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Article

Reactions of Hydrogen Sulfide with Singly and Doubly Tucked-in Titanocenes

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Hydrogen sulfide reacts with tucked-in titanocene complexes [Ti(III){η^5:η^1-$C_5Me_4(CH_2)$}Cp*] (Cp* = η^5-C_5Me_5) (**2**) and [Ti{η^4:η^3-$C_5Me_3(CH_2)_2$}Cp*] (**3**) and their precursors [Cp^*_2TiMe] (**2a**) and [$Cp^*_2Ti(\eta^2$-$Me_3SiC{\equiv}CSiMe_3)$] (**3a**), respectively, to give the corresponding titanocene hydrosulfides [Cp^*_2Ti(SH)] (**4**) and [$Cp^*_2Ti(SH)_2$] (**1**), respectively. Hydrogen sulfide also cleaves intramolecular σ- or π-Ti−C bonds in *ansa*-[$Ti^{III}(\eta^1{:}\eta^5{:}\eta^5$-$C_5Me_4SiMe_2CHCH_2SiMe_2C_5Me_4$)] (**5**) and *ansa*-[$Ti^{II}(\eta^2{:}\eta^5{:}\eta^5$-$C_5Me_4SiMe_2CH{=}CHSiMe_2C_5Me_4$)] (**6**), affording hydrosulfides *ansa*-[(η^5-$CH_2Me_2SiC_5Me_4)_2Ti(SH)$] (**7**) and *ansa*-[($\eta^5$-$CH_2Me_2SiC_5Me_4)_2Ti(SH)_2$] (**8**). The S−H bonds of hydrosulfides **4** and **7** were able to react with the Ti−C bonds in **2** and **5**, affording titanocene sulfides [($Cp^*_2Ti^{III})_2$S] (**11**) and *ansa*-[{(η^5-$CH_2Me_2SiC_5Me_4)_2Ti^{III}\}_2$S] (**12**), respectively. Combination of **7** with **2a** gave rise to the mixed titanocene sulfide [*ansa*-{(η^5-$CH_2SiMe_2C_5Me_4)_2$Ti}S(TiCp^*_2)] (**13**). The titanium(III) d^1 electrons in **11**−**13** form an electronic triplet state well observable by EPR spectra in toluene glass. All the hydrosulfides were decomposed by sunlight. Compound **1** eliminated Cp*H and H_2S, while **4** mainly Cp*H. Apparently formed transient [Cp*TiS] species probably gave rise to the serendipitously isolated cluster [{Cp*Ti(S)}$_4$] (**14**). Crystal structures of the all complexes were determined by X-ray diffraction analysis.

Introduction

Hydrogen sulfide is one of the most toxic gases;[1a] however, it is also considered to be, in addition to NO and CO, a gaseous hormone endogenously produced, e.g., by enzymatic decomposition of cysteine and homocysteine.[1b] This important signaling biological compound has been shown to play important roles, e.g., in central nervous and cardiovascular systems,[1c−e] and its physiological as well as pathophysiological effects are intensely studied. A long known, however, still intensely studied are sulfide complexes of biogenic transition metals (Fe, Co, Ni) that constitute a family of life-important enzymes,[2a−c] whereas the sulfides of some other transition metals (Mo, W, Ru, Os, Rh, Ir, Re) gained importance as catalysts for sulfur removal from petroleum via hydrodesulfurization.[2d−g] These applications stimulate the unceasing interest in investigation of the whole range of mononuclear as well as homo- and heteropolynuclear transition metal complexes containing sulfur ligands as bridging moieties.[3] Titanocene-sulfide chemistry, in spite of undoubted progress since the 1960s, remained relatively less developed,[3g] needing some basic knowledge on simple highly substituted titanocene (Ti^{IV} and Ti^{III})-hydrosulfide and sulfide complexes.

Titanocene-sulfur chemistry was opened by the discovery of titanacyclohexasulfane complex [Cp_2TiS_5] (Chart 1, I) by E. Samuel in 1966[4a] and independently by H. Köpf et al.[4b] The X-ray crystal structures of both of its two crystallographic modifications revealed the chair structure of its six-membered ring,[5] which appeared to be suitable for insertion[6a] and substitution reactions with organic reagents.[6b] Simple titanocene dihydrosulfide [$Cp_2Ti(SH)_2$]

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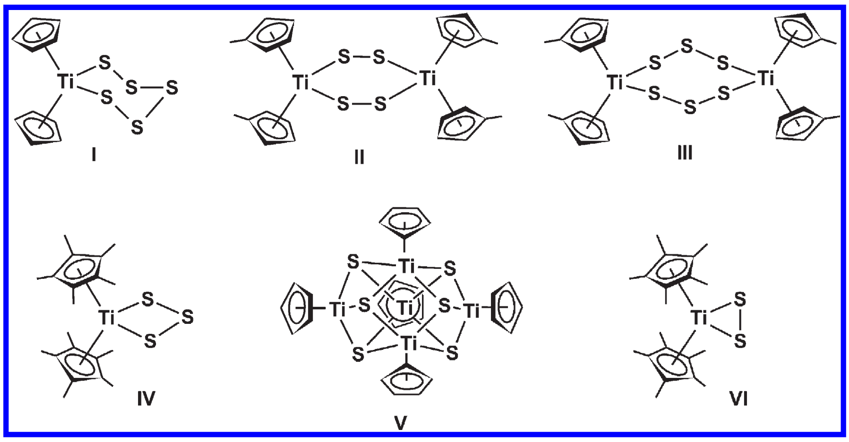
Chart 1



was prepared from $[Cp_2TiCl_2]$ and H_2S in the presence of NEt_3.[7a] Attempts to use it for preparation of titanacyclosulfanes with different sulfur content largely yielded $[Cp_2TiS_5]$;[7a] however, a better crystallizing $[(C_5H_4Me)_2Ti(SH)_2]$ has been suggested to dehydrogenate to give $[(C_5H_4Me)_2Ti(\mu\text{-}S_2)]_2$, forming 1,4-dititanacyclohexasulfane (Chart 1, II). This compound was actually obtained by partial desulfurization of $[(C_5H_4Me)_2TiS_5]$ with PBu_3.[7b] Similarly, the 1,5-dititanacyclooctasulfane complex (Chart 1, III) was obtained from I using PPh_3 as a desulfurization agent.[7c] Both mentioned titanocene dihydrosulfides were shown to have low-reactive S−H bonds; however, their sulfur atoms were able to coordinate $M(CO)_4$ (M = Mo, W) moieties, giving rise to $[Cp_2Ti(\mu\text{-}SH)_2M(CO)_4]$ complexes.[7d] Deprotonation of $[Cp_2Ti(SH)_2]$ appeared to be feasible with NaH[7e] or LiBu,[7f] affording the ionic complex $[Na_2\{CpTiS(\mu\text{-}S)\}_2\cdot 4THF]_2$. This was proved to be an intermediate in the formation of intermetallic clusters $[CpTi(\mu_3\text{-}S)_3M_3(\text{diolefin})_3]$ (M = Rh, Ir) from $[\{M(\mu\text{-}Cl)(\text{diolefin})\}_2]$ and $[Cp_2Ti(SH)_2]$ in the presence of LiBu.[7f] The deprotonation of $[Cp_2Ti(SH)_2]$ with leaving anionic ligand (A) from $[M(A)(\text{diolefin})_2]$ (M = Rh, Ir, A = acac, quinol) afforded trinuclear complexes $[Cp(A)Ti(\mu_3\text{-}S)_2\{M(\text{diolefin})_2\}_2]$.[7g] Deprotonation of the adduct of $[Cp_2Ti(SH)_2]$ with [Cp*RuCl] afforded a pseudocubane cluster composed of two [CpTiS] and two [Cp*RuS] moieties.[7h]

The sterically more congested $[Cp^*{}_2TiCl_2]$ was shown to be inert toward H_2S in the presence of NEt_3; however, when reacted with Li_2S_5 it afforded the first permethyltitanocene-sulfur complex containing a titanacyclobutasulfane ring (Chart 1, IV).[8] A convenient entry to the permethyltitanocene dihydrosulfide, $[Cp^*{}_2Ti(SH)_2]$ (**1**), was discovered by F. Bottomley et al.,[9a] who explored the titanium(II) complex $[Cp^*{}_2Ti(CO)_2]$ in a redox reaction with H_2S under condition that the latter was not in excess during the reaction. The overall stoichiometry of the reaction is given in eq 1.

$$Cp^*{}_2Ti(CO)_2 + 2H_2S \rightarrow Cp^*{}_2Ti(SH)_2 + H_2 + 2CO \qquad (1)$$

Analogous treatment of $[Cp_2Ti(CO)_2]$ with H_2S yielded mainly the cluster $[(CpTi)_5S_6]$ (Chart 1, V),[9b] similar to an extremely stable oxygen complex $[(CpTi)_6O_8]$ prepared analogously from $[Cp_2Ti(CO)_2]$ and water.[9c] The analogous zirconium dicarbonyls $[Cp_2Zr(CO)_2]$ and $[Cp^*{}_2Zr(CO)_2]$ afforded dehydrogenated dimeric sulfides, with the crystal structure determined for $[Cp_2Zr(\mu\text{-}S)]_2$ only.[9a] The tucked-in zirconocene complex $[ZrI\{\eta^5{:}\eta^1\text{-}C_5Me_4(CH_2)\}Cp^*]$ was reacted with H_2S to give $[Cp^*{}_2Zr(SH)I]$, which afforded the highly reactive $[Cp^*{}_2Zr{=}S]$ species.[9d] An elegant method exploring thermally stable Ti(II) titanocene complexes was also applied by R. A. Andersen et al. for synthesis of the sulfide $[Cp^*{}_2Ti({=}S)(\text{pyridine})]$ and the disulfide $[Cp^*{}_2Ti(S_2)]$ (Chart 1, VI) complexes from $[Cp^*{}_2Ti(\eta^2\text{-}C_2H_4)]$ and stoichiometric amounts of sulfur. Molecular hydrogen was shown to convert the sulfide complex to $[Cp^*{}_2TiH(SH)]$ and the disulfide VI to **1**, proving thus the hydrogenation step in the desulfurization reaction.[10]

Here, we report reactions of hydrogen sulfide with tucked-in titanocene complexes $[Ti(III)\{\eta^5{:}\eta^1\text{-}C_5Me_4(CH_2)\}(Cp^*)]$ (**2**)[11a] and $[Ti\{\eta^4{:}\eta^3\text{-}C_5Me_3(CH_2)_2\}(Cp^*)]$ (**3**)[12a] and their

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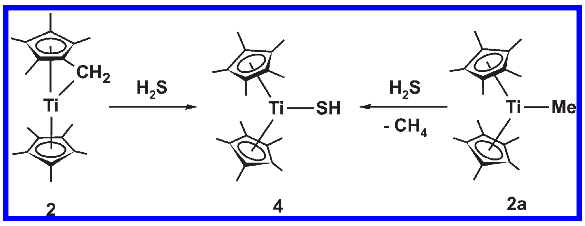
precursors [Cp*$_2$TiMe] (**2a**)[11b] and [Cp*$_2$Ti(η^2-Me$_3$SiC≡CSiMe$_3$)] (**3a**),[12b] respectively, yielding the corresponding titanocene hydrosulfide [Cp*$_2$TiSH] (**4**) and dihydrosulfide **1**, respectively. Hydrogen sulfide was also reacted with intramolecular σ- or π-Ti−C bonds in recently described complexes *ansa*-[Ti^{III}(η^1:η^5:η^5-C$_5$Me$_4$SiMe$_2$CHCH$_2$SiMe$_2$C$_5$Me$_4$)] (**5**) and *ansa*-[Ti^{II}(η^2:η^5:η^5-C$_5$Me$_4$SiMe$_2$CH=CHSiMe$_2$C$_5$Me$_4$)] (**6**)[13] in order to demonstrate the general applicability of this access to titanocene hydrosulfides. The S−H bonds of the obtained titanocene hydrosulfides **4** and **7** were able to react with the Ti−C bonds in **2** and **5**, affording titanocene sulfides Ti^{III}−S−Ti^{III}. A serendipitious isolation of the cluster [{Cp*Ti(μ_3-S)}$_4$] (**14**) justified preliminary investigations of thermolysis and photolysis of **1** and **4**.

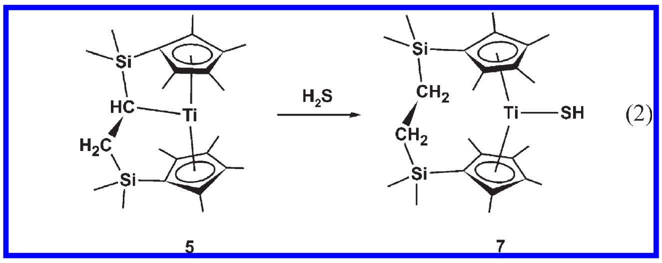
Results and Discussion

Protolytic reactions of H$_2$S with the singly tucked-in titanocene [Ti(III){η^5:η^1-C$_5$Me$_4$(CH$_2$)}(Cp*)] (**2**)[11a] and its precursor [Cp*$_2$TiMe] (**2a**)[11b] are shown in Scheme 1, and those with the doubly tucked-in [Ti{η^4:η^3-C$_5$Me$_3$(CH$_2$)$_2$}(Cp*)] (**3**)[12a] and its precursor [Cp*$_2$Ti(η^2-Me$_3$SiC≡CSiMe$_3$)] (**3a**)[12b] are shown in Scheme 2.

The reactions are visually observable since purple **2** or green **2a** affords the violet [Cp*$_2$TiSH] (**4**), and blue **3** or yellow **3a** give rise to the known[9a] red [Cp*$_2$Ti(SH)$_2$] (**1**). The use of the tucked-in compounds **2** and **3** is advantageous in the sense of "optimum atom economy", as no other products are formed in stoichiometric reactions, whereas methane and hydrogenated bis(trimethylsilyl)ethyne derivatives are formed from **2a** and **3a**, respectively. All the reactions proceed at ambient temperature, compound **2** reacting somewhat faster than compound **3**, and both their precursors **2a** and **3a** faster than the tucked-in compounds **2** and **3**, in accord with their energy content.[14] The protolytic reactions of H$_2$S also run smoothly with the intramolecular Ti−C bond of the paramagnetic *ansa*-titanocene compound *ansa*-[Ti(III){η^1:η^5:η^5-C$_5$Me$_4$SiMe$_2$CHCH$_2$SiMe$_2$C$_5$Me$_4$}] (**5**) having the *ansa*-chain tethered to titanium (eq 2) and with the back-bonding Ti−C bonds of the π-coordinated double bond of the *ansa*-chain in [Ti(II){η^2:η^5:η^5-C$_5$Me$_4$SiMe$_2$CH=CHSiMe$_2$C$_5$Me$_4$}] (**6**) (eq 3).

Scheme 1





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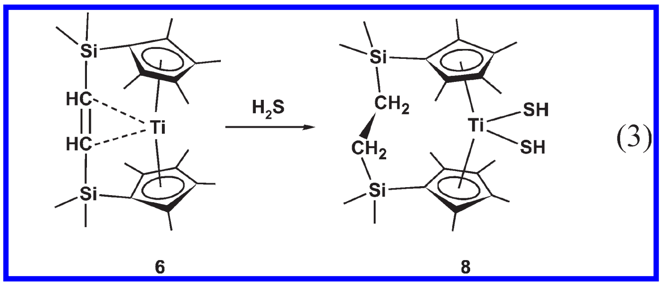
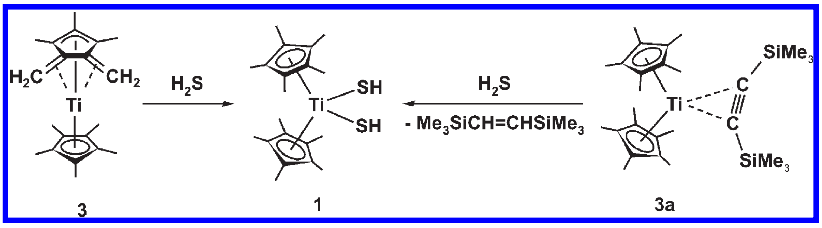


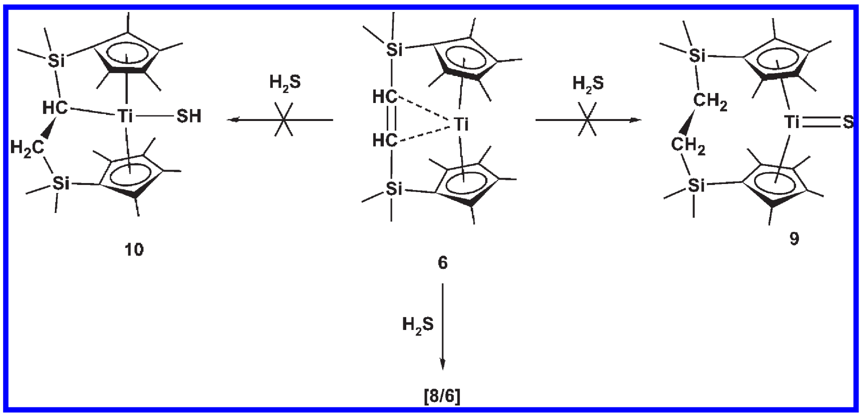
(3)

These reactions were also accompanied by color changes as brown **5** afforded violet *ansa*-[(η^5-CH$_2$Me$_2$SiC$_5$Me$_4$)$_2$Ti(SH)]

Scheme 2



Scheme 3



(**7**) and yellow **6** gave blood-red *ansa*-[(η^5-$CH_2Me_2SiC_5Me_4)_2Ti(SH)_2$] (**8**). Due to uncertainty in dosing exact amounts of gaseous H_2S, a 1.1−1.5-fold molar excess of H_2S over the stoichiometry was used in order to avoid the case of its insufficiency. Warming to 40 °C for up to 10 min was used to accomplish the reaction, which was then terminated by evaporation of all volatiles under vacuum. No byproducts that could arise, e.g., from protolysis of cyclopentadienyl ligands or other reactions of excessive H_2S, were detected throughout this work. The only experiment without the presence of excess H_2S was the reaction of **6** with approximately one molar equivalent of H_2S, which could yield, for example, products **9** and **10**, depicted in Scheme 3.

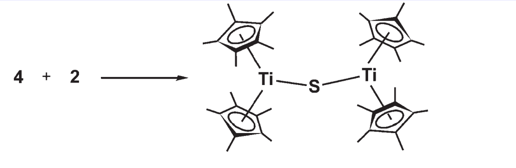
Surprisingly, the main ocher-red crystalline product denoted [**8**/**6**] contained **8** and **6**, one molecule each in its unit cell, showing that the formation of **8** is preferred to other possible products **9** and/or **10**.

Structures of all the compounds were identified by X-ray single-crystal diffraction analysis (see below), and their properties determined by current spectroscopic and analytical methods. Paramagnetic d^1 titanocene hydrosulfides **4** and **7** extend the class of [Cp^*_2TiL] compounds, binding an electronegative element in ligand L (L = halide, amide, and alkoxide). Accordingly, they show very similar EPR *g*-tensors and two electronic transitions in the visible spectral region assigned to $1a_1 \rightarrow 2a_1$ and $1a_1 \rightarrow b_1$ transitions.[15a] The electronic absorption band in the attainable near-infrared region (800−2000 nm) due to $1a_1 \rightarrow b_2$ transition, which indicates the extent of π-donation from electronegative element (N, O or F) to Ti(III),[15] was not observed for Ti−S bonds in **4** and **7**. This does not imply the absence of the π-donation at all since the corresponding transition could occur at wavelength above 2000 nm, where its observation could be difficult because of a large line-width of the electronic transition compared to by orders more intensive C−H valence vibration absorption bands. The red color of **1** and **8** comes from the absorption band at 490 nm, which is a Cp* → Ti or S → Ti LMCT transition.[16a] It is of interest that an analogous absorption band for [$Cp^*_2TiCl_2$] is observed at a much higher wavelength of 560 nm.[16b]

Both **4** and **7** displayed their EI-MS spectra with high-abundant molecular ions; however, their fragmentation depended on the titanocene moiety. Compound **4** gave fragments $[M - HS]^+$ and $[M - H_2S]^+$ as virtually equal intensity base peaks, while the $[M - Cp^*]^+$ fragment was much less abundant. Compound **7** showed the abundant fragment $[M - H_2S - 2H_2]^+$ and $[HSiMe_2]^+$ as a base peak. The extensive loss of hydrogen that is typical for fragmentation patterns of *ansa*-[(η^5-$CH_2Me_2SiC_5Me_4)_2$-Ti] derivatives[13] accompanies the H_2S elimination to give the former ion. On the other hand, diamagnetic compounds **1** and **8** showed very low-abundant molecular ions and their $[M - 2\,H]^+$ fragments and abundant $[M - HS]^+$ and $M - H_2S]^+$ ions. Compound **1** showed also abundant $[M - Cp^*]^+$ and $[M - Cp^* - H_2S]^+$ ions and $[HCp^*]^+$ base peak. Compound **8** further displayed the $[M - 2\,SH - 5\,H]^+$ ion and $[HSiMe_2]^+$ as a base peak. The EI-MS spectra of composed crystal [**8**/**6**] displayed mostly the fragmentation of **8**, whereas the base peak of **6** ($M^{\cdot+}$, *m*/*z* 430)[13] was negligible.

The ν(S−H) vibration of very low intensity was well discernible in a narrow range, 2590−2607 cm^{-1}, the monohydrosulfides absorbing at higher wavenumbers than the dihydrosulfides. For comparison, ν(S−H) for CH_3SH absorbs at 2550 cm^{-1},[17a] and H_2S in Xe matrix at 17 K in the range 2580−2630 cm^{-1}.[17b] The discrepancy between the reported[9a] value of 2580 cm^{-1} and the present 2600 cm^{-1} for **1** can be due to different medium (Nujol mull/KBr pellet) or different crystal modification (see below). The reported δ_H 2.73 ppm for S−H of **1** agrees with the present δ_H 2.85 ppm provided the solvent effect ($CDCl_3/C_6D_6$) is considered.

Formation of Titanocene Sulfides. The titanocene hydrosulfide **4** and *ansa*-titanocene hydrosulfide **7** maintain the protolytic capability of their S−H moiety, as demonstrated by reactions of **4** with **2** (eq 4) and **7** with **5** (eq 5).



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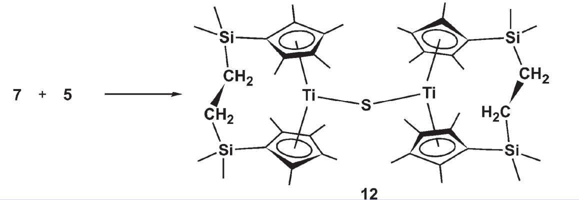
(4)



12

(5)

Both reactions afforded green paramagnetic sulfides [$(Cp^*_2Ti)_2S$] (**11**) and *ansa*-[{(η^5-$CH_2SiMe_2C_5Me_4)_2Ti\}_2S$] (**12**) in virtually quantitative yields. Heating to 60 °C for 30 min was necessary to complete the reaction since reactivity of the hydrosulfide group in **4** and **7** was decreased compared to H_2S due to its lower acidity and sterical congestion. Compounds **11** and **12** could also be obtained by applying a half molar equivalent of H_2S to **2** or **2a** and **5**, respectively. Their formation was indicated by a transient green coloration after about half portions of H_2S were added to **2** or **5** in the synthesis of **4** and **7**, respectively. Reactions between a titanocene hydrosulfide and a titanocene alkyl can be used for preparation of sulfides with different metallocene moieties. This was exemplified by reacting **7** with **2a**, which resulted in the

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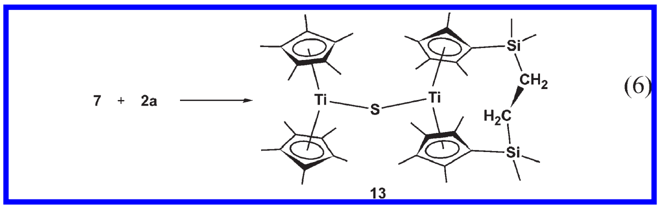
formation of [*ansa*-{(η^5-CH$_2$SiMe$_2$C$_5$Me$_4$)$_2$Ti}S(TiCp*$_2$)] (**13**) (eq 6).



(6)

13

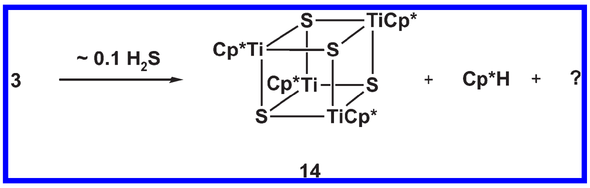
Compounds **11**−**13** are paramagnetic green crystalline solids forming bright green toluene solutions. Their EI-MS spectra showed low-abundant molecular ions for **11** and **13**, whereas for **12** the M$^+$ ion was not observed at all. The reason lies in the high temperatures of evaporation, which facilitate dissociation of the Ti−S bond upon electron impact. Accordingly, the base peaks [Cp*$_2$Ti]$^+$ for **11** and [(CH$_2$Me$_2$SiC$_5$Me$_4$)$_2$Ti]$^+$ for **13** were observed, and for **12** the [HSiMe$_2$]$^+$ base peak was accompanied with a highly abundant retro-fragment [**5**]$^+$ (m/z 431). The IR spectra gave evidence for the presence of Cp* and (CH$_2$Me$_2$SiC$_5$Me$_4$)$_2$ ligands only, and the ^{1}H NMR spectrum of **11** displayed a very broad line typical of paramagnetic shift and broadening.

The other spectroscopic properties were discernibly changing in the order **11** → **13** → **12**, reflecting the different influence of the [Cp*$_2$Ti] and *ansa*-[(η^5-CH$_2$SiMe$_2$C$_5$Me$_4$)$_2$-Ti] moieties. The green color of the compounds is due to an absorption band that moves slightly its position from 635 nm for **11** to 655 nm for **12**. The two Ti(III) d^1 electrons form an electronic triplet state of rhombic symmetry, as evidenced by EPR spectra of their frozen toluene solutions (see Supporting Information). The g-tensor and zero-field splitting parameters D and E could be determined[18] for only **11** (g_z = 1.980, g_y = 1.967, g_x = 1.968; D = 0.01678 cm^{-1} and E = 0.00163 cm^{-1}), as Ti(III) impurities in **12** and **13** obscured the central part of their ESR spectra. For **11**, a simplified relationship (eq 7)[19] between experimental dipole−dipole zero-field parameter D_d and

$$D_d = \frac{-\beta^2}{3R^3}\left[2g_z^2 + \frac{g_x^2 + g_y^2}{2}\right] \tag{7}$$

the Ti−Ti distance R afforded R = 4.66 Å, shorter by 0.05 Å than the crystallographic distance. The outer features of the EPR triplet-state spectra (ΔH_{zz}), which mainly determine the magnitude of D_d, were slightly increasing in the order **11** → **13** → **12** (364−376 G), whereas the crystallographic Ti−Ti distances were slightly increasing from an average 4.7117(7) Å for **11** to 4.7476(4) Å for **13** and to 4.7701(4) Å for **12** (see below). This disagrees with the inversely proportional relationship between D_d and R of eq 8; however, differences in the Ti−Ti distance determined by single-crystal X-ray diffraction and by the EPR method in toluene glass as large as 0.05 Å are quite common due to the different molecular geometry in the glass and in the single crystal.[20] It is of interest that analogous [(Cp′$_2$Ti)$_2$O] compounds are known only for the less bulky cyclopentadienyl ligands, e.g., Cp′ = 1,3-C$_5$Me$_3{}^t$Bu$_2$ with linear Ti−O−Ti linkage[21] or Cp′ = Cp with the Ti−O−Ti angle of 170.9(4)°.[22] The EPR spectrum of [(Cp$_2$Ti)$_2$O] in toluene glass at 2 K afforded the axially symmetric triplet-state spectrum (D = 0.0249 cm^{-1}, E = 0) indicative of the linear Ti−O−Ti arrangement, however.[23] In contrast, the rhombic symmetry of the EPR parameters for **11** proves that the molecule retains the bent structure as found by X-ray crystallography (see below) in the toluene glass. The other related compound, the telluride [(Cp*$_2$Ti)$_2$Te] with the Ti−Te distance of 2.70 Å and Ti−Te−Ti angle of 168.62(8)°, surprisingly exerted only a weak magnetic coupling between the Ti(III) atoms, not displaying the EPR spectra of the electronic triplet state.[24]

Scheme 4



14

Thermolytic and Photolytic Decomposition of 1 and 4. All the above hydrosulfides appeared to be thermally unstable at elevated temperature and photosensitive to sunlight. Heating of an m-xylene solution of **1** in the dark to 140 °C for 2 h turned the solution greenish-brown, and pentamethylcyclopentadiene (C$_5$Me$_5$H (Cp*H)), fulvene (C$_5$Me$_4$CH$_2$), and pentamethylcyclopentadienylthiol (C$_5$Me$_5$SH) were detected in volatiles by GC-MS in the molar ratio ca. 12:1.7:1. The ^{1}H NMR spectra of the thermolytic residue displayed a number of resonances of apparently C$_5$Me$_5$ ligands, not allowing any conclusion on the thermolytic products. On the other hand, the solution of **4** in m-xylene remained clear violet until 150 °C and turned gray at 220 °C for 5 h with elimination of mainly Cp*H and much less Cp*H dimers. The EI-MS spectra of the residue after evaporation of volatiles revealed in addition to the molecular ion of **4** (m/z 351) a pattern of peaks m/z 571−575 and some other high-mass low-abundant peaks varying with the temperature of evaporation. Similar spectra were also obtained from the residue of **1** after 140 °C, not giving any lead to a possible cluster composition.

Exposure of toluene solutions of **1** and **4** to sunlight resulted in their color change to brown within 1−2 h. The photolysis of **1** in C$_6$D$_6$ was followed in a sealed NMR tube: compound **1** disappeared after 1 h, and Cp*H and H$_2$S were liberated in approximately equimolar amounts as identified from ^{1}H and ^{13}C NMR spectra. Unfortunately, a tangle of ^{1}H and ^{13}C NMR resonances attributable to different C$_5$Me$_5$ ligands did not allow determining any titanium-containing product. The GC-MS analysis of volatiles from photolysis of **4** revealed the presence of far overwhelming Cp*H. This indicates that a highly coordinatively unsaturated [Cp*TiS] species is formed (eq 8), which can stabilize by

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Table 1. Important Common Bond Lengths (Å) and Valence and Dihedral Angles (deg) for Hydrosulfides 4, 1, 7, 8, and [8/6]

	4	1	7	8	[8/6]
			Bond Lengths (Å)		
Ti(1)−Cg(1)[a]	2.0618(9)	2.1323(7)	2.0667(7)	2.1445(7)	2.1424(11)
Ti(1)−Cg(2)[a]	2.0629(8)	2.1359(7)	2.0634(7)	2.1384(7)	2.1402(11)
Ti(1)−S(1)	2.3957(6)	2.4128(5)	2.3958(5)	2.3984(5)	2.4127(8)
Ti(1)−S(2)		2.4129(4)		2.3991(5)	2.3910(7)
S(1)−H(1)	1.210	1.052	1.015	1.167[g]	1.175
S(2)−H(2)		1.025		0.928	1.078
			Valence Angles (deg)		
Cg(1)−Ti(1)−Cg(2)[a]	143.76(4)	137.71(3)	145.12(3)	140.37(3)	140.47(5)
Cg(1)−Ti(1)−S(1)	109.32(3)	101.77(2)	105.45(2)	102.85(3)	100.48(4)
Cg(2)−Ti(1)−S(1)	106.91(3)	106.18(2)	109.18(3)	102.22(3)	103.73(4)
Cg(1)−Ti(1)−S(2)		102.85(2)		102.09(3)	105.80(4)
Cg(2)−Ti(1)−S(2)		105.21(2)		105.73(3)	103.42(4)
S(1)−Ti−S(2)		95.699(17)		95.035(19)	93.48(3)
Ti(1)−S(1)−H(1)	104.0	101.6	107.7	112.7[h]	101.9
Ti(1)−S(2)−H(2)		103.1		101.6	103.8
			Dihedral Angles (deg)		
φ[b]	36.76(8)	44.16(4)	36.86(5)	46.49(4)	45.01(8)
$\tau 1$[c]	4		−1		
$\tau 2$[d]	−173		175		
$\omega 1$[e]		80.96(3)		69.31(1)[i]	42.60(3)
$\omega 2$[f]		78.09(3)		73.15(1)	74.28(2)

[a] Cg(1) and Cg(2) are centroids of the C(1−5) and C(11−15) cyclopentadienyl rings, respectively. [b] Dihedral angle between the least-squares planes of cyclopentadienyl rings. [c] Torsion angle Cg(1)−Ti(1)−S(1)−H(1). [d] Torsion angle Cg(2)−Ti(1)−S(1)−H(1). [e] Dihedral angle between the plane defined by Ti(1), S(1), and S(2) and the plane defined by Ti(1), S(1), and H(1). [f] Dihedral angle between the plane defined by Ti(1), S(1), and S(2) and the plane defined by Ti(1), S(2), and H(2). [g] Atom H(1) is resolved in two orthogonal positions, H(11) and H(12). The distance S(1)−H(11) is given in the table; Si(1)−H(12) is 1.176 Å. [h] The value for Ti(1)−S(1)−H(11); Ti(1)−S(1)−H(12) is 100.8°. [i] The dihedral angle involving the Ti(1)−S(1)−H(11) plane; the dihedral angle involving the Ti(1)−S(1)−H(12) plane is 53.80(1)°.

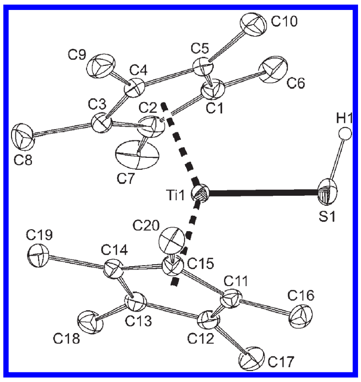

Figure 1. PLATON drawing of compound **4** at the 30% probability level with atom-labeling scheme. The hydrogens on carbon atoms are omitted for clarity.

constituting various clusters using μ-S or μ_3-S bridging atoms.

$$\mathrm{Cp^*_2TiSH} \xrightarrow{\nu} \mathrm{Cp^*H} + [\mathrm{Cp^*TiS}] \qquad (8)$$

Compound **1** affords probably the same [Cp*TiS] species, however, in a more complex process since the established elimination of Cp*H and H_2S would result in a proton-deficient species. Nevertheless, the formation of [Cp*TiS] seems to be justified by a serendipitous finding of several crystals of the tetramer $[\mathrm{Cp^*Ti}(\mu_3\text{-S})]_4$ (**14**), which grew up from a hexane solution of **3** mixed, accidentally, with only about one tenth of a molar equivalent of H_2S after 16 months standing in a laboratory shelf (Scheme 4).

The structure of **14** was determined by single-crystal X-ray diffraction analysis (see below), and the composition was corroborated by EI-MS spectra revealing the molecular ion (*m*/*z* 860) and plausible fragment ions corresponding to elimination of Cp*, 2 Cp*H, 3 Cp*H, and M^{2+} ion (*m*/*z* 430). Diamagnetism of **14** and equivalency of all Cp* ligands was established by ^{1}H and ^{13}C NMR spectra exhibiting one single resonance for protons and two resonances of carbon atoms. The mechanism of formation of **14** remains unclear since its NMR signals were not observed in the above thermolytic as well as photolytic products of **1**. We suggest that **14** was formed from **1** (arisen from **3**, Scheme 1) under diffuse light on a laboratory shelf. The photolytically liberated H_2S was apparently consumed with excess **3** to give **1**, which was photolyzed until its complete disappearance with elimination of Cp*H. This was proved by GC-MS of volatiles from the mother liquor. The structurally similar cluster $[\{(\eta^5\text{-}C_5H_4Me)\mathrm{Ti}(\mu_3\text{-S})\}_4]$ was prepared by the reaction of $[(C_5H_4Me)\mathrm{TiCl_2(THF)_2}]$ with an equimolar amount of $(Me_3Si)_2S$, eliminating Me_3SiCl. The cluster formation was proposed to proceed via the dimer $[(C_5H_4Me)\mathrm{TiS}]_2$ solvated with THF.[25] Here, the formation of crystalline **14** in hexane, in which it is practically insoluble, was apparently conditioned by a very slow photolysis of **1**, generating a very low concentration of the [Cp*TiS] species. Attempts to reproduce the preparation of **14** in sunlight or by heating to thermolytic temperature of **1** (140 °C) were unsuccessful.

Crystal Structures. All the prepared crystalline compounds were characterized by single-crystal X-ray diffraction methods. Important geometric parameters for titanocene hydrosulfides **1**, **4**, **7**, and **8** and composed crystal [**8**/**6**] are listed in Table 1. The monohydrosulfides **4** (Figure 1)

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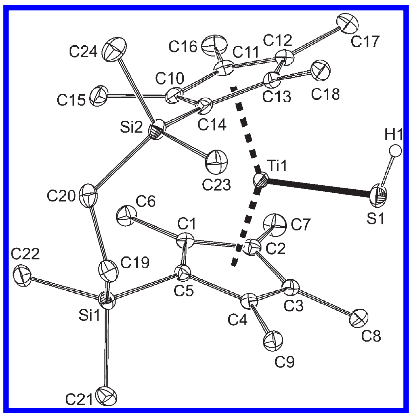

Figure 2. PLATON drawing of compound **7** at the 30% probability level with atom-labeling scheme. The hydrogens on carbon atoms are omitted for clarity.

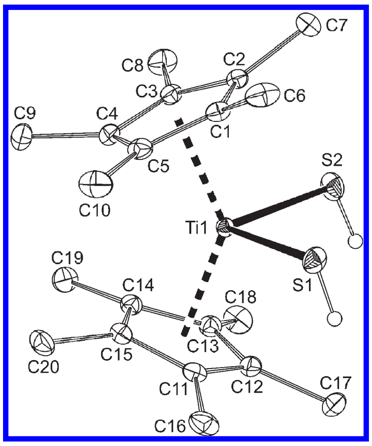

Figure 3. PLATON drawing of compound **1** at the 30% probability level with atom-labeling scheme. The hydrogens on carbon atoms are omitted for clarity.

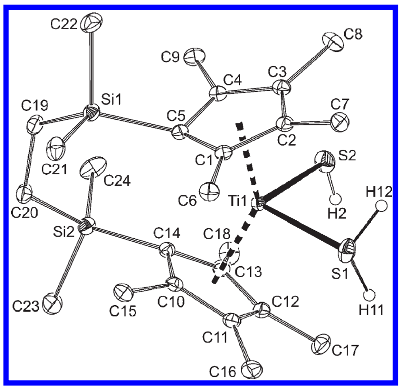

Figure 4. PLATON drawing of compound **8** at the 30% probability level with atom-labeling scheme. The hydrogen H1 is disordered over two positions (H11, H12) with equal occupancy factors. The hydrogens on carbon atoms are omitted for clarity.

and **7** (Figure 2) with trigonally coordinated titanium(III) show considerably stronger bonding of cyclopentadienyl ligands than the tetrahedrally coordinated titanium(IV) dihydrosulfides **1** (Figure 3) and **8** (Figures 4 and 5), as indicated by about 0.06 Å shorter Ti−Cg bonds.

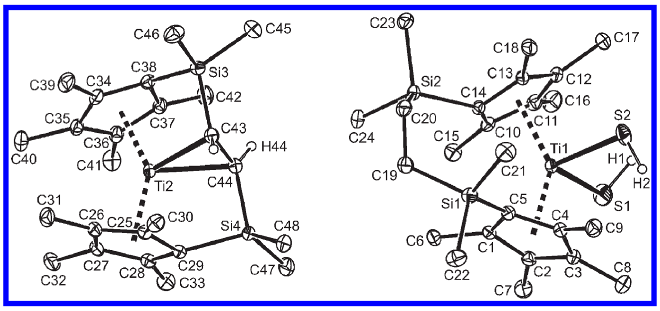

Figure 5. PLATON drawing of compounds **6** and **8** in [**8**/**6**] at the 30% probability level with atom-labeling scheme. The hydrogens on carbon atoms except those on C43 and C44 are omitted for clarity.

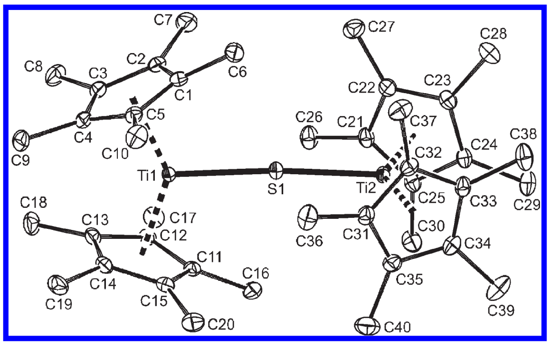

Figure 6. PLATON drawing of compound **11** at the 30% probability level with atom-labeling scheme. Hydrogens are omitted for clarity.

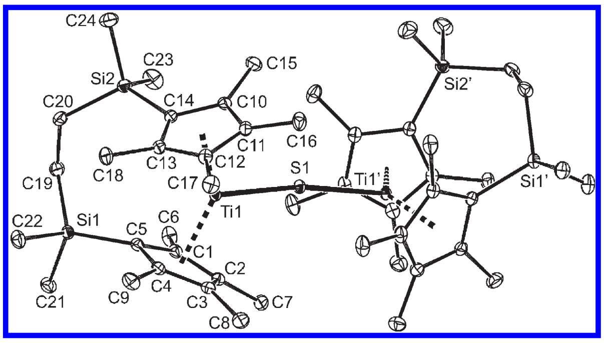

Figure 7. PLATON drawing of compound **12** at the 30% probability level with atom-labeling scheme. Hydrogens are omitted for clarity.

A discernibly shorter Ti−S bond is found for **4** compared to **1**; however, for the *ansa*-compounds **7** and **8** the difference is close to a three-times esd only. The hydrogen atoms in S−H bonds were always found on difference Fourier maps; however, their position was not refined since a large electron density from the sulfur atom in the vicinity of hydrogen resulted in an unrealistic short distance (close to 1.0 Å) (Table 1). In spite of this limitation it was established that the Ti−S−H angles of slightly above 100° are orientated close to the Cg(1)−Ti−Cg(2) plane (see values of τ for **4** and **7**) and ω for **1**, **8**, and [**8**/**6**] (Table 1). This orientation of the Ti−S−H moiety causes a decrease of the Ti−S bond from the axis of the Cg(1)−Ti−Cg(2) angle to gain a somewhat larger space for the S−H bond. For **1**, the variation in spatial orientation of S−H bonds leads to an extensive polymorphism. In addition to the monoclinic crystal of **1** described in Table 1, an orthorhombic crystal (**1a**) described in detail in the Supporting Information was also obtained by crystallization

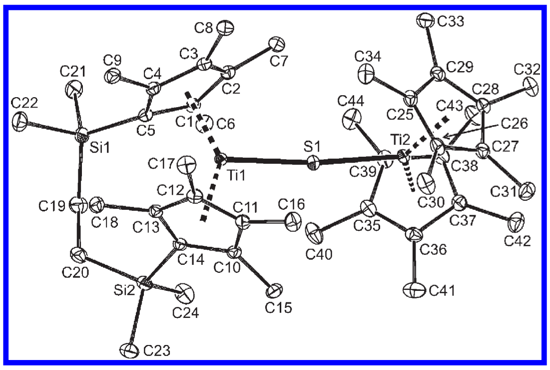

Figure 8. PLATON drawing of compound **13** at the 30% probability level with atom-labeling scheme. Hydrogens are omitted for clarity.

Table 2. Important Common Bond Lengths (Å) and Valence and Dihedral Angles (deg) for Sulfides 11−13

	11[a]	**12**[b]	**13**
	Bond Lengths (Å)		
Ti(1)−Cg(1)[c]	2.0944(13) 2.0990(15)	2.1145(7)	2.1015(7)
Ti(1)−Cg(2)[c]	2.0990(13) 2.0994(14)	2.0937(7)	2.0860(8)
Ti(2)−Cg(3)[c]	2.1056(13) 2.1016(13)		2.1096(7)
Ti(2)−Cg(4)[c]	2.1045(14) 2.1077(13)		2.1062(8)
Ti(1)−S(1)	2.3604(8) 2.3589(8)	2.3942(3)	2.3772(4)
Ti(2)−S(1)	2.3524(8) 2.3634(8)		2.3806(4)
Ti(1)−Ti(2)	4.7069(7) 4.7165(7)	4.7701(4)	4.7476(4)
	Valence Angles (deg)		
Cg(1)−Ti(1)−Cg(2)[c]	138.87(5) 139.16(6)	138.83(3)	139.06(3)
Cg(3)−Ti(2)−Cg(4)[c]	139.26(5) 138.76(5)		137.98(3)
Cg(1)−Ti(1)−S(1)	110.87(4) 110.58(5)	112.25(3)	111.49(3)
Cg(2)−Ti(1)−S(1)	110.26(4) 110.26(4)	108.77(2)	109.34(2)
Cg(3)−Ti(2)−S(1)	109.91(5) 110.73(4)		110.75(3)
Cg(4)−Ti(2)−S(1)	110.78(4) 110.50(4)		111.27(3)
Ti(1)−S(1)−Ti(2)	174.37(4) 174.33(4)	169.97(3)	172.479(19)
	Dihedral Angles (deg)		
$\varphi 1$[d]	39.69(11) 39.85(12)	41.10(7)	40.96(8)
$\varphi 2$[e]	39.91(12) 39.72(10)		40.40(8)
ω[f]	85.99(12) 87.72(11)	88.27(8)	89.91(9)

[a] Data for two nonequivalent molecules in the unit cell: molecule 1 and molecule 2. [b] Symmetry operation used to generate equivalent positions: $-x + 1, y, -z + 1/2$. [c] Cg(1) and Cg(2) are centroids of the C(1−5) and C(11−15) cyclopentadienyl rings, respectively, and Cg(3) and Cg(4) are centroids of the C(21−25) and C(31−35) cyclopentadienyl rings, respectively. [d] Dihedral angle between the least-squares planes of the C(1−5) and C(11−15) cyclopentadienyl rings. [e] Dihedral angle between the least-squares planes of the C(21−25) and C(31−35) cyclopentadienyl rings. [f] Dihedral angle between the plane defined by Cg(1), Ti(1), and Cg(2) and the plane Cg(3), Ti(2), and Cg(4).

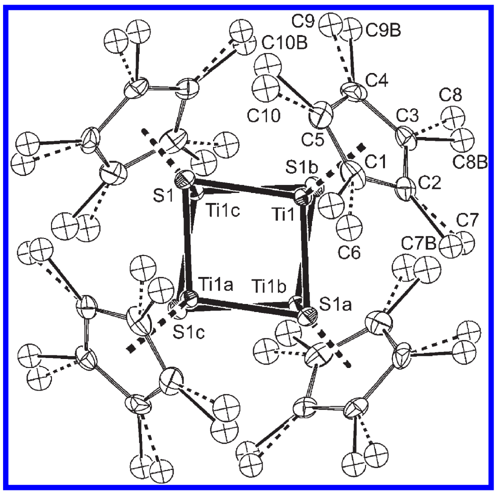

Figure 9. PLATON drawing of compound **14** at the 30% probability level with atom-labeling scheme. The carbon atoms of methyl moieties are disordered into two positions. Hydrogens are omitted for clarity.

from the same solvent (hexane), probably at somewhat different temperature. The unit cell of **1a** contained the two independent molecules, one with the S−H bonds on one side of the Ti, S(1), S(2) plane and the other with the S−H bonds on both sides. Nonetheless, Bottomley et al.[9a] described another, tetragonal structure of **1** ($I4_1/a$, $a,b = 31.140(6)$ Å, $c = 8.350(1)$ Å, $Z = 16$, $V = 8097(2)$ Å^3) with the hydrogen atoms on opposite sides of the Ti, S(1), S(2) plane and ω angles about 65°, and mentioned yet another monoclinic structure (Cm, $a = 8.202(1)$ Å, $b = 14.941(1)$ Å, $c = 9.255(1)$ Å, $\beta = 116.29(1)°$, and $Z = 2$). Different positions of the S−H bonds were also found for **8** and [**8**/**6**]. In **8** the S(1)−H(1) bond was disordered on both sides of the plane as H(11) and H(12) (Figure 4), witnessing close probability of occurrence of any of the two orientations. For [**8**/**6**] the S−H bonds in **8** were found on opposite sides of the Ti, S(1), S(2) plane, and the molecule of **6** did not differ remarkably from that recently described (Figure 5).[13]

The sulfides **11**−**13** (Figures 6−8) contain trigonally coordinated Ti(III) atoms bonded to the sulfur atom in near-linear arrangements.

The geometric parameters gathered in Table 2 show that the structures of **11**−**13** differ negligibly. The Ti−Cg distances for **11** and **12** are discernibly longer compared to those for titanocene(TiIII) hydrosulfides **4** and **7**, and the Cg−Ti−Cg angles are more acute, however, very similar for all **11**−**13** compounds. The Ti−S bonds are becoming slightly longer and the Ti−S−Ti angles marginally less obtuse in the order **11** < **13** < **12**. In the same order the Ti−Ti distance as well as the sum of Ti−S distances are increasing. The conformation of the *ansa*-[(η^5-$CH_2SiMe_2C_5Me_4)_2Ti$] species in a number of complexes has been recently discussed.[13] The staggered conformation of the $Cp^*{}_2Ti$ mioety and substantial deviation of the Cp* methyl groups from the ring least-squares plane are common here and in all known structures of $Cp^*{}_2Ti$ complexes.[15]

The cluster **14** is formed from four equivalent [Cp*Ti(μ_3-S)] moieties forming a distorted cubane structure composed of Ti and S atoms (Figure 9). The Cp* ligands are rotationally disordered, which resulted in larger thermal parameters of its ring carbon atoms and resolution of the methyl carbon atoms into two positions. The least-squares plane of the cyclopentadienyl ring C(1−5) is nearly parallel with the plane of three sulfur atoms (S(1), S(1a), and S(1b)) attached to the common Ti(1) atom (dihedral angle of 1.22(20)°). The equivalent positions of the $(C_5Me_5)Ti(1)S(1)$ moiety are formed by symmetry operations $-x + 1$, $-y$, z (atoms denoted 1a), $-x + 1/2$, $y + 1/2$, $-z + 1/2$ (atoms denoted 1b), and $x - 1/2$, $-y + 1/2$, $-z + 1/2$ (atoms denoted 1c). The bond length Ti(1)−S(1) is 2.3748(9) Å, Ti(1)−S(1a) and Ti(1a)−S(1) are identical (2.3811(9) Å), and the same is true for Ti(1)−S(1b) and Ti(1c)−S(1) bonds (2.3999(9) Å). The valence angles S−Ti−S are 99.73(3)−101.98(3)° and Ti−S−Ti are 77.04(3)−78.47(3)°. The Ti−Ti distances in the cluster molecule are 2.9776(8)−3.0081(9) Å. These geometry parameters do not differ from those for $[\eta^5\text{-}C_5H_4Me)Ti(\mu_3\text{-}S)]_4$ more than by 3-times esd. This allows us to adopt conclusions of T. B. Rauchfuss and A. L. Rheingold et al.[25] for bonding in **14**: four titanium(III)-based electrons are delocalized in the cluster with participation of electron-deficient Ti−Ti bonds.

Conclusions

The reaction of hydrogen sulfide with low-valent permethyltitanocene derivatives affords a clean and convenient access to corresponding titanocene hydrosulfides **1**, **4**, **7**, and **8**, whose further chemistry can be a subject of interest. The S−H bonds of **4** and **7** were shown to be highly reactive in protolysis of Ti−C bonds, affording dititanocene sulfides **11**−**13**, and this gives a good prospect for their reactivity in hydrothiolation of alkynes. The mode of terminal acetylene insertion will be of relevance to the recently reported insertion of the HC≡CR triple bond into the Zr−SR′ bond in a catalytic cycle effecting the catalytic hydrothiolation of terminal alkynes, yielding Markovnikov products.[26] Although the sulfur atoms in the S−H bonds are more sterically hindered and weaker electron donors than those in nonsubstituted titanocene hydrosulfides, they should be attempted for the synthesis of titanium−late transition metal complexes following the methodology known for $[Cp_2Ti(SH)_2]$.[7d,f−h] A decreased electropositivity of titanium in the Cp*Ti moiety could be used to tune the catalytic properties of such complexes.[27] Similarly, titanocene thiolates can be used to coordinate late transition metal complexes;[28] however, the steric congestion in permethyltitanocene thiolates would require using half-sandwich titanocene thiolates instead. An easy photodecomposition of **1** and **4** is being explored in the search for new cluster complexes containing [Cp*TiS] building units.

Experimental Section

General Considerations. Reactions with Ti(III) and Ti(II) complexes with H_2S were performed with exclusion of direct sunlight in sealed glass devices equipped with breakable seals on a vacuum line. This was operated by metal valves and finally driven by active charcoal at −196 °C to give a pressure of about 2×10^{-4} Torr. ^1H (300 MHz), ^{13}C (75 MHz), and ^{29}Si (59.6 MHz) NMR spectra were recorded on a Varian Mercury 300 spectrometer in C_6D_6 solutions at 25 °C. Chemical shifts (δ/ppm) are given relative to solvent signals or tetramethylsilane. EI-MS spectra were measured on a VG-7070E mass spectrometer at 70 eV. The crystalline samples in sealed capillaries were opened and inserted into a direct inlet probe under argon. IR spectra of samples in KBr pellets were measured in an air-protecting cuvette on a Nicolet Avatar FT IR spectrometer in the range 400−4000 cm^{-1}. KBr pellets were prepared in a Labmaster 130 (mBraun) glovebox under purified nitrogen. X-Band ESR spectra were recorded on an ERS-220 spectrometer (Center for Production of Scientific Instruments, Academy of Sciences of GDR, Berlin, Germany) operated by a CU-1 unit (Magnettech, Berlin, Germany). g-Values were determined by using an Mn^{2+} standard at $g = 1.9860$ ($M_I = -1/2$ line). A variable-temperature STT-3 unit was used for measurements in the range −140 to +25 °C. UV−near-IR spectra in the range 300−2000 nm were measured on a Varian Cary 17D spectrometer in sealed quartz cells (Hellma). GC-MS measurements were performed on a Thermo Focus DSQ using a Thermo TR-5MS (15 m × 0.25 mm i.d. × 0.25 μm) capillary column. Elemental analyses were carried out on a FLASH EA1112 CHN/O automatic elemental analyzer (Thermo Scientific). Melting points were measured on a Koffler block in sealed glass capillaries under nitrogen and are uncorrected. These melting points should be taken with caution since the observed sample darkening for **1** and **4** can indicate the photoinduced decomposition on the Koffler block. Photolysis experiments were performed in summer with sunlight that passed through 2 × 2.5 mm glass windows and 2 mm Pyrex glass of the ampule.

Chemicals. The solvents hexane, toluene, and benzene-d_6 were dried by refluxing over $LiAlH_4$ and stored as solutions of dimeric titanocene $[(\mu\text{-}\eta^5\text{:}\eta^5\text{-}C_5H_4C_5H_4)(\mu\text{-}H)_2\{Ti(\eta^5\text{-}C_5H_5)\}_2]$.[29] Compound **2** and $[Cp^*{}_2TiMe]$ (**2a**) were obtained from $[Cp^*{}_2TiCl_2]$ (Aldrich) as described elsewhere.[11c] Compound **3** was prepared from $[Cp^*{}_2Ti(\eta^2\text{-}Me_3SiC{\equiv}CSiMe_3)]$ (**3a**) as reported.[12b] The titanocene dichloride *ansa*-$[TiCl_2(\eta^5\text{-}CH_2SiMe_2C_5Me_4)_2]$[30] was used for obtaining *ansa*-$[Ti(III)\{\eta^1\text{:}\eta^5\text{:}\eta^5\text{-}C_5Me_4SiMe_2CHCH_2SiMe_2\text{-}C_5Me_4\}]$ (**5**) and $[Ti(II)\{\eta^2\text{:}\eta^5\text{:}\eta^5\text{-}C_5Me_4SiMe_2CH{=}CHSiMe_2\text{-}C_5Me_4\}]$ (**6**) as described recently.[13] H_2S was obtained by hydrolysis of aluminum sulfide (Al_2S_3) (granular, <4 mesh, Aldrich) as follows. Granular Al_2S_3 (3.0 g, 20 mmol) was degassed in an ampule (2 L) on a vacuum line, and degassed water (0.18 mL, 10.0 mmol) was condensed in under cooling with liquid nitrogen. After sealing off, the aluminum sulfide was repeatedly spread over the ampule and poured into the bottom, where also all volatiles were condensed. After 2 days the gaseous H_2S was transferred into a storage ampule (5 L) on a vacuum line by condensing at −196 °C. The reactor line was equipped with a mercury manometer, allowing dosing of requested amounts of H_2S to the reagent solution (Hg was exposed to H_2S only for the time to restore the pressure of up to 30 Torr).

Preparation of $[Cp^*{}_2TiSH]$ (4). Gaseous H_2S (total amount of 1.2 mmol) was slowly added to a solution of **2** (0.25 g, 0.8 mmol) in 5 mL of toluene under stirring. The purple color of **2** turned intense green when about one-half of the H_2S was consumed; however, addition of the whole amount of H_2S by condensing at liquid nitrogen temperature followed by warming to room temperature resulted in obtaining a clear violet solution. The unreacted H_2S and all volatiles were immediately evaporated under vacuum to a trap cooled with liquid nitrogen, and the violet residue was dissolved in ca. 5 mL of hexane. Crystallization from a concentrated solution at −28 °C yielded violet crystalline aggregates. Yield: 0.23 g (83%). Slow recrystallization

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from hexane afforded crystals suitable for X-ray diffraction analysis.

Data for **4** are as follows. Mp: violet crystals turned brown at 168 °C, melting at 205−210 °C. EI-MS (140 °C): *m*/*z* (relative abundance) 352 (30), 351 (M$^+$; 72), 350 (12), 335 ([M − MeH]$^+$; 6), 319 (26), 318 ([M − SH]$^+$; 100), 317 ([M − SH$_2$]$^+$; 95), 316 (30), 315 (38), 313 (14), 217 (19), 216 (18), 215 ([M − Cp*H]$^+$; 32), 214 (24), 213 (26), 212 ([M − Cp*H − 3 H]$^+$; 30), 211 (15), 210 (15), 209 (15), 183 (12), 182 (16), 181 ([M − Cp*H − SH$_2$]$^+$; 26), 180 (19), 179 (18), 178 ([M − Cp*H − 3 H − SH$_2$]$^+$; 31), 177 (22), 176 (17), 135 ([Cp*]$^+$; 12), 121 (14), 119 (36), 117 (15), 105 (31), 93 (19), 91 (31), 80 (18), 77 (21). IR (KBr, cm^{-1}): 2968 (s), 2940 (s), 2905 (vs), 2858 (s), 2721 (vw), 2606 (vw) ν(S−H), 1488 (m), 1433 (m,b), 1378 (vs), 1243 (vw), 1160 (vw), 1064 (w), 1023 (m), 951 (vw), 802 (vw), 433 (s). ^{1}H NMR (C$_6$D$_6$): 17.6 (br s, 1900 Hz, 30H, C$_5$*Me*$_5$); S*H* not found. EPR (toluene): g_{iso} = 1.964, ΔH = 14 G; (toluene, −140 °C): g_1 = 2.000, g_2 = 1.983, g_3 = 1.912, g_{av} = 1.965. UV−vis (toluene, nm): 545 > 670 (sh). Anal. Calcd for C$_{20}$H$_{31}$STi (351.41): C, 68.36; H, 8.89. Found: C, 68.42; H, 8.93.

Preparation of 4 from Cp*$_2$TiMe (2a). Cp*$_2$TiMe (0.22 g, 0.66 mmol) was dissolved in C$_6$D$_6$ (2.0 mL), and gaseous H$_2$S (∼0.3 mmol) was condensed to the frozen solution at −196 °C. After warming to room temperature an intense bright green solution was formed (of apparently compound **11**). Volatiles were condensed into an NMR tube under cooling with liquid nitrogen, and the tube was sealed off. The green solid was dissolved in toluene (5 mL), and about 0.5 mmol of gaseous H$_2$S was condensed in. After warming to room temperature, the solution turned intense blue. After a 5 min warming to 40 °C, all volatiles were condensed to a trap cooled to −196 °C. The residue was dissolved in 2 mL of hexane and crystallized by slow distillation of the solvent in a refrigerator. A residual mother liquor (ca. 0.3 mL) was removed, and fine violet crystals were washed with condensing hexane vapor and dried under vacuum. Yield: 0.19 g (82%). The crystals gave virtually identical EI-MS, IR, EPR, and UV−vis spectra to those of **4**. The collected volatiles in C$_6$D$_6$ contained methane as identified by an NMR singlet signal at δ_H 0.16 ppm[31] and H$_2$S at δ_H 0.18 ppm (published value 0.20 ppm).[3b]

Preparation of [Cp*$_2$Ti(SH)$_2$] (1). Gaseous H$_2$S (1.2 mmol) was condensed to a blue solution of **3** (0.32 g, 1.0 mmol) in 10 mL of toluene under cooling with liquid nitrogen. After warming to room temperature a stirred solution was warmed to 60 °C for 10 min, changing color to ocher-red. Then all volatiles were evaporated under vacuum, and the residue was dissolved in hexane. An ocher-red crystalline solid was obtained from a saturated solution by cooling to −28 °C. Yield: 0.34 g (89%).

Data for **1** are as follows. Mp: darkening at 210 °C, melting at 325 °C, brown liquid. ^{1}H NMR (C$_6$D$_6$): 1.84 (s, 30H, C$_5$*Me*$_5$); 2.85 (s, 2H, S*H*). ^{13}C{^{1}H} NMR (C$_6$D$_6$): 12.99 (C$_5$*Me*$_5$); 122.54 (*C*$_5$Me$_5$). EI-MS (200 °C): *m*/*z* (relative abundance) 384 (M$^{+\cdot}$; 2), 382 ([M − 2H]$^+$; 8), 355 (10), 354 (12), 353 (38), 352 (35), 351 ([M − SH]$^+$; 56), 350 (47), 349 (24), 348 (10), 319 (21), 318 ([M − 2 SH]$^+$; 53), 317 (42), 316 (18), 315 (15), 253 (18), 251 (23), 249 ([M − Cp*]$^+$; 37), 219 (13), 218 (25), 217 (40), 216 (41), 215 ([M − Cp* − H$_2$S]$^+$; 73), 214 (26), 213 (49), 212 (31), 211 (19), 209 (15), 182 (11), 181 (30), 179 (13), 178 (23), 177 (18), 137 (12), 136 ([Cp*H]$^+$; 100), 135 (85), 134 (25), 121 (41), 120 (21), 119 (92), 117 (15), 105 (65), 91 (48), 79 (23), 77 (24). IR (KBr, cm^{-1}): 2980 (m), 2949 (m), 2895 (vs), 2857 (s), 2719 (vw), 2600 (vw) ν(S−H), 1491 (m), 1432 (s), 1377 (vs), 1309 (vw), 1243 (w), 1160 (vw), 1064 (vw), 1021 (m), 954 (vw), 808 (vw), 600 (vw). UV−vis (toluene, nm): 490. Anal. Calcd for C$_{20}$H$_{32}$S$_2$Ti (384.49): C, 62.25; H, 8.39. Found: C, 62.34; H, 8.34.

Preparation of 1 from 3a. Gaseous H$_2$S (1.2 mmol) was condensed to a yellow solution of **3a** (0.49 g, 1.0 mmol) in 10 mL of toluene under cooling with liquid nitrogen. After warming to room temperature a stirred solution turned ocher-red within 20 min. Then all volatiles were distilled at finally 60 °C under vacuum into a cooled trap, and the residue was dissolved in hexane. Ocher-red crystalline **1** was obtained from a saturated solution by cooling to −28 °C. Yield: 0.32 g (85%). The crystalline product gave virtually identical ^{1}H and ^{13}C NMR spectra in C$_6$D$_6$ as **1**. The GC-MS analysis of the volatiles established the presence of 1,2-bis(trimethylsilyl)ethenes (*m*/*z* 172).

Preparation of *ansa*-[(η^5-CH$_2$SiMe$_2$C$_5$Me$_4$)$_2$TiSH] (7). Compound **5** (0.61 g, 1.41 mmol) was dissolved in 10 mL of toluene, giving a brown solution, and gaseous H$_2$S (1.5 mmol) was condensed in under cooling with liquid nitrogen. After warming to room temperature a clear blue solution was formed. After 30 min, all volatiles were evaporated to dryness, and the residue was dissolved in 10 mL of hexane and crystallized from a saturated solution at −28 °C. A blue crystalline solid was separated from a brown mother liquor and recrystallized analogously from hexane to give blue rhomboid crystals. Yield: 0.51 g (78%).

Data for **7** are as follows. Mp: decomposition at 185 °C. EI-MS (180 °C): *m*/*z* (relative abundance) 468 (9), 467 (25), 466 (34), 465 (M$^+$; 80), 464 (12), 463 (12), 433 (7), 432 (14), 431 ([M − H$_2$S]$^+$; 17), 430 (9), 429 (53), 428 (42), 427 ([M − H$_2$S − 2H$_2$]$^+$; 74), 426 (40), 425 (22), 259 (7), 258 (15), 257 (10), 244 (7), 243 (8), 242 (11), 241 (15), 240 (9), 163 (10), 119 (19), 105 (10), 85 (21), 73 ([SiMe$_3$]$^+$; 89), 59 ([SiMe$_2$H]$^+$; 100). IR (KBr, cm^{-1}): 2974 (m), 2947 (s), 2920 (s), 2900 (s), 2866 (m), 2799 (w), 2729 (vw), 2607 (w) ν(S−H), 1481 (w), 1450 (w), 1432 (w), 1412 (w), 1388 (w), 1378 (m), 1349 (w), 1331 (s), 1246 (s), 1130 (w), 1078 (vw), 1022 (m), 830 (vs),797 (m), 766 (s), 709 (m), 682 (m), 594 (m), 572 (w), 444 (m). EPR (toluene, 22 °C): $g = 1.966$, $\Delta H = 7$ G; (toluene, −140 °C): $g_1 = 2.000$, $g_2 = 1.984$, $g_3 = 1.918$, $g_{av} = 1.967$. UV−vis (toluene, nm): 350 (sh) ≫ 547 > 666 (sh). Anal. Calcd for C$_{24}$H$_{41}$SSi$_2$Ti (465.71): C, 61.90; H, 8.87. Found: C, 61.96; H, 8.94.

Preparation of *ansa*-[(η^5-CH$_2$SiMe$_2$C$_5$Me$_4$)$_2$Ti(SH)$_2$] (8). Compound **6** (0.34 g, 0.80 mmol) was dissolved in 20 mL of toluene to give a yellow-orange solution, and gaseous H$_2$S (∼1.9 mmol) was condensed in under cooling with liquid nitrogen. When the reaction solution warmed to room temperature, it turned bright red. All volatiles were evaporated under vacuum, and the residue was dissolved in 20 mL of warm hexane. Slow cooling to −5 °C yielded a crop of red crystals. A concentrated mother liquor afforded another crop of crystals of the same appearance. Combined yield: 0.33 g (0.83%).

Data for **8** are as follows. Mp: 170 °C. ^{1}H NMR (C$_6$D$_6$): 0.17 (s, 12H, Si*Me*$_2$); 0.95 (s, 4H, SiC*H*$_2$); 2.03, 2.08 (2 × s, 2 × 12H, C$_5$*Me*$_4$); 2.93 (s, 2H, S*H*). ^{13}C{^{1}H} NMR (C$_6$D$_6$): 1.54 (*SiMe*$_2$), 12.70 (Si*C*H$_2$); 14.14, 16.83 (C$_5$*Me*$_4$); 113.18 (*C$_{ipso}$*), 130.10, 132.09 (*C*$_5$Me$_4$). ^{29}Si{^{1}H} NMR (C$_6$D$_6$): −4.91 (*Si*Me$_2$). EI-MS (160 °C): *m*/*z* (relative abundance) 498 (M$^{+\cdot}$; 5), 497 (6), 496 ([M − 2H]$^+$; 10), 469 (8), 468 (7), 467 (14), 466 (27), 465 ([M − SH]$^+$; 35), 464 (28), 463 (14), 433(10), 432 ([M − 2 SH]$^+$; 25), 431 (10), 429 (19), 428 (13), 427 ([M − 2 SH − 5 H]$^+$; 23), 379 (12), 258 (17), 257 (11), 241 (14), 179 (9), 178 (7), 177 (10), 145 (23), 143 (15), 119 (18), 105 (17), 91 (7), 85 (22), 73 ([SiMe$_3$]$^+$; 86), 59 ([SiMe$_2$H]$^+$; 100). IR (KBr, cm^{-1}): 2978 (m), 2950 (m), 2921 (s), 2900 (s), 2851 (m), 2796 (w), 2723 (vw), 2590 (w) ν(S−H), 1474 (m), 1454 (m), 1413 (m), 1375 (m), 1346 (w), 1328 (m), 1254 (s), 1243 (s), 1145 (vw), 1126 (m), 1087 (vw), 1065 (w), 1018 (m), 951 (vw), 836 (vs), 800 (m), 768 (s), 703 (m), 683 (w), 660 (vw), 636 (vw), 598 (m), 578 (vw), 457 (m), 434 (w). Anal. Calcd for C$_{24}$H$_{42}$S$_2$Si$_2$Ti (498.78): C, 57.79; H, 8.49. Found: C, 57.86; H, 8.54.

Preparation of Composed Crystals [8/6]. Compound **6** (0.43 g, 1.0 mmol) was suspended in 15 mL of hexane to give a pale yellow solution, and H$_2$S was slowly added under stirring. As the reaction proceeded, the solid **6** was dissolved until at about 1.0 mmol H$_2$S consumed the solid **6** disappeared while the solution turned ocher. The solution was evaporated, and an ocher residue was dissolved in hexane and crystallized by slow cooling

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to −5 °C. A crop of ocher-red crystals was obtained. After concentration of the mother liquor another portion of crystals of the same appearance was collected. Combined yield: 0.34 g (73%). The X-ray diffraction analysis revealed that the unit cell contained molecules of **8** and **6** in a 1:1 abundance.

Data for [**8/6**] are as follows. Mp: 161 °C. EI-MS (150 °C): *m*/*z* (relative abundance) [**8**]$^{+\cdot}$ 498 not observed, 467 (63), 465 ([**8** − SH]$^+$; 95), 463 (11), 465 (30), 433 (51), 432 ([**8** − 2 SH]$^+$; 100), 431 ([**8** − H_2S − HS]$^+$; 78), 430 ([**6**]$^{+\cdot}$; 13), 429 (22), 428 (22), 427 (29), 426 (55), 425 (24), 119 (13), 105 (32), 91 (15), 85 (8), 83 (15), 73 ([$SiMe_3$]$^+$; 95), 59 ([$SiMe_2H$]$^+$; 39). IR (KBr, cm^{-1}): 3040 (vw), 2970 (m,sh), 2953 (m), 2902 (s), 2859 (m), 2800 (w,sh), 2729 (vw), 2593 (vw) ν(S−H), 1476 (w), 1453 (w), 1433 (w), 1418 (w), 1376 (m), 1348 (w), 1328 (m), 1247 (s), 1123 (m), 1064 (vw), 1020 (m), 846 (vs), 801 (m), 767 (s), 704 (m), 682 (w), 662 (m), 642 (w), 598 (w), 575 (vw), 498 (vw), 467 (m), 444 (w). ^{1}H, ^{13}C, and ^{29}Si NMR spectra revealed the presence of **8** and **6**[13] in equimolar quantities.

Preparation of [(Cp^*_2Ti)$_2$S] (11). Compound **4** was prepared from **2** (0.25 g, 0.8 mmol) and H_2S (1 mmol) as described above, and all volatiles were evaporated. A purple solution of **2** (0.25 g, 0.8 mmol) in 5 mL of toluene was added to the violet solid of **4** under stirring. A bright green solution was obtained after warming to 60 °C for 15 min. Green prisms of **11** were obtained after cooling of the concentrated solution to −28 °C. The mother liquor after its volume reduction afforded crystals of the same appearance. Combined yield: 0.47 g (88%).

Data for **11** are as follows. Mp: decomposition at 340 °C. EI-MS (270 °C): *m*/*z* (relative abundance) 670 (5), 669 (6), 668 (M$^{+\cdot}$; 11), 601 (6), 573 (8), 352 ([M − Cp*Ti($C_5Me_3(CH_2)_2$)]$^+$; 14), 351 ([Cp^*_2TiSH]$^+$; 10), 320 (12), 319 (58), 318 ([Cp^*_2Ti]$^+$; 100), 317 (70), 316 (29), 216 ([Cp*TiSH]$^+$; 12), 212 (10), 182 (9), 181 (12), 179 (7), 178 (9), 136 (12), 135 (12), 119 (18), 105 (16), 95 (11), 91 (14), 79 (9). IR (KBr, cm^{-1}): 2982 (m,sh), 2966 (m), 2901 (vs), 2858 (s), 2716 (vw), 1491 (w), 1439 (m,b), 1377 (s), 1309 (vw), 1242 (w), 1166 (w), 1064 (vw), 1023 (m). ^{1}H NMR (C_6D_6): 15.5 (br s, 2600 Hz, 60H, C_5Me_5). EPR (toluene, 22 °C): $g_{iso} = 1.970$, $\Delta H = 10$ G; (toluene, −140 °C): electronic triplet state $g_z = 1.980$, $g_y = 1.967$, $g_x = 1.969$, $D = 0.01678$ cm^{-1}, $E = 0.00163$ cm^{-1}, $\Delta M_s = 2$: singlet, $\Delta H = 10$ G at $g = 3.941$. UV−vis (toluene, nm): 372 > 397 (sh) ≫ 550 (sh) < 635. Anal. Calcd for $C_{40}H_{60}STi_2$ (668.75): C, 71.84; H, 9.04. Found: C, 71.80; H, 8.98.

Preparation of *ansa*-[{(η^5-$CH_2SiMe_2C_5Me_4$)$_2$Ti}$_2$S] (12). Compound **7** (0.30 g, 0.64 mmol) in 10 mL of toluene was poured onto solid **5** (0.28 g, 0.64 mmol), and the mixture was kept at 60 °C for 5 h to give a yellowish-green solution. All volatiles were evaporated under vacuum, and the residue was dissolved in 30 mL of hexane at 60 °C. Slow cooling to −5 °C afforded green, nearly rectangular prisms. Yield: 0.32 g (56%).

Data for **12** are as follows. Mp: decomposition at 185 °C. EI-MS (180 °C): *m*/*z* (relative abundance) M$^{+\cdot}$ 896 not observed, 465 (17), 464 ([M − Cp′$_2$Ti]$^+$; 16), 463 (11), 433 (16), 432 (45), 431 ([M − Cp′$_2$Ti − HS]$^+$; 75), 430 (27), 429 (40), 428 (32), 427 (25), 426 (10), 119 (12), 105 (17), 91 (12), 85 (19), 83 (27), 73 ([$SiMe_3$]$^+$; 95), 59 ([$SiMe_2H$]$^+$; 100). IR (KBr, cm^{-1}): 2947 (s,sh), 2919 (vs), 2854 (s), 2800 (w,sh), 1481 (w), 1452 (w), 1410 (w), 1381 (w), 1349 (w), 1331 (m), 1248 (s), 1154 (vw), 1130 (w), 1090 (vw), 1072 (vw), 1024 (m), 832 (vs),799 (m), 766 (s), 706 (m), 681 (w), 595 (w), 571 (vw), 435 (m). EPR (toluene, 22 °C): impurity 1 (Cp′$_2$TiOR): $g = 1.978$, $\Delta H = 3.3$ G, $a_{Ti} = 7.9$ G; impurity 2 (Cp′$_2$TiSR): $g = 1.963$, $\Delta H = 13$ G; (toluene, −140 °C): electronic triplet state: $\Delta H_{zz} = 376$ G, $g_z = 1.981$, ΔH_{yy}. = 226 G, $g_y = 1.969$, ΔH_{xx} obscured by impurities, $\Delta M_s = 2$: singlet, $\Delta H = 10$ G at $g = 3.942$; impurity 1: $g_1 = 2.000$, $g_2 = 1.984$, $g_3 = 1.955$, $g_{av} = 1.980$; impurity 2: $g_1 = 2.000$, $g_2 = 1.984$, $g_3 = 1.910$, $g_{av} = 1.965$. UV−vis (toluene, nm): 385 > 420 (sh) ≫ 655. Anal. Calcd for $C_{48}H_{80}SSi_4Ti_2$ (897.34): C, 64.25; H, 8.99. Found: C, 64.18; H, 8.96.

Preparation of [*ansa*-{(η^5-$CH_2SiMe_2C_5Me_4$)$_2$Ti}S(TiCp^*_2)] (13). A solution of **2a** (0.5 mmol in 4 mL of hexane) was poured onto crystalline **7** (0.21 g, 0.45 mmol), and the mixture was stirred at 60 °C for 20 min. A clear green solution was cooled to −28 °C for 2 days. The mother liquor containing a highly soluble excess of **2a** was separated from a crystalline product. The latter was recrystallized from warm hexane and dried under vacuum to give a green crystalline solid. Yield: 0.25 g, (71%). Crystals suitable for X-ray diffraction analysis were obtained from a toluene solution.

Data for **13** are as follows. Mp: 240 °C. MS EI-MS (240 °C): *m*/*z* (relative abundance) 782 (M$^{+\cdot}$; 4), 468 (4), 467 (7), 466 (5), 465 ([M − Cp*($C_5Me_4CH_2$)Ti]$^+$; 6), 464 (4), 434 (16), 433 (50), 432 ([M − Cp^*_2TiS]$^+$; 100), 431 (36), 430 (14), 429 (12), 319 (19), 318 ([Cp^*_2Ti]$^+$; 54), 317 (17), 316 (9), 216 ([Cp*TiSH]$^+$; 6), 179 (7), 121 (7), 91 (7). IR (KBr, cm^{-1}): 2954 (s), 2904 (vs), 2858 (s), 2717 (vw), 1485 (w), 1459 (w), 1444 (m,b), 1413 (w), 1377 (m), 1332 (m), 1246 (s), 1152 (vw), 1130 (w), 1070 (vw), 1023 (m), 832 (vs), 797 (w), 766 (m), 703 (w), 679 (vw), 595 (vw), 570 (vw), 433 (m). EPR (toluene, 22 °C): impurity 1 (Cp′$_2$TiOR): $g = 1.978$, $\Delta H = 3.4$ G; impurity 2 (Cp′$_2$TiSR): $g = 1.967$, $\Delta H = 10$ G; (toluene, −140 °C): electronic triplet state: $g_z = 1.980$, $\Delta H_{zz} = 372$ G, $g_z = 1.980$, ΔH_{yy}. = 246 G, $g_y = 1.967$, ΔH_{xx} obscured by impurities, $\Delta M_s = 2$: singlet, $\Delta H = 10$ G at $g = 3.942$; impurity 1: $g_1 = 2.000$, $g_2 = 1.985$, $g_3 = 1.955$, $g_{av} = 1.980$; impurity 2: $g_1 = 2.000$, $g_2 = 1.985$, $g_3 = 1.919$, $g_{av} = 1.968$. UV−vis (toluene, nm): 385 ≫ 550(sh) < 645. Anal. Calcd for $C_{44}H_{70}SSi_2Ti_2$ (783.04): C, 67.49; H, 9.01. Found: C, 67.82; H, 9.08.

Preparation of [(Cp*TiS)$_4$] (14). Compound **3** (0.3 g, 0.95 mmol) in 15 mL of hexane was exposed by an experimental fault to an unknown, much substoichiometric amount of H_2S, and a dark blue solution was left standing in a sealed ampule. After 16 months in diffuse daylight at room temperature, the presence of several square-pyramidal crystals of gray-metallic appearance was observed. The blue mother liquor was separated, and the crystals were washed with condensing hexane vapor and dried under vacuum. Yield: 0.03 g (0.035 mmol). Further crystallization from the mother liquor after volume reduction afforded only pure **3**. Volatiles of the mother liquor were distilled under vacuum into a trap cooled with liquid nitrogen. The GC-MS analysis of the distillate revealed besides hexanes only the presence of C_5Me_5H (*m*/*z* 136) and a trace of $C_5Me_5H_3$ (*m*/*z* 138). The nonvolatile residue was dissolved in C_6D_6 for ^{1}H and ^{13}C NMR analysis. Tangles of weak resonances did not allow identification of any product except **3**, whose spectra are known.[12]

Data for **14** are as follows. Mp > 360 °C. EI-MS (340 °C): *m*/*z* (relative abundance) 862 (10), 861 (13), 860 (M$^{+\cdot}$; 16), 859 (9), 725 ([M − Cp*]$^+$; 2), 679 (13), 678 (8), 677 ([M − Cp*Ti]$^+$; 13), 661 (10), 455 (10), 430 ([M/2]$^+$; 6), 368 (11), 279 (13), 278 ([M − 3 Cp*Ti − SH]$^+$; 67), 256 (10), 219 (9), 185 (13), 170 (12), 157 (16), 141 (9), 136 (10), 135 (13), 133 (10), 131 (10), 129 (12), 121 (14), 119 (16), 97 (9), 96 (9), 83 (11), 81 (10), 69 (38), 57 (26), 55 (31), 51 (12). ^{1}H NMR (C_6D_6): 2.56 (s, 60H, C_5Me_5). ^{13}C{^{1}H} NMR (C_6D_6): 14.55 (C_5Me_5); 119.84 (C_5Me$_5$). IR (KBr, cm^{-1}): 2971 (m), 2946 (m), 2904 (vs), 2852 (m), 2718 (vw), 1494 (w), 1484 (w), 1454 (m), 1430 (m), 1373 (vs), 1309 (vw), 1244 (w), 1158 (vw), 1064 (vw), 1025 (m), 802 (vw). Anal. Calcd for $C_{40}H_{60}S_4Ti_4$ (860.70): C, 55.82; H, 7.03. Found: C, 56.02; H, 6.97.

Thermolysis of 1. A solution of **1** (0.22 g, 0.57 mmol) in *m*-xylene (5 mL) was heated to 140 °C for 4 h in an oven, turning the initial red color to brown. All volatiles were distilled at 100 °C under high vacuum to a cooled trap and analyzed by GC-MS: C_5Me_5H, *m*/*z* 136, (92%), fulvene $C_5Me_4CH_2$, *m*/*z* 134, (5%), C_5Me_5SH, *m*/*z* 168, (3%).

Thermolysis of 4. Compound **4** (0.18 g, 0.5 mmol) was dissolved in *m*-xylene (5.0 mL), sealed in a glass ampule, and subsequently heated. The blue color of **4** faded only after 168 °C, and the final gray solution was worked up after heating to 250 °C for 2 h. Volatiles were collected in a cooled trap and analyzed with GC-MS: *m*/*z* 136 (Cp*H) 98%, *m*/*z* 270 (Cp^*_2) 1%, *m*/*z* 272 (Cp*H)$_2$ 1%. Only a minor part of the nonvolatile residue was extracted into hexane. The residue was largely soluble in toluene; however, some black solid remained insoluble. The soluble fractions gave no crystallizing product, and their ^{1}H and ^{13}C NMR spectra showed a tangle of resonances for Cp* ligands. EI-MS spectra (150−250 °C) of the residue from the hexane extract indicated still the presence of $\mathbf{4}^+$ (m/z 351 and its fragment ions) and low-intensity peaks at m/z 602, 574, 573, 559, 545, 430, and 414, which could indicate a cluster formation.

Photolysis of 1 in an NMR Tube. A C_6D_6 solution of **1** (38 mg) in a sealed NMR tube was exposed to sunlight, and the photolysis progress was followed by ^{1}H NMR spectroscopy. The signals belonging to **1** vanished within 2 h. The ^{1}H NMR spectrum of the photolyzed sample contained the resonance of H_2S at $\delta_H = 0.18$ ppm (published value $\delta_H = 0.20$ ppm)[3c] and resonances of pentamethylcyclopentadiene[32] in integral ratio close to 1:1. Furthermore, the spectrum showed the presence of several Cp* moieties, which could not be assigned. Then the NMR tube was opened under vacuum, and volatiles were distilled into a trap at 60 °C. The GC-MS analysis revealed the presence of Cp*H (60%) and fulvene ($C_5Me_4CH_2$) (40%).

Photolysis of 4 in Benzene. A solution of **4** (0.14 g, 0.4 mmol) in benzene (5 mL) was exposed to sunlight for 5 h. All volatiles were distilled under vacuum into a trap cooled to −196 °C, and after warming to ambient temperature in air the liquid was analyzed by GC-MS. The products consisted of Cp*H (84%) and $C_5Me_4CH_2$ (16%).

X-ray Crystallography. Single crystals or crystal fragments of **1**, **1a**, **4**, **7**, **8**, **8**/**6**, and **11**−**14** were mounted into Lindemann glass capillaries in a Labmaster 130 glovebox (mBraun) under purified nitrogen. Diffraction data for all complexes were collected on a Nonius KappaCCD diffractometer (Mo Kα radiation, $\lambda = 0.71073$ Å) and processed by the HKL program package.[33] The phase problem was solved by direct methods (SIR97),[34] followed by consecutive Fourier syntheses, and refined by full-matrix least-squares on F^2 (SHELXL-97).[35] Relevant crystallographic data are gathered in the Supporting Information. All non-hydrogen atoms were refined anisotropically, except those of disordered methyl moieties in **14**. The C−H hydrogen atoms were found on a difference Fourier map, recalculated into idealized positions (riding model), and assigned temperature factors either $H_{iso}(H) = 1.2U_{eq}$(pivot atom) or $H_{iso}(H) = 1.5U_{eq}$(pivot atom), except for H(43) and H(44) of **8**/**6**. These were refined isotropically without any restraints. The hydrogen atoms of S−H moieties were found on difference Fourier maps and refined as riding on corresponding S atoms with restricted displacement parameters. PLATON/SQUEEZE[36] was used to correct the data of **13** for the presence of the disordered solvent. One potential solvent volume of 376 Å^3 was found at a special position; 103 electrons per unit cell worth of scattering were located in the void, corresponding well to two molecules of toluene. Molecular graphics was carried out with the PLATON program.[37]

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Supporting Information Available: CIF files for the structures **1**, **1a**, **4**, **7**, **8**, **8**/**6**, **11**, **12**, **13**, and **14**. EPR spectrum of **11** in frozen toluene glass. Tables of crystallographic data and data collection and structure refinement details for **1**, **1a**, **4**, **7**, **8**, **8**/**6**, **11**, **12**, **13**, and **14**. This material is available free of charge via the Internet at http://pubs.acs.org.

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