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The preparation of four- and six-membered chalcogenametallacyclic derivatives of group 4 metallocenes

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Abstract

Four-membered metallacycles $[(RC_5H_4)_2M(\mu\text{-}E)]_2$ (M = Zr, Hf; **1**, E = Se; **2**, E = S) were obtained by UV irradiation of dialkyl- or diaryl-metallocenes and equimolecular amounts of elemental chalcogen, but this method works only for bulky R groups. A more general route to compounds **1** and **2** involves the reaction of metallocene dichloride with chalcogenide anions. Six-membered metallacyclohexasulfanes $(t\text{-}BuC_5H_4)_2MS_5$ (**3**, M = Zr, Hf) are obtained rather than compounds **2** when an excess of sulfur is used in the photolytic experiments, whereas compounds **1** were still formed when an excess of selenium was used. The observed difference is explained in terms of the solubility of the chalcogen in the solvent used for the reaction.

Introduction

Chalcogen complexes of transition metals can be regarded as the result of the deoligomerisation [1,2] of the stable forms of the chalcogen elements induced by highly reactive organometallic species [3–7]. These reactions lead to a wide variety of compounds which act as soluble chalcogen reservoirs [8,9] or precursors of new chalcogen molecules such as S_n ($n = 6$, 7 [10]; $n = 10$, 15 or 20 [11] or Se_2S_5 [12]). Other compounds with chalcogen–carbon bonds are efficient reagents for synthesis of organic chalcogen-containing molecules [13–15].

Three types of chalcogen-containing ligands are known. The most common is a thiolate or selenolate ligand, which can be either monodentate [16,17] or bidentate [18]. The hydrochalcogenide ligand belongs to this family. In the second type, the ligand is a chelated chain of chalcogen atoms [20–22] forming a metallacycle. The third type involves bridging $(E)_x$-ligands. Titanium complexes bearing two such ligands are well-known for $x = 2$ [8a,22], or 3 [22,23]. When $x = 1$, the central ring is four-membered: we have previously described such complexes containing t-butyl-

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cyclopentadienyl groups linked to zirconium or hafnium [7b,9b]. However, as early as 1980, Shaver [20a] mentioned a chance preparation of $[Cp_2Zr(\mu\text{-}S)]_2$ [20b], whose crystal structure has recently been studied [24a,24b]. A quite similar compound has been reported by Herrmann [24c].

Up to now the preparation of these four-membered bimetallic complexes involved use of photo- [7b,9c] or thermally-generated low-valent metallocene units [9b], but this approach is confined to molecules containing cyclopentadienyl ligands bearing a bulky alkyl group. We describe below a more general route to such species, and account for the different behaviour of transient metallocenic species towards selenium and sulfur.

Results and discussion

While several complexes containing two metals linked by sulfur [20,22–27] or selenium atoms [25g,26] have been reported, very few involve transition metals [20,24,25d,26]. We obtained [7b,9c] the first four-membered zirconacycles involving chalcogen atoms (Fig. 1) by photolysis of dialkyl- or diaryl-metallocenes in presence of elemental selenium as represented in eq. 1. The procedure worked equally well when a stoichiometric amount of sulfur was used instead of selenium.

$$\begin{array}{lll} 2(\text{t-BuCp})_2MR_2 + 2E & \xrightarrow{UV} (\text{t-BuCp})_2M(\mu\text{-}E)_2M(\text{t-BuCp})_2 & (1) \\ (M = Zr, Hf;\ R = Ph, Me) & \quad (\mathbf{1}\text{: } E = Se; & \\ & \quad \mathbf{2}\text{: } E = S) & \end{array}$$

Compounds **1** and **2** (Fig. 1) were characterized by elemental analysis, cryoscopy, and proton NMR and mass spectrometry. A preliminary X-ray analysis showed that the central core of **1** (M = Zr) is very close to a perfect square [28a], but the complete structure was not determined. However, the crystal structure of the analogue of **1** containing tellurium in place of selenium agrees well with the indicated geometry of **1** [28b].

The occurrence of reaction 1 can be easily understood when starting from a diarylmetallocene: in this case it is known that the photolysis induces intramolecular coupling of the two aryl ligands [29a] leading to transient metallocenic species which can be stabilized by complexation [29]. When R = Me, the UV irradiation presumably involves the homolytic cleavage of the alkyl–metal bond, but in this case the formation of the metallocenic species has not been definitely proved [30].

The presence of an alkyl group on the cyclopentadienyl ligands appears to be necessary. Where the unsubstituted diphenylzirconocene is used, a complex mixture was obtained instead of the expected **1** or **2**. This failure can be accounted for in

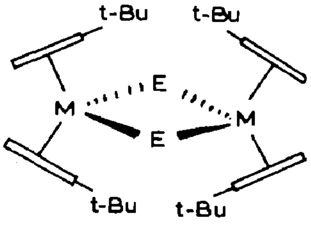

Fig. 1. Structure of compounds 1 and 2.

terms of two factors. First, the photochemical cleavage is very fast, giving species more prone to dimerize [31] than to react with chalcogen molecules, especially in the case of insoluble polymeric grey selenium. Secondly, sulfur and selenium are able to insert into the metal–carbon bond of the less hindered complexes [9c] to give unexpected by-products.

We have reported preliminary results showing that another preparation of the bimetallacyclotetrachalcogenanes **1** and **2** involves reaction of metallocene dichlorides with chalcogenide anions in THF [32]. The reaction can be represented as in equation 2.

$$\begin{array}{lll} 2(\mathrm{RCp})_2\mathrm{MCl}_2 & \xrightarrow{+2\mathrm{E}^{2-},\ -4\mathrm{Cl}^-} & [(\mathrm{RCp})_2\mathrm{M}(\mu\text{-E})]_2 \\ (\mathrm{R} = \mathrm{H, Me, t\text{-}Bu}) & & (\mathbf{1}\text{: E} = \mathrm{Se}; \\ & & \ \mathbf{2}\text{: E} = \mathrm{S}) \end{array} \qquad (2)$$

In our hands the use of commercial sodium selenide resulted in failure. The required anhydrous nucleophilic species can be generated by reduction of the chalcogen either by metallic sodium [33] or by lithium triethylborohydride [34]. As a suitable reagent for preparation of catenated chalcogen derivatives of early transition metals had previously been prepared by Shaver [20] and Rauchfuss [13] by use of lithium triethylborohydride, we chose the second approach, as shown in the equation 3

$$2\ \mathrm{LiBEt_3H} + 1/n\mathrm{E}_n \rightarrow \mathrm{Li_2E} + \mathrm{H_2} + 2\ \mathrm{BEt_3} \qquad (3)$$

The reagent thus obtained was allowed to react with metallocene dichlorides according to equation 2. The data for the isolated compounds are reported in Table 1.

The rate of reaction 2 is very sensitive to steric hindrance: the slowest reaction was observed for complex **1c**. Moreover in the case of the hafnium analogue of **1c** the reaction mixture still contained half of the starting dichloride after two weeks at room temperature.

The variations in the yields shown in Table 1, and especially the low values for **1a** and **1d**, can be explained in terms of the lower solubility and higher sensitivity towards hydrolysis of the unsubstituted complexes compared with their alkylated homologues.

Table 1

Yields and ^{1}H NMR data of $(\mathrm{RCp})_2\mathrm{M}(\mu\text{-E})_2\mathrm{M}(\mathrm{RCp})_2$

	M	R	E	Rdt. (%)	^{1}H NMR, δ (ppm)	Ref.
1a	Zr	H	Se	5	6.34s	
1b	Zr	Me	Se	55	6.30m, 16H; 2.11s, 2H	
1c	Zr	t-Bu	Se	55	6.52, 16H; 1.28s, 36H	7b
1d	Hf	H	Se	13	6.28s	
2a	Zr	H	S	61	6.26s	20b
2b	Zr	Me	S	39	6.20ps, 16H; 2.14, 12H	
2c	Zr	t-Bu	S	78	6.42ps, 16H; 1.30s, 36H	
2d	Hf	H	S	47	6.22s	
2e	Hf	Me	S	55	6.16ps, 16H; 2.18s, 12H	
2f	Hf	t-Bu	S	35	6.37m, 16H; 1.32s, 36H	

The isolated compounds are bimetallic and their dimeric character is retained even in solution, as was shown by cryometric measurements. For the cyclopentadienyl protons, the ^1H NMR spectra displays either the singlet characteristic of the unalkylated ligand or an AA′BB′ system of spins accounting for two anisochronous sets of two enantiotopic protons, as is usually observed for an η^5-alkylcyclopentadienyl ligand in a symmetrical complex [35]. The chance observed for compound **2c** disappears in $CDCl_3$, giving the expected pseudo-triplet signals.

Reaction 1 above implies equimolar amounts of metallocenic compounds and chalcogen atoms. In fact, compounds **1** were readily obtained even in presence of a large excess of selenium, showing that the 1/1 stoechiometry is not a prerequisite. Unlike selenium, sulfur had to be used in exact proportion, otherwise metallacyclohexasulfanes **3** were obtained instead of the desired binuclear compounds (equation 4). This result was not completely unexpected since it is known that UV-irradiation

$$(\text{t-BuCp})_2\text{MPh}_2 + 5/8\text{S}_8 \rightarrow \underset{\substack{(\mathbf{3c}:\ \text{M} = \text{Zr};\\ \mathbf{3f}:\ \text{M} = \text{Hf})}}{(\text{t-BuCp})_2\text{MS}_5} + \text{Ph} - \text{Ph} \qquad (4)$$

of Cp_2TiMe_2 in the presence of sulfur leads to Cp_2TiS_5 [6]. Moreover, we obtained **3c** from the corresponding butadienezirconocene complex [9b].

The compounds **3c** and **3f** were characterized by elemental analysis and shown to be identical with authentic samples prepared from $(\text{t-BuCp})_2MCl_2$ by the method used by Shaver [20] and Rauchfuss [13] for similar compounds. It involves partially reducing sulfur with $LiBEt_3H$ and treating the so-formed reagent with metallocene dichloride. The size of the obtained metallacycle mainly depends on the bulk of cyclopentadienyl ligands: if they bear only one alkyl group the six-membered metallacycles $(RCp)_2MS_5$ (M = Ti, Zr, Hf; R = H, Me, i-Pr, $SiMe_3$) are obtained [13,20,22], whereas $(C_5Me_5)_2MCl_2$ gives $(C_5Me_5)_2MS_x$ (M = V, $x = 2$ [36]; M = Ti, $x = 3$ [21]). In the case of $(\text{t-BuCp})_2MCl_2$ it is clear that the reaction gives the six-membered metallacycles **3c** or **3f**.

Further characterization of **3c** and **3f** was achieved by studying their ^1H NMR spectra; at room temperature the signals from the t-BuCp groups are isochronous but, as the temperature is lowered splitting of the signals occurs. This observation is consistent [20] with a cyclohexane-like ME_5 metallacycle bearing two formally diastereotopic cyclopentadienyl rings, respectively in an axial and an equatorial conformation, in accordance with the recent study of the RX structure of the well-known Cp_2ME_5 (M = Zr, Hf; E = S [37]; M = Ti; E = Se [38]). At room temperature the signals from the t-BuCp ligands in **3c** and **3f** are isochronous owing to rapid inversion of the ring (Fig. 2).

Starting from the low-temperature limit spectrum two coalescences were observed: one related to the cyclopentadienyl protons and the other to t-butyl groups. The ring inversion barriers for compounds **3** were calculated by standard methods [39,40]; the values (Table 2) are very similar to those reported for other zircona- and hafna-cyclohexasulfanes [20b]. The replacement of one hydrogen atom of each cyclopentadienyl ligand by a t-butyl group increases $\Delta G^{\neq}$ by about 3kJ mol^{-1}. This increase is in good agreement with the difference between $\Delta G^{\neq}$ values (5.7 kJ mol^{-1}) corresponding to the ring inversion for $(Me_3SiC_5H_4)_2TiS_5$ [20b] and Cp_2TiS_5 [41].

From our results, it is clear that the photochemical reaction 1 or 3 gives the

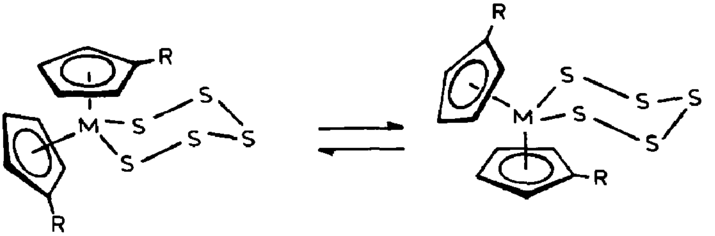

Fig. 2. Inversion of the six-membered ring of compounds 3, R = t-Bu.

bimetallacycle **2** or pentasulfide **3** depending on the amount of sulfur present. It is very likely that one of the two products **2** or **3** is an intermediate in the reaction sequence for the formation of the other one. The second step of the reaction can be represented either by equation 5 or 6.

$$\underset{(\mathbf{2})}{[(\text{t-BuCp})_2\text{M}(\mu\text{-S})]_2} + \text{S}_8 \rightarrow \underset{(\mathbf{3})}{2(\text{t-BuCp})_2\text{MS}_5} \tag{5}$$

$$\underset{(\mathbf{3})}{2(\text{t-BuCp})_2\text{MS}_5} + 8(\text{t-BuCp})_2\text{MPh}_2 \xrightarrow{\text{UV}} \underset{(\mathbf{2})}{5[(\text{t-BuCp})_2\text{M}(\mu\text{-S})]_2} + 8\text{PhPh} \tag{6}$$

Equation 5 is based on the assumption that complex **2** is the initial product, and that **2** then reacts with more elemental sulfur with opening of the four-membered metallacycle. In reaction 6, the metallacyclohexasulfane **3**, which is in this case assumed to be the first product serves as a very soluble sulfur reservoir able to react with the metallocenic species formed by photolysis of the diarylmetallocene.

We prefer the suggestion that the overall reaction begins with formation of the pentasulfide **3** with **3** then reacting as in equation 6. This hypothesis implies a progressive cleavage of the molecular sulfur S_8, leading first to S_5 fragments and then to sulfide ligands by cleavage of the metallacycle **3**. The direct formation of the binuclear compound **2** in the first step would require the less plausible cleavage of S_8 molecules into monoatomic species. Our results are consistent with our favoured interpretation, since irradiation of a mixture of pentasulfide **3** and diphenylmetallocene according to equation 6 readily gave the corresponding binuclear complex **2**. However, the other possibility cannot be ruled out, since we found that a mixture of complex **2** and molecular sulfur leads to pentasulfide **3**, as shown in eq. 5.

In the case of selenium we obtained only the binuclear four-membered metallacycle **1**. This result can be readily understood by taking into account the high

Table 2

Free activation enthalpy of ring inversion of metallacyclohexasulfanes

No. or ref.	compound	*T* coalesc. (K)	ΔG^* (kJ mol^{-1})
20b	Cp_2ZrS_5		48.6
20b	Cp_2HfS_5		58.0
3c	$(t\text{-}BuCp)_2ZrS_5$	243(Cp)	51.6
	$(t\text{-}BuCp)_2ZrS_5$	239(t-Bu)	52.1
3f	$(t\text{-}BuCp)_2HfS_5$	283(Cp)	61.2
	$(t\text{-}BuCp)_2HfS_5$	277(t-Bu)	61.3

insolubility of polymeric chains of grey selenium in organic solvents [33,42]. In this heterogeneous reaction mixture the life-time of an hypothetic soluble metallacyclohexaselenane $(RCp)_2MSe_5$ would be very short, because it would act as a soluble selenium reservoir, more able to react with metallocenic species than the insoluble grey-selenium.

Experimental

Reactions with organometallic materials were carried out under argon at room temperature by Schlenk techniques. Solvents were dried, desoxygenated, and distilled from sodium-benzophenon 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 (δ scale in ppm, s = singlet, d = doublet, t = triplet, m = multiplet, ps = pseudo-singlet). Mass spectra were obtained with a Finnigan 3300 spectrometer at 70 eV; the *m/e* values shown are for the ions containing the most abundant isotopes. Microanalyses were carried out by Service Central d'Analyses du CNRS, Lyon. Selenium and sulfur were sublimed and stored under argon; $LiHBEt_3$ (superhydride) was purchased from Aldrich as a solution in THF. Cp and RCp respectively represent the ligands η^5-C_5H_5 and alkylcyclopentadienyl. M denotes a transition metal and E a chalcogen atom. Compounds $(t\text{-}BuCp)_2MPh_2$ were prepared as previously described [9c].

*$Cp_2Zr(\mu\text{-}Se)_2ZrCp_2$ (**1a**)*

A mixture of selenium (0.197 g, 2.50 mmol), $LiHBEt_3$ (5.25 mmol), and Cp_2ZrCl_2 [43] (0.584 g, 2.00 mmol) in THF (15 ml) was stirred for six days. The green solid was extracted with 25 ml CH_2Cl_2, and after centrifugation, the clear extract was evaporated and the residue dissolved in hot toluene. Cooling, gave green crystals (0.03 g, 0.05 mmol, 5%) of **1a**; m.p. > 260 °C. Anal. found: C, 39.85; H, 3.37; Se, 24.70; Zr, 30.15. $C_{20}H_{20}Se_2Zr_2$ calcd.: C, 39.99; H, 3.55; Se, 26.29; Zr, 30.30%. MS: 600 (*M*), 535 (*M* – Cp), 470 (*M* – 2Cp), 455 (*M* – Cp – Se), 405 ($CpSe_2Zr_2$), 300 (Cp_2SeZr), 235 (CpSeZr), 220 (Cp_2Zr). Cryometry (benzene): Calcd. 600; found 589.

*$(MeCp)_2Zr(\mu\text{-}Se)_2Zr(CpMe)_2$ (**1b**)*

A solution of $(MeCp)_2ZrCl_2$ [44] (0.640 g, 2.00 mmol) in 15 ml of THF was added to a mixture of selenium (0.197 g, 2.50 mmol) and $LiHBEt_3$ (5.25 mmol). After six days stirring, the solvent was evaporated and the residue extracted with hot toluene. The extract was filtered and the solvent distilled off. Recrystallization of the residue from toluene gave green crystals (0.361 g, 0.55 mmol, 55%); m.p. 180–184 °C. Anal. Found: C, 43.92; H, 4.30; Se, 24.24; Zr, 27.84. $C_{24}H_{28}Se_2Zr_2$ calcd.: C, 43.88; H, 4.29; Se, 24.04; Zr, 27.77%. MS: 656 (*M*), 577 (*M* – MeCp).

*$(t\text{-}BuCp)_2Zr(\mu\text{-}Se)_2Zr(Cpt\text{-}Bu)_2$ (**1c**)*

A mixture of selenium (0.166 g, 2.10 mmol), $LiHBEt_3$ (4.2 mmol), and $(t\text{-}BuCp)_2ZrCl_2$ [35b, 45] (0.808 g, 2.00 mmol) in THF (20 ml) was stirred for 18 h. The solvent was removed and the residue extracted with toluene. Work up of the clear solution obtained after centrifugation and recrystallisation from toluene/

heptane gave the known product [7b,9b,9c] (0.45 g, 0.54 mmol, 55%). Cryometry (benzene): found 833; calcd. 824.

*$Cp_2Hf(\mu\text{-}Se)_2HfCp_2$ (**1d**)*

By the procedure used for **1a**, selenium (0.197 g, 2.5 mmol), $LiHBEt_3$ (5.25 mmol) and Cp_2HfCl_2 [43b] (0.76 g, 2.00 mmol) in THF (10 ml) gave complex **1d** as green crystals; m.p. > 260 °C. Anal. Found: C, 32.16; H, 2.88; Se, 19.68. $C_{20}H_{20}Hf_2Se_2$ calcd.: C, 30.98; H. 2.60; Se, 20.37%. MS: 780 (M), 715 ($M-$ Cp), 650 ($M-$ 2Cp), 635 ($M-$ Cp $-$ Se), 585 ($M-$ 3Cp), 390 (Cp_2HfSe), 325 (CpHfSe), 310 (Cp_2Hf).

*$Cp_2Zr(\mu\text{-}S)_2ZrCp_2$ (**2a**)*

To a mixture of sulfur (0.08 g, 2.50 mmol) and $LiHBEt_3$ (5.25 mmol) was added a solution of Cp_2ZrCl_2 (0.58 g, 2 mmol) in 15 ml of THF. After overnight stirring the supernatent ligand was decanted and the residue dissolved in CH_2Cl_2. The solution was centrifuged, then the residue was crystallized from hot toluene to give the compound isolated previously by Shaver [20]; m.p. > 260 °C. Anal. Found: 47.18; H, 4.03; S, 11.81; Zr, 36.00. $C_{20}H_{20}S_2Zr_2$ calcd.: C, 47.98; H, 3.97; S, 12.64; Zr, 35.98%. MS: 504 (M), 439 ($M-$ Cp), 407 ($M-$ Cp $-$ S), 374 ($M-$ 2Cp), 252 (Cp_2ZrS), 220 (Cp_2Zr).

*$(MeCp)_2Zr(\mu\text{-}S)_2Zr(CpMe)_2$ (**2b**)*

To a mixture of sulfur (0.220 g, 6.87 mmol) and 14.0 mmol $LiHBEt_3$ was added a solution of $(MeCp)_2ZrCl_2$ [44] (2.00 g, 6.25 mmol) in 15 ml of THF. After overnight stirring the solvent was distilled off and the residue washed with pentane then recrystallised from hot toluene as blue crystals (0.70 g, 1.23 mmol, 39%); m.p. 218–220 °C. Anal. Found: C, 51.18; H, 5.04; S, 11.50; Zr, 31.79. $C_{24}H_{28}S_2Zr_2$ calcd.: C, 51.19; H, 5.01; S, 11.39; Zr, 32.40%. MS: 560 (M), 481 ($M-$ MeCp); 402 ($M-$ 2MeCp), 323 ($M-$ 3MeCp), 244 ($M-$ 4MeCp).

*$(t\text{-}BuCp)_2Zr(\mu\text{-}S)_2Zr(Cpt\text{-}Bu)_2$ (**2c**)*

A procedure analogous to that used for **2b** except that heptane was used instead of toluene, gave green crystals (1.15 g, 1.57 mmol, 78%) m.p. > 260 °C from $(t\text{-}BuCp)_2ZrCl_2$ [35b,45] (1.630 g, 4.00 mmol). Anal. Found: C, 59.53; H, 7.37; S, 8.65; Zr, 25.42. $C_{36}H_{52}S_2Zr_2$ calcd.: C, 59.12; H, 7.16; S, 8.77; Zr, 24.94. MS: 730 (M); 607 ($M-$ t-BuCp); 575 ($M-$ t-BuCp $-$ S); 454 $(t\text{-}BuCp)_2Zr_2S$; 365 $(t\text{-}BuCp)_2ZrS)$; 333 $(t\text{-}BuCp)_2Zr$. Cryometry (benzene): found 728; calcd.: 730.

*$Cp_2Hf(\mu\text{-}S)_2HfCp_2$ (**2d**)*

To a solution of lithium sulfide (2.5 mmol) as prepared for **2b**, was added a solution of Cp_2HfCl_2 [43b] (0.76 g, 2.00 mmol) in 10 ml THF. The mixture was stirred for five days then the red solid was filtered off and extracted with CH_2Cl_2 (12 ml). The clear solution obtained after centrifugation was evaporated, and the residual red solid was recrystallised from toluene (0.39 g, 0.47 mmol, 47%); m.p. > 260 °C. Anal. Found: C, 35.09; H, 3.04; Hf, 52.38; S, 9.48. $C_{20}H_{20}Hf_2S_2$ calcd.: C, 35.25; H, 2.96; Hf, 52.38; S, 9.41%. MS: 684 (M); 619 ($M-$ Cp); 587 ($M-$ Cp $-$ S); 554 ($M-$ 2Cp); 342 (Cp_2HfS); 277 (CpHfS).

*$(MeCp)_2Hf(\mu\text{-}S)_2Hf(CpMe)_2$ (**2e**)*

By the procedure used for **2b**, sulfur (0.040 g, 1.25 mmol), $LiHBEt_3$ (2.6 mmol), and $(MeCp)_2HfCl_2$ [46] (0.407 g, 1.00 mmol) gave red crystals (0.20 g, 0.27 mmol, 55%) after recrystallization from heptane/toluene; m.p. 228–230 °C. Anal. Found: C, 40.53; H, 3.92; Hf, 48.06; S, 8.70. $C_{24}H_{28}Hf_2S_2$ calcd.: C, 39.08; H, 3.82; Hf, 48.39; S, 8.69%. MS: 740 (*M*); 661 (*M* − MeCp); 646 (*M* − MeCp − Me); 582 $(MeCp)_2Hf_2S_2$; 370 $(MeCp)_2HfS$.

*$(t\text{-}BuCp)_2Hf(\mu\text{-}S)_2Hf(Cpt\text{-}Bu)_2$ (**2f**)*

By the method used for **2c**, lithium sulfide (2.5 mmol) and $(t\text{-}BuCp)_2HfCl_2$ [35b,46] in THF (10 ml) gave red crystals (0.32 g,. 0.35 mmol, 35%); m.p. > 260 °C. Anal. Found: C, 48.72; H, 5.98; Hf, 37.17; S, 6.89. $C_{36}H_{52}Hf_2S_2$ calcd.: C, 47.73; H, 5.78; Hf, 39.40; S, 7.08. MS: 908 (*M*); 851 (*M* − t-Bu); 819 (*M* − t-Bu − S); 787 (*M* − t-BuCp); 698 ($(t\text{-}BuCp)_2CpHf_2S$); 680 ($Cp_4Hf_2S_2$); 648 (Cp_4Hf_2S); 666 ($(t\text{-}BuCp)_2Hf_2S_2$); 454 $(t\text{-}BuCp)_2HfS$. Cryometry (benzene): found 892; calcd. 905.

*Photochemical synthesis of **1c**, **1f** and **2c**, **2f***

A typical procedure was as follow. To the chalcogen (0.75 mmol) was added a solution of 0.72 mmol of diphenylmetallocene in toluene (40 ml). The mixture was irradiated for 3 h (Zr complexes) or 15 h (Hf complexes). The solvent was evaporated and the residue washed twice with pentane then dried. Recrystallization from heptane gave the same compounds as those obtained by the substitution method (see above).

*$(t\text{-}BuCp)_2ZrS_5$ (**3c**)*

A mixture of sulfur (0.484 g, 15.1 mmol) and $LiHBEt_3$ (6.05 mmol) was stirred for 20 min at room temperature and then a solution of $(t\text{-}BuCp)_2ZrCl_2$ [35b,45] (1.2 g, 3 mmol) in THF (15 ml) was slowly added. Stirring was maintained overnight, the solvent then distilled off and the residual solid extracted with toluene. The extract was centrifuged, and the solution evaporated to leave a solid, which was recrystallized from methylene dichloride/pentane to give yellow crystals of the product (1.06 g, 2.15 mmol, 71%), which was identical to that described previously [9b]; m.p. 164–166 °C. ^1H NMR: 5.85 t 4H (Cp); 5.68 t 4H (Cp); 1.10 s 18H (t-Bu). MS: 492 (*M*); 428 $(t\text{-}BuCp)_2ZrS_3$; 396 $(t\text{-}BuCp)_2ZrS_2$; 371 $(t\text{-}BuCp)ZrS_5$; 364 $(t\text{-}BuCp)_2ZrS$; 346 $(C_5H_4)_2ZrS_4$; 332 $(t\text{-}BuCp)_2Zr$; 307 $(t\text{-}BuCp)ZrS_3$; 211 $(t\text{-}BuCp)Zr$.

*$(t\text{-}BuCp)_2HfS_5$ (**3f**)*

In a procedure similar to that used for **3c**, a solution of $(t\text{-}BuCp)_2HfCl_2$ [35b,46] (1.47 g, 3.0 mmol) in THF (20 ml) was added to a solution made from sulfur (0.489 g, 15.28 mmol) and $LiHBEt_3$ (6.2 mmol) in THF. Yellow crystals (0.85 g, 1.46 mmol, 48%); m.p. 168–170 °C. ^1H NMR: 5.81 m 4H (Cp); 5.65 m 4H (Cp); 1.11 s 18H (t-Bu). Anal. Found: C, 37.52; H, 4.58; Hf, 29.42; S, 27.68. $C_{18}H_{26}S_5Hf$ calcd.: C, 37.20; H, 4.51; Hf, 30.72; S, 27.59%. MS: 582 (*M*), 518 $(t\text{-}BuCp)_2HfS_3$, 486 $(t\text{-}BuCp)_2HfS_2$, 461 $(t\text{-}BuCp)HfS_5$, 429 $(t\text{-}BuCp)HfS_4$, 397 $(t\text{-}BuCp)HfS_3$, 308 (HfS_4), 301 $(t\text{-}BuCp)Hf$.

Synthesis of 3c, 3f starting from $(t\text{-}BuCp)_2MPh_2$

Irradiation for 5 h of a mixture of $(t\text{-BuCp})_2\text{MPh}_2$ (M = Zr, Hf) (0.78 mmol) and sulfur (3.9 mmol) in toluene (20 ml) followed by washing of the crude product with pentane and recrystallisation, gave the same products as those obtained by LiHBEt_3 method.

Photochemical synthesis of **2c**, **2f** *starting from* **3c**, **3f**

A toluene solution of $(t\text{-BuCp})_2\text{MS}_5$ (M = Zr, Hf) (0.21 mmol) and the appropriate $(t\text{-BuCp})\text{MPh}_2$ (M = Zr, Hf) (0.84 mmol) was irradiated for 3 h (M = Zr) or 15 h (M = Hf). The solvent was evaporated off and the solid residue was washed with pentane then recrystallized and shown to be identical with the compounds **2c** and **2f**, described above.

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