Synthesis of *ansa*-[*n*]Silacyclopentadienyl–Cycloheptatrienyl–Chromium Complexes (*n* = 1, 2): Novel Precursors for Polymers Bearing Chromium in the Backbone

Alexandra Bartole-Scott,[b] Holger Braunschweig,*[a] Thomas Kupfer,[a] Matthias Lutz,[a] Ian Manners,[b] Thi-loan Nguyen,[a] Krzysztof Radacki,[a] and Fabian Seeler[a]

Abstract: Reaction of [(η^5-C_5H_4Li)(η^7-C_7H_6Li)Cr]·tmeda with a variety of dialkyl(dichloro)silanes in aliphatic solvents afforded the corresponding [1]silatrochrocenophanes. Structural characterization by X-ray diffraction analysis of the [1]silatrochrocenophanes bearing Me_2Si, (*i*Pr)$_2$Si, and silacyclobutane bridges revealed tilt angles α of 15.56(12)°, 15.8(1)°, and 16.33(17)°, respectively. Analogously, a [2]silatrochrocenophane (**6**) was prepared in excellent yield by reaction of [(η^5-C_5H_4Li)(η^7-C_7H_6Li)Cr]·tmeda with 1,2-dichloro-1,1,2,2-tetramethyldisilane. This complex also was characterized structurally and exhibited a tilt angle α of 2.60(15)°. The [1]silatrochrocenophane bearing the Me_2Si bridge underwent facile and regioselective carbon–silicon bond cleavage with [Pt(PEt$_3$)$_4$] to give a very high yield of an oxidative addition product. The ring-opening polymerization of these novel [1]silatrochrocenophanes afforded ring-opened chromium-based polymers.

Keywords: *ansa*-silametallocenes · chromium · metallocenes · metallopolymers · oxidative addition · ring-opening polymerization · silicon

Introduction

Tilted sandwich compounds have attracted recent interest owing to their unique structure, bonding, and reactivity patterns as well as their potential utility as precursors for metal-containing macromolecules.[1] Among them [1]silaferrocenophanes are the most thoroughly investigated strained sandwich compounds due to their propensity to give facile access to polyferrocenylsilanes by ring-opening polymerization (ROP), which can be triggered thermally or by anionic or transition metal mediated catalysis.[2] However, structural motifs other than ferrocene are rarely studied and comprise only a few derivatives of bis(benzene)chromium[3] and bis(benzene)vanadium[4] as well as cobaltocenophanes[5] and ruthenocenophanes.[6] Moreover, only recently have

metallopolymers of this type that do not contain a ferrocenyl repeat unit been reported in the literature.[3a, 6a, 8c, 9, 10]

During our current study of compounds that are isoelectronic with bis(benzene)chromium, we became interested in cyclopentadienyl–cycloheptatrienyl–chromium[7] ([(η^7-C_5H_5)-(η^7-C_7H_7)Cr] = trochrocene),[8] whose derivatization to form a [2]boratrochrocenophane[8] we have reported. Recently, the first two examples of *ansa*-silametallocenes with heteroleptic ligand moieties around the metal centre have been reported. These complexes were obtained by reaction of [(η^5-C_5H_5)(η^7-C_7H_7)Ti] (troticene)[8c, 9] or [(η^5-C_5H_5)(η^7-C_7H_7)V] (trovacene)[9, 10] with *n*BuLi in the presence of *N,N,N',N'*-tetramethylethylenediamine (TMEDA) and subsequent treatment with dialkyl(dichloro)silanes.[9, 10] In this contribution we report on: 1) syntheses of the first examples of [*n*]silatrochrocenophanes (*n* = 1, 2); 2) the reactivity of [1]silatrochrocenophane (**2**) towards [Pt(PEt$_3$)$_4$]; and 3) the formation of a poly(silatrochrocene) by transition metal catalyzed ring-opening polymerization.

Results and Discussion

Synthesis of [*n*]Silatrochrocenophanes (*n* = 1 and 2): An essential prerequisite for the synthesis of *ansa*-metalloceno-

[a] Prof. Dr. H. Braunschweig, T. Kupfer, Dr. M. Lutz, T.-l. Nguyen, Dr. K. Radacki, F. Seeler
Institut für Anorganische Chemie, Bayerische Julius-Maximilians-Universität Würzburg
Am Hubland, 97074 Würzburg (Germany)
Fax: (+49) 931-888-4623
E-mail: h.braunschweig@mail.uni-wuerzburg.de

[b] A. Bartole-Scott, Prof. Dr. I. Manners
Inorganic Rings and Macromolecules, Dept. of Chemistry
80 St. George St., Toronto, Ontario M5S 3H6 (Canada)

phanes is to access a suitable precursor that can be transformed subsequently into the desired product. The two most commonly applied methods of preparing *ansa*-metallocenophanes are: 1) build-up of the bridging ligand scaffold, followed by double deprotonation, usually with *n*BuLi, and subsequent reaction with a suitable transition metal halide (A, Scheme 1); and 2) the double deprotonation of a metallocene followed by reaction with a bridging element dihalide (B, Scheme 1).[11]
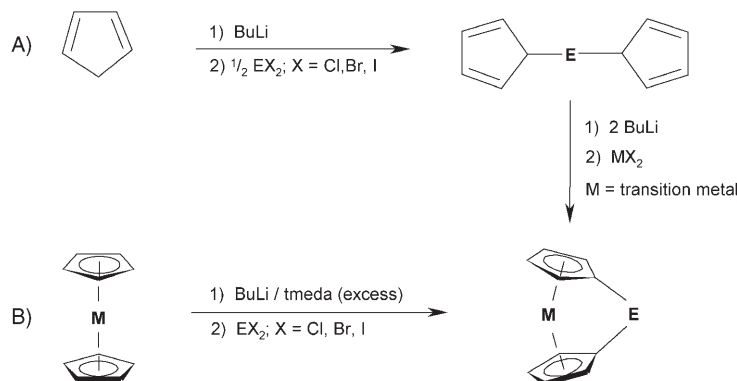
Scheme 1. The two principal methods of preparation of *ansa*-metallocenes exemplified by the formation of an *ansa*-bis(η^5-cyclopentadienyl) transition metal complex.

Hitherto, a reliable route to lithiate trochrocene has not been described in the literature.[7a, 12] To this end we accomplished double metallation of trochrocene by employing *t*BuLi/TMEDA in aliphatic solvents to afford the base-stabilized compound [(η^5-C$_5$H$_4$Li)(η^7-C$_7$H$_6$Li)Cr]·tmeda (**1**) in high yield.[8a] Subsequent reaction of the dilithio complex (**1**) with a variety of dialkyl(dichloro)silanes gave, after work-up, the [1]silatrochrocenophanes (**2**, **3**, **4**, **5**) in yields ranging from 42% to 67% (Scheme 2). All complexes were isolated as dark blue solids, which proved to be very sensitive towards air and moisture but could be stored at ambient temperature under a protective atmosphere for a long time without degradation.

Attempts to obtain higher yields were thwarted by the inherent solubility of these compounds in all common organic solvents, although the progress of the reaction as detected by ^{1}H NMR spectroscopy indicated quantitative conversion of the starting materials. Pertinent features in the ^{1}H NMR spectra include the splittings of the Cp resonances into two pseudo-triplets (**2**: δ = 3.66 and 3.70 ppm; **3**: δ = 3.69 and 3.76 ppm; **4**: δ = 3.67 and 3.74 ppm; **5**: δ = 3.67 and 3.74 ppm) and of the cycloheptatrienyl (Cht) resonances into three multiplets (**2**: δ = 5.14–5.88 ppm; **3**: δ = 5.14–5.93 ppm; **4**: δ = 5.12–5.91 ppm; **5**: δ = 5.20–5.82 ppm). The ^{13}C NMR spectra exhibit high-field shifted resonances for the *ipso* carbons (**2**: δ = 51.66 and 60.10 ppm; **3**: δ = 51.67 and 60.17 ppm; **4**: δ = 51.39 and 60.10 ppm; **5**: δ = 49.9 and 60.2 ppm), which are significantly deshielded compared with those found for [1]silaferrocenophanes[13] and

[1]silachromoarenophanes,[3c, d, 4b] but are drastically high-field shifted with respect to the ^{13}C NMR resonances for the *ipso* carbons found in the corresponding Ti congener.[8c, 9]

Similarly to the preparation of [1]silatrochrocenophanes, the dilithio compound (**1**) reacted with 1,2-dichloro-1,1,2,2-tetramethyldisilane to afford the disila-bridged trochrocenophane (**6**) in 69% yield as dark blue crystals. As expected, the incorporation of the disila bridge in **6** imposed less molecular strain, which is manifested in solution in the deshielding of the Cp resonances in the ^{1}H NMR spectrum (δ = 3.88 and 4.04 ppm) as well as the low-field shift of the *ipso* carbons in the ^{13}C NMR spectrum (δ = 81.4 and 91.4 ppm). Furthermore, in its ^{29}Si NMR spectrum **6** exhibits two distinct resonances (δ = −14.8 and 6.9 ppm) for the disila bridge due to chemical inequivalence of the silicon atoms. To assess unequivocally the structural patterns of such silatrochrocenophanes, single-crystal structure determinations of **2**, **3** (Figure 1) and **5** (Figure 2) were carried out. Whereas **2** crystallizes in the monoclinic space group $P2_1/n$, **3** and **5** crystallize in the orthorhombic space groups $Pca2_1$ and $Pbca$, respectively (Table 1). However, **5** exhibits a disorder in the silacylobutane ring moiety, and therefore the structure was refined isotropically. Comparison with structurally related *ansa* complexes, namely [1]silachromoarenophanes [(η^6-C$_6$H$_5$)-Me$_2$Si-(η^6-C$_6$H$_5$)Cr][3c] and [(η^6-C$_6$H$_5$)-Ph$_2$Si-(η^6-C$_6$H$_5$)Cr],[3d] reveals that the tilt angles α, as previously defined, are very similar to the values measured for the [1]silatrochrocenophanes reported here (**2**: α = 15.6(1)°; **3**: α = 15.8(1)°; **5**: α = 16.33(17)°; versus [(η^6-C$_6$H$_5$)-Me$_2$Si-(η^6-C$_6$H$_5$)Cr]: α = 16.6(3)°;[3c] [(η^6-C$_6$H$_5$)-Ph$_2$Si-(η^6-C$_6$H$_5$)Cr]: α = 14.4°[3d]). Yet α values reported for the [1]silatroticenophane [(η^5-C$_5$H$_4$)-SiMe$_2$-(η^7-C$_7$H$_6$)Ti],[8c] the [1]silatrovacenophane [(η^5-C$_5$H$_4$)-SiMe$_2$-(η^7-C$_7$H$_6$)V],[10] the [1]silavanadoarenophane [(η^6-C$_6$H$_5$)-Si(CH$_2$)$_3$-(η^6-C$_6$H$_5$)V],[4b] and the [1]silaferrocenophane [(η^5-C$_5$H$_4$)-Me$_2$Si-(η^5-C$_5$H$_4$)Fe][13] are all significantly higher, undoubtedly because of the longer interannular distance in the Ti, V, and Fe systems. As expected, the interatomic C–Cr distances are significantly shorter than those found in the titanium congener[8c] but significantly longer than the carbon–metal separation reported for related [1]silaferrocenophanes.[13] The C-(arene)-Si-C(arene) angles θ in **2** (93.91(9)°), **3** (94.14(7)°), and **5** (94.67(14)°) deviate significantly from the tetrahedral angle for an sp^3-hybridized silicon atom. The smaller angle θ results in a slight scissoring effect at silicon, with a widening of the C(R)-Si-C(R) (**2**, C(R) = Me; **3**, C(R) = *i*Pr) angle to 110.74(13)° in **2** and 115.28(8)° in **3**. This difference in angles between **2** and **3** is presumably due to the increased steric demand of the Si(*i*Pr)$_2$ bridging element in **3**. This scissoring effect in **5** is not detectable [average θ = 80.3°] owing to the ring strain in the silacyclobutane unit. The Cr−Si distances in **2** (2.909 Å), **3** (2.915 Å) and **5** (2.889 Å) are significantly greater than the sum of the covalent radii (2.42 Å).[14] These distances indicate that any interaction between the Cr centre and silicon atom is weak at best. This finding is in agreement with previously found Fe−B distances in [1]boraferrocenophanes.[15]
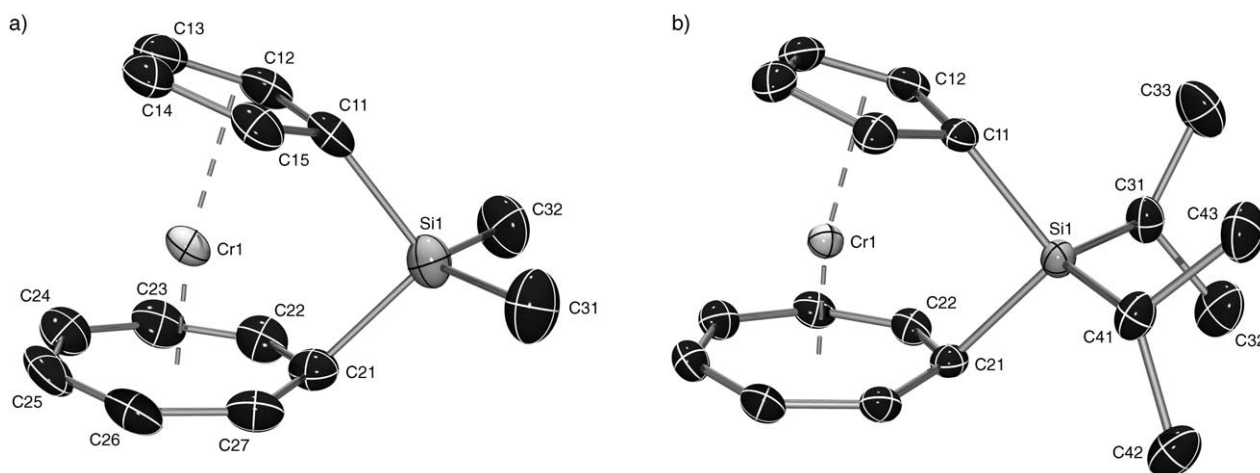
Figure 1. Molecular structure of **2** (a) and **3** (b) (ref. [16]). Selected bond lengths [Å] and angles [°] of **2** (values for **3** are given in square brackets): Cr1−C11 2.148(2) [2.1576(16)], Cr1−C12 2.160(2) [2.1683(16)], Cr1−C13 2.206(2) [2.2139(17)], Cr1−C14 2.210(2) [2.2224(17)], Cr1−C15 2.165(2) [2.1809(18)], Cr1−C21 2.108(2) [2.1139(16)], Cr1−C22 2.141(2) [2.1476(17)], Cr1−C23 2.174(2) [2.174(2)], Cr1−C24 2.163(2) [2.1825(17)], Cr1−C25 2.170(2) [2.1843(16)], Cr1−C26 2.171(2) [2.1784(15)], Cr1−C27 2.144(2) [2.1452(15)], Si1−C11 1.886(2) [1.891(2)], Si1−C21 1.902(2) [1.907(2)] Si1−C31 1.856(3) [1.889(2)], Si−C32 1.863(2) [1.887(2)], Cr1−X_{Cp} 1.813 [1.840], Cr1−X_{Cht} 1.436 [1.442]; C11-Si1-C21 93.91(9) [94.14(7)], C31-Si1-C32 110.74(13) [115.28(8)] X_{Cp}-Cr1-X_{Cht} 167.50 [167.36] (X = centroid).
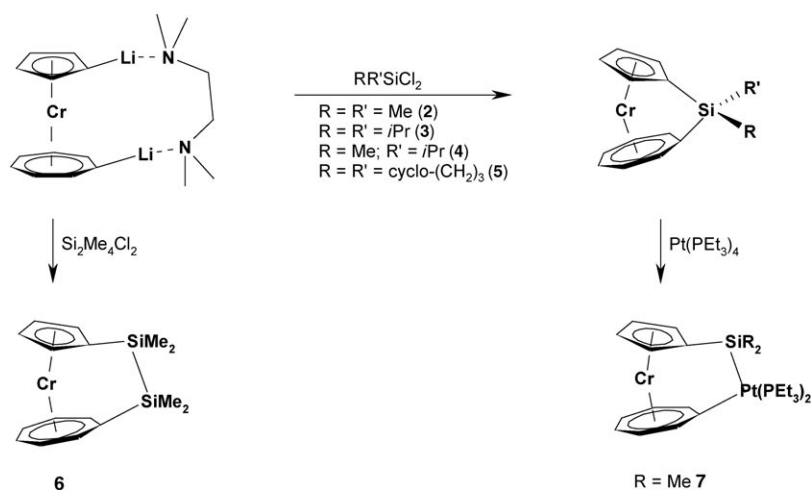
Scheme 2. Preparation of [1]silatrochrocenophanes and regioselective Pt⁰-mediated C−Si bond cleavage.

The formation of the disila bridge in **6** was confirmed by a single-crystal diffraction study. The [2]silatrochroceno-phane **6** crystallizes in the monoclinic space group $P2_1$ (Figure 3) and is therefore isomorphous with previously reported [2]silatrovacenophane.[10] As expected, **6** exhibits only weak molecular strain with a tilt angle α [2.60(15)°] in accord with tilt angles found in structurally related [2]silafer-rocenophanes[17] and [2]silatrovacenophane.[10] The tilt angle of the latter, for example, is 3.8(3)°.[10] The scissoring effect in [1]silatrochrocenophanes is less pronounced in **6** because it has less ring strain; thus, the angles around the silicon cen-tres adopt more regular tetrahedral angles (C11-Si1-Si2 104.30(7)°, C21-Si2-Si1 101.76(6)°, C31-Si1-C32 109.10(12)°, C41-Si2-C42 108.15(10)°). The methyl substituents around the silicon centres adopt a mutually eclipsed conformation

with a dihedral angle of 2.9°. These findings are in contrast to the tilt angle α of 8.9° and the dihedral angle of 40.6° found for previously reported [2]bora-trochrocenophane;[8a] arguably, the shorter B−B bond enforces a more strained geometry.

Oxidative addition of the Si−C bond to [Pt(PEt₃)₄]: Strained [1]silametallocenophanes are known to react with plati-num(0) complexes with oxida-tive addition of the Si−C bond.[9,18] This aspect of carbon–silicon bond cleavage has been demonstrated success-fully for [1]silaferrocenopha-nes[18a,b] and [1]silatroticenophanes;[9] stoichiometric addition of [Pt(PEt₃)₃][19] resulted in the formation of isolable [2]platinasilaferrocenophanes[18a,b] and [2]platinasilatrotice-nophane,[9] respectively. Interestingly, in the case of the [1]si-latroticenophane the carbon−silicon bond cleavage occurred regioselectively, exclusively at the silicon−Cht linkage, thus affording [2]platinasilatroticenophane[9] as a green solid in low yields. Similarly [1]silatrochrocenophane (**2**) reacted with stoichiometric amounts of [Pt(PEt₃)₃] to afford [2]plati-nasilatrochrocenophane (**7**) in moderate yields as turquoise crystals. The ³¹P{¹H} NMR spectrum of **7** exhibits two dis-tinct ³¹P NMR resonances in very close proximity (δ = 8.9 and 9.1, ²$J_{P,P}$ = 17 Hz) (Figure 4) flanked by P–Pt satellites with coupling constants of 2007 Hz and 1028 Hz, respective-ly. The latter is considerably lower due to the strong *trans*
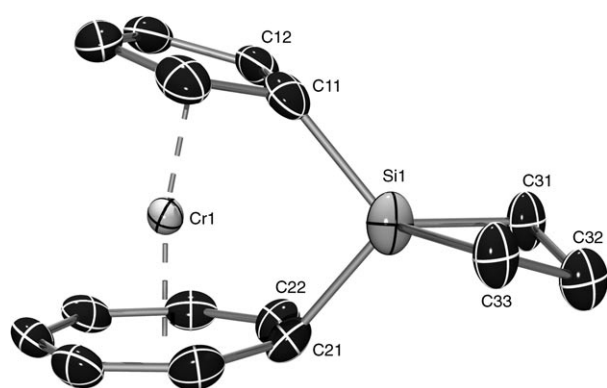
Figure 2. The molecular structure of **5**.[16] Selected bond lengths [Å] and angles [°]: Cr1−C11 2.148(3), Cr1−C12 2.162(3), Cr1−C13 2.210(3), Cr1−C14 2.212(3), Cr1−C15 2.162(3), Cr1−C21 2.102(3), Cr1−C22 2.138(3), Cr1−C23 2.163(3), Cr1−C24 2.173(3), Cr1−C25 2.170(3), Cr1−C26 2.179(3), Cr1−C27 2.139(3), Si1−C11 1.877(4), Si1−C21 1.885(4), Cr1−X_{Cp} 1.816, Cr1−X_{Cht} 1.432; C11-Si1-C21 94.67(14), C31a-Si1-C33a 79.5(2), C31b-Si1-C33b 81.1(3), X_{Cp}-Cr1-X_{Cht} 168.00 (X = centroid).

influence exerted by the silyl substituent. In addition, the observation of a doublet of doublets resonance in the ^{29}Si NMR at $\delta = 11.5$ with Si–P coupling constants of 182 Hz and 17 Hz and strong Pt–Si couplings of 1392 Hz supports a regioselective carbon–silicon bond cleavage (Figure 5).

Regioselective C−Si bond activation in **7** was unequivocally confirmed by a single-crystal diffraction analysis (Figure 6). Complex **7** crystallizes in the orthorhombic space group $P2_12_12_1$ and is therefore isomorphous with the previously reported [2]platinasilatroticenophane and the [2]platinasilatrovacenophane (Table 1).[9] Incorporation of an additional bridging atom in **6** relaxes the molecular strain that exists in the parent molecule; this is manifested in the tilt angle α of 7.51(7)°. As expected, the chromium congener is less strained than the corresponding titanium ($\alpha = 13.5°$) and vanadium compounds ($\alpha = 10.6°$); furthermore, the interatomic C−Cr distances are shorter than the Ti−C and V−C separations.[9] Owing to the strong *trans* influence conferred by the silyl group, the Pt−P distances deviate considerably, with Pt1−P1 = 2.3745(10) Å and Pt1−P2 = 2.3057(12) Å. These values lie in the expected range known

Table 1. Crystal data and structure refinement for **2**, **3**, **5**, **6**, and **7**.

|	2	3	5	6	7
molecular formula	$C_{14}H_{16}CrSi$	$C_{18}H_{24}CrSi$	$C_{15}H_{16}CrSi$	$C_{16}H_{22}CrSi_2$	$C_{26}H_{46}CrP_2PtSi$
M_r	264.36	320.46	276.37	322.52	695.75
temperature [K]	173(2)	193(2)	193(2)	173(2)	193(2)
wavelength [Å]	0.71073	0.71073	0.71073	0.71073	0.71073
crystal system	monoclinic	orthorhombic	orthorhombic	monoclinic	orthorhombic
space group	$P2_1/n$	$Pca2_1$	$Pbca$	$P2_1$	$P2_12_12_1$
Z	4	4	8	2	4
a [Å]	11.0223(14)	14.7816(11)	7.7123(5)	6.6512(5)	7.9214(7)
b [Å]	7.8437(10)	9.5663(7)	17.3600(12)	13.0734(11)	17.6925(15)
c [Å]	14.4376(18)	10.9911(8)	18.7104(13)	9.4128(8)	20.1885(17)
α [°]	90	90	90	90	90
β [°]	97.649(3)	90	90	105.1320(10)	90
γ [°]	90	90	90	90	90
volume [Å³]	1237.1(3)	1554.2(2)	2505.1(3)	790.10(11)	2829.4(4)
ρ_{calcd} [g cm⁻¹]	1.419	1.370	1.466	1.356	1.633
absorption coefficient [mm⁻¹]	0.990	0.801	0.981	0.860	5.491
F(000)	552	680	1152	340	1392
crystal size [mm³]	0.24 × 0.16 × 0.03	0.13 × 0.11 × 0.06	0.03 × 0.03 × 0.32	0.09 × 0.24 × 0.26	0.39 × 0.19 × 0.12
θ range for data collection [°]	2.19–25.21	2.50–26.43	2.35–26.05	2.24–26.03	2.30–26.14
limiting indices	$-13 \le h \le 13$ $-9 \le k \le 9$ $-17 \le l \le 17$	$-18 \le h \le 18$ $-11 \le k \le 11$ $-13 \le l \le 13$	$-9 \le h \le 9$ $-21 \le k \le 21$ $-22 \le l \le 23$	$-8 \le h \le 8$ $-16 \le k \le 16$ $-11 \le l \le 11$	$-9 \le h \le 9$ $-21 \le k \le 21$ $-24 \le l \le 24$
reflections collected	13607	25537	21765	8938	30861
independent reflections ($R_{int.}$)	2450 (2073)	3185 (3105)	2466 (2046)	3143 (3035)	5626 (5484)
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
data/restraints/parameters	2450/0/145	3185/1/181	2466/13/153	3143/1/172	5626/0/280
goodness-of-fit on F^2	1.038	1.060	1.083	1.064	1.068
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0345$ $wR_2 = 0.0915$	$R_1 = 0.0227$ $wR_2 = 0.0616$	$R_1 = 0.0240$ $wR_2 = 0.0599$	$R_1 = 0.0482$ $wR_2 = 0.1082$	$R_1 = 0.0216$ $wR_2 = 0.0528$
R indices (all data)	$R_1 = 0.0429$ $wR_2 = 0.0961$	$R_1 = 0.0234$ $wR_2 = 0.0620$	$R_1 = 0.0253$ $wR_2 = 0.0605$	$R_1 = 0.0605$ $wR_2 = 0.1138$	$R_1 = 0.0225$ $wR_2 = 0.0530$
largest diff. peak and hole [e Å⁻³]	0.408 and −0.283	0.228 and −0.255	0.278 and −0.168	0.724 and −0.411	1.957 and −0.838
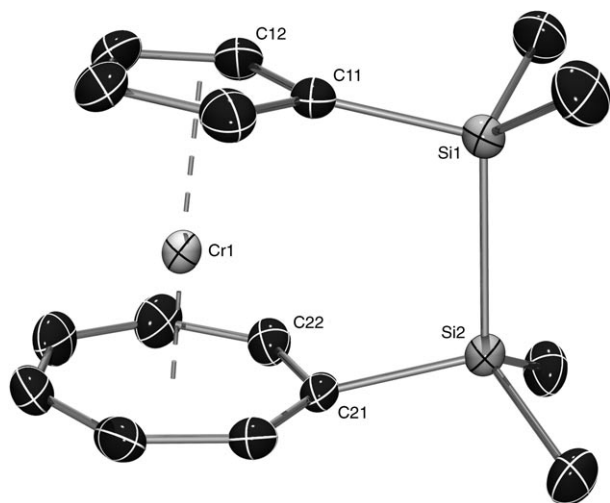
Figure 3. The molecular structure of **6**.[16] Selected bond lengths [Å] and angles [°]: Cr1−C11 2.197(2), Cr1−C12 2.190(2), Cr1−C13 2.191(2), Cr1−C14 2.181(2), Cr1−C15 2.184(2), Cr1−C21 2.1750(17), Cr1−C22 2.146(2), Cr1−C23 2.161(2), Cr1−C24 2.157(2), Cr1−C25 2.166(2), Cr1−C26 2.168(2), Cr1−C27 2.155(2), C11−Si1 1.879(2), C21−Si2 1.902(2), Si1−Si2 2.3507(8), Cr1−X_{Cp} 1.829, Cr1−X_{Cht} 1.429; X_{Cp}-Cr1-X_{Cht} 177.24 (X = centroid).

Figure 6. Molecular structure of **7** (ref. [16]. Selected bond lengths [Å] and angles [°]: Cr1−C11 2.173(4), Cr1−C12 2.150(4), Cr1−C13 2.145(4), Cr1−C14 2.147(4), Cr1−C15 2.149(4), Cr1−C16 2.141(5), Cr1−C17 2.141(4), Cr1−C21 2.150(4), Cr1−C22 2.173(4), Cr1−C23 2.201(4), Cr1−C24 2.185(4), Cr1−C25 2.163(4), Pt1−C21 2.087(4), Pt1−P1 2.3745(10), Pt1−P2 2.3057(12), Pt1−Si1 2.4229(13); C21-Pt1-P2 174.58(11), C21-Pt1-P1 85.63(11), P1-Pt1-P2 99.34(4), C21-Pt1-Si1 82.82(11), P2-Pt1-Si1 92.51(4), P1-Pt1-Si1 166.42(4), X_{Cp}-Cr-X_{Cht} 174.9 (X = centroid).

presence of a platinum catalyst has been reported recently.[3a, 9] A solution of **2** in C_6D_6 was treated with Karstedt's catalyst (Pt^0) both at ambient temperature and at elevated temperatures. In both cases ^{1}H NMR characterization of the reaction mixture demonstrated 90% conversion of the silatrochrocenophane (Scheme 3). The polymeric product (**8**)

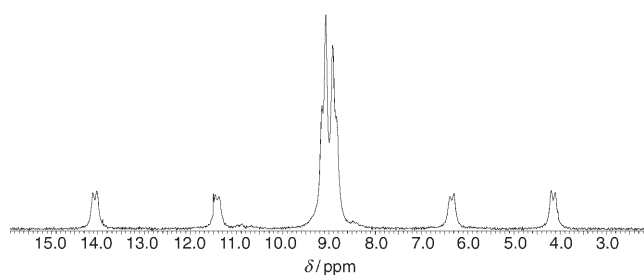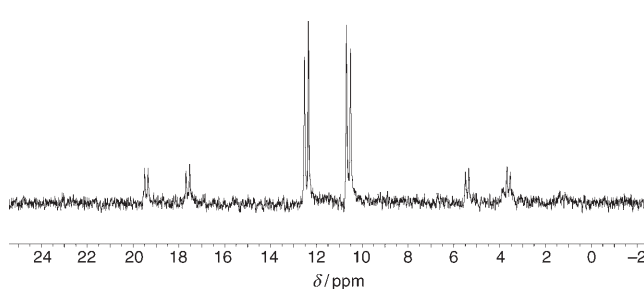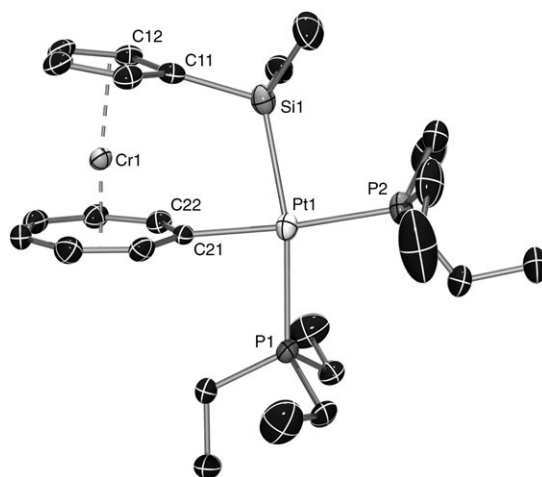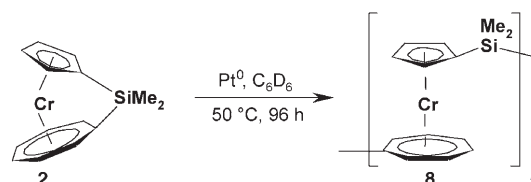Figure 4. ^{31}P NMR spectrum of **7**.

Figure 5. ^{29}Si NMR spectrum of **7**.

from [2]platinasilaferrocenophanes, as do Pt1−C21 (2.087(4) Å) and Pt1−Si1 (2.4229(13) Å).[18a,b]

Ring-opening polymerization of [1]silatrochrocenophane (2): Transition metal catalyzed ring-opening polymerization (ROP) of [1]silaferrocenophanes has been shown to be an efficient method for the preparation of high molecular weight polyferrocenylsilanes.[18e,g] In addition, the ROP of [1]silachromarenophanes and [1]silatroticenophane in the

Scheme 3. Ring-opening polymerization of **2** and formation of the polymer **8**.

was precipitated in hexanes to yield a light green powder in 52% yield. The change in the chemical shift of the $SiMe_2$ group in both the ^{1}H and the ^{29}Si NMR spectra to 0.8 and −2.7, respectively, compared with 0.61 and −6.4 in **2**, was important. The polymer **8** was found to be air-sensitive and sparingly soluble in THF; characterization of the powder by gel permeation chromatography (GPC) revealed a moderate molecular weight [M_w = 6.4×10^3, M_n = 4.0×10^3 (PDI = 1.6)].

We also attempted copolymerization of **2** with [(η^5-C_5H_4)-SiR(R′)-(η^5-C_5H_4)Fe] (R = R′ = Me, or R = Me, R′ = Ph) in the presence of a platinum catalyst in order to increase the solubility of the polymer product in organic solvents. After 48 h at room temperature, however, only the

FULL PAPER

corresponding polyferrocenylsilane homopolymer could be detected by ^{1}H NMR spectroscopy in the crude mixture and in the isolated product. This result suggests that [1]silaferrocenophanes undergo metal-catalyzed ROP much more rapidly than species **2**.

Photolytic ring-opening polymerization has been shown recently to be successful in the ROP of [1]silaferrocenophanes to give polyferrocenylsilanes with efficient molecular weight control.[20] We attempted to induce photolytic ring opening of compound **2** in an analogous manner. Solutions of **2** in THF were treated with Na[C$_5$H$_5$] or alternatively with 1,2-bis(diphenylphosphino)ethane at 5°C under a UV light source for several hours. In each case, however, photolytic treatment did not result in ring opening as determined by ^{1}H NMR spectroscopy.

Conclusion

Novel [1]silatrochrocenophanes **2**--**5** have been synthesized and characterized. Single-crystal X-ray diffraction studies of **2** and **3** revealed the presence of strained, ring-tilted structures. The incorporation of a disila bridge in the trochrocene moiety afforded the [2]silatrochrocenophane **6**. X-ray diffraction studies revealed a less strained structure than those of **2** and **3**. Upon treatment of **2** with [Pt(PEt$_3$)$_4$] a regioselective Si−C bond activation occurred, which afforded the oxidative addition product **7**, which was also characterized structurally and showed only moderate molecular strain ($\alpha = 7.5°$). Testing of the propensity of **2** to form metallopolymers **8** via transition metal mediated ring-opening polymerization yielded a metallopolymer with a moderate molecular weight ($M_w = 6.4\times10^3$, $M_n = 4.0\times10^3$ (PDI = 1.6)) as determined by GPC. Utilization of these strained precursors in ring-opening polymerization is being studied in our laboratories.

Experimental Section

All manipulations were conducted under a protective atmosphere of dry argon, by standard Schlenk techniques or in a glove-box. All solvents were purified by standard methods. The NMR spectra were recorded on a Bruker Avance 400 (^{1}H: 400.13 MHz; ^{13}C: 100.61 MHz; ^{29}Si: 79.49 MHz) and a Bruker AV 500 (^{1}H: 500.13 MHz; ^{13}C: 125.76 MHz; ^{29}Si: 99.36 MHz) FT-NMR spectrometer, respectively, and were referenced relative to TMS. The mass spectra were recorded on a Finnigan MAT 8200 spectrometer (EI-positive: 70 eV). Exact masses were recorded on a Finnigan MAT 90 spectrometer (EI-positive: 70 eV). NMR characterization of the polymerization experiments was obtained on Varian Unity 400 or Varian Mercury 300 spectrometers (^{1}H: 400 or 300 MHz; ^{13}C: 100.5 MHz; ^{29}Si: 79.5 MHz). Solid-state CP-MAS ^{13}C spectra were obtained on a Bruker DSX 200 instrument with a spin rate of 8 kHz. Molecular weights were estimated by GPC using a Viscotek GPC MAX liquid chromatograph equipped with a Viscotek Triple Detector Array consisting of a differential refractometer and Ultrastyragel columns with pore sizes of 10^3–10^5 Å. Polystyrene standards were purchased from Aldrich and were used for calibration purposes. The flow rate was 1.0 mL min^{-1}, and the eluent was THF. Photoirradiation was performed by placing the reaction flask next to a 125 W high–pressure Hg arc lamp

(Philips). The emission was filtered through Pyrex glass ($\lambda \approx 300$ nm). [(η^5-C$_5$H$_5$)(η^7-C$_7$H$_7$)Cr],[7a] [(η^5-C$_5$H$_4$Li)(η^7-C$_7$H$_6$Li)Cr]·tmeda[8a] (**1**), [Pt-(PEt$_3$)$_4$],[19] [(η^5-C$_5$H$_5$)-SiMe$_2$-(η^5-C$_5$H$_4$)Fe],[2] and [(η^5-C$_5$H$_5$)-SiMe(Ph)-(η^5-C$_5$H$_4$)Fe][2] were synthesized according to published procedures. Karstedt's catalyst was purchased from Gelest; Na[η^5-C$_5$H$_5$] (2.0 M in THF) and 1,2-bis(diphenylphosphino)ethane were purchased from Aldrich and were used as received. The dichlorodialkylsilanes and tetramethyldichlorodisilane employed in the syntheses were purchased commercially, distilled before use at ambient pressure, and stored under argon.

[(η^5-C$_5$H$_4$)SiMe$_2$-(η^7-C$_7$H$_6$)Cr] (2): A solution of Me$_2$SiCl$_2$ (768 mg, 722 μl, 5.95 mmol) in pentane (20 mL) was added dropwise to a suspension of [(η^5-C$_5$H$_4$Li)(η^7-C$_7$H$_6$Li)Cr]·tmeda (**1**) (2.00 g, 5.95 mmol) in pentane (50 mL) over a 30 min period at −78°C. After the addition was complete, the reaction mixture was stirred for 2 h at −78°C and subsequently warmed to ambient temperature over a 6 h period while the suspension changed from pale yellow to turquoise. It was filtered through Celite, and **2** was isolated by crystallization at −30°C as a dark blue solid (850 mg, 3.21 mmol, 54%). ^{1}H NMR (500.13 MHz, C$_6$D$_6$, 297 K): δ = 0.61 (s, 6H; Si(CH$_3$)$_2$), 3.66 (m, 2H; C$_5$H$_4$), 3.70 (m, 2H; C$_5$H$_4$), 5.14 (m, 2H; α-C$_7$H$_6$), 5.44 (m, 2H; β-C$_7$H$_6$), 5.88 ppm (m, 2H; γ-C$_7$H$_6$); ^{13}C{^{1}H} NMR (125.77 MHz, C$_6$D$_6$, 297 K): δ = −2.79 (Si(CH$_3$)$_2$), 51.66 (ipso-carbon), 60.10 (ipso-carbon), 78.28 (C$_5$H$_4$), 80.61 (C$_5$H$_4$), 86.83 (C$_7$H$_6$), 91.59 (C$_7$H$_6$), 99.97 ppm (C$_7$H$_6$); ^{29}Si{^{1}H} (99.36 MHz, C$_6$D$_6$, 297 K): δ = 6.44 ppm; MS (EI): m/z (%): 264 (42) [M^+], 249 (2) [M^+−Me], 234 (1) [M^+−2 Me], 208 (28) [Tr$^+$], 144 (4) [Cr(C$_5$H$_4$Si)$^+$], 117 (11) [Cr(C$_5$H$_5$)$^+$], 91 (9) [C$_7$H$_7^+$], 52 (100) [Cr$^+$]; HR MS: m/z 264.04206 [M^+] (requires 264.04209); elemental analysis (%) calcd for C$_{14}$H$_{16}$CrSi (264.36): C 63.61, H 6.10; found: C 63.36, H 6.23.

[(η^5-C$_5$H$_4$)-Si(iPr)$_2$-(η^7-C$_7$H$_6$)Cr] (3): A procedure analogous to the preparation of **2**, employing **1** (0.30 g, 0.89 mmol) in hexanes (25 mL) and (iPr)$_2$SiCl$_2$ (0.16 g, 0.89 mmol) in hexanes (5 mL), afforded **3** (0.15 g, 0.48 mmol, 54%) as dark blue crystals after crystallization and drying in vacuo. ^{1}H NMR (200 MHz, C$_6$D$_6$): δ = 1.35 (d, ^{3}J(H,H) = 7.33 Hz, 6H; Me), 1.53 (d, ^{3}J(H,H) = 7.32 Hz, 6H; Me), 1.74 (m, 2H; C$_{iPr}$H), 3.69 (m, 2H; C$_5$H$_4$), 3.76 (m, 2H; C$_5$H$_4$), 5.14 (m, 2H; α-C$_7$H$_6$), 5.45 (m, 2H; β-C$_7$H$_6$), 5.93 ppm (m, 2H; γ-C$_7$H$_6$); ^{13}C{^{1}H} NMR (50 MHz, C$_6$D$_6$): δ = 11.62 (Me), 17.49, 18.17 (C$_{iPr}$H), 51.67 (ipso-carbon), 60.17 (ipso-carbon), 78.45 (C$_5$H$_4$), 81.31 (C$_5$H$_4$), 86.73 (C$_7$H$_6$), 92.32 (C$_7$H$_6$), 99.85 ppm (C$_7$H$_6$); ^{29}Si{^{1}H} NMR (40 MHz, C$_6$D$_6$): δ = 12.5 ppm; MS (EI): m/z (%): 320 (100) [M^+], 278 (5) [M^+−C$_3$H$_6$], 235 (24) [M^+−C$_3$H$_6$−iPr], 208 (6) [Tr$^+$], 52 (51) [Cr$^+$]; HR MS: m/z 320.10495 [M^+] (requires 320.10469); elemental analysis (%) calcd for C$_{18}$H$_{24}$CrSi (320.46): C 67.46, H 7.55; found: C 67.71, H 7.33.

[(η^5-C$_5$H$_4$)-SiMe(iPr)-(η^7-C$_7$H$_6$)Cr] (4): In a procedure analogous to the preparation of **2**, employing **1** (1.00 g, 2.97 mmol) in pentane (50 mL) and Me(iPr)SiCl$_2$ (467.3 mg, 2.97 mmol) in pentane (20 mL) afforded **4** (567 g, 2.00 mmol, 67%) as dark blue crystals after crystallization and drying in vacuo. ^{1}H NMR (400 MHz, C$_6$D$_6$): δ = 0.55 (s, 3H; Me), 1.18 (d, ^{3}J(H,H) = 7.45 Hz, 3H; Me), 1.41 (d, ^{3}J(H,H) = 7.32 Hz, 3H; Me), 1.63 (m, 1H; C$_{iPr}$H), 3.67 (m, 2H; C$_5$H$_4$), 3.74 (m, 2H; C$_5$H$_4$), 5.12 (m, 1H; α-C$_7$H$_6$), 5.15 (m, 1H; α-C$_7$H$_6$), 5.46 (m, 2H; β-C$_7$H$_6$), 5.91 ppm (m, 2H; γ-C$_7$H$_6$); ^{13}C{^{1}H} NMR (101 MHz, C$_6$D$_6$): δ = −8.29 (Me), 10.53 (Me), 16.33, 16.50 (C$_{iPr}$H), 51.39 (ipso-carbon), 60.10 (ipso-carbon), 78.33 (C$_5$H$_4$), 78.42 (C$_5$H$_4$), 80.64 (C$_5$H$_4$), 81.12 (C$_5$H$_4$), 86.79 (C$_7$H$_6$), 86.88 (C$_7$H$_6$), 91.73 (C$_7$H$_6$), 92.20 (C$_7$H$_6$), 99.84 (C$_7$H$_6$), 99.94 ppm (C$_7$H$_6$); ^{29}Si{^{1}H} NMR (79 MHz, C$_6$D$_6$): δ = 12.0 ppm; MS (EI): m/z (%): 292 (77) [M^+], 277 (2) [M^+−Me], 262 (2) [M^+−Me−Me], 249 (20) [M^+−iPr], 234 (3) [M^+−iPr−Me], 208 (27) [Tr$^+$], 144 (8) [Cr(C$_5$H$_4$Si)$^+$], 91 (10) [C$_7$H$_7^+$], 52 (100) [Cr$^+$]; HR MS: m/z 292.07367 [M^+] (requires 292.7339); elemental analysis (%) calcd for C$_{16}$H$_{20}$CrSi (292.41): C 65.72, H 6.89; found: C 65.44, H 6.81.

[(η^5-C$_5$H$_4$)-Si(CH$_2$)$_3$-(η^7-C$_7$H$_6$)Cr] (5): A procedure analogous to the preparation of **2**, employing **1** (600 mg, 1.78 mmol) in pentane (50 mL) and (CH$_2$)$_3$SiCl$_2$ (251.7 mg, 1.78 mmol, 210 μL) afforded dark blue crystals of **5** (207 mg, 0.75 mmol, 42%) after crystallization and drying in vacuo. ^{1}H NMR (500.13 MHz, C$_6$D$_6$): δ = 1.56–1.63 (m, 2H; CH$_2$), 1.72–1.79 (m, 2H; CH$_2$), 2.35–2.41 (m, 1H; CH$_2$), 2.44–2.54 (m, 1H; CH$_2$), 3.67 (m, 2H; C$_5$H$_4$), 3.74 (m, 2H; C$_5$H$_4$), 5.20 (s, 1H; C$_7$H$_6$), 5.21 (s, 1H;

C_7H_6), 5.53 (m, 2H; C_7H_6), 5.82 ppm (m, 2H; C_7H_6); $^{13}C\{^1H\}$ NMR (125.77 MHz, C_6D_6): δ = 17.1 (CH_2), 17.2 ($SiCH_2$), 49.9 (*ipso*-carbon), 60.2 (*ipso*-carbon), 78.1 (C_5H_4), 80.2 (C_5H_4), 87.2 (C_7H_6), 90.4 (C_7H_6), 100.1 ppm (C_7H_6); $^{29}Si\{^1H\}$ NMR (99.36 MHz, C_6D_6): δ = 15.3; MS (EI): *m/z* (%): 276 (80) [M^+], 248 (68) [$M^+-C_2H_4$], 234 (2) [$M^+-C_3H_6$], 208 (2) [Tr^+], 144 (32) [$Cr(C_5H_4Si)^+$], 117 (6) [$Cr(C_5H_5)^+$], 106 (4) [$(C_6H_6Si)^+$], 93 (10) [$(C_5H_5Si)^+$], 52 (100) [Cr^+]; HR MS: *m/z* 276.04135 [M^+] (requires 276.04209); elemental analysis (%) calcd for $C_{15}H_{16}CrSi$ (276.37): C 65.19, H 5.84; found: C 65.31, H 5.76.

[(η^5-C_5H_4)-(SiMe$_2$)$_2$-(η^7-C_7H_6)Cr] (6): A procedure analogous to the preparation of **2**, employing **1** (376 mg, 1.12 mmol) in heptane (50 mL) and $(CH_3)_4Si_2Cl_2$ (208 mg, 1.12 mmol), afforded **6** (250 mg, 0.78 mmol, 69%) as dark blue crystals after crystallization and drying in vacuo. ^1H NMR (500.13 MHz, C_6D_6): δ = 0.29 (s, 6H; Si(CH$_3$)$_2$), 0.62 (s, 6H; Si-(CH$_3$)$_2$)), 3.88 (m, 2H; C_5H_4), 4.04 (m, 2H; C_5H_4), 5.55 (m, 2H; C_7H_6), 5.67 (m, 2H; C_7H_6), 5.89 ppm (m, 2H; C_7H_6); $^{13}C\{^1H\}$ NMR (125.77 MHz, C_6D_6): δ = -2.3 (SiCH$_3$), -1.4 (SiCH$_3$), 78.3 (C_5H_4), 81.4 (*ipso*-carbon), 81.8 (C_5H_4), 86.7 (C_7H_6), 90.4 (C_7H_6), 91.4 (*ipso*-carbon), 92.4 ppm (*ipso*-carbon); $^{29}Si\{^1H\}$ (99.36 MHz, C_6D_6): δ = -14.8, 6.9 ppm; MS (EI): *m/z* (%): 322 (100) [M^+], 307 (4) [M^+-Me], 264 (21) [M^+-SiMe_2], 208 (19) [Tr^+], 117 (11) [$Cr(C_5H_5)^+$], 52 (55) [Cr^+]; HR MS: *m/z* 322.06611 [M^+] (requires 322.06597); elemental analysis (%) calcd for $C_{16}H_{22}CrSi_2$ (322.51): C 59.59, H 6.88; found: C 59.95, H 6.51.

[(η^5-C_5H_4)-SiMe$_2$-Pt(PEt$_3$)$_2$-(η^7-C_7H_6)Cr] (7): A resealable bulb was charged with [Pt(PEt$_3$)$_4$] (253 mg, 0.379 mmol) and heated for 20 min at 60°C under vacuum. [(η^5-C_5H_4)-SiMe$_2$-(η^7-C_7H_6)Cr] (**2**) (100 mg, 0.378 mmol) and benzene (2 mL) were added to the resulting red oil. The mixture was heated at 60°C for two days and subsequently dried in vacuo. The residue was taken up in heptane (20 mL) and filtered through a short pad of Celite. The solution was concentrated to about 3 mL and then cooled to -78°C. The greenish crystals that separated were decanted from the mother liquid, washed with two portions of pentane (3 mL), and dried in vacuo to yield **6** (200 mg, 0.287 mmol, 76%). ^1H NMR (500.13 MHz, C_6D_6, 297 K): δ = 0.78 (m, 15H; PCH$_2$C*H*$_3$ and Si(CH$_3$)$_2$), 0.98 (m, 9H; PCH$_2$C*H*$_3$), 1.22 (m, 6H; PCH$_2$C*H*$_3$), 1.68 (m, 6H; PC*H*$_2$CH$_3$), 3.87 (m br, 2H; C_5H_4), 4.44 (m br, 2H; C_5H_4), 5.75 ppm (m br, 6H; C_7H_6); $^{13}C\{^1H\}$ NMR (125.77 MHz, C_6D_6): δ = 8.0 ($J_{C,Pt}$ = 11.0 Hz, P(CH$_2$C*H*$_3$)), 8.5 (d, $^3J_{C,P}$ = 11.9 Hz, Si(CH$_3$)$_2$), 8.8 ($J_{C,Pt}$ = 22.0 Hz, P(CH$_2$C*H*$_3$)$_3$), 15.5 (d, $^1J_{C,P}$ = 18.3 Hz, $J_{C,Pt}$ = 11.0 Hz, P-(C*H*$_2$CH$_3$)$_3$), 18.4 (d, $^1J_{C,P}$ = 31.2 Hz, $J_{C,Pt}$ = 22.9 Hz, P(C*H*$_2$CH$_3$)$_3$), 75.7 (C_5H_4), 81.7 (C_5H_4), 85.5 (C_7H_6), 87.1 (*ipso*-C_5H_4), 93.2 (d, $J_{C,P}$ = 6.4 Hz, $J_{C,Pt}$ = 72.4 Hz, C_7H_6), 93.9 ($J_{C,Pt}$ = 44.0 Hz, C_7H_6), 94.7 (t, $J_{C,P}$ = 6.4 Hz, $J_{C,Pt}$ = 59.6 Hz, *ipso*-C_7H_6); $^{29}Si\{^1H\}$ NMR (99.36 MHz, C_6D_6): δ = 11.5 ppm (dd, $^2J_{Si,P}$ = 182.14 *trans* to PEt$_3$, $^2J_{Si,P}$ = 16.95 *cis* to PEt$_3$, $^1J_{Si,Pt}$ = 1391.7 Hz); $^{31}P\{^1H\}$ NMR (202.45 MHz, C_6D_6): δ = 8.9 (d, $^2J_{P,P}$ = 17.23 Hz, $^1J_{P,Pt}$ = 1027.51 Hz, PEt$_3$ *cis* to SiMe$_2$), 9.1 ppm (d, $^2J_{P,P}$ = 17.23 Hz, $^1J_{P,Pt}$ = 2007.03 Hz, PEt$_3$ *trans* to SiMe$_2$); elemental analysis (%) calcd for $C_{26}H_{46}CrP_2PtSi$ (695.75): C 44.88 H 6.66; found: C 44.81, H 6.73.

Ring-opening polymerization of 2 with platinum(0)

At room temperature: Karstedt's catalyst (0.5% wt, 5.2 µL) was added to a deep blue solution of **2** (20 mg, 75.7 µmol) in C_6D_6 (1 mL). The solution was kept under an inert atmosphere and was allowed to react at 25°C for approximately 72 h. The product was precipitated into hexanes and yielded a light green powder. This powder was air-sensitive and sparingly soluble in organic solvents. Yield: 12 mg (60%). ^1H NMR (C_6D_6, 300 MHz): δ = 5.5 (v br, 6H; C_7H_6), 3.9 (br, 2H; C_5H_4), 3.8 (br, 2H; C_5H_4), 0.8 ppm (br, 6H; SiMe$_2$).

At 50°C: In a similar manner, Karstedt's catalyst (0.5% wt., 5.2 µL) was added to a solution of **2** (20 mg, 75.7 µmol) in C_6D_6 (1 mL). Upon addition of the platinum(0) catalyst, the solution immediately turned green and its ^1H NMR showed only the presence of **2**. The solution was kept under an inert atmosphere and allowed to react for 96 h at 50°C. ^1H NMR of the crude reaction mixture showed 90% conversion from **2**. The light green product was precipitated into hexanes and yielded a powdery material which was air-sensitive and sparingly soluble in polar organic solvents. Yield: 10.5 mg (52%). For polymer **8**: ^1H NMR (C_6D_6, 300 MHz) δ = 5.85 (br, 2H; C_7H_6), 5.57 (br, 2H; C_7H_6), 5.52(br, 2H;

C_7H_6), 3.93 (br, 2H; C_5H_4), 3.80 (br, 2H; C_5H_4), 0.80 ppm (br, 6H; SiMe$_2$); Cp-MAS $^{13}C\{^1H\}$ NMR (100.6 MHz, kv_{rot} = 5 KHz, 25°C): δ = 1.3 (br, Si(CH$_3$)$_2$), 75 (br, C_5H_4), 81 (br, C_5H_4), 88 (br, C_7H_6), 90.5 (br, C_7H_6), 93 ppm (br, C_7H_6); $^{29}Si\{^1H\}$ NMR (C_6D_6, 400 MHz): δ = -2.7 ppm (s, SiMe$_2$); GPC (THF): M_n = 4.0×10^3, M_w = 6.4×10^3, PDI = 1.6.

Attempted copolymerization of 2 with [1]silaferrocenophanes: Under an inert atmosphere, toluene (2 mL) was added to a vial containing: a) [(η^5-C_5H_4)-SiMe$_2$-(η^7-C_7H_6)Cr] (11 mg, 41.7 µmol) and [(η^5-C_5H_4)-SiMe$_2$-(η^5-C_5H_4)Fe] (5 equiv, 50 mg, 0.21 mmol); or b) [(η^5-C_5H_4)-SiMe$_2$-(η^7-C_7H_6)Cr] (9 mg, 34.1 µmol) and [(η^5-C_5H_4)-SiMe(Ph)-(η^5-C_5H_4)Fe] (5 equiv, 50 mg, 0.16 mmol). Karstedt's catalyst (0.5% wt, 15.5 µL) was added by using a syringe to each vial. Each mixture was allowed to react under an inert atmosphere for 48 h at 25°C. In each case, ^1H NMR revealed only polyferrocenylsilane homopolymer both in the crude mixture and in the product precipitated from hexanes.

Attempted stoichiometric, photolytic ring-opening of 2: To deep blue solutions of [(η^5-C_5H_4)-SiMe$_2$-(η^7-C_7H_6)Cr] (100 mg, 0.38 mmol) in THF (2 mL) was added: a) (Na[η^5-C_5H_5] (1 equiv, 0.19 mL, 2.0 M in THF); or b) bis(diphenylphosphino)ethane (1 equiv, 0.15 g). The solutions were irradiated for up to 6 h and kept at a temperature of 5°C in a water bath. In each case, only unreacted **2** could be detected by ^1H NMR spectroscopy.

Acknowledgements

[1] a) D. A. Foucher, C. H. Honeyman, J. M. Nelson, B. Z. Tang, I. Manners, *Angew. Chem.* **1993**, *105*, 1843–1845; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1709–1711; b) I. Manners, *Adv. Organomet. Chem.* **1995**, *37*, 131–168; M. Herberhold, *Angew. Chem.* **1995**, *107*, 1985–1987; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1837–1839.

[2] a) I. Manners, *Chem. Commun.* **1999**, 857–865; b) P. Nguyen, P. Gómez-Elipe, I. Manners, *Chem. Rev.* **1999**, *99*, 1515–1548; c) I. Manners, U. Vogel, in *Modern Cyclophane Chemistry* (Eds.: R. Gleiter, H. Hopf), Wiley-VCH, Weinheim, **2004**, p. 415.

[3] a) A. Berenbaum, I. Manners, *Dalton Trans.* **2004**, 2057–2058; b) H. Braunschweig, M. Homberger, C. Hu, X. Zheng, E. Gullo, G. Clentsmith, M. Lutz, *Organometallics* **2004**, *23*, 1968–1970; c) K. C. Hultzsch, J. M. Nelson, A. J. Lough, I. Manners, *Organometallics* **1995**, *14*, 5496–5502; d) C. Elschenbroich, J. Hurley, B. Metz, W. Massa, G. Baum, *Organometallics* **1990**, *9*, 889–902.

[4] a) C. Elschenbroich, E. Schmidt, R. Gondrum, B. Metz, O. Burghaus, W. Massa, S. Wocadlo, *Organometallics* **1997**, *16*, 4589–4596; b) C. Elschenbroich, A. Bretschneider-Hurley, J. Hurley, A. Behrendt, W. Massa, S. Wocadlo, E. Reijerse, *Inorg. Chem.* **1995**, *34*, 743–745; c) C. Elschenbroich, A. Bretschneider-Hurley, J. Hurley, W. Massa, S. Wocadlo, J. Pebler, *Inorg. Chem.* **1993**, *32*, 5421–5424.

[5] a) M. J. Drewitt, S. Barlow, D. O'Hare, J. M. Nelson, P. Nguyen, I. Manners, *Chem. Commun.* **1996**, 2153–2154; b) S. Fox, J. P. Dunne, M. Tacke, D. Schmitz, R. Dronskowski, *Eur. J. Inorg. Chem.* **2002**, 3039–3046.

[6] a) U. Vogel, A. J. Lough, I. Manners, *Angew. Chem.* **2004**, *116*, 3383–3387; *Angew. Chem. Int. Ed.* **2004**, *43*, 3321–3325; b) J. M. Nelson, A. J. Lough, I. Manners, *Angew. Chem.* **1994**, *106*, 1019–1021; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 989–991.

[7] a) E. O. Fischer, S. Breitschaft, *Chem. Ber.* **1966**, *99*, 2905–2917; b) E. O. Fischer, S. Breitschaft, *Angew. Chem.* **1963**, *75*, 94–95; *Angew. Chem. Int. Ed. Engl.* **1963**, *2*, 44–45.

[8] For the introduction of the trivial name trochrocene, see: a) H. Braunschweig, M. Lutz, K. Radacki, *Angew. Chem.* **2005**, *117*, 5792–5796; *Angew. Chem. Int. Ed. Engl.* **2005**, *44*, 5647–5651. This is in accord with the naming of [(η^5-C_5H_5)V(η^7-C_7H_7)] as trovacene and [(η^5-C_5H_5)Ti(η^7-C_7H_7)] as troticene; see, for example: b) C. Elschen-

broich, O. Schiemann, O. Burghaus, K. Harms, *J. Am. Chem. Soc.* **1997**, *119*, 7452–7457; c) M. Tamm, A. Kunst, T. Bannenberg, E. Herdtweck, P. Sirsch, C. J. Elsevier, J. M. Ernsting, *Angew. Chem.* **2004**, *116*, 5646–5650; *Angew. Chem. Int. Ed.* **2004**, *43*, 5530–5534.

[9] M. Tamm, A. Kunst, E. Herdtweck, *Chem. Commun.* **2005**, 1729–1731.

[10] C. Elschenbroich, F. Paganelli, M. Nowotny, B. Neumüller, O. Burghaus, *Z. Anorg. Allg. Chem.* **2004**, *630*, 1599–1606.

[11] a) H. L. Lentzner, W. E. Watts, *Tetrahedron* **1971**, *27*, 4343–4350; b) J. M. Nelson, P. Nguyen, R. Petersen, H. Rengel, P. M. Macdonald, A. J. Lough, I. Manners, N. P. Raju, J. E. Greedan, S. Barlow, D. D. O'Hare, *Chem. Eur. J.* **1997**, *3*, 573–584.

[12] C. J. Groenenboom, H. J. De Liefde, E. W. Meijer, F. Jellinek, *J. Organomet. Chem.* **1974**, *69*, 235–240.

[13] a) W. Finckh, B.-Z. Tang, D. A. Foucher, D. B. Zamble, R. Ziembinski, A. Lough, I. Manners, *Organometallics* **1993**, *12*, 823–829; b) M. J. MacLachlan, A. J. Lough, W. E. Geiger, I. Manners, *Organometallics* **1998**, *17*, 1873–1883; c) J. K. Pudelski, D. A. Foucher, C. H. Honeyman, A. J. Lough, I. Manners, *Organometallics* **1995**, *14*, 2470–2479; d) S. Barlow, M. J. Drewitt, T. Dijkstra, J. C. Green, D. O'Hare, C. Whittingham, H. H. Wynn, D. P. Gates, I. Manners, J. M. Nelson, J. K. Pudelski, *Organometallics* **1998**, *17*, 2113–2120.

[14] J. G. Stark, H. G. Wallace, *Chemistry Data Book*, John Murray, London, **1975**.

[15] a) H. Braunschweig, R. Dirk, M. Müller, P. Nguyen, R. Resendes, D. P. Gates, I. Manners, *Angew. Chem.* **1997**, *109*, 2433–2435; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2338–2340; b) A. Berenbaum, H. Braunschweig, R. Dirk, U. Englert, J. C. Green, F. Jäkle, A. J. Lough, I. Manners, *J. Am. Chem. Soc.* **2000**, *122*, 5765–5774.

[16] The crystal data for **2**, **3**, **5**, **6**, and **7** were collected with a Bruker APEX diffractometer with a CCD area detector and graphite-mono-chromated $Mo_{K\alpha}$ radiation. The structure was solved using direct methods, refined with a Shelx software package (G. Sheldrick, University of Göttingen, **1997**), and expanded using Fourier techniques. Details of the X-ray crystal structure determination can be found in the Supporting Information. CCDC-275102 (**2**), CCDC-275103 (**3**), CCDC-275104 (**5**), CCDC-275101 (**6**), and CCDC-275100 (**7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the CambridgeCrystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[17] a) V. V. Dement'ev, F. Cervantes-Lee, L. Parkanyi, H. Sharma, K. H. Pannell, *Organometallics* **1993**, *12*, 1983–1987; b) W. Finckh, B.-Z. Tang, D. A. Foucher, D. B. Zamble, R. Ziembinski, A. Lough, I. Manners, *Organometallics* **1993**, *12*, 823–829.

[18] a) N. P. Reddy, N. Choi, S. Shimada, M. Tanaka, *Chem. Lett.* **1996**, *25*, 649–650; b) J. B. Sheridan, A. J. Lough, I. Manners, *Organometallics* **1996**, *15*, 2195–2197; c) J. B. Sheridan, K. Temple, A. J. Lough, I. Manners, *J. Chem. Soc. Dalton Trans.* **1997**, 711–713; d) K. Temple, A. J. Lough, J. B. Sheridan, I. Manners, *J. Chem. Soc. Dalton Trans.* **1998**, 2799–2805; e) K. Temple, F. Jäkle, J. B. Sheridan, I. Manners, *J. Am. Chem. Soc.* **2001**, *123*, 1355–1364; f) W. Y. Chan, A. Berenbaum, S. B. Clendenning, A. J. Lough, I. Manners, *Organometallics* **2003**, *22*, 3796–3808; g) P. Gómez-Elipe, R. Resendes, P. M. Macdonald, I. Manners, *J. Am. Chem. Soc.* **1998**, *120*, 8348–8356.

[19] T. Yoshida, T. Matsuda, S. Otsuka, *Inorg. Synth.* **1990**, *28*, 120–123.

[20] a) T. Mizuta, Y. Imamura, K. Miyoshi, *J. Am. Chem. Soc.* **2003**, *125*, 2068–2069; b) M. Tanabe, I. Manners, *J. Am. Chem. Soc.* **2004**, *126*, 11434–11435.