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Synthesis and Structure of 1,4-[(RCp)$_2$Ti]$_2$Se$_4$ and Its Application to the "Chalcogenospecific" Synthesis of 1,2,5,6-Se$_4$S$_4$

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The synthesis of 1,4-[(RCp)$_2$Ti]$_2$Se$_4$ (R = H (**3a**), Me (**3b**), *i*-Pr (**3c**) is described together with their applications to the preparation of 1,2,5,6-Se$_4$S$_4$ (**4**). The deselenization of (RCp)$_2$TiSe$_5$ (**2a–c**) with organophosphines gives **3a–c** isolated as purple microcrystalline solids. The same compounds could also be prepared from the reaction of (RCp)$_2$TiCl$_2$ with solutions of Li$_2$Se$_2$. *R*Cp labeling studies show that these Ti$_2$Se$_4$ compounds do not exchange their (RCp)$_2$TiSe$_2$ fragments. ^{77}Se NMR studies indicate that **3c** has one type of Se atom while three resonances are observed for the pentaselenide **2c**. Compound **3b** crystallizes in the triclinic space group $C\bar{1}$ with a = 9.577 (2) Å, b = 15.145 (2) Å, c = 8.359 (1) Å, α = 97.08 (1)°, β = 92.02 (1)°, γ = 89.89 (1)°. A total of 1772 data were processed to a final R_F = 0.0382, R_{wF} = 0.0444. The compound adopts a centrosymmetric chair conformation with Ti–Se and Se–Se distances of 2.55 and 2.34 Å, respectively. The reaction of **3a** and **3b** with CS$_2$ solutions of S$_2$Cl$_2$ in a molar ratio 1:2 gave **4** in good yield. The single-crystal X-ray diffraction analysis of **4** indicates the presence of a cyclic crown conformer with the atomic positions occupied statistically by either S or Se due to rotational disorder. Raman spectra show three sets of lines assigned to bond stretching modes $\nu_{\text{Se-Se}}$, $\nu_{\text{Se-S}}$, and $\nu_{\text{S-S}}$. The ^{77}Se NMR spectrum of **4** exhibits only one line at 651.5 ppm. Upon heating, **4** undergoes two endothermic transformations assigned to polymerization to (Se$_2$S$_2$)$_n$ followed by melting at 112.5 °C.

Introduction

Organotransition-metal chemistry has a well-established and growing place in the synthesis of hydrocarbons. In contrast, the application of transition-metal organometallics to the synthesis of main-group compounds is in its infancy. The prospects, however, are bright, particularly given the burgeoning interest in main-group chemistry.

A premier example of the role of transition metals in main-group chemistry is the use of Cp$_2$TiS$_5$[2] (Cp = η^5-C$_5$H$_5$) for the synthesis of sulfur homocycles (eq 1). This reaction type has

$$\mathrm{Cp_2TiS_5 + S_nCl_2 \rightarrow Cp_2TiCl_2 + S_{n+5}} \qquad (1)$$

$$n = 1, 2, 4, 6, 7, 8$$

provided access to many new allotropes of sulfur, some for the first time, the study of which has revolutionized our view of this complex element.[3] The related reaction of Cp$_2$TiSe$_5$ and Se$_2$Cl$_2$ is the only route to pure samples of Se$_7$. The cross-reactions of Cp$_2$TiSe$_5$ with S$_n$Cl$_2$ and Cp$_2$TiS$_5$ with Se$_2$Cl$_2$ have given six-, seven-, and eight-membered rings with segregated sulfur and selenium sequences, SeS$_5$, Se$_2$S$_5$, Se$_3$S$_5$, Se$_5$S$_2$, and Se$_6$S$_2$.[4,5] This methodology has also been applied to the synthesis of Me$_2$C-substituted polysulfanes[6] from the reactions of sulfur dihalides and 1,4-Cp$_2$TiS$_4$CMe$_2$.[7,8]

The fact that the Cp$_2$TiE$_5$ reagents reliably deliver a pentachalcogenide fragment is both a strength and a limitation. It is a severe limitation since it would be desirable to have a source of E$_n$ where $n \neq 5$. The availability of compounds of the type [(RCp)$_2$TiE$_n$]$_2$[8-10] was therefore of interest because, by using reactions analogous to that in eq 1, these materials could serve as sources of the E$_n$ fragments where $n < 5$. This report describes the realization of this concept in the forms of the chalcogenospecific synthesis of 1,2,5,6-Se$_4$S$_4$, which has been accomplished by using the dimeric titanium diselenides 1,4-[(RCp)$_2$Ti]$_2$Se$_4$ whose preparation is described. Traditional routes to selenium sulfides are nonselective, giving mixtures of Se$_n$S$_{8-n}$; our method is highly selective, hence the term "chalcogenospecific".

Compounds of the formula Se$_n$S$_{8-n}$ have been known for a very long time.[11] Selenium sulfides occur naturally[12] and are industrially synthesized via the reaction of SeO$_2$ and H$_2$S.[11] More commonly mixtures of Se$_n$S$_{8-n}$ molecules have been prepared from melts of the two elements.[13-15] Since the band gap of selenium sulfides is a function of the selenium content,[16] selective synthesis provide a means to control the properties of semiconducting polymers.

Results and Discussion

Synthesis and Properties of 1,4-[(RCp)$_2$Ti]$_2$Se$_4$. Two methods were developed for the synthesis of the Ti$_2$Se$_4$ heterocycles, both of which begin with the titanocene dichlorides (RCp)$_2$TiCl$_2$, where R = H (**1a**), Me (**1b**), *i*-Pr (**1c**). The first method is an adaptation of our synthesis of Ti$_2$S$_4$ rings[7,9] by desulfurization of the corresponding pentasulfides. The second method involves the direct reaction of Se$_2^{2-}$ with (RCp)$_2$TiCl$_2$.

Treatment of dichloromethane solutions of (RCp)$_2$TiSe$_5$ (**2a–c**) with triphenyl- or tributylphosphine gives compounds **3a–c** in 40–65% yields. All three Ti$_2$Se$_4$ compounds were obtained as analytically pure purple crystals. In contrast to the reactions of (RCp)$_2$TiS$_5$ with phosphines,[10] we observed no evidence for hexachalcogenides, i.e., 1,4-[(MeCp)$_2$Ti]$_2$Se$_6$.

A more convenient synthesis of **3b** and **3c** involves the reaction of THF solutions of Li$_2$Se$_2$ with (RCp)$_2$TiCl$_2$. The Li$_2$Se$_2$ reagent is prepared by the reaction of polymeric gray selenium and 2 equiv of LiBHEt$_3$, "Super Hydride" (Aldrich), as described by Gladysz.[17]

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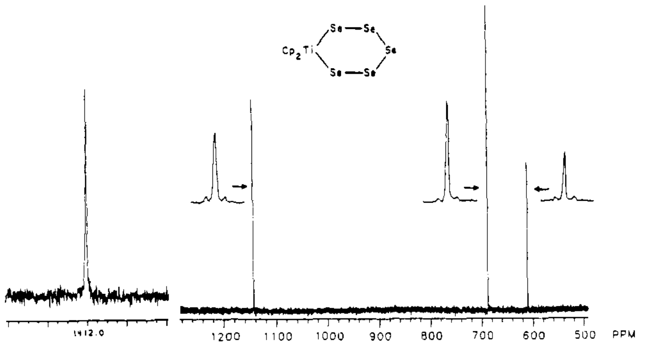
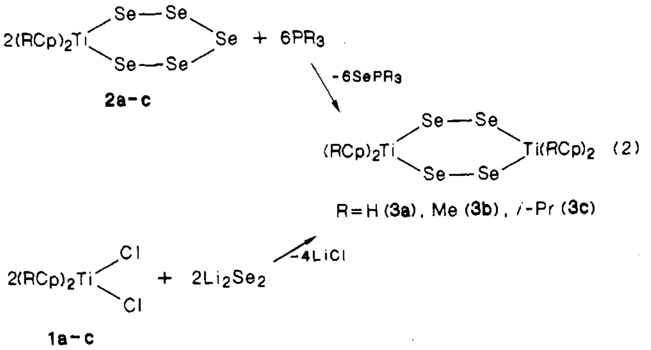


Figure 1. 47.7-MHz ^{77}Se NMR spectra of (*i*-PrC$_5$H$_4$)$_2$TiSe$_5$ (**2c**) and 4-[(*i*-PrC$_5$H$_4$)$_2$Ti]$_2$Se$_4$ (**3c**).

The reaction of THF solutions of **1** and Li$_2$Se$_2$ at room temperature gives the desired products **3** in about 65% yield (eq 2). In comparison with the method described in the preceding paragraph, the Li$_2$Se$_2$ procedure obviates the need to prepare the pentaselenide intermediates. Interestingly, it had previously been shown that the reaction of Li$_2$S$_2$ with (RCp)$_2$TiCl$_2$ gives complex mixtures comprised largely of the pentasulfido chelate.[7]



The Ti$_2$Se$_4$ compounds appear to be mildly air and moisture sensitive, the solubility varies with the substituents on the cyclopentadienyl group. The unsubstituted complex **3a** was almost completely insoluble in all solvents while **3b** and particularly **3c** exhibited good solubility and could be further recrystallized from dichloromethane–hexane. Solutions of **3b** and **3c** are unstable; after an hour, decomposition to the pentaselenides **2** and other unidentified insoluble species was observed. As such, **3b** is insufficiently stable in boiling dichloromethane solution to react directly with even electrophilic acetylenes like dimethyl acetylenedicarboxylate and methyl propiolate. The corresponding diselenenes do form but they appear to arise via the pentaselenides,[18] which are obtained when dichloromethane solutions of **3b** are heated.

The ^{1}H NMR spectrum of **3b** consists of two methyl singlets and three RC$_5H_4$ multiplets (2:2:4) consistent with the chair conformation. The expected four RC$_5H_4$ resonances (2:2:2:2) are well resolved in the case of the *i*-PrCp dimer **3c**. The ^{1}H NMR spectrum of the poorly soluble **3a** shows only one signal although two are expected for the chair conformer in the absence of a dynamic ring inversion. The ^{77}Se NMR spectrum of **3c** consists of a single line at 1412 pm vs Me$_2$Se. The ^{77}Se NMR spectrum of the corresponding pentaselenide **2c** showed three resonances at 1147, 688, and 610 ppm in an approximate 2:2:1 intensity ratio, respectively (Figure 1). The high-frequency peak in the pentaselenide spectrum is therefore assigned to the coordinated Se atoms.

Since the ^{1}H NMR signals for **3b** and **3c** were well resolved, we investigated the possibility of crossover reactions. Although these Ti$_2$Se$_4$ compounds were shown to be unstable with respect to the pentaselenides **2b** and **2c**, no evidence was obtained in support of 1,4-[(MeCp)$_2$Ti][(*i*-PrCp)$_2$Ti]Se$_4$. This experiment indicates that monometallic (RCp)$_2$TiSe$_2$ compounds are unimportant in understanding the reactivity of these unusual heterocycles. However, in view of the existence of (C$_5$Me$_5$)$_2$VS$_2$,[20] it is reasonable that (RCp)$_2$TiSe$_2$ is an intermediate in the formation of **3**. We had previously reported the synthesis of 1,4-[Cp$_2$Ti][(*i*-PrCp)$_2$Ti]S$_4$.[7]

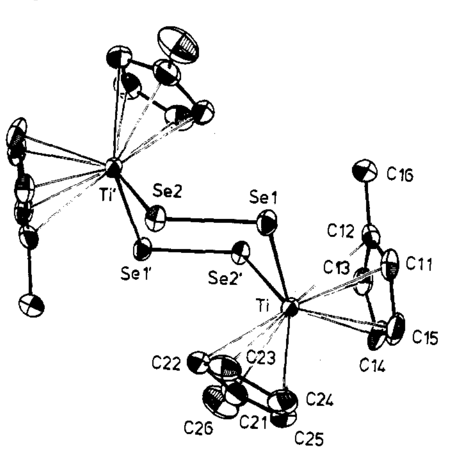


Figure 2. Structure of 1,4-[(MeC$_5$H$_4$)$_2$Ti]$_2$Se$_4$ (**3b**) with thermal ellipsoids drawn at the 50% probability level.

Table I. Important Bond Distances (Å) and Angles (deg) in 1,4-[(MeCp)$_2$Ti]$_2$Se$_4$ (**3b**)

Ti–Se1	2.563 (1)	C11–C12	1.391 (6)
Ti–Se2	2.542 (1)	C11–C15	1.403 (7)
Se1–Se2	2.343 (1)	C12–C13	1.425 (7)
Ti–C11	2.423 (4)	C12–C16	1.525 (6)
Ti–C12	2.481 (4)	C13–C14	1.384 (7)
Ti–C13	2.409 (5)	C14–C15	1.431 (8)
Ti–C14	2.339 (5)	C21–C22	1.401 (7)
Ti–C15	2.354 (4)	C21–C25	1.373 (7)
Ti–C21	2.414 (5)	C21–C26	1.500 (7)
Ti–C22	2.361 (4)	C22–C23	1.404 (7)
Ti–C23	2.396 (5)	C23–C24	1.420 (7)
Ti–C24	2.358 (5)	C24–C25	1.415 (8)
Ti–C25	2.399 (5)		
Se(1)–Ti–Se(2)	94.2 (1)	Se(1)–Se(2)–Ti	113.0 (1)
Se(2)–Se(1)–Ti	106.6 (1)		

Structure of 1,4-[(MeCp)$_2$Ti]$_2$Se$_4$ (3b). Compound **3b** was characterized by single-crystal X-ray diffraction (Figure 2, Table I). The molecule is crystallographically centrosymmetric; the Ti$_2$Se$_4$ core adopts a chair conformation in the lattice. The Ti–Se (2.563 (1) Å) and Se–Se (2.343 (1) Å) bond lengths resemble those for Cp$_2$TiSe$_5$.[21] The TiSeSeTi torsional angles are 77.90 (7)°. It is interesting to note that the valence electron count for **3b** is two less than that for the recently reported [W(CO)$_5$]$_2$Se$_4^{2+}$.[22] The latter compound adopts a nonclassical[23] structure featuring four bonding Se–Se contacts, two of which are very long at 3.015 (2) Å.

Reactivity of 3a and 3b toward S$_2$Cl$_2$. The aforementioned Ti$_2$Se$_4$ heterocycles offered for the first time the opportunity to synthesize a mixed sulfur–selenium heterocycle with alternating Se$_n$ and S$_n$ sequences. Indeed, CS$_2$ solutions of S$_2$Cl$_2$ and **3a** react to give 1,2,5,6-Se$_4$S$_4$ (**4**) according to eq 3, provided the reactants are mixed in the correct stoichiometric ratio. The reaction was complete in a few minutes at room temperature. After removing the precipitated byproduct **1a** by filtration, the desired product was crystallized from the CS$_2$ by cooling to −78 °C. After a single recrystallization, we obtained a 73% yield of **4**. According to the HPLC analysis the product is contaminated with a few percent

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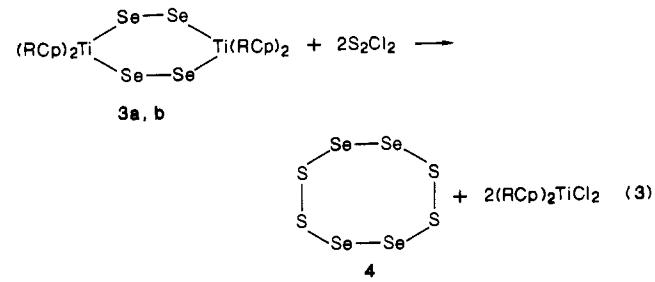

3a, b

4

(3)

of Se_6S_2, which can be removed by repeated recrystallization from cold CS_2.

Compound **3b** was also used for the synthesis of 1,2,5,6-Se_4S_4. In this case the higher solubility of **1b** results in simultaneous crystallization of the two products on cooling and requires that the selenium sulfide product be purified by mechanical separation.

Characterization of 1,2,5,6-Se_4S_4 (4). Under standard conditions, the HPLC retention times of the cyclic selenium sulfides depend on the ring size, the number of selenium atoms, and the number of Se–S bonds in the molecule.[24] Because of this, the retention time of each Se_4S_4 isomer can be fairly reliably predicted after a large number of cyclic selenium sulfides have been investigated by HPLC.[4,5,24] The chromatogram of **4** is shown in Figure 3. Under standardized conditions,[24] **4** is distinguished from the minor impurity of Se_6S_2, which elutes more slowly. Compound **4** was obtained as orange rod-shaped crystals, which are stable at 20 °C in air for months. The ^{77}Se NMR spectrum of **4** showed only a singlet in accordance with the expected symmetry (Figure 3). With the exception of 1,3,5,7-Se_4S_4, all other isomers of Se_4S_4 are expected to show more than one ^{77}Se NMR signal. The chemical shift of 651.5 ppm versus Me_2Se conforms with the expectation for an eight-membered ring containing Se atoms linked to one sulfur and one selenium atom.[15]

An X-ray diffraction study of **4** indicated monoclinic symmetry with $a = 8.702$ (1) Å, $b = 9.104$ (3) Å, $c = 11.324$ (2) Å and $\beta = 91.56$ (1)°. The most likely space group is $P2_1/n$. The crystallography of Se_nS_{8-n} rings had previously been studied for materials prepared from mixed selenium–sulfur melts and related nonselective reactions. Those studies had shown that eight-membered rings of compositions from α-Se_8 to $Se_{4.7}S_{3.3}$ crystallized in the space group $P2_1/n$. The results of the present study show that this range extends to Se_4S_4. The more sulfur-rich phases crystallize in the monoclinic space group $P2/c$ with distinctly different lattice constants.[11] In the lattice, the molecules of **4** are in eight-membered rings that are rotationally disordered, thereby preventing determination of useful bond lengths and angles. The electron density map of **4** clearly showed the crown-shaped, eight-membered ring. Importantly, the calculated crystal density of 3.29 g cm^{-3} is in good agreement with the arithmetic mean of the densities of both α-S_8 (2.07 g cm^{-3}) and α-Se_8 (4.43 g cm^{-3}), which is 3.25 g cm^{-3}, as can be expected for a compound of composition Se_4S_4.

Evidence supporting the structure proposed for **4** also comes from its Raman spectrum (Figure 4, Table II). The totally symmetric bending mode appears as a very strong line at 168 cm^{-1} (calculated as 173 cm^{-1}).[13] Based on our previous work, this frequency is characteristic of an eight-membered ring with a high Se content.[14] The presence of only one Se–Se bond type is supported by the observation of only one line in the Se–Se stretching frequency region. Vibrational coupling between the two Se_2 units is low because they are not directly connected. Consequently, the two SeSe stretching modes of the molecule are accidentally degenerate or almost so. The same holds for the SeS stretching vibrations, which appear as a strong line at 353 cm^{-1} with shoulders on the high-frequency side, which is typical for nonneighboring SeS bonds. Were the SeS bonds neighboring, well-separated ν_{SeS} Raman lines would be expected.[9] Of the three relatively weak bands near 460 cm^{-1} assigned to ν_{ss}, one must be due to intermolecular coupling, combination vibrations, or the presence of an impurity since only two lines are expected for a 1,2,5,6-Se_4S_4 molecule. In comparison with all other Se_4S_4 isomers, the observed spectrum fits that previously predicted for the 1,2,5,6-isomer[14] best.

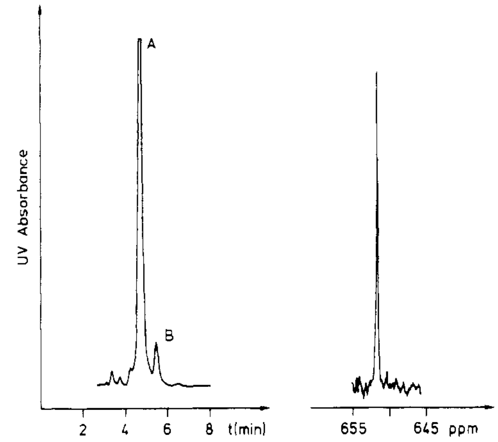

Figure 3. HPLC trace (left) and ^{77}Se NMR spectrum (right) of a recrystallized sample of 1,2,5,6-Se_4S_4. The ratio of the chromatographic peak areas of Se_4S_4 (peak A) and Se_6S_2 (peak B) is 9.09. The small peaks left of peak A are caused by unidentified seven- and eight-membered selenium sulfide heterocycles.

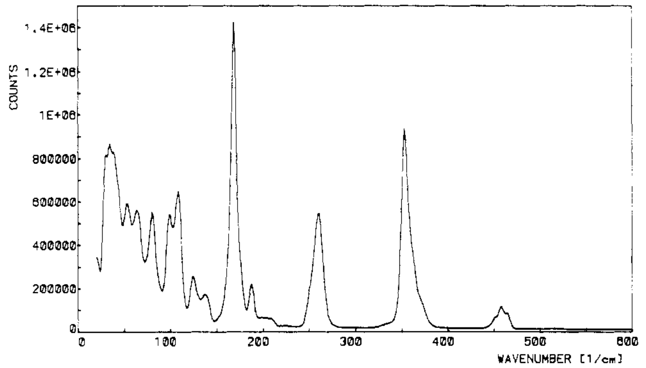

Figure 4. Raman spectrum of 1,2,5,6-Se_4S_4 (4).

Table II. Raman Spectral Data for 1,2,5,6-Se_4S_4 (−100 °C)

wavenumber, cm^{-1}	assgnt[14]	wavenumber, cm^{-1}	assgnt[14]
30	lattice modes	168 vs	bending modes
35		188 w	
39		260 s	ν_{SeSe}
53 m	torsional modes	353 vs	ν_{SeSe}
64 m		368 sh	
81 m	bending modes	452 vw, sh	ν_{SS}
99 m		458 w	
109 s		464 vw, sh	
125 w			
137 w			

On heating, the color of a twice-recrystallized sample of **4** changed from orange to deep red and then, beginning at 85 °C to silver; the sample melts at 112.5 °C (uncorrected). After being recooled to room temperature, the sample was insoluble in CS_2. When the properties of **4** were studied by differential thermal calorimetry, two broad endothermic peaks were observed beginning at 84 and 101 °C. The process that begins at 84 °C was complete at 91 °C and is believed to represent a polymerization to a chain, possibly containing alternating Se_2 and S_2 subunits. The second process, which occurred over the range of 101–116 °C, represents the melting of the polymer.

Conclusions

In this report we have described the synthesis of a series of cyclic Ti_2Se_4 compounds and their application to the first synthesis of

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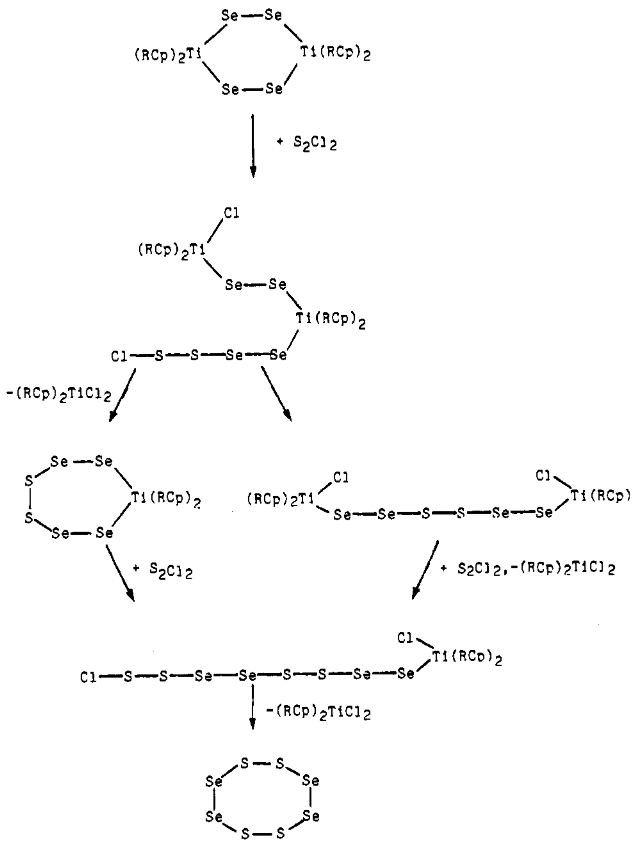
Scheme I



a single isomer of Se_4S_4 that has alternating Se_2 and S_2 units. The titanium diselenide compounds could be prepared via two methods. The Ti_2Se_4 rings differ in terms of their solubilities, depending on the substituents on the cyclopentadienyl rings. The structures of these species were confirmed by using ^1H and ^{77}Se NMR spectroscopy as well as by single-crystal X-ray diffraction.

The Ti_2Se_4 reagents were found to react with S_2Cl_2 in a 1:2 molar ratio to give $1,2,5,6\text{-}Se_4S_4$ in good yield. HPLC as well as Raman and ^{77}Se NMR spectroscopies demonstrate that *this synthesis is selective for but one of the thirty $Se_{8-n}S_n$ rings*,[25] there being seven diastereoisomers, of Se_4S_4 alone. The accessibility of the reagents and the stability of the products indicate that the isolation of individual isomers of these rings is a realistic goal.

The synthesis of **4** provides some useful and interesting mechanistic insights concerning the mode of action of the titanocene-based chalcogen-transfer reagents. A suggested mechanism is presented in Scheme I. The first step must be the scission of one Ti–Se bond with the formation of acyclic $Cl(RCp)_2TiSeSe(RCp)_2TiSeSeSSCl$. This species could undergo two intramolecular reactions, both of which would afford the Ti–Se–Se–S–S–Se–Se–Ti sequence, which in turn would be reactive toward S_2Cl_2 to give **4**. Explicit in our mechanistic proposal is that all four Se atoms in each molecule of **4** are derived from the same Ti_2Se_4 ring. The involvement of more than one Ti center in a titanocene-based polychalcogen synthesis had been invoked previously to explain the formation of S_{5n} (n = 2, 3, 4) from the reaction of Cp_2TiS_5 with SO_2Cl_2.[26]

The only significant contaminant formed with **4** is $1,2,3,4,5,6\text{-}Se_6S_2$. We had previously shown that this hexaselenide can arise from the dismutation of Se_5S_2 (eq 4).[5] In contrast to

$$2Se_5S_2 \rightarrow Se_6S_2 + Se_4S_2 \qquad (4)$$

Se_6S_2, the Se_4S_2 byproduct of eq 4 does not form solid solutions with **4**, so it is easily removed by recrystallization. The Se_5S_2 is proposed to arise from the known reaction of S_2Cl_2 and $(RCp)_2TiSe_5$, which in turn results from the slow decomposition of $1,4\text{-}[(RCp)_2Ti]_2Se_4$ in solution.

Table III. Crystallographic Data for $1,4\text{-}[(MeCp)_2Ti]_2Se_4$ (**3b**)

formula	$C_{24}H_{28}Se_4Ti_2$
temp, °C	22 (2)
space group	$C\bar{1}$
a, Å	9.577 (2)
b, Å	15.145 (2)
c, Å	8.359 (1)
α, deg	97.08 (1)
β, deg	92.02 (1)
γ, deg	89.89 (1)
V, Å^3	1202.4
fw	728.12
Z	2
radiation	Mo Kα
detector aperture, mm	
horiz	2.0–2.5
vert	4.0
cryst size, mm	0.30 × 0.30 × 0.10
max 2θ, deg	50
scan type	ω–2θ
no. of reflcns measd	2040
no. of obsd data ($F^2 > 2.0\sigma(F^2)$)	1772
abs cor	empirical (ψ scan)
coeff, cm^{-1}	65.5
transmissn coeff	
max	0.99
min	0.27
final residuals	
R_F	0.0382
R_{wF}	0.0444
weighting scheme	$w = 1/(\sigma^2(F) + 0.004F^2)$
esd of unit weight observn	1.90
largest shift/error value of final cycle	0.17
largest peak in final diff Fourier, e/Å^3	0.68
no. of variables	142

Table IV. Positional Parameters

atom	x	y	z	B_{eq},[a] Å^2
Se1	0.1829 (0)	0.0789 (0)	0.4239 (1)	2.10
Se2	0.0355 (0)	−0.0136 (0)	0.2472 (1)	1.95
Ti	−0.2196 (1)	−0.0017 (0)	0.3216 (1)	1.63
C11	−0.3457 (5)	−0.1413 (3)	0.2678 (6)	2.57
C12	−0.2198 (4)	−0.1581 (3)	0.1917 (5)	2.18
C13	−0.2118 (5)	−0.0993 (3)	0.0717 (6)	2.47
C14	−0.3332 (5)	−0.0494 (4)	0.0738 (6)	3.03
C15	−0.4191 (5)	−0.0748 (4)	0.1973 (6)	3.06
C16	−0.1157 (6)	−0.2310 (3)	0.2206 (6)	3.33
C21	−0.2057 (5)	0.1533 (3)	0.2827 (6)	2.97
C22	−0.1662 (5)	0.1440 (3)	0.4428 (6)	2.67
C23	−0.2817 (5)	0.1168 (3)	0.5235 (6)	3.17
C24	−0.3928 (5)	0.1031 (4)	0.4061 (7)	3.66
C25	−0.3436 (5)	0.1286 (3)	0.2608 (7)	3.21
C26	−0.1199 (7)	0.1897 (4)	0.1589 (8)	4.51

[a] $B_{eq} = {}^4/_3(B_{11}a^2 + B_{22}b^2 + B_{33}c^2 + B_{12}ab(\cos\gamma) + B_{13}ac(\cos\beta) + B_{23}bc(\cos\alpha))$.

The successful application of $1,4\text{-}[(RCp)_2Ti]_2Se_4$ to the synthesis of specifically substituted heterocyclic rings suggests that other titanocene chalcogenides such as $1,5\text{-}[(RCp)_2Ti]_2S_n$ (n = 4, 6) would also be useful reagents in the synthesis of new main-group compounds. It has in fact been observed that **4** can also be prepared from $[Cp_2Ti]_2S_4$[7,9] by reaction with 2 mol of Se_2Cl_2.[27]

Experimental Section

Reagents were obtained from commercial sources and were used without further purification. $(MeCp)_2TiCl_2$ was prepared according to our recently published procedure for $(i\text{-}PrCp)_2TiCl_2$.[7] The apparatus and protocols for the HPLC[24] have been described previously. $1,2,5,6\text{-}Se_4S_4$ was eluted after 4.24 min (flow rate of 2 mL/min, dead time of 1.2 min). **4** has almost the same retention time as $1,2,3\text{-}Se_3S_5$. Raman spectra were recorded at −100 °C by using a krypton ion laser at 647.1 nm and an ISA double monochromator Raman spectrometer.[28] Mass spectra were re-

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(25) These isomers are depicted in ref 15 although the authors missed the $1,2,4,7\text{-}Se_4S_4$ isomer.

(26) Steudel, R.; Strauss, R. *J. Chem. Soc., Dalton Trans.* **1984**, 1775.

(27) Steudel, R.; Jensen, D., unpublished results.

(28) Steudel, R.; Holz, B. *Z. Naturforsch., B: Chem. Sci.* **1987**, *42B*, 691.

Table V. Anisotropic Temperature Factors for **3b**

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{12}	U_{13}
Se1	0.0237 (0)	0.0303 (0)	0.0263 (0)	0.0056 (0)	−0.0022 (0)	−0.0074 (0)
Se2	0.0216 (0)	0.0305 (0)	0.0219 (0)	−0.0010 (0)	0.0008 (0)	−0.0018 (0)
Ti	0.0172 (0)	0.0226 (0)	0.0221 (1)	0.0014 (0)	−0.0017 (0)	0.0004 (0)
C11	0.0249 (1)	0.0391 (1)	0.0336 (1)	0.0003 (1)	−0.0052 (1)	−0.0126 (1)
C12	0.0283 (1)	0.0233 (1)	0.0300 (1)	−0.0065 (1)	−0.0084 (1)	−0.0048 (1)
C13	0.0317 (1)	0.0352 (1)	0.0261 (1)	−0.0066 (1)	−0.0041 (1)	−0.0027 (1)
C14	0.0410 (1)	0.0432 (1)	0.0305 (1)	0.0034 (1)	−0.0190 (1)	−0.0082 (1)
C15	0.0242 (1)	0.0483 (1)	0.0428 (1)	−0.0061 (1)	−0.0104 (1)	−0.0090 (1)
C16	0.0500 (1)	0.0244 (1)	0.0506 (1)	−0.0071 (1)	−0.0144 (1)	0.0062 (1)
C21	0.0507 (1)	0.0214 (1)	0.0409 (1)	0.0007 (1)	0.0054 (1)	0.0023 (1)
C22	0.0314 (1)	0.0244 (1)	0.0446 (1)	−0.0065 (1)	−0.0077 (1)	−0.0003 (1)
C23	0.0466 (1)	0.0329 (1)	0.0407 (1)	−0.0047 (1)	0.0096 (1)	0.0132 (1)
C24	0.0340 (1)	0.0365 (1)	0.0687 (1)	−0.0030 (1)	0.0100 (1)	0.0155 (1)
C25	0.0400 (1)	0.0277 (1)	0.0541 (1)	0.0018 (1)	−0.0067 (1)	0.0142 (1)
C26	0.0730 (1)	0.0349 (1)	0.0653 (1)	0.0101 (1)	0.0127 (1)	−0.0031 (1)

corded on a Varian MAT 311A instrument in the EI mode at 70 eV (**3a**). ^{77}Se NMR spectra were recorded at 76.313 MHz (**4**) with a pulse width of 7 μs and a delay time of 7 s on a Bruker MSL-400 or at 47.752 MHz (**2c**, **3c**) with a pulse width of 25 μs and a delay time of 25 s on a home-built 250-MHz instrument. ^{1}H NMR spectra were recorded on a Varian XL-200 at 200 MHz.

(*i*-PrCp)$_2$TiSe$_5$ (2c). A slurry of 5.93 g of gray selenium in 10 mL of THF was treated with 30 mL of 1 M LiBHEt$_3$. This slurry was refluxed for 35 min and was then added via cannula to a solution of 4.99 g (14.98 mmol) of (*i*-PrCp)$_2$TiCl$_2$[7] in 50 mL of THF. The reaction mixture was stirred at room temperature for 1 h followed by stirring at room temperature for 1 h. The evaporated reaction mixture was extracted with 150 mL of CH$_2$Cl$_2$, and the dark purple solution was filtered through a pad of Celite. The purple filtrate was diluted with 30 mL of hexane and concentrated to 50 mL. After storage at −25 °C for 90 min, 8.12 g of dark purple crystals was collected (82.5%). Anal. Calcd for C$_{16}$H$_{22}$Se$_5$Ti: C, 29.25; H, 3.37; Se, 60.09; Ti, 7.29. Found C, 29.50; H, 3.60; Se, 59.93; Ti, 7.05. ^{1}H NMR (CDCl$_3$ solution): δ 6.31 (m, 2 H), 6.14 (m, 2 H), 5.96 (m, 4 H), 3.09 (sept, 1 H, J = 6.2 Hz), 2.69 (sept, 1 H, J = 6.2 Hz), 1.29 (d, 3 H, J = 6.2 Hz), 1.09 (d, 3 H, J = 6.2 Hz). ^{77}Se NMR (CH$_2$Cl$_2$ solution): 1147, 688, 610 ppm downfield of neat Me$_2$Se. This procedure is applicable to **2a** and **2b**, although these products are considerably less soluble.

1,4-[Cp$_2$Ti]$_2$Se$_4$ via Cp$_2$TiSe$_5$. A solution of PPh$_3$ (1.4 g) in 20 mL of CH$_2$Cl$_2$ was added over the course of 45 min to a refluxing solution of **2a** (1 g) in 350 mL of CH$_2$Cl$_2$. After a further hour of refluxing, the deep violet microcrystals of **3a** were collected by filtration and washed with pentane. Yield: 380 mg (64%). Anal. Calcd for C$_{20}$H$_{20}$Se$_4$Ti$_2$: C, 35.75; H, 2.98; Se, 47.0. Found: C, 37.75; H, 3.00; Se, 47.0. ^{1}H NMR (CDCl$_3$ solution): 6.59 (s). An analogous procedure was tested with (MeCp)$_2$TiSe$_5$, giving 40% yield of **3b**.

1,4-[(MeCp)$_2$Ti]$_2$Se$_4$ (3b) via the Li$_2$Se$_2$ Method. Gray selenium (0.158 g, 2 mmol) was treated with 2 mL of 1 M LiBHEt$_3$ in THF. The brown solution was heated under reflux for 30 min. After cooling, the red brown slurry was treated with a slurry of 0.277 g (1 mmol) of (MeCp)$_2$TiCl$_2$ in 15 mL of THF resulting in an immediate color change to purple. After 15 min the solution was evaporated to dryness, and the product was extracted with CH$_2$Cl$_2$; dilution with hexane followed by concentration afforded 0.238 g of dark purple crystals (65%). Anal. Calcd for C$_{24}$H$_{28}$Se$_4$Ti$_2$: C, 39.59; H, 3.88; Se, 43.38; Ti, 13.16. Found: C, 39.13; H, 4.07; Se, 43.34; Ti, 13.26. ^{1}H NMR (CDCl$_3$ solution): δ 6.53 (m, 2 H), 6.20 (m, 4 H), 5.80 (m, 2 H), 2.65 (s, 3 H), 1.73 (s, 3 H).

An analogous procedure was used to prepare the *i*-PrCp complex **3c**. Anal. Calcd for C$_{32}$H$_{44}$Se$_4$Ti$_2$: C, 45.74; H, 5.28; Se, 37.58; Ti, 11.40. Found: C, 45.16; H, 5.01; Se, 37.22; Ti, 11.60. ^{1}H NMR (CDCl$_3$ solution): δ 6.60 (m, 2 H), 6.27 (m, 2 H), 6.08 (m, 2 H), 5.87 (m, 2 H), 3.42 (sept, 1 H, J = 5.5 Hz), 2.60 (sept, 1 H, J = 5.5 Hz), 1.30 (d, 3 H, J = 5.5 Hz), 0.90 (d, 3 H, J = 5.5 Hz). ^{77}Se NMR (CH$_2$Cl$_2$ solution): 1412 ppm downfield of neat Me$_2$Se.

The ^{1}H NMR spectrum of equimolar CDCl$_3$ solutions of **3b** and **3c** was measured by 300-MHz NMR. All resonances could be assigned to **3b** and **3c**; within a few hours, resonances for **2b** and **2c** appeared due to decomposition of the Ti$_2$Se$_4$ species.

1,2,5,6-Se$_4$S$_4$ (4). At 20 °C, a stirred slurry of 270 mg of **3a** in 200 mL of CS$_2$ was treated with a solution of 108 mg of S$_2$Cl$_2$ in 7 mL of CS$_2$. After the mixture was stirred for 3 min, the precipitated **1a** was removed by filtration and the volume of the filtrate was reduced to 50 mL. On cooling to −78 °C, orange crystals formed; recrystallization from CS$_2$ (dissolution at 20 °C followed by cooling to −78 °C) resulted in 120 mg of almost pure **4** (73%). Anal. Calcd for Se$_4$S$_4$: Se, 71.12. Found (by oxidation with HNO$_3$/H$_2$SO$_4$, followed by iodometric titration): Se, 69.5. ^{77}Se NMR (CS$_2$ solution): 651.5 ppm (s), downfield of Me$_2$Se in toluene.

X-ray Diffraction Study of 1,4-[(MeCp)$_2$Ti]$_2$Se$_4$ (3b). Preliminary examination and data collection were performed with Mo Kα radiation on an Enraf-Nonius CAD4 diffractometer equipped with a graphite-crystal, incident-beam monochromator. Cell constants and an orientation matrix for data collection were obtained from least-squares refinement, by using the setting angles of 25 reflections. The crystal shows triclinic symmetry, space group $P\bar{1}$, with lattice constants a = 8.952 Å, b = 8.967 Å, c = 8.359 Å, α = 97.06°, β = 94.90°, and γ = 64.62°. For data collection and structure determination a nonstandard C-centered cell was taken with a = 9.577 (2) Å, b = 15,145 (2) Å, c = 8.359 (1) Å, α = 97.08 (1), β = 92.02 (1), and γ = 89.90 (1)°, because of an approximate orthogonality of the centered cell. Reflections were measured in the range 2° ≤ 2θ ≤ 50°, with a scan width of (1.0 + 0.35 tan θ). Lorentz and polarization corrections were applied, as well as an empirical absorption correction. The structure was solved by Patterson methods. The refinement included 142 parameters. Hydrogen atoms were included at calculated positions with fixed temperature factors U = 0.08 Å^2. Full-matrix least-squares refinement converged to R_F = 0.038 ($R_F = \sum||F_o - F_c|/\sum|F_o|$) and R_{wF} = 0.044 ($R_{wF} = [(\sum w(|F_o| - |F_c|)/\sum|F_o|^2)]^{1/2}$). A final difference electron density map showed no evidence of disorder. Crystallographic data for the structure refinement are given in Table III, while positional parameters and anisotropic temperature factors are given in Tables IV and V, respectively.

X-ray Diffraction Study of 1,2,5,6-Se$_4$S$_4$ (4). Instrumentation and experimental conditions were the same as for **3b**. The crystal is monoclinic, space group most probably $P2_1/n$ (nonstandard setting of $P2_1/c$, No. 14), with lattice constants a = 8.702 (1) Å, b = 9.104 (3) Å, c = 11,324 (2) Å, and β = 91.56 (1)°. Reflections were measured in the range 2 ≤ 2θ ≤70°; Lorentz and polarization corrections as well as an empirical absorption correction were applied. The structure was solved by direct methods. The results clearly show that the structure is built up from eight-membered rings, but due to a rotational disorder, sulfur and selenium atoms could not be distinguished; attempts to refine the structure by using several disorder models were not successful. A refinement assuming a statistical distribution of Se and S atoms in the rings resulted in an R_F of about 0.11.

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Registry No. **1a**, 1271-19-8; **1b**, 1282-40-2; **1c**, 12130-65-3; **2a**, 12307-22-1; **2b**, 78614-88-7; **2c**, 97732-75-7; **3a**, 114860-19-4; **3b**, 106191-39-3; **3c**, 106162-11-2; **4**, 75935-37-4; S$_2$Cl$_2$, 10025-67-9.

Supplementary Material Available: Tables of hydrogen atom parameters and important bond angles (3 pages); a table of structure factors (5 pages). Ordering information is given on any current masthead page.