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Pyrolysis of metallocene complexes $(\eta C_5H_4R)_2MR'_2$: an organometallic route to metal carbide (MC) materials (M = Ti, Zr, Hf)

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The following compounds were prepared and their pyrolysis in a stream of argon was studied: $(\eta^5\text{-}C_5H_5)_2Ti(C{\equiv}CC_6H_5)_2$, $(\eta^5\text{-}C_5H_4SiMe_3)_2\text{-}Ti(SH)_2$, $[(\eta^5\text{-}C_5H_5)Ti(\mu\text{-}CH_2)]_2$, $(\eta^5\text{-}C_5H_5)_2ZrR_2\text{-}(R{=}CH_2, CH_2C_6H_5, N(CH_3)_2)$, $(\eta^5\text{-}C_5H_4CH_3)_2\text{-}Zr(C{\equiv}CC_6H_5)_2$, $[(\eta^5\text{-}C_5H_4SiMe_3)_2Zr(\mu\text{-}S)]_2$, $[(\eta^5\text{-}C_5H_4SiMe_3)_2Hf(\mu\text{-}S)]_2$ and $(\eta^5\text{-}C_5H_4SiMe_3)_2Hf\text{-}(C{\equiv}CC_6H_5)_2$. The products of bulk pyrolysis of these materials were formed in 20–40% yield, based on the charged sample weight, and consisted mainly of titanium carbide together with small amounts of amorphous carbon.

Keywords: Pyrolysis, ceramic, metallocene, titanium, zirconium, hafnium, low temperature route

Introduction

Metal carbides such as titanium, zirconium and hafnium carbides (Tic, ZrC and HfC) are hard materials; titanium carbide, especially, is one of the hardest known and possesses high thermal stability.[1] For example, titanium carbide is used commercially for coatings on different cutting tools, as a low-friction coating for bearings and as a protective wall coating for fusion reactors.[1] The traditional powder metallurgical preparative methods require high temperatures and yield a product that must be further processed.[1]

In a more recent development, organometallic compounds may be used as precursors for ceramic materials: For example, the MetalOrganic Chemical Vapor Deposition (MOCVD) technique is used as a low temperature route for preparing thin films of titanium carbide:[2] thermolysis of tetraneopentyltitanium at around 150 °C and $\leq 10^{-5}$ torr has been used to deposit thin films of TiC on different substrates such as Pyrex glass slides, copper or potassium bromide (KBr).[2] Also, the titanocene derivatives $(\eta\text{-}C_5H_5)TiCl_3$ or $(\eta\text{-}C_5H_5)_2TiCl_2$,[3] $(\eta\text{-}C_5H_5)_2Ti(R)(Cl)$[4] [R = CH_3, C_2H_5, $CH_2CH(CH_3)_2$, C_6H_5, $CH_2C_6H_5$, $C_2H_4C_6H_5$] and $(\eta\text{-}C_5H_5)_2TiR_2$[5,6] (R = CH_3, C_6H_5, $CH_2C_6H_5$) can be used in the preparation of titanium carbide, and in the most recent work, Brown showed that even the pseudohalide derivatives of bis(cyclopentadienyl)titanium(IV), $(\eta\text{-}C_5H_5)_2TiX_2$ (X = SCN, OCN, N_3), decompose thermally at a low temperature to yield titanium carbide.[7]

We report here further examples of the use of molecular organotitanium compounds, in particular, $(\eta\text{-}C_5H_4R)_2MR'_2$ [M = Ti, Zr, Hf; R = H, CH_3, $Si(CH_3)_3$; R′ = CH_3, $CH_2C_6H_5$, $C{\equiv}CC_6H_5$, $N(CH_3)_2$, SR], $[(\eta\text{-}C_5H_5)_2Ti(\mu\text{-}CH_2)]_2$ and $\{[(\eta\text{-}C_5H_4Si(CH_3)_3]_2M(\mu\text{-}S)\}_2$ (M = Zr, Hf) in the preparation of the carbides (TiC, as well as ZrC and HfC).

RESULTS AND DISCUSSION OF REACTION CHEMISTRY

Synthesis of starting materials

The compounds $(\eta\text{-}C_5H_5)_2Ti(C{\equiv}CC_6H_5)_2$ (**1**),[8] $(\eta\text{-}C_5H_5)_2Zr(CH_3)_2$ (**3**),[9] $(\eta\text{-}C_5H_5)_2Zr(CH_2C_6H_5)_2$ (**4**),[10] $(\eta\text{-}C_5H_4CH_3)_2Zr(C{\equiv}CC_6H_5)_2$ (**5**),[11] $(\eta\text{-}C_5H_5)_2Zr[N(CH_3)_2]_2$ (**6**),[12] and $[(\eta\text{-}C_5H_5)_2Ti(\mu\text{-}CH_2)]_2$ (**8**),[13] were synthesized according to published procedures. The new compounds $[\eta\text{-}C_5H_4Si(CH_3)_3]_2Ti(SH)_2$ (**2**),

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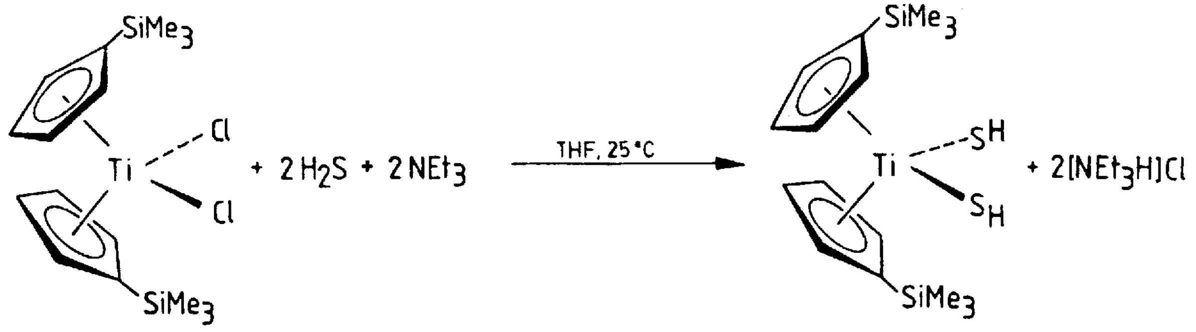


Scheme 1 **2**

$[(\eta\text{-}C_5H_4Si(CH_3)_3]_2Hf(C{\equiv}CC_6H_5)_2$ (**7**), and $\{[\eta\text{-}C_5H_4Si(CH_3)_3]_2M(\mu\text{-}S)\}_2$ (M = Zr, **9**; M = Hf, **10**) were prepared as described below (Experimental section).

Purple bis(trimethylsilylcyclopentadienyl)titanium(IV)dithiol, $[\eta\text{-}C_5H_4Si(CH_3)_3]_2Ti(SH)_2$ (**2**), was prepared in 96% yield by reaction of $[\eta\text{-}C_5H_4Si(CH_3)_3]_2TiCl_2$ [14] with H_2S in the presence of NEt_3 at rooom temperature in THF (Scheme 1).

The pale yellow bis(phenylethinyl)hafnocene compound **7**, $[\eta\text{-}C_5H_4Si(CH_3)_3]_2Hf(C{\equiv}CC_6H_5)_2$, was prepared in good yield by reaction of the appropriate hafnocene dihalide $[\eta\text{-}C_5H_4Si(CH_3)_3]_2HfCl_2$ [14] with two molar equivalents of lithium or sodium phenylacetylide in diethyl ether at room temperature (Scheme 2).

Metallocene dichlorides $[\eta\text{-}C_5H_4Si(CH_3)_3]_2MCl_2$ [14] (M = Zr, Hf) react with *in-situ* generated Li_2S [15] in tetrahydrofuran at room temperature in the dark to give the dinuclear bis-μ-sulfido bridged compounds $\{[\eta\text{-}C_5H_4Si(CH_3)_3]_2M(\mu\text{-}S)\}_2$ (M = Zr, **9**; M = Hf, **10**) in yields of around 60%. Compounds **9** and **10** were isolated as high-melting crystals (Scheme 3).

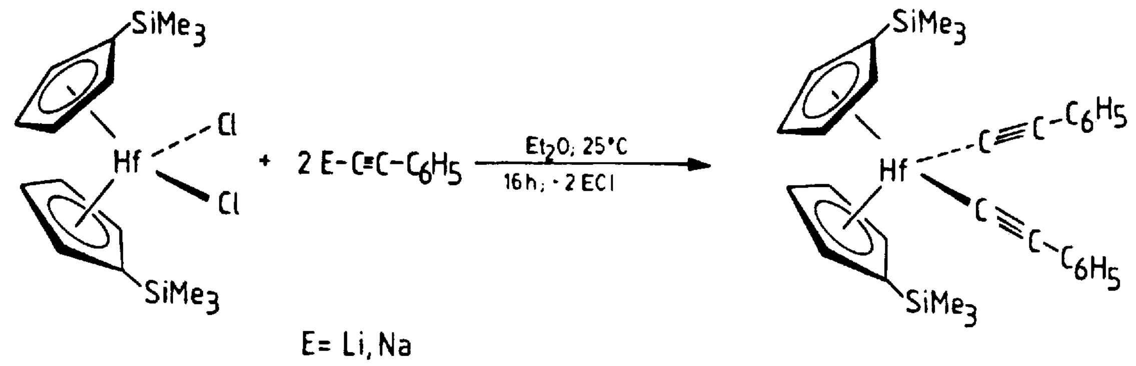
IR, ^1H and ^{13}C NMR, and electron impact mass spectra of these compounds are consistent with the proposed formulation of compound **2** and **7** as mononuclear[16, 17] and of **9** and **10** as dinuclear[18] metallocene complexes.

Most informative are the proton NMR spectra of these compounds, which show an AA′XX′ resonance pattern for the cyclopentadienyl protons in the region of δ 5.7–6.9 for compounds **2** and **7**, whereas in the compounds **9** and **10** the cyclopentadienyl protons are more deshielded. The presence of the functional groups SH (**2**) and $C{\equiv}CC_6H_5$ (**7**) is demonstrated by their infrared spectra. Bands of medium intensity at 2557 cm^{-1} (**2**) are evidence for the HS—, [16] and at 2072 cm^{-1} (**7**) for the C≡C—,[8, 11, 17] moieties (for details see the Experimental section).

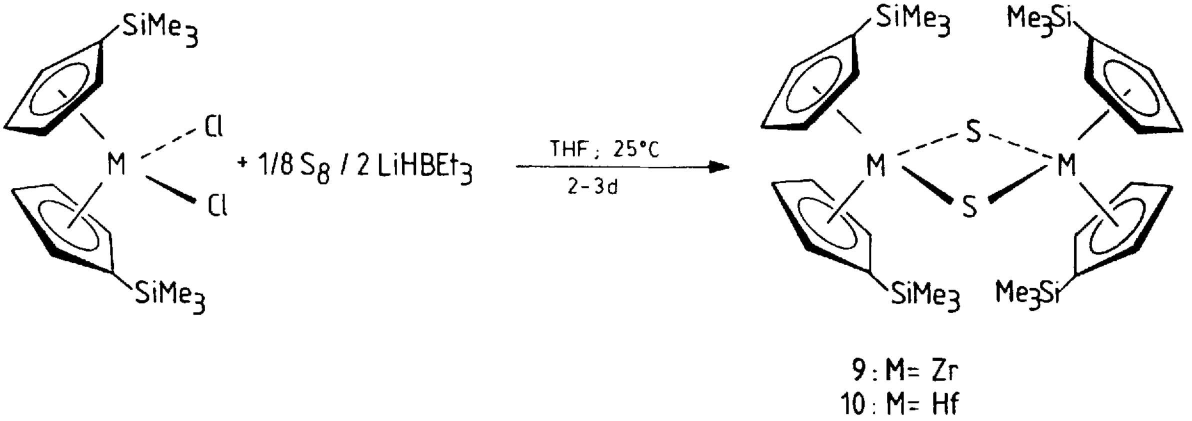
Thermal decomposition

Thermogravimetric studies were carried out as indicated in Scheme 4. As they showed (Fig. 1), compounds **1**–**10** begin to decompose at low temperature. Typical TGA traces are shown in Fig. 1 for $(\eta\text{-}C_5H_5)_2Ti(C{\equiv}CC_6H_5)_2$ (**1**) and $[\eta\text{-}C_5H_4Si(CH_3)_3]_2Hf(C{\equiv}CC_6H_5)_2$ (**7**).

The TGA yields of ceramic materials based on mono- or di-nuclear starting compounds were 20–



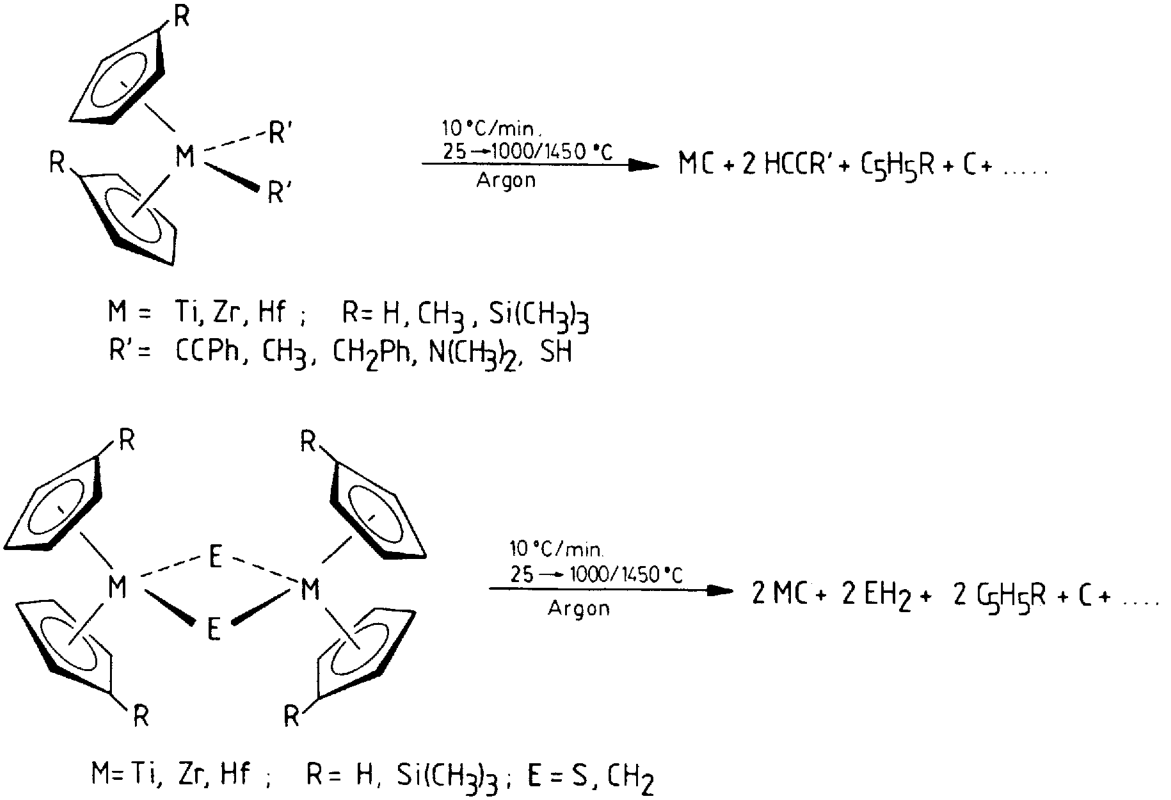
Scheme 2 **7**



Scheme 3

40% based on the weight of sample charged (Table 1, Scheme 4), depending on the substituent R'.

In a typical bulk pyrolysis experiment (Experimenal section), pyrolysis was conducted in a slow stream of nitrogen. The samples were heated with a heating rate of 10 °C min^{-1} to 1000 °C and were held at this temperatue for 30 min. The ceramic product was a black powder, and by X-ray diffraction (Cu-K$_\alpha$ with Ni filter) it showed only very small and broad peaks, which indicated the presence of mostly amorphous ceramic materials. To obtain crystalline materials, the ceramic products obtained above were heated quickly to 700 °C, held there for 30 min, and then were heated slowly to 1450 °C and were held at 1450 °C



Scheme 4

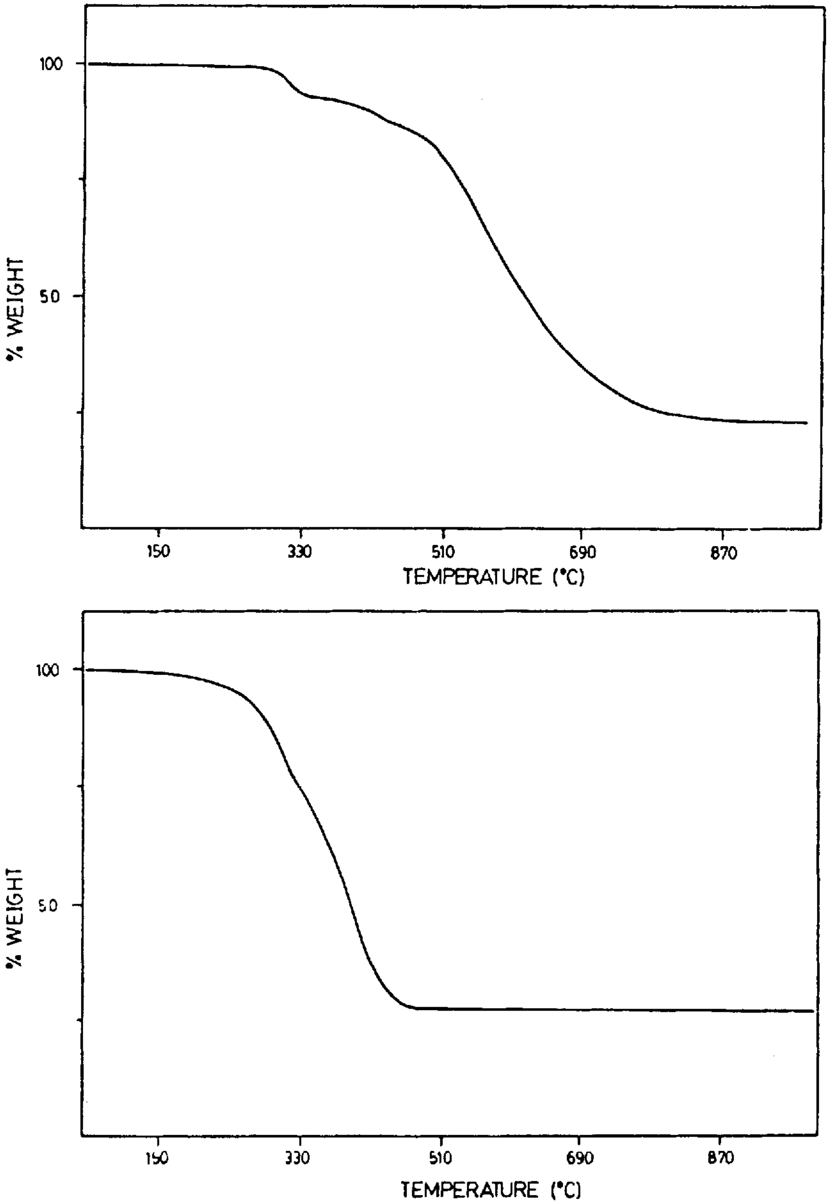


Figure 1 TGA traces of the compounds (η-C_5H_5)$_2$Ti(C$\equiv$CC_6H_5)$_2$ (**1**), above, and [η-$C_5H_4Si(CH_3)_3$]$_2$Hf(C$\equiv$CC_6H_5)$_2$ (**7**), low. Heating rate: 10 °C min^{-1}; 40 °C to 1000 °C.

between 5 and 15 h (Table 2). After this annealing procedure, X-ray powder diffraction showed only the very sharp peaks characteristic of the respective metal carbide MC (M = Ti, Zr, Hf).

In all cases (bulk as above, and TGA), the yields of ceramic products based on the starting complexes **1**–**10** were between 20 and 40% based on the weight of sample charged (Tables 1 and 2). The ceramic materials contained small amounts (2–9%) of amorphous carbon;^{7} the formation of metal-silicides (**2**, **7**, **9**, **10**) or metal sulfides (**2**, **9**, **10**) was not observed under the pyrolysis conditions used (Experimental section).

The volatile decomposition products which were formed during thermolysis are cyclopentadiene, phenylacetylene (**1**, **5**, **7**), toluene (**4**), hydrogen sulfide (**2**, **9**, **10**) or dimethylamine (**6**), depending on the nature of the ligands R′ in the metallocenes (C_5H_4R)$_2$N(R′)$_2$. The pyrolysis may be represented as shown in Scheme 5.

Table 1 TGA yields of the ceramic materials obtained by pyrolysis of the compounds **1–10** to temperatures of 1000 °C

Compound	M	R	R′	Lit. Ref.	TGA yield (%)[a]
1	Ti	H	$C\equiv CC_6H_5$	8	23
2	Ti	$Si(CH_3)_3$	SH	—	18
3	Zr	H	CH_3	9	37
4	Zr	H	$CH_2C_6H_5$	10	28
5	Zr	CH_3	$C\equiv CC_6H_5$	11	31
6	Zr	H	$N(CH_3)_2$	12	39
7	Hf	$Si(CH_3)_3$	$C\equiv CC_6H_5$	—	35
8	Ti	H	μ-CH_2	13	37
9	Zr	$Si(CH_3)_3$	μ-S	—	23
10	Hf	$Si(CH_{3)3}$	μ-S	—	41

[a] **Yield of ceramic materials, calculated as MC.**

In a series of experiments the volatile decomposition products were condensed into a liquid-nitrogen trap and analyzed (see the Experimental section). The metallocenes $(C_5H_4R)_2MR'_2$ (**1–10**) decompose with evolution of R′H as volatile products. Dehydrogenation of the cyclopentadienyl rings must occur to provide hydrogen for the evolution of R′H. Similar observations have been made in earlier thermal decomposition studies[3–7] of the compounds $(\eta$-$C_5H_5)_2TiR_2$ ($R = C_6H_5$, $CH_2C_6H_5$) and $(\eta$-$C_5H_5)_2Ti(Cl)(R)$ ($R = CH_3$, C_2H_5, C_6H_5, $CH_2C_6H_5$ . . .).[3–7] The reactions proceed by hydrogen abstraction from the cyclopentadienyl ligands.[3–7] The volatile products isolated in labeling experiments have shown that these reactions (thermolysis of $(\eta$-$C_5H_5)_2TiR_2$ and $(\eta$-$C_5H_5)_2Ti(Cl)(R)$; $R = C_6H_5$, $CH_2C_6H_5$) proceed either inter- or intram-olecularly with a cyclopentadienyl ligand providing the hydrogen for the evolution of RH.[3–7]

That the ceramic materials contain between 2 and 9% amorphous carbon is a result of the dehydrogenation of the cyclopentadienyl ligands.[7]

EXPERIMENTAL

General comments

All reactions were carried out under an atmosphere of nitrogen by using standard Schlenk techniques or in a Vacuum Atmospheres HE-43 DriLab glove box. Tetrahydrofuran (THF) was purified by distillation from sodium/benzophenone ketyl, n-pentane, n-hexane and diethyl ether by distillation from lithium aluminum hydride and dichloromethane by distillation from phosphorus pentoxide.

Infrared spectra were obtained using a Perkin–Elmer 1430 double-beam grating spectrometer. Proton nuclear magnetic resonance spectra were recorded on a JEOL FX-90 spectrometer and ^{13}C NMR spectra were recorded on a Bruker WM-270 spectrometer operating at 67.9 MHz in the Fourier transform mode. Chemical shifts are reported in δ units, downfield from tetramethylsilane and using the solvent as reference signal. EI mass spectra were recorded on a Finnigan 3200 spectrometer operating at 70 eV (m/z values given corresponding to isotopes of highest natural abundance). For the pyrolysis experiments, a Linde tube furnace was used. Melting points, determined using analytically pure samples (which were sealed in nitrogen-purged capillaries) on a Büchi melting-point apparatus, are uncorrected. Microanalyses were performed by Scandinavian Microanalytical Laboratories, Herlev, Denmark. Samples were sent sealed in evacuated vials.

Starting materials $(\eta$-$C_5H_5)_2MCl_2$ ($M = Ti$, Zr), $(\eta$-$C_5H_4CH_3)_2ZrCl_2$,[19] $[\eta$-$C_5H_4Si(CH_3)_3]_2MCl_2$ ($M = Ti$, Zr, Hf)[14] as well as the complexes $(\eta$-$C_5H_4Si(CH_3)_3]_2Ti(C\equiv CC_6H_5)_2$,[8] $(\eta$-$C_5H_5)_2Zr(CH_3)_2$,[9] $(\eta$-$C_5H_5)_2Zr(CH_2C_6H_5)_2$,[10] $(\eta$-$C_5H_4CH_3)_2Zr(C\equiv CC_6H_5)_2$,[11] $(\eta$-$C_5H_5)_2Zr[N(CH_3)_2]_2$[12] and $[(\eta$-$C_5H_5)_2Ti(\mu$-$CH_2)]_2$[13] were prepared according to published procedures.

Synthesis of $[\eta$-$C_5H_4Si(CH_3)_3]_2Ti(SH)_2$ (2)

Bis(trimethylsilylcyclopentadienyl)titanium dichloride (2.0 g; 5.08 mmol) was dissolved in 100 cm^3 of tetrahydrofuran (THF) at room temperature and H_2S was bubbled through the solution for 15 min to obtain an H_2S-saturated THF solution. Two molar equivalents of triethylamine were then slowly added. The reaction mixture gradually turned dark red–purple. It was stirred for 2 h at room temperature while a slow stream of H_2S was bubbled through it. The solvent was evaporated at reduced pressure and the resulting dark purple residue was extracted with n-pentane/toluene. The extracts were filtered through a pad of silica gel. Evaporation of the solvents under reduced pressure and recrystallization from n-pentane at −20 °C gave 1.9 g (4.89 mmol) of deep purple needles of **2** in 96% yield, m.p. 132 °C (decomp).

Table 2 Bulk pyrolysis data of the metallocene compounds **1**–**10** (Heating rate: 10 °C min^{-1}; final temperature: 1450 °C)

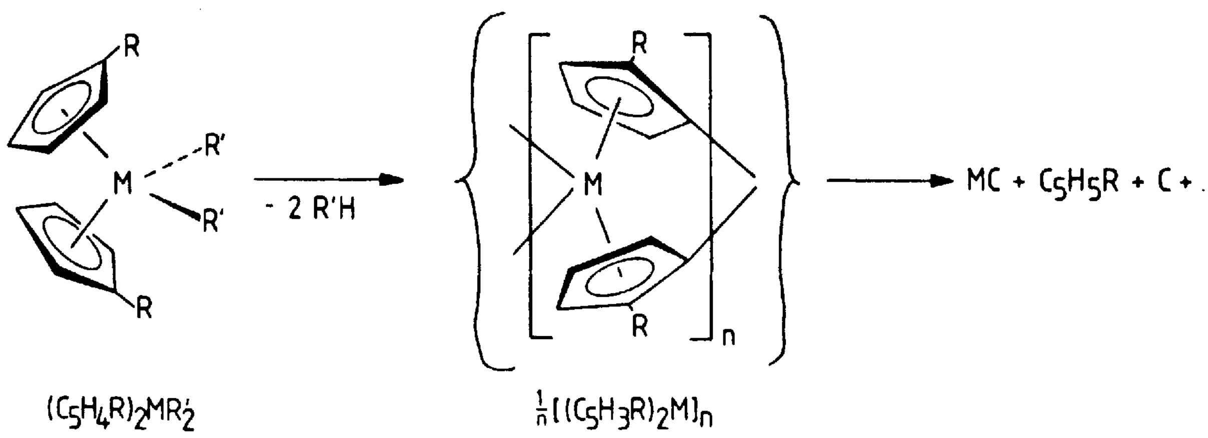
Compound	Sinter time 1450 °C (h)	Obtained ceramic yields at 1450 °C mg (%)[a]	Calculated yields for hypothetical MC mg (%)[a, b]	Diff. obtained ceramic yield – calc. yield (MC) mg (%)[a, b]
1	15	160(22.9)	110.23(15.8)	49.77(7.1)
2	5	125(17.9)	107.80(15.4)	17.2(2.5)
3	7.5	240(34.3)[c]	288.03(41.2)[c]	– 48.03(6.9)[c]
4	8	200(28.6)	179.63(25.7)	20.37(2.9)
5	6.5	220(31.4)	160.00(22.9)	60.00(8.5)
6	8	270(38.6)	233.31(33.3)	36.69(5.2)
7	9.5	250(35.7)	203.84(29.1)	46.16(6.6)
8	7	260(37.1)	218.01(31.1)	41.99(6.0)
9	7	160(22.9)[c]	181.69(26.0)[c]	– 21.69(3.1)[c]
10	10	287(41.0)	274.43(39.2)	12.57(1.8)

[a] **Based on 700 mg starting-material 1–10**; % numbers in parentheses: obtained or calculated yields in %, based on 700 mg starting-material **1**–**10**. [b] Yields were calculated as Mc (M = Ti, Zr, Hf) based on Scheme 4. [c] Weight lost during pyrolysis due to vigorous gas evolution in the temperature range 200–400 °C.

IR (KBr), cm^{-1}: 3083 vw, 3053 w, 2940 m, 2880 w, 2557 vw (SH), 1443 vw, 1401 m, 1372 m, 1236 vs, 1217 w, 1196 w, 1168 s, 1096 w, 930 vw, 903 sh, 892 s, 824 vs, 742 s, 683 s, 658 m, 628 sh, 618 m. ^{1}H NMR (C_6D_6): δ 0.29 (s, 18H, $Si(CH_3)_3$), 3.70 (s, 2H, SH), 5.73 (t, 4H, $J_{HH} = 2.4$ Hz, C_5H_4), 6.15 (t, 4H, $J_{HH} = 2.4$ Hz, C_5H_4). EI mass spectrum: molecular ion at *m/z* (relative intensity) 388(4), $M^+ - 2Me$ 358(33), $M^+ - SH$ 355(19), $M^+ - SH - Me$ 340(11), $M^+ - SH - 2Me$ 325(90), $(C_5H_4SiMe_3)_2Ti^+$ 322(57), $(C_5H_4SiMe_3)Ti(SH_2^+$ 251(11), $(C_5H_4Si)_2Ti^+$ 232(14), $(C_5H_4Si)(C_5H_4)Ti^+$ 204(18), $(C_5H_5)_2Ti^+$ 178(10), $C_5H_5SiMe_3^+$ 138(23), $C_5H_5SiMe_2^+$ 123(47), $C_5H_5Si^+$ 92(11), $SiMe_3^+$ 73(100). Analysis: Calcd for $C_{16}H_{28}S_2Si_2Ti$: C, 49.46; H, 7.26. Found: C, 49.50: H, 7.28%.

Synthesis of $[C_5H_4Si(CH_3)_3]_2Hf(C{\equiv}C\text{-}C_6H_5)_2$ (7)

Bis(trimethylsilylcyclopentadienyl)hafnium dichloride (2.5 g; 4.77 mmol) and 1.18 g (9.54 mmol) of sodium phenylacetylide or 1.03 g (9.54 mmol) or lithium phenylacetylide in 200 cm^3 of diethyl ether were stirred for 16 h at room temperature. The solvent was removed *in vacuo*. The pale yellow solid residue then was extracted with



Scheme 5

ether/n-hexane (1:1). The extracts were filtered through a pad of Celite. Evaporation of the solvents under reduced pressure and recrystallization from ether/n-hexane gave 2.5 g (3.82 mmol) of **7** as a pale yellow crystalline solid in 80% yield; m.p. 100 °C (decomp.).

IR (KBr), cm^{-1}: 2072 (C≡C). ^1H NMR (acetone-d_6): δ 0.35 (s, 18H, $Si(CH_3)_3$), 6.43 (t, 4H, $J_{HH} = 2.4$ Hz, C_5H_4), 6.72 (t, 4H, $J_{HH} = 2.4$ Hz, C_5H_4), 7.22 (m, 10H, C_6H_5). Analysis: Calcd for $C_{32}H_{36}HfSi_2$: C, 58.65; H, 5.54. Found: C, 58.64; H, 5.60%.

Synthesis of $\{[C_5H_4Si(CH_3)_3]_2Zr(\mu\text{-}S)\}_2$ (9)

To lithium sulfide,[15] prepared from 213 mg (6.64 mmol) of S_8 in 80 cm^3 of THF and 1.4 g (13.22 mmol) of lithium triethylborohydride, was added at room temperature 2.9 g (6.64 mmol) of bis(trimethylsilylcyclopentadienyl)zirconium dichloride.[14] The reaction mixture was stirred in the dark at 25 °C for 2.5 days. During this time, it slowly turned blue–green. After the solvent had been evaporated in high vacuum, the resulting dark-coloured residue was extracted with n-hexane/toluene (1:1) and filtered through a pad of Celite. Evaporation of the solvents under reduced pressure and recrystallization from n-hexane/toluene gave 1.40 g (1.76 mmol) of deep blue–green crystals of **9** in 53% yield, mp 216 °C (decomp.).

IR (KBr), cm^{-1}: 3086 w, 2936 s, 2879 m, 1439 m, 1403 m, 1397 m, 1362 s, 1315 m, 1245 sh, 1238 vs, 1172 vs, 10070 w, 1062 vw, 1038 vs, 972 w, 896 s, 857 sh, 830 vs, 785 vs, 742 s, 676 s, 627 s. ^1H NMR (C_6D_6): δ 0.38 (s, 36H, $Si(CH_3)_3$), 6.69 (t, 8H, $J_{HH} = 2.4$ Hz, C_5H_5), 6.87 (t, 8H, $J_{HH} = 2.4$ Hz, C_5H_4). EI mass spectrum: molecular ion at *m/z* (relative intensity) 796(43), $M^+ - Me$ 781(8), $M^+ - SiMe_3$ 723(12), $(C_5H_4SiMe_3)_3Zr_2S_2^+$ 659(60), $(C_5H_4SiMe_3)_2(C_5H_4SiMe_2)Zr_2S_2^+$ 644(25), $(C_5H_4SiMe_3)_2(C_5H_4SiMe)Zr_2S_2^+$ 629(7), $(C_5H_4SiMe_3)_2C_5H_4Zr_2S^+$ 552(7), $(C_5H_4SiMe_3)_2Zr_2S^+$ 488(6), $(C_5H_4SiMe_3)(C_5H_4SiMe_2)Zr_2S^+$ 473(2), $(C_5H_4SiMe_3)_2ZrS^+$ 397(2), $(C_5H_4SiMe_3)(C_5H_4SiMe_2)ZrS^+$ 382(10), $(C_5H_4SiMe_3)(C_5H_4SiMe)ZeS^+$ 367(3), $(C_5H_4SiMe_3)(C_5H_4Si)ZrS^+$ 352(2), $(C_5H_4SiMe_3)C_5H_4ZrS^+$ 324(3), $(C_5H_4SiMe_2)C_5H_4ZrS^+$ 309(5), $(C_5H_4SiMe)C_5H_4ZrS^+$ 294(1), $(C_5H_4Si)C_5H_4ZrS^+$ 279(3), $C_5H_5SiMe_3^+$ 138(5), $C_5H_5SiMe_2^+$ 123(10), $C_5H_5SiMe^+$ 108(1), $C_5H_5Si^+$ 93(1), $SiMe_3^+$ 72(100), $SiMe_2^+$ 58(5), $SiMe^+$ 43(16). Analysis: Calcd for $C_{32}H_{52}Si_4S_2Zr_2$: C, 48.31; H, 6.59. Found: C, 48.31; H, 6.61%.

Synthesis of $\{[C_5H_4Si(CH_3)_3]_2Hf(\mu\text{-}S)\}_2$ (10)

To Li_2S[15] (for preparation and reaction scale, see above) was added 3.48 g (6.64 mmol) bis(trimethylsilylcyclopentaphenyl)hafnium dichloride[14] in one portion. The reaction mixture was stirred for three days at room temperature in the dark. Work-up similar to that used for the analogous zirconium compound (9) gave 1.9 g (1.96 mmol) of 10 as a deep red crystalline solid in 59% yield, m.p. 210 °C (decomp.).

IR (KBr), cm^{-1}: 3072 w, 2934 s, 2875 m, 1440 m, 1407 m, 1398 m, 1365 s, 1311 m, 1242 sh, 1238 sh, 1230 vs, 1172 vs, 1071 w, 1062 vw, 1038 vs, 896 s, 864 sh, 820 vs, 780 vs, 743 s, 680 s, 622 vs. ^1H NMR (C_6D_6): δ 0.37 (s, 36H, $Si(CH_3)_3$), 6.62 (t, 8H, $J_{HH} = 1.8$ Hz, C_5H_4), 6.86 (t, 8H, $J_{HH} = 1.8$ Hz, C_5H_4). EI mass spectrum: molecular ion at *m/z* (relative intensity) 970(68), $M^+ - Me$ 955(5), $M^+ - SiMe_3$ 897(7), $M^+ - SiMe_3\text{-}Me$ 882(8), $M^+ - SiMe_3\text{-}2Me$ 867(3), $M^+ - SiMe_3\text{-}3Me$ 852(3), $(C_5H_4SiMe_3)_3Hf_2S_2^+$ 832(48), $(C_5H_4SiMe_3)_2(C_5H_4SiMe_2)Hf_2S_2^+$ 817(19), $(C_5H_4SiMe_3)_2(C_5H_4SiMe)Hf_2S_2^+$ 802(3), $(C_5H_4SiMe_3)_2(C_5H_4Si)Hf_2S_2^+$ 787(2), $(C_5H_4SiMe_3)_2C_5H_4Hf_2S_2^+$ 759(2), $(C_5H_4SiMe_3)((C_5H_4SiMe_2)C_5H_4Hf_2S_2^+$ 744(10), $(C_5H_4SiMe_3)(C_5H_4SiMe)C_5H_4Hf_2S_2^+$ 729(8), $(C_5H_4SiMe_3)(C_5H_4Si)C_5H_4Hf_2S_2^+$ 714(2), $(C_5H_4SiMe_3)_2Hf_2S^+$ 633(3), $(C_5H_4SiMe_3)C_5H_4SiMe_2)Hf_2S^+$ 648(2), $(C_5H_4SiMe_3)_2HfS^+$ 484(1), $(C_5H_4SiMe_3)(C_5H_4SiMe_2)HfS^+$ 469(4), $(C_5H_4SiMe_3)(C_5H_4SiMe)HfS^+$ 454(2), $(C_5H_4SiMe_3)(C_5H_4Si)HfS^+$ 439(2), $(C_5H_4SiMe_3)C_5H_4HfS^+$ 411(1), $(C_5H_4SiMe_2)C_5H_4HfS^+$ 396(4), $(C_5H_4SiMe)C_5H_4HfS^+$ 381(2), $(C_5H_4Si)C_5H_4HfS^+$ 366(2), $C_5H_5SiMe_3^+$ 138(12), $C_5H_5SiMe_2^+$ 123(18), $C_5H_5SiMe^+$ 108(2), $C_5H_5Si^+$ 93(3), $SiMe_3^+$ 73(100). Analysis: Calcd for $C_{32}H_{52}Hf_2Si_4S_2$: C, 39.62; H, 5.40. Found: C 39.40; H, 5.46%.

Thermal decomposition of the compounds 1–10

In these experiments 700 mg of each of the compounds **1** (1.84 mmol), **2** (1.80 mmol), **3** (2.79 mmol), **4** (1.74 mmol), **5** (1.55 mol), **6** (2.26 mmol), **7** (1.07 mmol), **8** (1.82 mmol), **9**

(0.88 mmol) and **10** 0.72 mmol) was placed in a dry-box into a porcelain boat and then removed in a sealed container and quickly transferred to the tube furnace which was flushed with argon for 30 min. For a further 15 min nitrogen was bubbled through the tube and then the sample was heated slowly (10 °C min^{-1}) to 1000 °C and held at that temperature for 30 min. After cooling to room temperature the boat was transferred to the dry-box and the black ceramic material was ground in a mortar. The sample was then put into a carbon boat and heated (for technique see above) quickly to 700 °C, held there for 30 min, then heated slowly in 10 °C min^{-1} steps to 1450 °C. It was held at that temperature between 5 and 15 h (Table 2) and was then allowed to cool slowly to room temperature overnight. The ceramic product was black in color. Powder X-ray diffraction (Cu-K_α with Ni filter) showed only sharp peaks for TiC [TiC; d_0, Å (intensity): 2.51(80), 2.179(100), 1.535(50), 1.311(30), 1.255(10), 1.086(5), 0.997(5), 0.971(30)], ZrC [ZrC cubic; d_0, Å (intensity): 2.707(100), 2.345(80), 1.659(50), 1.415(45), 1.355(18), 1.174(10), 1.077(18), 1.05(20)] or HfC [HfC face-centered, cubic; d_0, Å (intensity): 2.68(100), 2.321(90), 1.641(70), 1.399(80), 1.34(30), 1.16(10), 1.065(50), 1.038(50), 0.9473(40)] depending on the pyrolyzed compounds **1**–**10**. The yields and pyrolysis conditions are summarized in Table 2.

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REFERENCES

1. (a) Toth, L E *Transition Metal Carbides and Nitrides*, Academic Press, New York, 1971. (b) Kübel, E *VDI-Berichte*, 1988, 670: 625

2. Girolami, G S, Jensen, J A, Pollina, D M, Williams, W S, Kaloyeros, A E and Alloca, C M *J. Am. Chem. Soc.* 1987, 109: 1579

3. (a) Norman, V and Whaley, T P US Patent 3061464 (1962); *Chem. Abstr.*, 1963, 58: 320d. (b) Norman, V and Whaley, T P US Patent 3061465 (1962); *Chem. Abstr.*, 1965, 62: 15866c

4. (a) Waters, J A, Vickroy, V V and Mortimer, G A *J. Organomet. Chem.*, 1971, 33: 41. (b) Waters, J A and Mortimer, G A *J. Organomet. Chem.*, 1970, 22: 417

5. (a) Boekel, C P, Teuben, J H and De Liefde Meijer, H J *J. Organomet. Chem.*, 1975, 102: 161. (b) Dvorak, J, O'Brien, R J and Santo, W J *Chem. Soc., Chem. Commun.*, 1970, 411

6. (a) Boekel, C P, Teuben, J H and De Liefde Meijer, H J *J. Organomet. Chem.*, 1975, 102: 317. (b) Boekel, C P, Teuben, J H and De Liefde Meijer, H J *J. Organomet. Chem.*, 1974, 81: 371. (c) Fachinetti, G and Floriani, C J *Chem. Soc., Chem. Commun.*, 1972, 654

7. Brown, G M *Inorg. Chem.*, 1989, 28: 3028 and literature cited therein

8. (a) Koepf, H and Schmidt, M *J. Organomet. Chem.*, 1967, 10: 383. (b) Teuben, J H and De Liefde Meijer, H J *J. Organomet. Chem.*, 1969, 17: 87. (c) Jimenez, R, Barral, M C, Moreno, V and Santos, A *J. Organomet. Chem.*, 1979, 174: 281. (d) Lang, H and Seyferth, D *Z. Naturforsch.* 1990, 45f, 212

9. (a) Hunter, W E, Hrncir, D C, Bynum, R V, Penttila, R A and Atwood, J L *Organometallics* 1983, 2: 750. (b) Wailes, P C, Weigold, H and Bell, A P *J. Organomet. Chem.* 1972, 34: 155

10. Brindley, P B and Scotton, M J *J. Chem. Soc., Perkin Trans. II*, 1981, 419

11. (a) Jimenez, R, Barral, M C, Moreno, V and Santons, A *J. Organomet. Chem.*, 1972, 182:353. (b) Jenkins, A D, Lappert, M F and Srivastava, R C *J. Organomet. Chem.*, 1970, 23: 165

12. Chandra, G and Lappert, M F *J. Chem. Soc. (A)* 1968, 1939

13. (a) Van de Heisteg, B J J, Schat, G, Akkerman, O S and Bickelhaupt, F *J. Organomet. Chem.* 1986, 308: 1. (b) Bickelhaupt, F *Pure Appl. Chem.*, 1986, 58: 537. (c) Van de Heisteg, B J J, Schat, G, Akkerman, O S and Bickelhaupt, F *Organometallics*, 1985, 4: 141

14. Lappert, M F, Pickett, Ch J, Riley, P I and Yarrow, P I W *J. Chem. Soc., Dalton Trans.*, 1981, 805

15. Gladysz, J A, Wang, V K and Jick, B S *Tetrahedron*, 1979, 35: 2329

16. Shaver, A and McCall, J A *Organometallics*, 1984, 3: 1823

17. Barral, M C, Jimenez, R and Santos, A *Inorg. Chim. Acta*, 1982, 63: 257

18. (a) Beckhauser, R and Thiele, K H *Z. Anorg. Allg. Chem.*, 1989, 573: 195. (b) Tainturier, G, Gautheron, B and Fakim, M *J. Organomet. Chem.*, 1985, 290: C4

19. (a) Reynolds, L T and Wilkinson, G *J. Inorg. Nucl. Chem.*, 1959, 9: 86. (b) Wilkinson, G and Birmingham, P *J. Am. Chem. Soc.*, 1954, 76:4281. (c) *Idem, ibid.*, 1953, 75: 1011