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# Thermal stability and reaction of chalcogen-containing metallocenic compounds with elemental chalcogens

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## Abstract

Dissymmetrical four-membered bimetallocenacycles $(t\text{-BuC}_5H_4)_2M(\mu\text{-S})_2M'(RC_5H_4)_2$ ($M, M' = Zr, Hf$; $R = H$, t-Bu) have been prepared and found to give redistribution products in solution at 190 °C; identification of these products shows that the reaction involves exclusive cleavage of a metal–sulfur bond. Elemental sulfur and selenium react with chalcogen-containing complexes. The reaction is shown to involve the introduction of chalcogenic species in place of the $\sigma$-ligands of the complex to give either four-membered bimetallic complexes or catenated pentachalcogen metallocenic compounds. Some examples of insertion of sulfur and tellurium into the zirconium–methyl bond are also described.

## Introduction

Many complexes containing a hafnocene– or zirconocene–chalcogen bond have been described [1–18]. In some of them, the chalcogen ligand is purely inorganic, as in the well-known metallahexacyclic compounds $(\eta^5\text{-RC}_5H_4)_2ZrE_5$ ($M = Zr$, Hf; $E = S$, Se) [4,6,7h,8a,17,18] or in the four-membered bimetallacyclic $[(\eta^5\text{-RC}_5H_4)_2Zr(\mu\text{-E})]_2$ [6a,6c,7c,7f–h,8,12a,14,18]. These compounds can be prepared either from the corresponding zirconocene dichlorides by classical metathetical reactions [6,7f,8a,18] or by reaction of highly reactive organometallic species with the stable forms of elemental chalcogen [4,7c,7g,8,18]. In previous papers we described some preparations involving reactions of photochemically- or thermally-generated low-valent metallocenic species [7c,7g,8,18a] or dimeric metallocenic hydrides [7h,18b] with sulfur, selenium, and tellurium.

Another type of a chalcogen-bonded metallocenic compound involves organic ligands such as thiolate or selenolate. Most of them have been prepared by metathetical syntheses [1–3,5,7a,7g,11,14,16], but they can also be made by insertion

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of a selenium atom into zirconium–carbon bonds [7a,7g,14,16] or oxidative addition of dialkyl- or diaryl-diselenides to photochemically-generated low-valent metallocenic species [7b,7g].

Very little is known about the reactions of chalcogen derivatives of hafnocene and zirconocene in comparison with the extensive knowledge of the behaviour of the related $(C_5H_5)_2TiS_5$ [17]. In this paper we describe some chemical properties of these compounds. Initially we present results of a study of the thermal stability of the central four-membered core of the bimetallacyclic compounds $[(\eta^5\text{-}RC_5H_4)_2M(\mu\text{-}S)]_2$. Then we deal with reactions of elemental chalcogens with chalcogen-containing complexes of zirconocene. The results provide explanations of the subsequent transformations of the initial products of the insertion of chalcogen atoms into the zirconium–carbon bond. Finally we describe the previously unobserved insertion of sulfur and tellurium into the zirconium–methyl bond.

## Results and discussion

### *Thermolysis of $[(\eta^5\text{-}RC_5H_4)_2M(\mu\text{-}S)]_2$*

The four-membered bimetallacyclic compounds $[(\eta^5\text{-}RC_5H_4)_2M(\mu\text{-}E)]_2$ can be regarded as resulting from dimerization of the hypothetical $[(\eta^5\text{-}RC_5H_4)_2M{=}E]$ (eq. 1).

$$2\left[(\eta^5\text{-}RC_5H_4)_2M{=}E\right] \rightleftharpoons \left[(\eta^5\text{-}RC_5H_4)_2M(\mu\text{-}E)\right]_2 \qquad (1)$$

To the best of our knowledge such compounds containing a terminal chalcogen atom bonded to a zirconium or a hafnium atom, were previously unknown, but the $[(C_5Me_5)_2Zr{=}O]$ fragment has been characterized in the mass spectrum of $(C_5Me_5)_2Zr(OH)_2$ [19]. In order to provide evidence to the existence of the equilibrium shown in eq. 1 we decided to study the thermal scrambling of metallocenic moieties in the dissymmetrical compounds **1**–**4**. These compounds were prepared by reaction of the hydrosulfides with various dimeric dihydrides, according to eq. 2.

$$2(\text{t-Bu}C_5H_4)_2M(SH)_2 + \left[(RC_5H_4)_2M'(H)(\mu\text{-}H)\right]_2 \rightarrow$$
$$(\text{t-Bu}C_5H_4)_2M(\mu\text{-}S)_2M'(RC_5H_4)_2 + 4\ H_2 \qquad (2)$$

(**1**: M = Zr, M′ = Zr, R = H;
**2**: M = Hf, M′ = Zr, R = H;
**3**: M = Zr, M′ = Hf, R = H;
**4**: M = Zr, M′ = Hf, R = t-Bu;
**4**: M = Hf, M′ = Zr, R = t-Bu)

Reaction 2 gave compounds **1** and **2** at 20 °C, but for preparation of compounds **3** and **4** which involves the less reactive hafnocene dihydride or bulkier dihydrides, a temperature of 50 °C had to be used. Compounds **1**–**4** were characterized by elemental analysis, mass spectrometry, and $^1H$ NMR spectroscopy. The attribution of the signals reported in the experimental section of this paper was based on the following features described previously for the symmetrical $[(\eta^5\text{-}RC_5H_4)_2M(\mu\text{-}S)]_2$ complexes [7f,18]: (a) the cyclopentadienyl protons are more deshielded when the

$\eta^5$-ligand is bonded to zirconium rather than to hafnium, and (b) the reverse result is usually the case for the protons of the alkyl group bonded to this ligand.

We tried to prepare the compound $(\eta^5\text{-t-BuC}_5H_4)_2Hf(\mu S)_2Hf(\eta^5\text{-}C_5H_5)_2$ from $(\eta^5\text{-t-BuC}_5H_4)_2Hf(SH)_2$ and $[(\eta^5\text{-}C_5H_5)_2Hf(H)(\mu\text{-}H)]_2$ according to eq. 2. The reaction was very slow at room temperature reflecting the lower reactivity of hafnocene dihydrides than of their zirconocene analogues [20]. Use of higher temperature gave a mixture containing the symmetrical complex $[(\eta^5\text{-}C_5H_5)_2Hf(\mu\text{-}S)]_2$ [7f,18] the formation of which implies an unexpected exchange of ligands between the bis-hydrosulfide and the hydride.

Another route (eq. 3) starting from dimethyl complexes instead of dihydrides, was explored:

$$(\text{t-BuC}_5H_4)_2M(SH)_2 + (RC_5H_4)_2M'Me_2 \rightarrow (\text{t-BuC}_5H_4)_2M(\mu\text{-}S)_2M'(RC_5H_4)_2 + 2\ CH_4 \quad (3)$$

This alternative seems to be confined to the preparation of **1**. For other compounds no reaction was observed at room temperature, and heating of the mixture always gave the well-known condensation [6c,17] of the metallocene bis-hydrogenosulfide to the corresponding symmetrical complexe **5** [18a], as shown in eq. 4.

$$2(\text{t-BuC}_5H_4)_2M(SH)_2 \rightarrow \underset{(\mathbf{5})}{[(\text{t-BuC}_5H_4)_2M(\mu\text{-}S)]_2} + 2\ H_2S \quad (4)$$

The thermal stability of compounds **1**, **2** and **4** was studied by keeping a solution in benzene-$d_6$ at 190 °C in a sealed NMR tube. Compounds **2** and **4** were practically unchanged after two days, whereas the disproportionation of **1** into the symmetrical complexes **5** and **6** [6c] (eq. 5) was shown by $^1$H NMR spectroscopy.

$$\underset{(\mathbf{1})}{2(\text{t-BuC}_5H_4)_2Zr(\mu\text{-}S)_2Zr(C_5H_5)_2} \rightleftharpoons \underset{(\mathbf{5})}{[(\text{t-BuC}_5H_4)_2Zr(\mu\text{-}S)]_2} + \underset{(\mathbf{6})}{[(C_5H_5)_2Zr(\mu\text{-}S)]_2} \quad (5)$$

After reaction at 140 °C, the products **5** and **6** were unambiguously detected and identified by $^1$H NMR spectroscopy. After 40 h at 190 °C, the mixture contained **1**, **5** and **6** in 2/1/1 ratio, and further heating did not cause any significant change, showing that the equilibrium corresponds to the statistical distribution of the metallocenic moieties. The reversal of reaction 5 was also studied; compounds **5** and **6** gave a mixture containing the expected dissymetrical compound **1** and unchanged **5** and **6** upon heating at 190 °C.

In neither case did we observe any additional signal in the NMR spectrum of the mixture at equilibrium. This shows that production of mixed compounds such as, for example, *cis*- or *trans*-$[(\text{t-BuC}_5H_4)(C_5H_5)Zr(\mu\text{-}S)]_2$ does not occur provided overheating is avoided, and implies that the structure of the metallocenic moieties $[(\text{t-BuC}_5H_4)_2Zr]$ and $[(C_5H_5)_2Zr]$ is unaffected by heating. Therefore reaction 5 must involve breaking of one metal–sulfur bond, presumably giving transient monomeric species as postulated in eq. 1.

### *Reactions with elemental chalcogens*

The previously described four-membered bimetallacyclic compounds readily react with elemental chalcogens to give the corresponding pentachalcogenide compounds, as shown in entries 1 to 13 of Table 1. Most of the experiments were performed in sealed tubes. In such cases the products were identified by comparison of the NMR spectra of the crude mixture with spectra of authentic samples [6c,7f,8a,18]. **7** and **8** are new compounds; they were found to be identical to samples prepared by an unambiguous method [6c,18a]. The overall reaction is represented by eq. 6.

$$[(\eta^5\text{-RC}_5\text{H}_4)_2\text{Zr}(\mu\text{-E})]_2 + 8\text{E} \rightarrow 2(\eta^5\text{-RC}_5\text{H}_4)_2\text{ZrE}_5 \qquad (6)$$

The rate of the reaction depends strongly on the bulk of the cyclopentadienyl ligands, as shown by comparison of entries 1 and 6. In fact, the reaction of the crowded $[(\text{t-BuC}_5\text{H}_4)_2\text{ZrS}]_2$ with sulfur in the dark, requires heating, and $[(\text{t-BuC}_5\text{H}_4)_2\text{ZrSe}]_2$ does not react with grey selenium. It is also quite clear that an excess of sulfur (lines 1 and 3) or selenium (lines 11 and 12) favours the reaction.

Entries 10 and 11 show the enhancement of the formation of the pentasulfide by UV irradiation. As it is known that cyclooctasulfur molecules are broken down by UV light [21], this result was not completely unexpected. Moreover, in this case photochemical cleavage of the metallacycle, such as has been observed for $(\text{C}_5\text{H}_5)_2\text{TiS}_5$ [22], cannot be excluded. In order to gain a better insight into the mechanism of the reaction, some cross-over experiments were performed. $[(\text{MeC}_5\text{H}_4)_2\text{ZrSe}]_2$ was found to react at room temperature with an excess of sulfur to give selenium and a mixture of the known sulfide $[(\text{MeC}_5\text{H}_4)_2\text{ZrS}]_2$ and pentasulfide $(\text{MeC}_5\text{H}_4)_2\text{ZrS}_5$ (Table 1, lines 14 and 15) together with an unidentified product. The reaction of grey selenium with the sulfide $[(\text{MeC}_5\text{H}_4)_2\text{ZrS}]_2$, which corresponds to the reverse of the reaction above, did not give the expected $[(\text{MeC}_5\text{H}_4)_2\text{ZrSe}]_2$, the NMR spectrum of the reaction mixture showed only the unidentified product mentioned above along with the unchanged metallacycle. Whatever is the structure of the product common to both reactions, the formation of sulfides from a selenium compound clearly shows that eq. 6 represent an oversimplification of the actual process and rules out a simple addition of chalcogen atoms to a chalcogen-containing complex. The suggestion of a substitution reaction involving exchange of the ligands and elemental chalcogen must be preferred. For the reaction shown in entry 14 we suggest a two-step process (eq. 7 and 8).

$$[(\text{MeC}_5\text{H}_4)_2\text{ZrSe}]_2 + \text{S} \rightarrow [(\text{MeC}_5\text{H}_4)_2\text{Zr}]_2(\mu\text{-S})(\mu\text{-Se}) + \text{Se} \qquad (7)$$

$$[(\text{MeC}_5\text{H}_4)_2\text{Zr}]_2(\mu\text{-S})(\mu\text{-Se}) + \text{S} \rightarrow [(\text{MeC}_5\text{H}_4)_2\text{ZrS}]_2 + \text{Se} \qquad (8)$$

In these reactions the unidentified product we observed when starting from $[(\text{MeC}_5\text{H}_4)_2\text{ZrSe}]_2$ and sulfur or from $[(\text{MeC}_5\text{H}_4)_2\text{ZrS}]_2$ and selenium, is assumed to be a dissymmetrically-bridged intermediate, in accordance with its NMR spectrum which shows for the cyclopentadienyl protons a complex pattern characteristic of two different $\sigma$-ligands. Unfortunately this compound could not be isolated.

The replacement of chalcogen-containing ligands by chalcogen atoms is not confined to metallacyclic zirconium complexes. Addition of sulfur or selenium at room temperature to a toluene solution of zirconocene bis-thiolate or bis-selenolate afforded (Table 2) the corresponding four-membered metallacyclic compounds, together with the organic bis-selenide or bis-sulfide resulting from the coupling of the ligands (eq. 9).

$$(\text{RC}_5\text{H}_4)_2\text{Zr}(\text{ER}')_2 + 2\text{E}' \rightarrow [(\text{RC}_5\text{H}_4)_2\text{ZrE}']_2 + \text{R}'\text{EER}' \qquad (9)$$

$(\text{R} = \text{Me, t-Bu})$

Table 1

Reaction of elemental sulfur and selenium with the four-membered bimetallacycles $[(RC_5H_4)_2Zr(\mu E)]_2$

| Starting material | ref. | Chalcogen | Temperature (°C) | Time (h) | Product | Ref. or number | Yield (%) |
|---|---|---|---|---|---|---|---|
| 1 $[(C_5H_5)_2Zr(\mu\text{-}S)]_2$ | [6c] | $S^a$ | 20 | 0.5 | $(C_5H_5)_2ZrS_5$ | [6c] | $20^b$ |
| 2 $[(C_5H_5)_2Zr(\mu\text{-}S)]_2$ | [6c] | $S^a$ | 20 | 16 | $(C_5H_5)_2ZrS_5$ | [6c] | $100^b$ |
| 3 $[(C_5H_5)_2Zr(\mu\text{-}S)]_2$ | [6c] | 8S | 20 | 60 | $(C_5H_5)_2ZrS_5$ | [6c] | $47^c$ |
| 4 $[(MeC_5H_4)_2Zr(\mu\text{-}S)]_2$ | [18a] | 8S | 35 | 10 | $(MeC_5H_4)_2ZrS_5$ | **7** | $72^c$ |
| 5 $[(t\text{-}BuC_5H_4)_2Zr(\mu\text{-}S)]_2$ | [8a] | $S^a$ | 45 | 66 | $(t\text{-}BuC_5H_4)_2ZrS_5$ | [8a] | $6^b$ |
| 6 $[(t\text{-}BuC_5H_4)_2Zr(\mu\text{-}S)]_2$ | [8a] | $S^a$ | 70 | 6 | $(t\text{-}BuC_5H_4)_2ZrS_5$ | [8a] | $10^b$ |
| 7 $[(t\text{-}BuC_5H_4)_2Zr(\mu\text{-}S)]_2$ | [8a] | $S^a$ | 100 | 16 | $(t\text{-}BuC_5H_4)_2ZrS_5$ | [8a] | $100^b$ |
| 8 $[(t\text{-}BuC_5H_4)_2Zr(\mu\text{-}S)]_2$ | [8a] | 8S | 90 | 21 | $(t\text{-}BuC_5H_4)_2ZrS_5$ | [8a] | $35^c$ |
| 9 $[(t\text{-}BuC_5H_4)_2Zr(\mu\text{-}S)]_2$ | [8a] | 8S | 20 | $22^d$ | $(t\text{-}BuC_5H_4)_2ZrS_5$ | [8a] | $100^b$ |
| 10 $[(t\text{-}BuC_5H_4)_2Zr(\mu\text{-}S)]_2$ | [8a] | 8S | 20 | $22^d$ | $(t\text{-}BuC_5H_4)_2ZrS_5$ | [8a] | $38^c$ |
| 11 $[(C_5H_5)_2Zr(\mu\text{-}Se)]_2$ | [18a] | $Se^a$ | 20 | 16 | $(C_5H_5)_2ZrSe_5$ | [6c] | $100^b$ |
| 12 $[(C_5H_5)_2Zr(\mu\text{-}Se)]_2$ | [18a] | 8Se | 20 | 32 | $(C_5H_5)_2ZrSe_5$ | [6c] | $40^c$ |
| 13 $[(MeC_5H_4)_2Zr(\mu\text{-}Se)]_2$ | [18a] | 8Se | 20 | 10 | $(MeC_5H_4)_2ZrSe_5$ | **8** | $49^c$ |
| 14 $[(MeC_5H_4)_2Zr(\mu\text{-}Se)]_2$ | [18a] | $S^a$ | 20 | 0.3 | $[(MeC_5H_4)_2Zr(\mu\text{-}S)]_2$ | [18a] | $20^b$ |
| 15 $[(MeC_5H_4)_2Zr(\mu\text{-}Se)]_2$ | [18a] | $S^a$ | 20 | 7 | $(MeC_5H_4)_2ZrS_5$ | **7** | $100^b$ |
| 16 $[(MeC_5H_4)_2Zr(\mu\text{-}Se)]_2$ | [7g] | $S^a$ | 40 | 6 | $[(t\text{-}BuC_5H_4)_2Zr(\mu\text{-}S)]_2$ | [8a] | $30^b$ |
|  |  |  |  |  | $(t\text{-}BuC_5H_4)_2ZrS_5$ | [8a] | $70^b$ |
| 17 $[(t\text{-}BuC_5H_4)_2Zr(\mu\text{-}Se)]_2$ | [7g] | 2S | 40 | 16 | $[(t\text{-}BuC_5H_4)_2Zr(\mu\text{-}S)]_2$ | [8a] | $40^b$ |

[a] Excess. [b] Estimated by $^1H$ NMR. [c] Weight of recrystallized product. [d] UV irradiation.

Table 2

Reactions [a] of elemental sulfur and selenium with bis-thiolates and selenolates $(RC_5H_4)_2Zr(ER')_2$

| Starting material | | Chal- cogen | Time | Product (h) | Ref. or number | Yield (%) |
|---|---|---|---|---|---|---|
| 1 $(MeC_5H_4)_2Zr(SeBz)_2$ [b] | **(9)** | Se [c] | 17 | $[(MeC_5H_4)_2Zr(\mu\text{-Se})]_2$ | [18a] | 65 [d] |
| 2 $(MeC_5H_4)_2Zr(SeBz)_2$ | **(9)** | S [c] | 3.5 | $[(MeC_5H_4)_2Zr(\mu\text{-S})]_2$ | [18a] | 100 [d] |
| 3 $(MeC_5H_4)_2Zr(SeBz)_2$ | **(9)** | S [c] | 24 | $(MeC_5H_4)_2ZrS_5$ | 7 | 100 [d] |
| 4 $(MeC_5H_4)_2Zr(SeBz)_2$ | **(9)** | 2S | 4 | $[(MeC_5H_4)_2Zr(\mu\text{-S})]_2$ | [18a] | 61 [e] |
| 5 $(MeC_5H_4)_2Zr(SePh)_2$ | **(10)** | S [c] | 7 | $[(MeC_5H_4)_2Zr(\mu\text{-S})]_2$ | [18a] | 55 [d] |
| 6 $(MeC_5H_4)_2Zr(SBz)_2$ [b] | **(11)** | S [c] | 6 | $[(MeC_5H_4)_2Zr(\mu\text{-S})]_2$ | [18a] | 70 [d] |
| 7 $(t\text{-}BuC_5H_4)_2Zr(SBz)_2$ [b] | **(12)** | 2S | 120 | $[t\text{-}BuC_5H_4)_2Zr(\mu\text{-S})]_2$ | [18a] | 25 [d] |

[a] Temperature 20 °C. [b] Bz = $CH_2C_6H_5$. [c] Excess. [d] Estimated by $^1H$ NMR. [e] Weight of recrystallized product.

We can exclude the possibility that the observed four-membered metallacycle is formed via a thermally induced decomposition of the starting bis-selenolate or bis-thiolate, since for example, $(MeC_5H_4)_2Zr(SeCH_2C_6H_5)_2$ is stable for days in $C_6D_6$ below 50 °C. After 5 days at 85 °C, $[(MeC_5H_4)_2ZrSe]_2$ was unambiguously identified in the mixture, but 93% of the starting compound remained unaffected, showing the slow rate of this reaction compared to that of reaction 9.

Table 2 shows that it is easy to replace a selenium-containing ligand by sulfur but, we could not bring about the reverse transformation. This is consistent with the difficulties encountered in bringing about a clean insertion of sulfur into a zirconium–carbon bond.

### *Insertion of sulfur and tellurium into the zirconium–carbon bond*

We have previously shown that grey selenium readily inserts into the zirconium- and hafnium-methyl bond to give the expected symmetrical complex [7a,7g] according to eq. 10.

$$(RC_5H_4)_2MR'_2 + 2\ E \rightarrow (RC_5H_4)_2M(ER')_2 \qquad (10)$$

$$(R = H,\ t\text{-}Bu;\ M = Zr,\ Hf;\ E = Se;\ R' = CH_3)$$

This reaction is not restricted to methyl ligands and selenium (Table 3). The rate of insertion depends on the nature of the chalcogen, decreasing in the sequence $S > Se > Te$. In most cases the reaction mixture contained substitution products

Table 3

Yields and NMR data for products of insertion into the zirconium–carbon bond

| Compound | $^1H$ NMR, $\delta$ (ppm) | Yield (%) |
|---|---|---|
| $(MeC_5H_4)_2Zr(SePh)_2$ **(10)** | 8.02 m 6H (Ph), 7.04 m 4H (Ph), 5.72 pt 4H ($C_5H_4$), 5.53 pt 4H ($C_5H_4$), 1.81 s 6H (Me) | |
| $(MeC_5H_4)_2Zr(SeMe)_2$ **(13)** | 5.78 pt 4H ($C_5H_4$), 5.62 pt 4H ($C_5H_4$), 2.51 s 6H (SeMe), 1.93 s 6H (MeCp) | 31 |
| $Cp_2Zr(SMe)_2$ **(14)** | 5.78 s 10H ($C_5H_5$), 2.55 s 6H (SMe) | 47 |
| $Cp_2Zr(TeMe)_2$ **(15)** | 5.69 s 10H ($C_5H_5$), 2.41 s 6H (TeMe) | 19 |

originating from reaction 9 in addition to the expected insertion product. This feature considerably restricts the use of reaction 10 for preparation of metallocene-chalcogenate compounds.

## Experimental

All the reactions were carried out in toluene, under argon at room temperature unless otherwise stated. Schlenk techniques were used. Solvents were dried, desoxygenated, and distilled from sodium-benzophenone ketyl just before use. Photochemical reactions were carried out in glass reactors with light from a medium pressure mercury lamp.

NMR spectra were recorded on a JEOL FX 100 spectrometer with $C_6D_6$ solutions. Chemical shifts are relative to $Me_4Si$ ($\delta$ scale in ppm, s = singlet, d = doublet, t = triplet, pt = pseudo-triplet, m = multiplet). Mass spectra were obtained with a Finnigan 3300 spectrometer at 70 eV; the *m/e* values refer to ions containing the most abundant isotopes. Microanalyses were performed by Service Central d'Analyses du CNRS, Lyon. Selenium and sulfur were sublimed and stored under argon, but tellurium (Aldrich Gold Label) was used as received. Cp and RCp respectively represent the ligands $\eta^5$-$C_5H_5$ and $\eta^5$-alkylcyclopentadienyl. M denotes a transition metal and E or E′ a chalcogen atom.

### *(t-BuCp)$_2$Zr($\mu$-S)$_2$Zr(Cp)$_2$* (**1**)

(A) A suspension of (t-BuCp)$_2$Zr(SH)$_2$ [18b] (0.12 g, 0.30 mmol) and [Cp$_2$ZrH($\mu$-H)]$_2$ [23] (0.07 g, 0.15 mmol) in 6 ml of toluene was stirred for 40 h. After evaporation of solvent the residual solid was washed with pentane and recrystallized from heptane-toluene. Cooling gave green crystals (0.12 g, 0.19 mmol, 66%) of **1**; m.p. 214 ° C. $^1$H NMR: 6.37 s 10H (Cp); 6.28 s 8H ($C_5H_4$); 1.30 s 18H (t-Bu). Anal. Found: C, 53.24; H, 5.32; S, 9.27; Zr, 32.83. $C_{28}H_{36}S_2Zr_2$ calcd.: C, 54.32; H, 5.86; S, 10.36; Zr, 29.41%. Mass spectrum 616 ($M$), 495 ($M$ − t-BuCp), 486 ((t-BuCp)$_2$ZrS$_2$), 374 (Cp$_2$Zr$_2$S$_2$), 309 (CpZr$_2$S$_2$).

(B) Cp$_2$ZrMe$_2$ [26] (0.15 g, 0.59 mmol) in 2 ml of toluene was added to a toluene (5 ml) solution of (t-BuCp)$_2$Zr(SH)$_2$ (0.23 g, 0.58 mmol). After 20 h, work-up as above afforded **1** (0.22 g, 0.36 mmol, 62%).

### *(t-BuCp)$_2$Hf($\mu$-S)$_2$Zr(Cp)$_2$* (**2**)

(t-BuCp)$_2$Hf(SH)$_2$ [18b] (0.43 g, 0.88 mmol) and [Cp$_2$ZrH($\mu$-H)]$_2$ (0.20 g, 0.45 mmol) gave after 3 days blue crystals (0.30 g, 0.42 mmol, 48%) m.p. 220 ° C. $^1$H NMR: 6.30 m 18H (Cp); 1.32 s 18H (t-Bu). Anal. Found: C, 47.90; H, 5.11; Hf, 25.24, S, 8.90; Zr, 13.33. $C_{28}H_{36}HfS_2Zr$ calcd.: C, 47.61; H, 5.14; Hf, 25.27, S, 9.07; Zr, 12.91%.

### *(t-BuCp)$_2$Zr($\mu$-S)$_2$Hf(Cp)$_2$* (**3**)

A suspension of (t-BuCp)$_2$Zr(SH)$_2$ (0.32 g, 0.80 mmol) and [Cp$_2$HfH($\mu$-H)]$_2$ [25] was stirred at 50 ° C for 20 h. The solvent was evaporated and the residue washed with pentane then recrystallized from hot toluene to give red crystals (0.28 g, 0.40 mmol, 50%); m.p. 210 ° C. $^1$H NMR: 6.40 m 8H ($C_5H_4$); 6.22 s 10H ($C_5H_5$); 1.29 s 18H (t-Bu). Anal. Found: C, 47.67; H, 5.09; Hf, 25.24; S, 8.46; Zr, 12.91. $C_{28}H_{36}HfS_2Zr$ calcd.: C, 47.61; H, 5.14; Hf, 25.27; S, 9.08; Zr, 12.91%. Mass spectrum: 706 ($M$), 585 ($M-$ t-BuCp), 576 ((t-BuCp)$_2$HfZrS$_2$), 496 (Cp$_3$ZrHfS), 464 (Cp$_2$ZrHfS$_2$).

*(t-BuCp)$_2$Zr($\mu$-S)$_2$Hf(t-BuCp)$_2$* (4)

A suspension of (t-BuCp)$_2$Hf(SH)$_2$ (0.41 g, 0.84 mmol) and [(t-BuCp)$_2$ZrH($\mu$-H)]$_2$ (0.28 g, 0.42 mmol) in toluene was kept at 60 ° C for 17 h. Work-up as above and recrystallisation from hot toluene/heptane gave blue crystals (0.39 g, 0.48 mmol, 57%); m.p. > 260 ° C. $^1$H NMR: 6.44 s 8H ((C$_5$H$_4$)$_2$Zr); 6.35 m 8H ((C$_5$H$_4$)$_2$Hf); 1.33 s 18H (t-Bu)(Hf); 1.29 s 18H (t-Bu)(Zr). Anal. Found: C, 53.90; H, 6.70; Hf, 20.15; S, 7.77; Zr, 12.75. $C_{36}H_{52}HfS_2Zr$ calcd.: C, 52,82; H, 6.40; Hf, 21.80; S, 7.83; Zr, 11.11%. Mass spectrum: 818 ($M$), 761 ($M-$ t-Bu), 697 ($M-$ t-BuCp), 665 ((t-BuCp)$_3$HfSZr), 647 (($M-$ t-Bu$_3$), 544 ((t-BuCp)$_2$HfSZr).

*Cp$_2$ZrS$_5$*

A mixture of sulfur (0.103 g, 0.40 mmol) and [Cp$_2$Zr($\mu$-S)]$_2$ [6c,18a] (0.20 g, 0.39 mmol) in 20 ml of toluene was stirred for 60 h, after which an orange solid and a yellow solution were present. The solution was filtered and the filtrate evaporated to dryness, and the residue recrystallized from a mixture of dichloromethane and pentane to give the yellow product, previously made by Shaver [6c] (0.14 g, 0.36 mmol, 47%); m.p. 160 ° C; $^1$H NMR 6.22 s (CDCl$_3$).

*(MeCp)$_2$ZrS$_5$* (7)

(A) Reaction 6: 0.10 g (3.16 mmol) of elemental sulfur was added to a solution of [(MeCp)$_2$Zr($\mu$-S)]$_2$ (0.22 g, 0.39 mmol) in 12 ml of toluene and the mixture was kept at 35 ° C for 10 h. The solvent was evaporated off and the residue was washed twice with pentane then recrystallized from hot toluene/heptane mixture to give yellow crystals (0.23 g, 0.56 mmol, 72%); m.p. 122° C. $^1$H NMR: 5.60 t 4H (C$_5$H$_4$); 5.46 t 4H (C$_5$H$_4$); 1.83 s 6H (Me). Anal. Found: C, 35.19; H, 3.46; S, 37.67; Zr, 22.13. $C_{12}H_{14}S_5Zr$ calcd.: C, 35.17; H, 3.44; S, 39.12; Zr, 22.26%. Mass spectrum 408 ($M$), 344 ($M-S_2$), 312 ($M-S_3$), 279 ($M-S_4$), 265 (MeCpZrS$_3$), 248 ((MeCp)$_2$Zr).

(B) From (MeCp)$_2$ZrCl$_2$ [6c]: 0.765 g (23.90 mmol) of sulfur was treated with 10 ml of LiHBEt$_3$ (Aldrich) in THF. After 20 min a solution of (MeCp)$_2$ZrCl$_2$ [26] (1.50 g, 4.69 mmol) in 15 ml of THF was added and the mixture was stirred overnight. The solvent was evaporated off, the residue shaken with toluene and the suspension filtrated. Evaporation of the filtrate and recrystallization of the solid from toluene and pentane gave 1.54 g (3.76 mmol, 80%) of yellow compound 7.

*(t-BuCp)$_2$ZrS$_5$*

(A) A solution of [(t-BuCp)$_2$Zr($\mu$-S)]$_2$ [8a] (0.23 g, 0.31 mmol) and sulfur (0.08 g, 2.48 mmol) in 10 ml of toluene was kept at 90 ° C for 21 h. The solution was filtered and the filtrate evaporated. The residue was washed three times with pentane and recrystallized from dichloromethane/pentane to give the yellow (t-BuCp)$_2$ZrS$_5$ [8a] (0.11 g, 0.23 mmol, 35%).

(B) A solution of [(t-BuCp)$_2$Zr($\mu$-S)]$_2$ (0.22 g, 0.30 mmol) and sulfur (0.24 g, 7.56 mmol) in 10 ml of toluene was irradiated for 22 h. Filtration, evaporation of the filtrate, and recrystallisation of the residue from dichloromethane and pentane afforded (t-BuCp)$_2$ZrS$_5$ (0.11 g, 0.23 mmol, 38%).

*$Cp_2ZrSe_5$*

To a suspension of grey selenium (0.106 g, 1.34 mmol) in THF was added a solution of $[Cp_2Zr(\mu\text{-}Se)]_2$ (0.10 g, 0.17 mmol) in 12 ml of toluene. After 32 h in the dark, the mixture was filtered and the solution evaporated to dryness. Recrystallization of the residue from dichloromethane/pentane afforded the known $Cp_2ZrSe_5$ [6c] (0.08 g, 0.13 mmol, 40%); m.p. 132–136 °C. $^1H$ NMR: 6.19 s ($C_5H_5$) ($CDCl_3$).

*$(MeCp)_2ZrSe_5$* (**8**)

(A) To a solution of $[(MeCp)_2Zr(\mu\text{-}Se)]_2$ [18a] (0.53 g, 0.81 mmol) in 15 ml of toluene was added grey selenium (0.52 g, 6.58 mmol). The mixture was stirred for 3 h then the red solid was dissolved by heating and the mixture was immediately filtered. Cooling gave **8** (0.51 g, 0.72 mmol, 49%); m.p. 136 °C. $^1H$ NMR: 5.53 m 8H ($C_5H_4$); 1.81 s 6H (Me). Anal. Found: C, 24.27; H, 2.33; Se, 57.60; Zr, 15.52. $C_{12}H_{14}Se_5Zr$ calcd.: C, 22.37; H, 2.19; Se, 61.28; Zr, 14.16%.

(B) The procedure described by Shaver et al. [6c] for similar compounds was used. Grey selenium (1.235 g, 15.63 mmol) was treated with 6.25 mmol of $LiBEt_3H$ in THF as described in ref. 27. After 0.5 h a solution of $(MeCp)_2ZrCl_2$ (1.00 g, 3.12 mmol) in 10 ml of THF was added, and the mixture stirred overnight. The solvent was evaporated, and the residue was recrystallized from hot toluene/pentane to give 1.08 g (1.68 mmol, 53%) of **8**; m.p. 136 °C.

*$[(t\text{-}BuCp)_2Zr(\mu\text{-}S)]_2$*

A solution of sulfur (0.018 g, 0.56 mmol) and $[(t\text{-}BuCp)_2Zr(\mu\text{-}Se)]_2$ [7g] (0.23 g, 0.28 mmol) in 10 ml of toluene was stirred at 40 °C for 16 h. The solvent was evaporated and the residue was washed twice with pentane then extracted with toluene. Filtration and evaporation of the extract gave 0.08 g (0.11 mmol, 40%) of green crystals identified as $[(t\text{-}BuCp)_2Zr(\mu\text{-}S)]_2$ [8a].

*$(MeCp)_2Zr(SeCH_2Ph)_2$* (**9**)

Dibenzyl diselenide (1.07 g, 3.14 mmol) in 10 ml of THF was treated with 6.3 mmol of $LiBEt_3H$. After 1 h stirring, 17 ml of toluene were added, and the mixture concentrated. A solution of $(MeCp)_2ZrCl_2$ (1.00 g, 3.14 mmol) in 40 ml of toluene was added and the mixture stirred overnight then filtered. The filtrate was evaporated, the residue washed twice with pentane, and the washings discarded. The product was recrystallized from hot toluene/heptane to give orange crystals of **9** (0.98 g, 1.66 mmol, 53%); m.p. 86 °C. $^1H$ NMR 7.46 m 4H (Ph), 7.14 m 6H (Ph), 5.83 pt 4H ($C_5H_4$), 5.65 pt 4H ($C_5H_4$), 4.35 s 4H ($CH_2$), 1.92 s 6H ($CH_3$). Anal. Found: C, 52.76; H, 4.79; Se, 26.73; Zr, 15.11. $C_{26}H_{28}Se_2Zr$ calcd.: C, 52.96; H, 4.98; Se, 26.78; Zr, 15.47%. Mass spectrum: 499 ($M - CH_2Ph$), 408 ($M - (CH_2Ph)_2$), 328 $(MeCp)_2ZrSe$, 249 $(MeCp)_2Zr$).

*$(MeCp)_2Zr(SePh)_2$* (**10**)

(A) Diphenyl diselenide (1.00 g, 3.2 mmol) in 7 ml of THF treated with 6.5 mmol of $LiBEt_3H$ in THF. After 1 h stirring, 10 ml of toluene were added and the mixture was concentrated. $(MeCp)_2ZrCl_2$ (1.02 g, 3.2 mmol) in 15 ml of toluene was added. After 1 h the mixture was filtered and the residue extracted with toluene. The combined extracts were evaporated to dryness, the oily residue was dissolved in the minimum of cold toluene, and heptane was added. The resulting solution was kept at −20 °C to give **10** (1.09 g, 1.26 mmol, 64%) as yellow crystals; m.p. 96 °C. $^1$H NMR: (see Table 3). Anal. Found: C, 51.31; H, 4.48; Se, 28.13; Zr, 16.08. $C_{24}H_{24}Se_2Zr$ calcd.: C, 51.32; H, 4.30; Se, 28.11; Zr, 16.24%.

(B) A mixture of $(MeCp)_2ZrPh_2$ (0.35 g, 0.87 mmol) and grey selenium (0.137 g, 1.74 mmol) in 15 ml of toluene was stirred for 3 days. Solid was filtered off and the filtrate evaporated. The product was recrystallized from toluene/hexane to give yellow crystals (0.20 g, 0.35 mmol, 40%). The product was shown to be identical with that described under A.

### *$(MeCp)_2Zr(SCH_2Ph)_2$* (**11**)

Dibenzyl disulfide (1.23 g, 5.00 mmol) and $LiBEt_3H$ (10.00 mmol) in 25 ml of THF were allowed to react for 1 h. 15 ml of toluene were added and the solution was concentrated by evaporation. A solution of $(MeCp)_2ZrCl_2$ (1.44 g, 4.5 mmol) in 35 ml of toluene was added and the mixture was stirred overnight at room temperature then evaporated to dryness. The residual oil was shaken with toluene and the suspension filtered. The filtrate was diluted with pentane and cooled to give pale yellow crystals of **11**, which melted at ca. 20 °C (1.99 g, 4.02 mmol, 89%). $^1$H NMR: 7.25 m 10H (Ph), 5.82 pt 4H ($C_5H_4$), 5.72 pt 4H ($C_5H_4$), 4.24 s 4H ($CH_2$), 2.01 s 6H (Me). Mass spectrum: 494 ($M$), 403 ($M - CH_2Ph$), 371 ($M - SCH_2Ph$), 91 ($PhCH_2$).

### *$(t\text{-}BuCp)_2Zr(SCH_2Ph)_2$* (**12**)

Treatment of dibenzyl disulfide (1.05 g, 4.20 mmol) with $LiBEt_3H$ (8.50 mmol) in 25 ml of THF was carried out as above. After addition of $(t\text{-}BuCp)_2ZrCl_2$ (1.53 g, 3.78 mmol) in 50 ml of toluene, overnight stirring, evaporation, dissolution in 20 ml of toluene, filtration and drying 2.06 g of yellow oil were obtained (3.55 mmol, 94%). Mass spectrum: 579 ($M$), 488 ($M - CH_2Ph$), 456 ($M - SCH_2Ph$), 3.97 ($M - 2(CH_2Ph)$), 333 ($M - 2(SCH_2Ph)$).

### *$[(MeCp)_2Zr(\mu\text{-}S)]_2$*

To a solution of 0.49 g (0.33 mmol) of **9** in 14 ml of toluene was added sulfur (0.026 g, 0.87 mmol). The mixture was stirred for 4 h and the solvent then evaporated off. The residue was washed three times with hexane and recrystallized from hot toluene to give blue crystals which were identified as the known $[(MeCp)_2Zr(\mu\text{-}S)]_2$ [18a] (0.14 g, 0.25 mmol, 61%). Evaporation of the washings gave diphenyl diselenide (0.22 g, 0.65 mmol, 78%).

### *$(MeCp)_2ZrPh_2$*

This compound was prepared by the metathetical reaction [24] between $(MeCp)_2ZrCl_2$ and PhLi and purified by recrystallisation from hot hexane (71%); m.p. 96 °C. $^1$H NMR: 7.33 m 10H (Ph); 5.68 m 8H ($C_5H_4$); 1.57 s 6H (Me). Anal. Found: C, 68.75; H, 5.93; Zr, 22.88. $C_{24}H_{24}Zr$ calcd.: C, 71.40; H, 5.99; Zr, 22.59%. Mass spectrum: 402 ($M$), 324 ($M$ − Ph), 248 ($(MeCp)_2Zr$).

### *$(MeCp)_2Zr(SeMe)_2$* (**13**)

A solution of $(MeCp)_2ZrMe_2$ [25] (0.44 g, 1.57 mmol) in 15 ml of heptane was stirred with grey selenium (0.25 g, 3.15 mmol) for 5 days. The mixture was filtered and the filtrate evaporated. The residue was dissolved in the minimum of pentane.

Cooling afforded orange crystals (0.22 g, 0.50 mmol, 31%); m.p. 88°C. $^1$H NMR (Table 3). Mass spectrum: 437 ($M$), 343 ($M-\mathrm{SeCH_3}$), 247 ($M-2(\mathrm{SeCH_3})$).

### *$Cp_2Zr(SMe)_2$* (**14**)

To a solution of $\mathrm{Cp_2ZrMe_2}$ [24] (0.55 g, 2.19 mmol) in 13 ml of heptane was added freshly sublimed sulfur (0.14 g, 4.38 mmol). The mixture was stirred overnight in the dark then the solvent was evaporated off. The residue was dissolved in the minimum of dichloromethane and pentane was added. Cooling gave pale yellow crystals (0.69 g, 2.19 mmol, 47%); m.p. 181°C. $^1$H NMR: (Table 3). Anal. Found: C, 46.20; H, 4.79; S, 20.11; Zr, 29.04. $\mathrm{C_{12}H_{16}S_2Zr}$ calcd.: C, 45.67; H, 5.11; S, 20.32; Zr, 28.90%. Mass spectrum: 314 ($M$), 267 ($M-\mathrm{SCH_3}$), 251($M-\mathrm{C_5H_4}$), 220 ($M-2(\mathrm{SCH_3})$), 187 ($M-\mathrm{C_{10}H_8}$).

### *$Cp_2Zr(TeMe)_2$* (**15**)

Tellurium powder (0.81 g, 6.36 mmol) was added to a solution of $\mathrm{Cp_2ZrMe_2}$ (0.80 g, 3.18 mmol) in 25 ml of heptane and the mixture was stirred for 5 days. The solvent was evaporated off and the residue extracted with dichloromethane. The extract was filtered and pentane was added to the filtrate. Cooling gave red crystals (0.63 g, 1.24 mmol, 19.5%) of compound **15**. $^1$H NMR (Table 3). Anal. Found: C, 28.16; H, 3.24; Te, 49.56; Zr, 17.59. $\mathrm{C_{12}H_{16}Te_2Zr}$ calcd.: C, 28.44; H, 3.18; Te, 50.36; Zr, 18.00%. Mass spectrum: 510 ($M$), 365 ($M-\mathrm{TeCH_3}$), 220 ($M-2(\mathrm{TeCH_3})$).

## References

1 (a) H. Köpf, J. Organomet. Chem., 14 (1968) 353; (b) H. Köpf and T.J. Klapötke, ibid., 310 (1986) 303; (c) H. Köpf and T.J. Klapötke, ibid., 307 (1986) 319; (d) H. Köpf and T.J. Klapötke, Chem. Ber., 119 (1986) 1986; (e) H. Köpf and T.J. Klapötke, Z. Naturforsch. B, 41 (1986) 971.

2 G.Chandra and M.F. Lappert, J. Chem. Soc. A, (1968) 1940.

3 M. Sato and T. Yoshida, J. Organomet. Chem., 67 (1974) 395.

4 E. Samuel and D. Giannoti, J. Organomet. Chem., 113 (1976) C17.

5 J.L. Petersen, J. Organomet. Chem., 166 (1979) 179.

6 (a) J.M. McCall and A. Shaver, J. Organomet. Chem., 193 (1980) C37; (b) P.H. Bird, J.M. McCall, A. Shaver and U. Siriwardane, Angew. Chem. Int. Ed. Engl., 21 (1982) 384; (c) A. Shaver and J.M. McCall, Organometallics, 3 (1984) 1823; (d) A. Shaver, J.M. McCall, V.W. Day and S. Vollmer, Can. J. Chem., 65 (1987) 1676.

7 (a) B. Gautheron, G. Tainturier and Ph. Meunier, J. Organomet. Chem., 209 (1981) C49; (b) S. Pouly, G. Tainturier and B. Gautheron, ibid., 232 (1982) C65; (c) B. Gautheron, G. Tainturier and S. Pouly, ibid., 268 (1984) C56; (d) B. Gautheron and G. Tainturier, ibid., 262 (1984) C30; (e) B. Gautheron, G. Tainturier, S. Pouly, F. Théobald, H. Vivier and A. Laarif, Organometallics, 3 (1984) 1495; (f) G. Tainturier, B. Gautheron and M. Fahim, J. Organomet. Chem., 290 (1985) C4; (g) G. Tainturier, B. Gautheron and S. Pouly, Nouv. J. Chim., 10 (1986) 625; (h) M. Fahim and G. Tainturier, J. Organomet. Chem., 301 (1986) C45.

8 (a) G. Erker, T. Mühlenbernd, R. Benn, A. Rufińska, G. Tainturier and B. Gautheron, Organometallics, 5 (1985) 1023; (b) G. Erker, T. Mühlenbernd, R. Nolte, J.L. Petersen, G. Tainturier and B. Gautheron, J. Organomet. Chem., 314 (1986) C21.

9 D.E. Laycock and H. Alper, J. Org. Chem., 46 (1981) 289–93.

10 P.B. Brindley and M.J. Scotton, J. Organomet. Chem., 222 (1981) 89–96.

11 (a) M.E. Silver and R.C. Fay, Organometallics, 2 (1983) 44; (b) M.E. Silver, O. Eisenstein and R.C. Fay, Inorg. Chem., 22 (1983) 759.

12 (a) F. Bottomley, D.F. Drummond, G.O. Egharevba and P.S. White, Organometallics, 5 (1986) 1620. (b) F. Bottomley, T-T. Chin, G.O. Egharevba, L.M. Kaul, D.A. Pataki and P.S. White, Organometallics, 7 (1988) 1214.

13 S.L. Buchwald and R.B. Nielsen, J. Am. Chem. Soc., 110 (1988) 3171.
14 L. Gelmini and D.W. Stephan, Organometallics, 6 (1987) 1515.
15 E.A. Mintz and A.S.J. Ward, J. Organomet. Chem., 307 (1986) C52.
16 P. Meunier, B. Gautheron and A. Mazouz, J. Organomet. Chem., 320 (1987) C39.
17 M. Draganjac and T.B. Rauchfuss, Angew. Chem. Int. Ed. Engl., 24 (1985) 742 and references therein.
18 (a) G. Tainturier, M. Fahim and B. Gautheron, J. Organomet. Chem., 362 (1989) 311; (b) G. Tainturier, M. Fahim and B. Gautheron, ibid., in press.
19 G.L. Hillhouse and J.E. Bercaw, J. Am. Chem. Soc., 106 (1984) 5472.
20 M.F. Lappert, C.J. Pickett, P.I. Riley and P.I.W. Yarrow, J. Chem. Soc. Dalton Trans., (1981) 805.
21 B. Meyer, Chem. Rev., 64 (1964) 429.
22 A.E. Bruce, M.R.M. Bruce and D.R. Tyler, J. Am. Chem. Soc., 106 (1984) 6660.
23 P.C. Wailes and H. Weigold, J. Organomet. Chem., 24 (1970) 405.
24 E. Samuel and M.D. Rausch, J. Am. Chem. Soc., 95 (1973) 6263.
25 S. Couturier, G. Tainturier and B. Gautheron, J. Organomet. Chem., 195 (1980) 291.
26 L.T. Reynolds and G. Wilkinson, J. Inorg. Nucl. Chem., 9 (1959) 86.
27 J.A. Gladysz, J.L. Hornby and J.E. Garbe, J. Org. Chem., 43 (1978) 1204.