany*
[b] *Anorganisch-Chemisches Institut der Technischen Universität München, Lichtenbergstrasse 4, D-85747 Garching, Germany*
[c] *Institut für Physikalische Chemie der Ludwig-Maximilians-Universität München, Butenandtstrasse 5-13, Haus E, D-81377 Munich, Germany*

Received 29 June 1999; accepted 14 July 1999

Abstract

The syntheses, properties and crystal structures of two isomeric ferrocenylethenylsilatranes and 1-(3-methylcymantrenyl)silatrane are reported. The organometallic moieties and the silatrane show little structural influence on each other. The Si–N distances remain in the expected range of 2.13–2.22 Å, asserting the hypervalency of silicon. The electron-donating effect of the silatrane group is transmitted through the C–C double bond to ferrocene, as shown by the redox potentials. The first hyperpolarizability of the ferrocene derivatives was determined by hyper-Rayleigh scattering. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Silatrane; Ferrocene; Cymantrene; Non-linear optics

1. Introduction

Silatranes (5-aza-2,8,9-trioxa-1-silabicyclo[3.3.3]-undecanes) are cage compounds which contain a hypervalent silicon atom with a transannular (comparatively weak) bond to nitrogen (bond length 2.0–2.4 Å). This bond is responsible for their chemical stability, e.g. towards hydrolysis [1–4]. Although a great variety of substituents at silicon were introduced, there are only a few silatranes containing transition metals (e.g. [5–7]). This is surprising, since interactions of the transition metal with the silatrane moiety are conceivable, and new applications can be envisaged. Thus, it was found that a silatrane moiety acts as a net electron donor towards a ferrocene directly connected to it [8,9]. We therefore decided to investigate silatranes as potential materials for applications in non-linear optics (NLO). Although transition metal compounds, in particular ferrocene derivatives, have been studied intensely with respect to NLO properties [10,11], nothing is known about silatranes.

In this article, we present the synthesis, structure and properties of silatranes connected to ferrocene via a double bond, and of the first silatrane containing a cymantrene moiety.

2. Syntheses

The synthesis of the ferrocene and cymantrene derivatives is straightforward and shown in Fig. 1. We first decided to use the Heck reaction [12] for the synthesis of the ferrocenylethenylsilatranes (iodoferrocene and 1-ethenylsilatrane **1** under palladium catalysis). The regioselectivity should be governed mainly by the donor/acceptor properties of the substituents at the olefinic double bond, where donor substituents (e.g. alkoxy groups) give a higher amount of α-product [13]. Since the silatrane moiety can be considered as a strong donor, as seen by its influence on the redox potentials of ferrocenylsilatranes [9], one might expect a mixture of α- and β-products with excess of the α-compound **2**. Surprisingly, we found *exclusively* the α-product, re-

---

[*] Corresponding author. Tel.: +49-89-28913325; fax: +49-89-28913329.

E-mail address: rherrman@nucleus.org.chemie.tu-muenchen.de (R. Herrmann)

[1] Present address: Centro de Química Estrutural, Complexo I, Instituto Superior Técnico, Avenida Rovisco Pais, P-1049-001 Lisbon, Portugal.

PII: S0022-328X(99)00440-4

gardless which conditions, solvents, or additives we used (see Section 4 for some variations). Considering the proposed mechanism [12] for the Heck reaction with oxidative addition of iodoferrocene to palladium, followed by insertion of the double bond into the ferrocene–palladium bond, one can see that the regioselectivity is biased towards the α-product probably for steric reasons, since both the ferrocene and the silatrane are very bulky substituents, and the formation of a σ-bonded intermediate where a CH_2-group is attached to palladium should be highly favored over a CH–Fc or CH–silatrane group in the same position.

To obtain the β-product **4**, we therefore used the hydrosilylation of ethinylferrocene **3** catalyzed by Speier's catalyst (H_2PtCl_6 in isopropanol). We found that the most convenient access to ethinylsilatrane is by the Corey–Fuchs procedure [14], starting with ferrocenecarboxaldehyde. This method has already been used by others for the synthesis of 1,2-diethinylferrocene [15]. The regioselectivity of the hydrosilylation strongly depends on the catalyst and the reaction conditions, as well as on properties of the substituent at the double bond and on the silicon reagent applied [16,17]. Thus, trichlorosilane leads to the *trans*-β-product preferentially, as exemplified by the reaction with 1-ethinyl-4-nitrobenzene where no α-product can be detected (see Section 4). On the other hand, the more convenient trimethoxysilane as hydrosilylation reagent gives an almost 1:1-mixture of α- and β-product with the same alkyne. Exactly the same tendency was observed for ethinylbenzene as well [18]. For the ferrocene derivatives, which are comparatively easy to oxidize, trichlorosilane can be expected to give lower yields of hydrosilylation products, and therefore trimethoxysilane is more promising; only alkyl- and arylsilanes (no chloro derivatives) were used for the hydrosilylation of ethenylferrocene [19]. Fortunately, ethinylferrocene **3** behaves very differently from 1-ethinyl-4-nitrobenzene and leads to the *trans*-β-product exclusively, even with trimethoxysilane. The direct products of the hydrosilylation reaction, the trichlorosilyl- or trimethoxysilylalkenes, were not isolated but converted directly to the corresponding silatranes, either by the acetic anhydride method [20] or by transesterification with boratrane [21], respectively.

To obtain the cymantrenylsilatrane **6**, we lithiated methylcymantrene with butyl lithium. The site of the lithiation of cymantrene is solvent dependent; in THF, the cp ring is attacked [22], while the carbonyl groups are preferred in diethyl ether [23]. We found also, that for methylcymantrene, the lithiation occurs at the cp ring when THF is used as solvent. Since the reaction product with tetraethoxysilane is of comparatively low stability, we converted it immediately to the silatrane

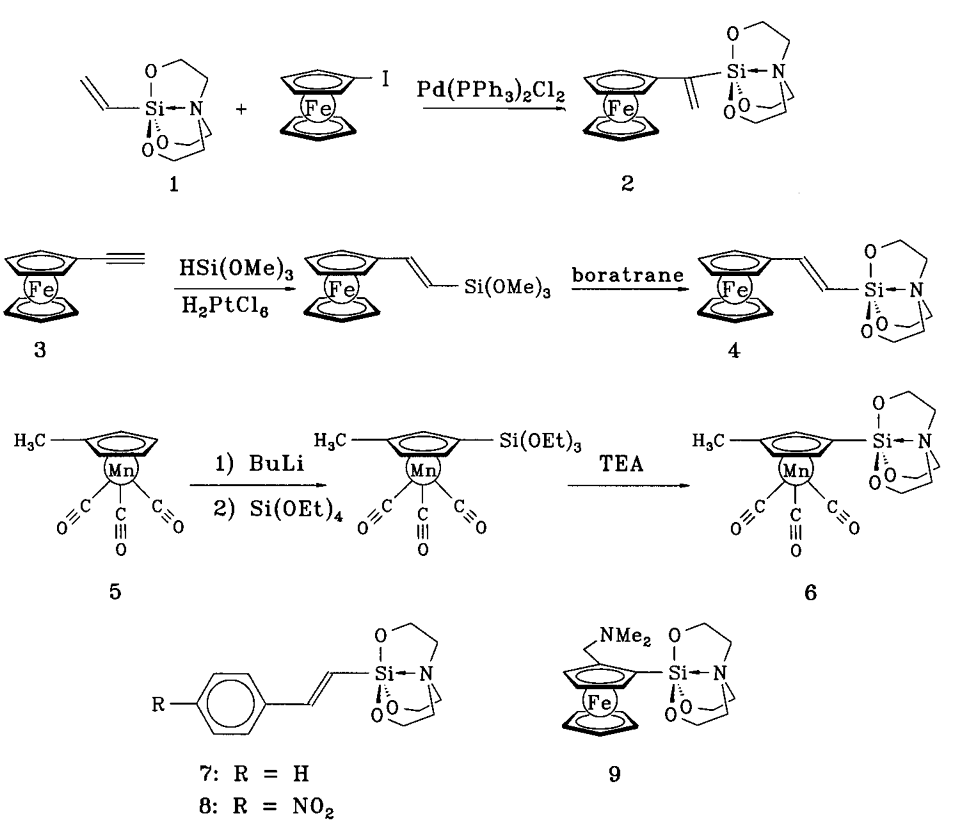

Fig. 1. Synthesis of the ferrocenylethenylsilatranes **2** and **4** and 1-(3-methylcymantrenyl)silatrane **6**.

Table 1
Selected bond lengths (Å) and angles (°) for compounds **2**, **4** and **6** [a]

2		**4**		**6**	
Bond lengths					
Si–N	2.222(2)	Si–N	2.198(2)	Si–N	2.138(2)
Si–C11	1.901(2)	Si–C12	1.872(2)	Si–C4	1.888(3)
C11–C12	1.328(3)	C11–C12	1.340(3)		
C10–C11	1.484(3)	C10–C11	1.471(4)		
Fe–C (cp, av.)	2.04(2)	Fe–C (cp, av.)	2.04(1)	Mn–C (cp, av.)	2.14(1)
C–C (fc, av.)	1.41(1)	C–C (fc, av.)	1.42(1)	C–C (cp, av.)	1.43(1)
C–C (sil, av.)	1.515(4)	C–C (sil, av.)	1.51(1)	C–C (sil, av.)	1.51(1)
Si–O (av.)	1.655(1)	Si–O (av.)	1.659(2)	Si–O (av.)	1.663(2)
O–C (av)	1.42(1)	O–C (av.)	1.416(4)	O–C (sil, av.)	1.417(5)
N–C (av)	1.47(1)	N–C (av.)	1.46(1)	N–C (av.)	1.474(5)
Bond angles					
N–Si–C11	179.6(1)	N–Si–C12	179.9(2)	N–Si–C4	178.7(1)
O–Si–O(av.)	118.1(1)	O–Si–O (av.)	118(2)	O–Si–O (av.)	119(2)
C–N–C (av.)	114.4(1)	C–N–C (av.)	114.5(5)	C–N–C (av.)	114(1)
Si–O–C (av.)	123.5(1)	Si–O–C (av.)	123.8(1)	Si–O–C (av.)	122.6(7)
C10–C11–C12	119.5(2)	C10–C11–C12	126.9(2)		
Si–C11–C12	120.1(2)	Si–C12–C11	126.8(2)		
				Mn–C7	1.779(4)
				Mn–C8	1.794(4)
				Mn–C9	1.795(3)
				O1–C7	1.155(5)
				02–C8	1.149(6)
				03–C9	1.146(4)
				C1–C2	1.508(5)

[a] Abbreviations: fc, ferrocene; cp, cyclopentadienyl; sil, silatrane; av., average.

by transesterification with triethanolamine (TEA). Because of the low yield, we cannot say for certain if the lithiation is site selective and produces 3-lithio-methylcymantrene exclusively, or if some 2-lithiated compound is formed as well. In the case of methylferrocene, no 2-metallated products are observed with pentyl sodium or pentyl potassium [24].

3. Properties of the compounds

The ferrocene derivatives **2** and **4** and the cymantrenylsilatrane **6** were characterized by X-ray crystallography. Details on data collection and refinement are given in Section 4 and in Table 3, selected bond lengths and angles in Table 1. The structures are shown in Figs. 2–4.

The influence of the organometallic moiety and the silatrane on each other's structural features is limited. Thus, the Si–N distances in 1-α-ferrocenylethenylsilatrane **2** (2.222(2) Å) and its 1-β counterpart **4** (2.198(2) Å) are close to the value in 1-ferrocenylsilatrane (2.181(2) β) [9]. In 1-β-phenylethenylsilatrane **7**, a Si–N distance of 2.127(4) Å was found [25]. The bulkiness of the ferrocene group when compared with phenyl might be responsible for the longer Si–N distance in **4** when compared with **7**, although an influence of the stronger electron donor properties of ferrocene may be considered as an additional reason. However, one should keep in mind that the weak Si–N bond is also strongly influenced by crystal packing effects, as one can see when comparing different modifications of 1-phenylsilatrane (α-modification, 2.193(5) Å [26]; γ-modification, 2.132(4) Å [27]). All other features of the silatranyl moiety are very similar in 1-β-phenylethenylsilatrane **7** and its ferrocene counterpart **4**. The olefinic double bond which is directly connected to the different aromatic residues is slightly shortened in the phenyl com-

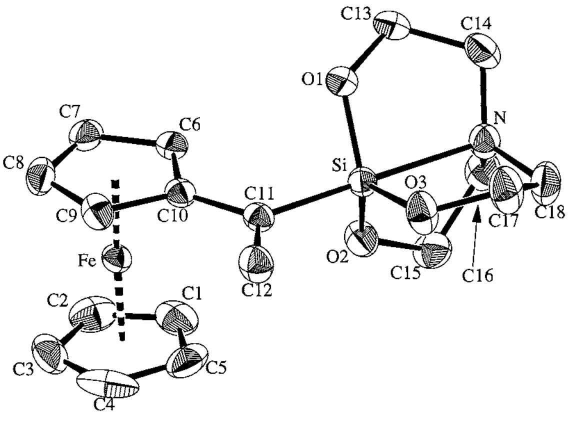

Fig. 2. PLATON plot of the molecular structure of 1-(1-ferrocenylethenyl)silatrane **2** (50% probability factor).

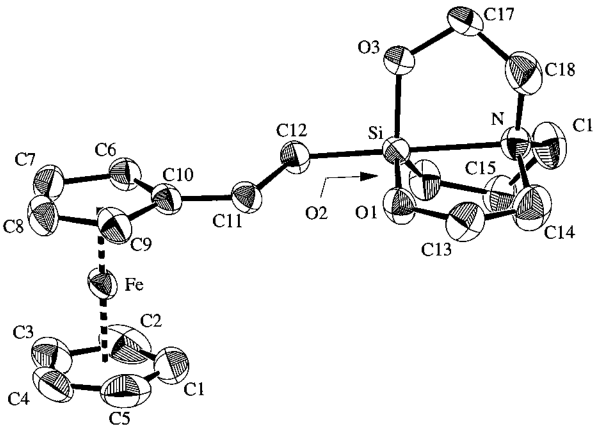

Fig. 3. PLATON plot of the molecular structure of 1-(2-ferrocenylethenyl)silatrane **4** (50% probability factor).

pound (C=C 1.312(6) Å in **7** [25] vs. 1.340(3) Å in **4**). The ferrocene groups adopt a rather unstrained geometry, since there is only a very small tilt of the two cp rings: The angle between the planes defined by both rings is 3.9(2)° in **2** and 2.2(2)° in **4** (and 3.1(1)° in 1-ferrocenylsilatrane [9]). In addition, the iron is well centered in the sandwich structure, since the centers of the cp rings form almost a straight line with the iron atom (angle centroid–Fe–centroid 177.0(2) and 178.7(2)°). Only slight distortions of the cp rings away from planarity and a narrow spread of the standard deviations in the average values of the C–C distances in the cp rings were found. In contrast to the observations made in 1-β-phenylethenylsilatrane **7**, no indication of disorder was detected, neither in the silatrane group (as in 1-β-phenylethenylsilatrane [25]), nor in any other part of the molecules.

The Si–N distance in the cymantrenylsilatrane **6** is shorter (2.138(2) Å) than in the ferrocene derivatives, a fact which might be due to the lower electron donating ability of cymantrene compared with ferrocene. As for the ferrocene derivatives, both the organometallic and the silatrane moieties remain almost undisturbed, which is reflected in very similar features for the silatrane groups in all three compounds studied (e.g. average N–C distance, 1.474(5) Å, angle N–Si–C4, 178.7(1)°, and average Si–O–C angle, 122.6(7)°). The organometallic part closely resembles the unsubstituted cymantrene [28], not only in the Mn–C distances to the cp ring, but also in the bonds to the carbonyl groups. Two of the three bonds are longer (1.794(4) and 1.795(3) Å), while the other is somewhat shorter (1.779(4) Å); a similar effect was observed in cymantrene (1.795(3), 1.797(3), and 1.788(3) Å). The difference in the carbonyl groups is not a mere crystal packing effect, since a considerable broadening of the ^{13}C-NMR signal is observed in solution, which points to a hindered rotation of the cp ring with respect to the positions of the CO groups in the Mn(CO)$_3$ unit.

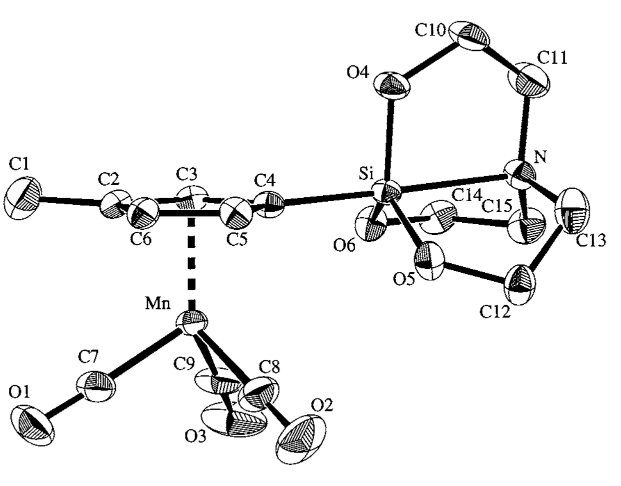

Fig. 4. PLATON plot of the molecular structure of 1-(3-methylcymantrenyl)silatrane **6** (40% probability factor).

When a silatrane group is directly attached to ferrocene, the oxidation potential of the Fe(II)/Fe(III) transition becomes considerably more negative when compared with that of triethoxysilylferrocene ($\Delta E = 0.26$ V). The effect is somewhat less pronounced when comparing the dimethylaminomethyl derivative **9** with its triethoxysilyl counterpart ($\Delta E = 0.14$ V), but still obvious. The ease of reduction of the ferrocenylsilatranes has been traced back to a high antibonding contribution of the Si–N bond to the HOMO [9]. In compounds **2** and **4**, the ferrocene and the silatrane are not directly connected, but separated by one (in **2**) or two (in **4**) carbon atoms. As expected for ferrocene derivatives, they show reversible Fe(II)/Fe(III) oxidations [29]. The oxidation potentials (quoted relative to the ferrocene/ferrocinium redox couple with $E_{1/2} = 0$ V) are very similar to that of **9**, despite the separation of the two groups (**2**, $E_{1/2} = -0.14$ V; **4**, $E_{1/2} = -0.08$ V; **9**, $E_{1/2} = -0.14$ V). Thus, the transmission of the net electron-donor effect of the silatrane correlates with the spatial separation of silatrane and ferrocene, and even when separated by two carbon atoms, the influence of the silatrane is still visible in the Fe(II)/Fe(III) redox potentials.

The observation of electronic communication between the silatrane and the ferrocene by electrochemistry suggests a correlation with non-linear optical (NLO) properties. Therefore, the first hyperpolarizability β for frequency doubling of the compounds **2** and **4** was determined by hyper-Rayleigh scattering (MRS) measurements [30], together with that of **7**, **8**, and **9**, for comparison. Experimental details have been described in Refs. [31,32]. The external reference method has been applied, using 4-nitroaniline ($\beta_{333}^{1064} = 6.2 \times 10^{-50}$ C m^3 V^{-2}, $\lambda_{max} = 348$ nm (CHCl$_3$), $\lambda_{max} = 350$ nm (CH$_2$Cl$_2$) [33]) as external reference compound for **7** and **8**, and 4-(*N*,*N*-dimethylamino)cinnamic aldehyde ($\beta_{333}^{1300} = 15.2 \times 10^{-50}$ C m^3 V^{-2}, $\lambda_{max} = 384$ nm (CHCl$_3$) [34])

Table 2
First hyperpolarizability β_{333} (in 10^{-50} C m^3 V^{-2}) for compounds **2**, **4**, **7**, **8**, and **9**, together with wavelength λ_{max} (in nm) and optical density ϵ (in m^2 mol^{-1}) of the maximum absorption, and fundamental wavelength λ_{ex} (in nm) [a]

Compound	λ_{max}	ϵ	λ_{ex}	β_{333}
2	446	23	1300	4.8
4	446	28	1300	8.4
7	257	1600	1064	3.7
8	320	1300	1064	4.8
9	400	12	1300	8.5

[a] Compounds **2** and **4** were measured in dichloromethane, all other compounds in chloroform as solvent.

for all other compounds. The dependence of the intensity of the HRS signal on the concentration was linear (range $0.6–6 \times 10^{-2}$ mol l^{-1}). No degradation of the compounds during measurement was observed, as verified by NMR measurements afterwards. The results are summarized in Table 2. The calculation of the diagonal component β_{333} of the hyperpolarizability tensor assumes a rod-like shape of the molecules. This is, however, only an approximation for **2** and **9**, and therefore the values should be considered with care [32,35].

Considering the silatrane as an electron donor, it is not surprising that the β_{333} value increases when a nitro group is introduced in the phenyl ring (compare **7** and **8**), since the introduction of an acceptor in the position opposite to a donor at a multiple bond makes the material more similar to classical organic NLO materials based on the familiar 'donor-conducting bridge-acceptor' model [10,11,36]. However, the silatrane is not a π-system as generally assumed in this model, and therefore one cannot expect that the analogy holds for all combinations with other groups. Thus, ferrocene is a rather strong electron donor when compared with phenyl, but the replacement of phenyl in **7** with ferrocenyl in **4** *increases* the β_{333} value instead of decreasing it, as one would expect according to the model. Also in contrast to the model, the introduction of the double bond (as conducting bridge) does not increase the hyperpolarizability, but leads to a very similar value as without it (compare **4** and **9**; the NMe_2 group of the side chain in **9** does not come close to the ferrocene nor to the silatrane [9] and should therefore be of negligible importance for the optical properties). On the other hand, the considerably lower value of the α-ferrocene compound **2** relative to the β-derivative **4** suggests that the relative orientation of the dipole moments of both ferrocene and silatrane is essential for the enhancement of the hyperpolarizability.

The absolute β_{333} values of the silatranes are not exceedingly high when compared with standard materials like 4-(*N*,*N*-dimethylamino)cinnamic aldehyde ($\beta_{333}^{1300} = 15.2 \times 10^{-50}$ C m^3 V^{-2}). However, their design is based on a different concept, since the silatrane moiety does not contain π-bonds, and an extended conducting bridge does not appear to increase the hyperpolarizability. Instead, this is achieved by the combination of both donor and acceptor groups with a silatrane (compare **4** and **8** with **7**). This unconventional behavior is under theoretical investigation in our group. The lack of extended π-systems also leads to an improved transparency in the visible range; the standard material 4-nitroaniline ($\beta_{333}^{1064} = 6.2 \times 10^{-50}$ C m^3 V^{-2}) has a λ_{max} of 348 nm with an optical density $\epsilon = 1400$ m^2 mol^{-1} (in chloroform) [37], with an extension to the visible range (yellow color), whereas the nitro-substituted silatrane **8** with almost the same β value, absorbs with a similar intensity only at $\lambda_{max} = 320$ nm and appears almost colorless to the eye. The ferrocene derivatives differ insofar as they all show the broad metal-to-ligand charge transfer band between 400 and 500 nm, but with only very low optical densities (e.g. 12 m^2 mol^{-1} at $\lambda_{max} = 400$ nm for **9**). Concluding, one can say that silatranes show a better 'nonlinearity/transparency tradeoff' [38] than classical NLO materials with similar structures.

4. Experimental

NMR spectra were measured with a Bruker AM 360 instrument, operating at 360.13 MHz for ^{1}H and 90.56 MHz for ^{13}C. Hyper-Rayleigh scattering measurements were performed with the equipment described [31,32]. Electrochemical studies were performed with an EG&G PAR 173 potentiostat and an EG&G Parc 175 universal programmer, using a 0.2 M solution of NBu_4BF_4 in THF, a platinum working electrode and a silver reference electrode. Potentials were determined relative to the internal cyanoferrocene/cyanoferrocinium redox couple ($E_{1/3}^{ox} = 0.89$ V vs. SCE) [29]. They are quoted relative to ferrocene/ferrocinium ($E_{1/3}^{ox} = 0$ V).

Single-crystal data for **2**, **4**, and **6** were collected on a kappa-CCD system from Nonius with a rotating anode generator (Nonius FR591; Mo–K$_\alpha$, $\lambda = 0.71073$ Å) in rotation mode (Φ-scans). Details on measurement and processing are given in Table 3. All frames were scaled using the Denzo-SMN program suite [39]. No crystal decay was observed. The structures were solved by direct methods [40] (all non-H atoms) and refined [41] by full-matrix least-squares (F^2) with all non-hydrogen atoms assigned anisotropic displacement parameters. For data analysis and visualization, the program PLATON [42] was used. Full crystallographic details, excluding structure factor tables, have been deposited at the Cambridge Crystallographic Data Center (CCDC). Any request to the CCDC for this material should quote the full literature citation and the reference numbers CCDC 133891–133893.

Iodoferrocene [43], 1-ethenylsilatrane **1** [44,20], 1-(2-phenylethenyl)silatrane **7** [45], 1-[2-(*N*,*N*-dimethylaminomethyl)ferrocenyl]silatrane **9** [9], and boratrane [21] were prepared as described. Commercial methylcymantrene **5** was purified by filtration over neutral alumina prior to use. Solvents were dried by standard techniques. Other chemicals were used as supplied.

4.1. 1-(1-Ferrocenylethenyl)silatrane **2**

1. 1-Ethenylsilatrane **1** (160 mg, 0.77 mmol) and iodoferrocene (240 mg, 0.77 mmol) were dissolved in 5 ml of dry DMF, and 0.20 ml of triethylamine (2.5 mmol) were added. The solution was degassed by three freeze–evacuate–thaw-cycles. After addition of 35 mg (0.05 mmol) of $Pd(PPh_3)_2Cl_2$, the mixture was heated to reflux overnight. After removal of all volatile components at 0.1 mm, the residue was chromatographed (silica, dichloromethane). The main yellow–orange band (R_f 0.70) contained the product **2** (280 mg, 90%), m.p. 215–220°C (dec.). ^{1}H-NMR ($CDCl_3$): 5.91 and 5.76 (2 × d, 1 H each, 4.1 Hz, $=CH_2$), 4.47 (t, 2 H, 2.0 Hz, Fc-α), 4.11 (t, 2 H, 2.0 Hz, Fc-β), 4.09 (s, 5 H, unsubst. cp), 3.85 (t, 6 H, 5.7 Hz, $O–CH_2$), 2.85 (t, 6 H, 5.7 Hz, $N–CH_2$). ^{13}C-NMR ($CDCl_3$): 147.0 (C=), 122.9 ($=CH_2$), 89.2 (Fc-*ipso*), 69.3 (unsubst. cp), 67.7, 67.4 (Fc-α, β), 58.1 ($O–CH_2$), 51.5 ($N–CH_2$). Anal. Found C, 56.5; H, 6.2; N, 3.3. $C_{18}H_{23}FeNO_3Si$ Anal. Calc. C, 56.1; H, 6.0; N, 3.6. Crystals suitable for X-ray crystal structure analysis were grown by slow evaporation of a solution in dichloromethane.
2. Iodoferrocene (1000 mg, 3.2 mmol) and 1-ethenylsilatrane 1 (670 mg, 3.2 mmol) were dissolved in 25 ml of diisopropylamine, and the solution was degassed. After addition of 220 mg of $Pd(PPh_3)_2Cl_2$ (0.32 mmol, 10 mol%), the solution was heated to reflux for 5 h. After removal of the solvent at 0.1 mm, the residue was chromatographed on silica to give 620 mg of the product **2** (50%), together with some ferrocene and decomposition products.
3. Palladium(II)acetate (6.7 mg, 0.03 mmol), PPh_3 (15.7 mg, 0.06 mmol), $AgNO_3$ (170 mg, 1.0 mmol), iodoferrocene (312 mg, 1.0 mmol), triethylamine (0.17 ml, 2.1 mmol), and 1-ethenylsilatrane **1** (241 mg, 1.2 mmol) were dissolved in 15 ml of degassed acetonitrile and heated to 100°C for 24 h. The solution was poured on a short (5 cm) column of neutral alumina. Elution with dichloromethane yielded the product **2** (290 mg, 75%)
4. 1-Ethenylsilatrane **1** (590 mg, 2.85 mmol) and iodoferrocene (610 mg, 0.95 mmol) were dissolved in 15 ml of degassed dimethylacetamide, and sodium acetate (320 mg, 3.5 mmol) and palladium(II)acetate (63 mg, 0.28 mmol, 10 mol%) were added. After heating to 100°C for 24 h, the solvent was removed

Table 3
Data collection and structure solution for compounds **2**, **4** and **6**

	2	**4**	**6**
Formula	$C_{18}H_{23}FeNO_3Si$	$C_{18}H_{23}FeNO_3Si$	$C_{15}H_{18}MnNO_6Si$
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	*P*21/*n* (No. 14)	*P*21/*c* (No. 14)	*P*21/*n* (No. 14)
a (Å)	16.5091(4)	13.4286(2)	10.2134(2)
b (Å)	7.4072(1)	10.5069(2)	13.1247(3)
c (Å)	13.9988(3)	12.6195(2)	13.3018(3)
α (°)	90	90	90
β (°)	96.3130(10)	107.497(9)	110.7777(11)
γ (°)	90	90	90
V (Å^3)	1701.48(6)	1698.14(10)	1667.11(6)
Crystal size (mm)	0.13 × 0.13 × 0.15	0.15 × 0.17 × 0.20	0.10 × 0.18 × 0.20
Temperature (K)	293	293	193
Θ_{min}, Θ_{max} (°)	4.6, 26.4	4.8, 30.5	4.5, 30.5
ϕ-scan, step (°)	0–360, 1	0–360,1	0–530,1
Dataset	$-19<h<19$ $-8<k<8$ $-17<l<17$	$-18<h<18$ $-14<k<14$ $-16<l<16$	$-9<h<9$ $-18<k<18$ $-17<l<18$
Total, unique data	22841, 3314	23210, 4140	24832, 4110
R_{int}	0.031	0.034	0.030
Observed data $I>2.0\sigma(I)$	2820	3490	3976
N_{ref}, N_{par}	3314, 217	4140, 217	4110, 217
R_1, wR_2 [a]	0.0318, 0.0877	0.0540, 0.1636	0.0541, 0.1535
Goodness-of-fit	1.06	1.07	1.06
Min/max resd. dens. (e Å^{-3})	−0.39, 0.26	−0.57, 1.55	−0.68, 1.52

[a] $R_1=\Sigma||F_o|-|F_c||/\Sigma|F_o|$. $wR_2=\{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)]^2\}^{1/2}$.

at 0.1 mm and the residue was chromatographed (silica, dichloromethane) to give 95 mg of ferrocene (20%) and 340 mg of the product **2** (30%).

4.2. *Ethinylferrocene* ***3***

Tetrabromomethane (16.6 g, 50 mmol), zinc powder (3.3 g, 50 mmol, activated by treatment with HCl) and PPh_3 (13.1g, 50 mmol) were suspended in 50 ml of dichloromethane. After stirring for 1.5 h, ferrocenecarboxaldehyde (5.35 g, 25 mmol) in 25 ml of dichloromethane was added dropwise. After 4 h stirring at room temperature (r.t.), the formed triphenylphosphine oxide was precipitated by addition of 350 ml of pentane. The precipitate (which includes much of the product) was filtered off, dissolved in dichloromethane and precipitated again with pentane. The procedure was repeated until the extracts remained almost colorless. The combined solutions were concentrated and chromatographed on silica (hexane). Yield 7.08 g (76%) of 2,2-dibromoethenylferrocene. By elution with hexane/ether (2:1), 1.45 g of ferrocenecarboxaldehyde (24%) could be recovered.

To a solution of 20 ml of butyl lithium (2.5 M in hexane, 50 mmol) in 20 ml of diethylether/THF (2:1) at − 78°C, a solution of 2,2-dibromoethenylferrocene (7.08 g, 19 mmol) in the same solvent mixture (50 ml) was added dropwise. After stirring for 2 h at − 78°C, the mixture was allowed to come to r.t. within 1 h. Stirring was continued for 2 h. After cooling to − 78°C, 10 ml of saturated aqueous ammonium chloride solution were added. After coming to r.t. and stirring for 10 min, the mixture was added to 20 ml of saturated sodium carbonate solution. The organic layer was separated, the aqueous layer extracted once with hexane, and the combined organic solutions were dried over sodium sulfate. Removal of the solvent yielded 3.91 g of ethinylferrocene **3** (98%), with properties identical to the ones reported [46].

4.3. *1-(2-Ferrocenylethenyl)silatrane* ***4***

Ethinylferrocene **3** (440 mg, 2.1 mmol), trimethoxysilane (300 mg, 2.5 mmol), and one drop of Speier's catalyst (0.1 M solution of H_2PtCl_6 in isopropanol) were heated to 50°C in a closed Schlenk tube overnight. Triethanolamine (300 mg, 2.0 mmol), 10 mg of KOH and 10 ml of toluene were added, and the mixture was heated to reflux for 24 h. After removal of the solvent at 0.1 mm, the residue was chromatographed (silica, dichloromethane), yielding 700 mg (90%) of the product **4**, R_f 0.7, m.p. 250–255°C (dec.). ^{1}H-NMR ($CDCl_3$): 6.77 (d, 1 H, 18.0 Hz, =CH(1)), 5.85 (d, 1 H, 18.0 Hz, =CH(2)), 4.31 and 4.09 (2 × s, 2 H each, Fc), 4.06 (s, 5 H, unsubst. cp), 3.81 (t, 6 H, 5.4 Hz, O–CH_2), 2.81 (t, 6 H, 5.4 Hz, N–CH_2). ^{13}C-NMR ($CDCl_3$): 140.5 (CH = (1)), 126.3 (=CH(2)), 86.0 (Fe-*ipso*), 69.0 (unsubst. cp), 68.0, 66.8 (Fc-α, β), 57.7 (O–CH_2), 51.0 (N–CH_2). Anal. Found C, 56.3; H, 6.0; N, 3.8. $C_{18}H_{23}FeNO_3Si$ Anal. Calc. C, 56.1; H, 6.0; N, 3.6. Crystals suitable for X-ray crystal structure analysis were grown by slow evaporation of a solution in dichloromethane.

4.4. *1-(3-Methylcymantrenyl)silatrane* ***6***

To a solution of methylcymantrene **5** (3.18g, 14.6 mmol) in 30 ml of THF, a 2.5 M solution of butyl lithium in hexane (18.0 mmol) was added at − 78°C. After warming to r.t., the solution was stirred overnight. Tetraethoxysilane (3.3 ml, 15.0 mmol) was added and the mixture stirred for 6 h. Then, 2.34 g (15.0 mmol) of boratrane were added and stirring continued overnight. After evaporation of the solvent, the residue was rapidly chromatographed over a short column (3 cm) of neutral alumina with pentane and ether to remove unreacted starting materials, and then with dichloromethane. This fraction was concentrated and subjected to a second chromatography (dichloromethane) under the same conditions to yield 210 mg (4%) of the product **6**. It is very unstable in solution and precipitates paramagnetic material, but can be stored as a solid under nitrogen at 0°C for longer periods. Microanalytical data could not be obtained because of its sensitivity. Crystals suitable for X-ray crystal structure analysis were grown by slow diffusion of a pentane layer to a dichloromethane solution at − 30°C. ^{1}H-NMR (C_6D_6): 1.61 (s, 3 H, Me), 1.80 (tr, 6 H, 5.9 Hz, CH_2–N), 3.35 (tr, 6 H, 5.9 Hz, CH_2–O), 4.18, 4.95, 5.00 (3 × s, 1 H each, cp). ^{13}C-NMR (C_6D_6): 13.3 (Me), 50.7 (CH_2–N), 57.4 (CH_2–O), 83.9, 90.9, 91.8 (CH (cp)), 92.5, 103.1 (C_q (cp)), 227.6 (CO).

4.5. *1-[2-(4-Nitrophenyl)ethenyl]silatrane* ***8***

1. To a solution of 1-ethinyl-4-nitrobenzene [47] (147 mg, 1.0 mmol) and trichlorosilane (163 mg, 1.2 mmol) in 1.0 ml of toluene, 1 drop of Speier's catalyst was added. The mixture was kept in a closed vessel at 70°C for 16 h. The solvent was evaporated in a vacuum, and to the residue was added sodium acetate (20 mg, 0.25 mmol) and acetic anhydride (310 mg, 3.0 mmol). The mixture was kept at 60°C for 5 h. All volatile components of the mixture were removed in a vacuum. The residue was dissolved in 15 ml of chloroform, and a solution of triethanolamine (150 mg, 1.0 mmol) in 10 ml of chloroform was added at 0°C dropwise within 30 min. Stirring was continued for 2 h at 0°C and at r.t. overnight. The solvent was removed in a vacuum and the residue purified by chromatography (silica,

2:1 dichloromethane–ethyl acetate), to give the product **8**, R_f 0.23, yield 120 mg (37%), m.p. 245–246°C. ^{1}H-NMR($CDCl_3$): 2.92 (t, 6 H, 5.9 Hz, CH_2–N), 3.88 (t, 6 H, 5.9 Hz), 6.58 and 7.15 (2 × d, 1 H each, 19.1 Hz, =CH), 7.54 and 8.11 (2 × d, 2 H each, 8.8 Hz, arom.). ^{13}C-NMR ($CDCl_3$): 51.0 (CH_2–N), 57.4 (CH_2–O), 136.4, 139.8 (=CH), 123.6, 126.8 (CH arom.), 145.9, 146.5 (C_q). Anal. Found C, 52.4; H, 5.5; N, 8.4. $C_{14}H_{18}N_2O_5Si$. Anal. Calc. C, 52.2; H, 5.6; N, 8.7.

2. To a solution of 1-ethinyl-4-nitrobenzene [47] (147 mg, 1.0 mmol) and trimethoxysilane (122 mg, 1.0 mmol) in toluene (1 ml) was added 1 drop of Speier's catalyst, and the mixture was heated to reflux overnight. The solvent was evaporated in a vacuum and the residue dissolved in 1.0 ml of xylene. Boratrane (160 mg, 1.0 mmol) and $AlCl_3$ (10 mg) were added and the mixture was refluxed for 1 day. After evaporation of the solvent, the residue was chromatographed (silica gel, 2:1 dichloromethane–ethyl acetate). The product **8** (R_f 0.23, 30 mg, 9%) was preceded by the isomeric 1-[1-(4-nitrophenyl)ethenyl]silatrane (R_f 0.48, 40 mg, 13%), m.p. 210–213°C. ^{1}H-NMR ($CDCl_3$): 2.89 (t, 6 H, 5.9 Hz, CH_2–N), 3.85 (t, 6 H, 5.9 Hz, CH_2O), 5.74 and 5.97 (2 × d, 1 H each, 3.9 Hz, =CH_2), 7.57 and 8.09 (2 × d, 2 H each, arom.). ^{13}C-NMR ($CDCl_3$): 51.2 (CH_2–N), 57.6 (CH_2–O), 128.8 (=CH_2), 122.9, 128.0 (CH, arom.), 145.8, 152.8, 154.6 (C_q). Anal. Found C, 52.5; H, 5.8; N, 8.3. $C_{14}H_{18}N_2O_5Si$. Anal. Calc. C, 52.2; H, 5.6; N, 8.7.

Acknowledgements

We wish to thank Professor Dr Fernanda N.N. Carvalho, Instituto Superior Técnico, Lisbon, Portugal, for help with electrochemical measurements, and Professor Dr Ivar Ugi, TU München, for general support. Financial support by Fonds der Chemischen Industrie is gratefully acknowledged.

References

[1] M.G. Voronkov, Pure Appl. Chem. 13 (1966) 35.

[2] M.G. Voronkov, V.M. Dyakov, S.V. Kirpichenko, J. Organomet. Chem. 233 (1982) 1.

[3] S.N. Tandura, M.G. Voronkov, N.V. Alekseev, Top. Curr. Chem. 131 (1986) 99.

[4] R.J.P. Corriu, J. Organomet. Chem. 400 (1990) 81.

[5] T.M. Chung, Y.-A. Lee, Y.K. Chung, I.N. Jung, Organometallics 9 (1990) 1976.

[6] Y.-A. Lee, Y.K. Chung, Y. Kim, J.H. Jeong, Organometallics 9 (1990) 2851.

[7] M.T. Attar-Bashi, C.E.F. Rickard, W.R. Roper, L.J. Wright, S.D. Woodgate, Organometallics 16 (1998) 504.

[8] G. Cerveau, C. Chuit, E. Colomer, R.J.P. Corriu, C. Reyé, Organometallics 9 (1990) 2415.

[9] M.J. Calhorda, P.E.M. Lopes, A. Schier, R. Herrmann, J. Organomet. Chem. 543 (1997) 93.

[10] N.J. Long, Angew. Chem. 107 (1995) 37. Angew. Chem. Int. Ed. Engl. 34 (1995) 21.

[11] D.R. Kanis, M.A. Ratner, T.J. Marks, Chem. Rev. 94 (1994) 195.

[12] S. Bräse, A. de Meijere, in: P.J. Stang, F. Diederich Jr. (Eds.), Metal-Catalyzed Cross Coupling Reactions, Wiley–VCH, Weinheim, 1997.

[13] C.-M. Andersson, A. Hallberg, G.D. Daves Jr., J. Org. Chem. 52 (1987) 3529.

[14] E.J. Corey, P.L. Fuchs, Tetrahedron Lett. (1972) 3769.

[15] U.H.F. Bunz, J. Organomet. Chem. 494 (1995) C8.

[16] E. Lukevics, Z.V. Belyakova, M.G. Pomerantseva, M.G. Voronkov, J. Organomet. Chem. Libr. 5 (1977) 1.

[17] I. Ojima, in: S. Patai, Z. Rappoport (Eds.), The Chemistry of Organic Silicon Compounds, vol. 2, Wiley, Chichester, 1989.

[18] L.I. Kopylova, N.D. Ivanova, V.I. Voropaev, É.N. Satsuk, N.I. Shergina, L.V. Sherstyannikova, M.G. Voronkov, Zh. Obshch. Khim. 58 (1988) 806 (English p. 713).

[19] S.M. Massarskaya, V.G. Dyatlova, L.K. Prokopova, Zh. Obsch. Khim. 43 (1973) 2706 (English p. 2684).

[20] M. Nasim, A.K. Saxena, I.P. Pal, L.M. Pande, Synth. React. Inorg. Metall. Org. Chem. 17 (1987) 1003.

[21] J.D. Nies, J.M. Bellama, N. Ben-Zvi, J. Organomet. Chem. 296 (1985) 315.

[22] A.N. Nesmeyanov, K.N. Anisimov, N.E. Kolobova, Y.V. Makarov, Izv. Akad. Nauk SSSR Ser. Khim. (1968) 686 (English p. 672).

[23] E.O. Fischer, A. Maasböl, Chem. Ber. 100 (1967) 2445.

[24] R.A. Benkeser, J.C. Bach, J. Am. Chem. Soc. 86 (1964) 890.

[25] M. Stradiotto, G. Crowe, R. Ruffolo, M.A. Brook, Acta Crystallogr. 53c (1997) 637.

[26] J.W. Turley, F.P. Boer, J. Am. Chem. Soc. 90 (1968) 4026.

[27] L. Párkányi, J. Nagy, K. Simon, J .Organomet. Chem. 101 (1975) 11.

[28] J. Cowie, E.J.M. Hamilton, J.C.V. Laurie, A.J. Welch, J. Organomet. Chem. 394 (1990) 1.

[29] M.E.N.P.R.A. Silva, A.J.L. Pombeiro, J.J.R. Fraústo da Silva, R. Herrmann, N. Deus, T.J. Castilho, M.F.C.G. Silva, J. Organomet. Chem. 421 (1991) 75.

[30] K. Clays, A. Persoons, Phys. Rev. Lett. 66 (1991) 2980.

[31] S. Stadler, R. Dietrich, G. Bourhill, C. Bräuchle, Opt. Lett. 21 (1996) 251.

[32] S. Stadler, R. Dietrich, G. Bourhill, C. Bräuchle, A. Pawlik, W. Grahn, Chem. Phys. Lett. 247 (1995) 271.

[33] M. Stähelin, D.M. Burland, J.E. Rice, Chem. Phys. Lett. 191 (1992) 245.

[34] E. Schmälzlin, K. Meerholz, S. Stadler, C. Bräuchle, H. Patzelt, D. Oesterhelt, Chem. Phys. Lett. 280 (1997) 551.

[35] R. Herrmann, B. Pedersen, G. Wagner, J.-H. Youn, J. Organomet. Chem. 571 (1998) 261.

[36] S.R. Marder, D.N. Beratan, B.G. Tieman, L.-P. Cheng, W. Tam, in: R.A. Hann, D. Bloor (Eds.), Organic Materials for Non-linear Optics, vol. II, The Royal Society of Chemistry, Cambridge, 1991.

[37] S. Stadler, G. Bourhill, C. Bräuchle, J. Phys. Chem. 100 (1996) 6927.

[38] J. Zyss, I. Ledoux, J.-F. Nicoud, in: J. Zyss (Ed.), Molecular Nonlinear Optics, Academic, Boston, 1994.

[39] Z. Otwinowski, W. Minor Jr., in: C.W. Carter Jr., R.M. Sweet (Eds.), Methods in Enzymology, vol. 276, Academic, Boston, 1997.

[40] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, J. Appl. Cryst. 26 (1993) 343.

[41] G.M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement, Universitat Gottingen, 1997.
[42] A.L. Spek, Acta Crystallogr. A 46 (1990) C34.
[43] R.W. Fish, M. Rosenblum, J. Org. Chem. 30 (1965) 1253.
[44] C.L. Frye, G.E. Vogel, J.A. Hall, J. Am. Chem. Soc. 83 (1961) 996.
[45] M.G. Voronkov, O.G. Yarosh, L.V. Shchukina, E.O. Tsetlina, S.N. Tandura, I.M. Korotaeva, Zh. Obshch. Khim. 49 (1979) 614.
[46] M. Rosenblum, N. Brawn, J. Papenmeier, M. Applebaum, J. Organomet. Chem. 6 (1966) 173.
[47] S.J. Cristol, W.P. Norris, J. Am. Chem. Soc. 76 (1954) 3005.