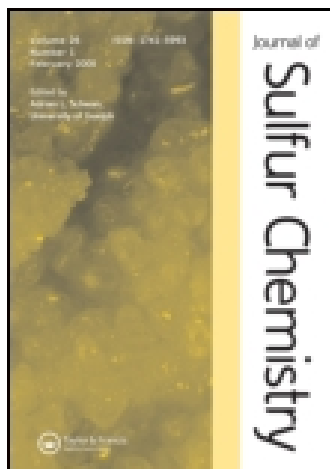


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Quest for diatomic selenium

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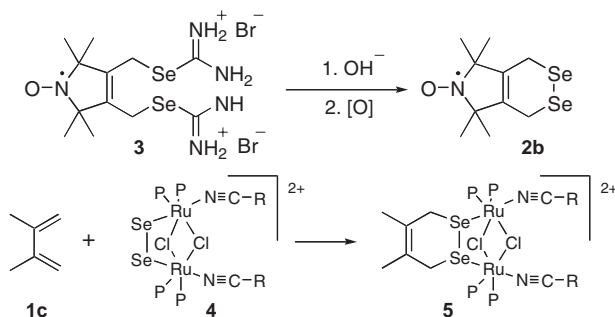
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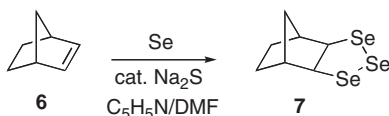
selenium-containing moieties in precursor **3** (**5**). In 2001, Matsumoto and co-workers (**6**) described the addition of diene **1c** to the diselenide ligand stabilized by dicationic ruthenium dichloride dimer **4** to give a coordinated dihydrodiselenin complex **5** (Scheme 1). This 4 + 2 cycloaddition product was obtained analogously to the previously reported dihydrodithiin complex (**7**).



Scheme 1. Dihydrodiselenin formation.

While there are earlier reports about the reaction of elemental selenium with dienes, only the formation of the corresponding selenophenes was observed (**8**);³ there were no reports concerning the underlying mechanism of the selenium transfer.

One of the most interesting approaches to selenium transfer was reported by Dirlikov (**9**). Norbornene was treated with selenium under the conditions mimicking those used for activated sulfur (**10**); norbornene triselenide formed in good yield (Scheme 2). No similar selenium transfer to dienes was reported.

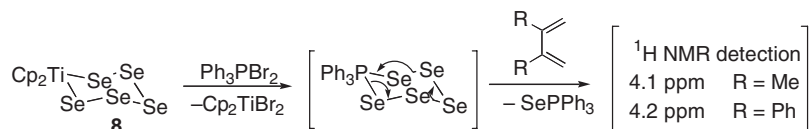


Scheme 2. Norbornene triselenide formation.

2. Results

In anticipation that some of the methodologies developed for the generation of diatomic sulfur might be successful in the elaboration of systems capable of delivering a diatomic selenium entity, Diels–Alder trapping experiments were carried out on appropriate precursors.

Earlier attempts in our laboratory at the *in situ* generation of diatomic selenium by Ph_3PBr_2 -induced fragmentation of titanocene pentaselenide (**8**) in the presence of 2,3-dimethyl-1,3-butadiene (**1c**) were unsuccessful (Scheme 3) (**11**).



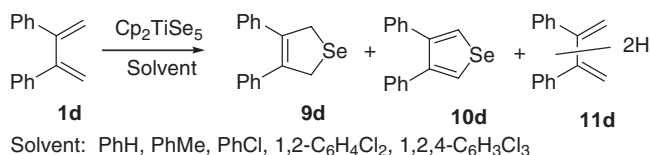
Scheme 3. Attempted trapping of Se_2 .

While ^1H NMR signals at 4.2 ppm for $\text{R} = \text{Ph}$ and 4.1 ppm for $\text{R} = \text{Me}$ were observed, no definite structural conclusions could be made due to rapid decomposition of the product. The difficulties experienced with the generation of diatomic selenium in this fashion to give dihydrodiselenins **2** are disappointing as the analogous sulfur-transfer experiments involving titanocene and zirconocene pentasulfides provided dihydrodithiins in ca. 20% yield (**2d**).

Work from our laboratory demonstrated that both elemental sulfur (**2i**) and metallocene polysulfides (**2j**) could be thermally induced to fragment and to transfer a two-sulfur unit. We anticipated that the analogous thermal fragmentation of elemental selenium and titanocene pentaselenide (**8**) might also lead to the transfer of a two-selenium unit that could be intercepted by a diene trap.

Initially, we attempted to transfer selenium to dienes applying conditions used by Dirlikov (**9**) (Scheme 2). However, even after a 15 h reflux, 2,3-diphenylbutadiene (**1d**) was unreactive. In a comparison with strained norbornene, dienes are significantly less reactive and might require even more vigorous conditions.

In an attempt to thermally transfer selenium, analogous to the reported sulfuration of dienes with metallocene polysulfides, titanocene pentaselenide (**8**) and 2,3-diphenyl-1,3-butadiene (**1d**) were refluxed in various solvents (Scheme 4) (**2j**). The progress of the reaction was monitored by ^1H NMR. Three products usually formed.



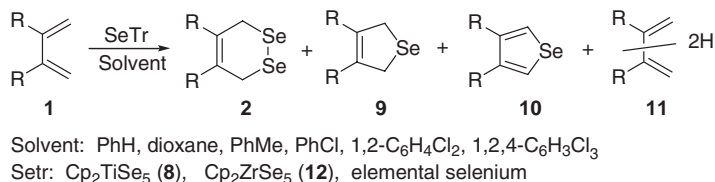
Scheme 4. Sulfuration of dienes with metallocene polysulfides.

Based on ^{13}C and ^{77}Se NMR as well as HRMS, two of these compounds were characterized as 2,5-dihydro-3,4-diphenylselenophene (**9d**) and 3,4-diphenylselenophene (**10d**). In high-boiling solvents, upon continued reflux, the concentration of compound **9d** gradually decreased concomitant with the formation of **10d** with a characteristic ^1H NMR singlet at 7.94 ppm. The third component consisted of varying amounts of mainly disubstituted 1- and some 2-butenes **11d**. Selenophene **10d** had been already reported as a product of the modified Hinsberg ring-closure reaction (**12**) (involving an α -diketone RCOCOR and bis[(alkoxycarbonyl)-methyl]selenanes $\text{R}'\text{CO}_2\text{CH}_2\text{SeCH}_2\text{CO}_2\text{R}'$) followed by decarboxylation.

Apparently, during the selenium transfer, some polymeric material formed as well as indicated by a broad multiplet in the aromatic region. It was also observed that during the reaction, titanocene pentaselenide (**8**) and the analogous zirconocene pentaselenide (**12**) (used to transfer selenium) was converted to an insoluble, black solid likely containing extruded elemental selenium together with polymerized metallocene moieties. Interestingly, the bulk of the reagent disintegrated in ca. 30 min in *o*-dichlorobenzene and even faster in 1,2,4-trichlorobenzene. With the decomposition of compound **8**, we believed it could release some active elemental selenium species, possible in a diatomic form.

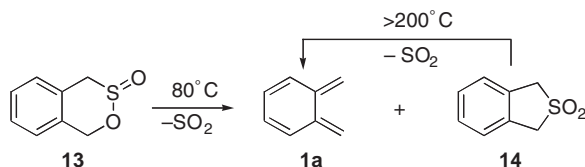
Although we did not observe any diselenin derivative, the mixture of products formed suggested the possibility that it might have had too short a lifetime to form in detectable amounts during the reaction. In order to study this possibility, we have carried out a detailed study using various dienes and selenium-transfer reagents.

Six different dienes were tested in refluxing solvents at various conditions (Scheme 5). It is interesting that the variety of products, *e.g.* diselenins **2**, selenophenes **10**, monoselenides **9** and dihydrobutadienes **11**, depend chiefly on the character of the diene and to a lesser extent on the nature of the selenium-transfer reagent (SeTr).



Scheme 5. Diene-selenium transfer reactions.

One of the dienes, 5,6-dimethylene-cyclohexa-1,3-diene (**1a**) is unstable and had to be generated *in situ* (Scheme 6). Usually, the corresponding sultine **13**, sulfone **14** or cyclobutene has been used for this purpose. Sultine **13** is a very convenient source of **1a** as upon a loss of SO₂ it converts to **1a** when heated at temperatures above 80°C (**13**). The reaction is not completely clean as sulfone **14** is formed (either from the reinsertion of SO₂ or internal rearrangement) as well as some unidentified side products. The other two sources of **1a** deliver the diene upon thermolysis at temperatures above 200°C making them incompatible with thermally unstable diselenium adducts. We have verified the reactivity of compound **14** at temperatures of 200°C and higher observing formation of ca. 20% of the corresponding monoselenide **9a** and no trace of dihydrodiselenin **2a** (**14**).⁴

Scheme 6. Generation of diene **1a**.

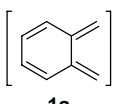

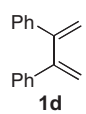

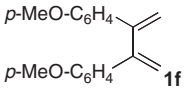
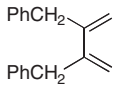
As we were focussed on the formation of Se₂-transfer products, we employed a variety of dienes for this type of reactivity in various solvents at their reflux temperatures. Only in the case of **1a** was the diatomic selenium-transfer product observed.

In fact, trapping took place in almost the whole range of temperatures applied, starting from 80°C in refluxing benzene (Entry 1, Table 1) up to 180°C in refluxing dichlorobenzene (Entry 2), with the best results clearly observed in 110–130°C range (Entries 3 and 4). Once the maximum yield of diselenin **2a** was reached, its concentration started to decrease. The subsequent decomposition of **2a** was so rapid that no trace of it was observed after 10 min in refluxing dichlorobenzene (with monoselenide **9a** present as the only product; Entry 6). Thus, the optimal reaction time under these conditions could only be estimated as shorter than 1 min (Entry 2). In refluxing benzene, a 4% yield of **2a** was obtained only after a 6 h long reflux (Entry 1).

The polarity of solvents did not seem to play a role in the selenium transfer; the use of dioxane resulted in an 8% yield (Entry 5), comparable with those obtained in toluene and chlorobenzene (Entries 3 and 4). Likely, this does not apply to solvents such as DMSO that decompose metallocene pentaselenides. An attempt to employ the selenium-transfer reaction in the latter solvent did not give any selenium-transfer products.

To find the optimal conditions favoring the formation of diselenin **2a**, not only solvents but selenium-transfer reagents were tested as well. Cp₂TiSe₅ was compared with Cp₂ZrSe₅ and with elemental selenium. In refluxing toluene (higher boiling solvents such as PhCl resulted in an immediate decomposition of zirconocene pentaselenide), the yield of **2a** (Entry 7) was similar to that obtained with titanocene pentaselenide (Entry 3; 11% and 8% yields, respectively). An

Table 1. Selenium transfer to diene with Cp₂TiSe₅ (**8**), Cp₂ZrSe₅ (**12**) and elemental selenium.

Dienes 1	Entry	SeTr	Optimized time (min)	Solvent	Yield (%)		
					2	9	11
 1a	1	Cp ₂ TiSe ₅	360 ^a	PhH	4	7	–
	2	Cp ₂ TiSe ₅	< 1 ^a	C ₆ H ₄ Cl ₂	ca. 5	ca. 15	–
	3	Cp ₂ TiSe ₅	30 ^a	PhMe	11	17	–
	4	Cp ₂ TiSe ₅	10 ^a	PhCl	11	14	–
	5	Cp ₂ TiSe ₅	60 ^a	Dioxane	8	11	–
	6	Cp ₂ TiSe ₅	10 ^b	C ₆ H ₄ Cl ₂	–	20	–
	7	Cp ₂ ZrSe ₅	30 ^a	PhMe	8	13	–
	8	Se	10 ^a	PhCl	2	26	–
	9	Cp ₂ TiSe ₅	5 + 1 ^c	PhCl	16	15	–
	10	Se	5 + 1 ^c	PhCl	6	23	–
 1c	11	Cp ₂ TiSe ₅	300	C ₆ H ₃ Cl ₃	–	1	–
	12	Se	300	C ₆ H ₃ Cl ₃	–	2	–
 1d	13	Cp ₂ TiSe ₅	240	C ₆ H ₄ Cl ₂	–	9	23
	14	Cp ₂ TiSe ₅	60	C ₆ H ₄ Cl ₂	–	10	29
	15	Se	100	C ₆ H ₃ Cl ₃	–	25	2
	16	Cp ₂ TiSe ₅ /Se	240	C ₆ H ₃ Cl ₃ , C ₆ H ₄ Cl ₂	–	9	22
 1e	17	Cp ₂ TiSe ₅	240	C ₆ H ₄ Cl ₂	–	1–2	–
	18	Se	240	C ₆ H ₄ Cl ₂	–	2	–
 1f	19	Cp ₂ TiSe ₅	60	C ₆ H ₃ Cl ₃	–	6	19
	20	Se	30	C ₆ H ₃ Cl ₃	–	15	2
 1g	21	Cp ₂ TiSe ₅	30	C ₆ H ₃ Cl ₃	–	13	34
	22	Cp ₂ TiSe ₅	240	C ₆ H ₄ Cl ₂	–	11	33
	23	Cp ₂ ZrSe ₅	240	C ₆ H ₄ Cl ₂	–	15	29
	24	Se	130	C ₆ H ₃ Cl ₃	–	27	15

Notes: ^aGeneration of **1a** from **13**. ^bGeneration of **1a** from **14** in a microwave oven. ^cSlow addition of the **1a** precursor to a refluxing solution of SeTr.

analogous reaction with elemental selenium carried out in chlorobenzene gave only 2% of **2a** (Entry 8).

In another experiment, we refluxed titanocene pentaselenide in chlorobenzene adding a solution of sultine **13** over a period of 5 min followed by additional 1 min reflux (Entry 9). Indeed, the yield of diselenin **2a** increased from 11% to 16%.

By an analogous procedure with elemental selenium instead of titanocene pentaselenide, we obtained a 6% yield of **2a** when compared with 2% obtained under standard conditions (Entry 10).

The formation of diselenin **2a**, the desired product of the selenium transfer, was adversely affected by the formation of analogous monoselenide **9a**. With metallocene pentaselenides, **9a** and **2a** were usually present in a 1.5:1 ratio, except for Entry 9 with a slow addition of **13**, where **2a** was slightly predominant. The **9a** to **2a** ratio was considerably higher (13:1 to 4:1) for reactions with elemental selenium (Entries 8 and 10). While we cannot entirely account for this negative

correlation linking monoselenide **9c** with diselenin **2a**, we have determined that the conversion of **9c** to **2c** does not occur under the reaction conditions.

Interestingly, no formation of diselenins was observed with any of the other dienes. Although examined under a variety of conditions, they converted to the corresponding monoselenides. The reactivity of the dienes varied significantly. Two of them, **1c** and **1e**, were practically unreactive toward the selenium-transfer reagents regardless of the reaction conditions (the use of a large excess of diene, SeTr or extended reaction times; Entries 11 and 12 and 17 and 18, respectively). While **1c** reacted better in trichlorobenzene, refluxing diene **1e** in this solvent resulted in its disappearance and no product formed at all. Corresponding monoselenides **9c** and **9e** were isolated in 1–2% yields only; no other products were detected.

Selenium transfer to dienes **1d**, **1f** and **1g**, however, was significantly faster. With metallocene pentaselenides, even in times as short as 4 h, dienes were completely converted to products. Although their reaction rates were low in refluxing chlorobenzene (*e.g.* an overnight reaction yielded only 2–3% of **9d**), the reaction temperature could be safely raised. Thus, increasing it from 180°C to 220°C shortened the reaction times from 5 to 6 h (Entries 13, 16, 22 and 23) to 30–60 min (Entries 14, 15, 19, 20, 21 and 24). The distribution of products was not affected by this change.

The formation of three products, monoselenides **9**, selenophenes **10** and butenes **11**, was another characteristic feature of the selenium transfer to **1d**, **1f** and **1g**. A typical pattern of this reaction is shown in Figure 1 with the example of 2,3-di(*p*-methoxyphenyl)butadiene (**1f**). This diene was selected for illustrative purposes as its reaction rate with elemental selenium is the fastest and allows for a complete conversion (selenophene and butenes as the final products) in a reasonable (10 h) time. Its unsubstituted 2,3-diphenylbutadiene analog (**1d**) requires days for this reaction to complete.

Initially, the rapid formation of monoselenide **9f** occurs. Compound **9f** is thermally unstable and converts to selenophene **10f** and dihydrobutadienes **11f**. Selenophene **10f** forms at a rate roughly comparable to that of butenes **11f**. The yields are relatively low, mainly due to polymerization that occurs to a significant extent. Indeed, an oily fraction characterized by multiple peaks with chemical shifts characteristic for the methoxy group was separated by column chromatography. Only later, when butenes slowly polymerize, does selenophene **10f** become the most prominent component of the reaction mixture. We have verified that the amount of selenium employed does

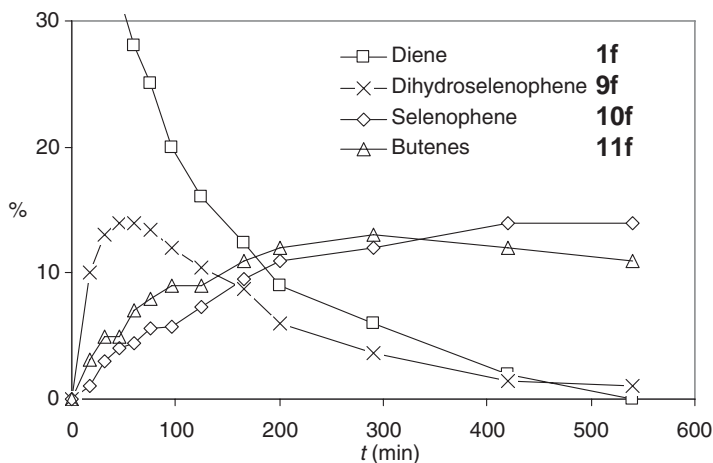


Figure 1. Selenium transfer to 2,3-di(*p*-methoxyphenyl)butadiene (**1f**) with elemental Se.

not change the reaction outcome provided that an excess is used. Similar behavior was observed for other selenium-transfer reaction of dienes **1d** and **1g** with elemental selenium as a SeTr.

Quite a different pattern is observed when metallocene pentaselenides are used as SeTr. A comparison of the efficiency of selenium transfer to diene **1d** with elemental selenium and titanocene pentaselenide is shown in Figure 2.

In both cases, significantly higher yields of **9d** are observed mainly because diene **1d** does not undergo polymerization as easily as **1f**. In general, the pattern observed for **1d** with elemental selenium parallels that of **1f**. This pattern is, however, almost completely reversed with Cp_2TiSe_5 as the SeTr. In this situation, butene **11d** becomes the main product and the yield of monoselenide **9d** does not even grow above 10%. In both cases, small amounts of selenophene **10d** form but they were not shown for clarity. Apparently, the formation of **11d** is from a primary reaction with titanocene pentaselenide.

Selenium transfer to 2,3-dibenzylbutadiene (**1g**) with elemental selenium gave monoselenide **9g** in a similar yield (27%), as observed in an analogous reaction of diene **1d**; however, the amount of corresponding butenes was by far higher (15% instead of 2%). The analysis of hydrogen-transfer products formed in this case suggests that the methylene protons from the benzylic moieties might have been the hydrogen source.

In an attempt to optimize selenium transfer, titanocene pentaselenide was used in varying amounts. The results are shown in Figure 3.

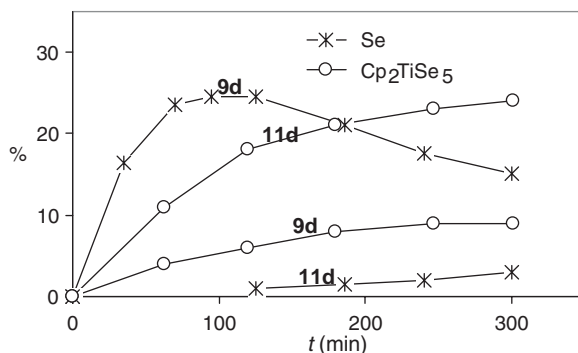


Figure 2. Comparison of selenium transfer to 2,3-diphenylbutadiene **1d** with elemental selenium (4 equivalents, *) and titanocene pentaselenide (0.25 equivalents, ○) in refluxing dichlorobenzene.

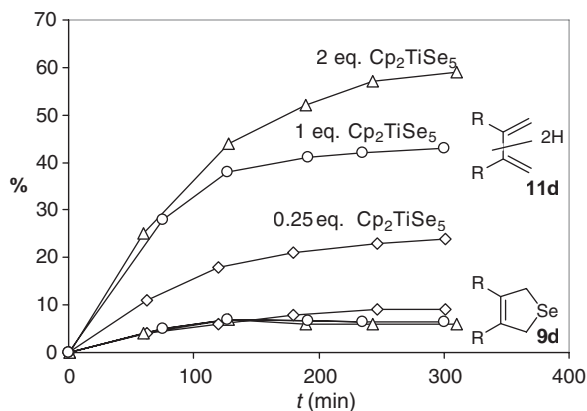


Figure 3. Distribution of monoselenide **9d** and butenes **11d** as a function of the amount of Cp_2TiSe_5 .

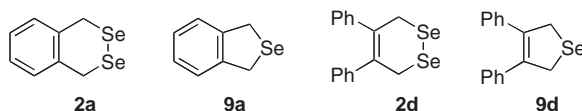
Contrary to expectations, no increase in the formation of monoselenide **9d** was observed when more and more titanocene pentaselenide was used. Indeed, its concentration does not exceed 10%. On the other hand, it is obvious that the formation of butenes **11d** is positively correlated with the amount of SeTr. A reasonable yield (60%) of partially hydrogenated butadiene forms with two equivalents of Cp_2TiSe_5 in 5 h.

The only likely source of hydrogen atoms available to dienes **1** is the SeTr itself. Both titanocene and zirconocene pentaselenides (**8** and **12**) decompose very rapidly under the reaction conditions to produce an insoluble black precipitate. In an attempt to quench this decomposition, the selenium transfer to diene **1d** was carried out in refluxing dichlorobenzene with a mixture of 0.25 equivalents of titanocene pentaselenide and elemental selenium. The results were virtually the same as observed with titanocene pentaselenide alone.

2.1. Possible intermediates in the selenium transfer

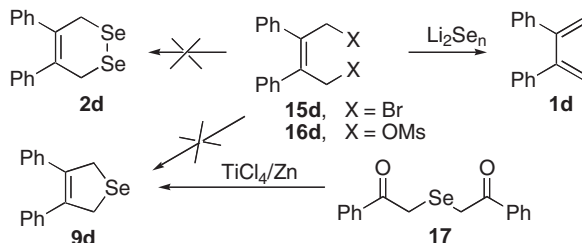
Analysis of the selenium-transfer products did not reveal the presence of any dihydrodiselenin product. This is not surprising, as unsubstituted 1,2-diselenins **2** are considered an unstable class of compounds. This inherent instability corroborates our inability to observe any diselenium cycloadduct **2** in our thermally induced selenium-transfer reactions.

It is reasonable, however, that diselenins in fact form, but convert immediately to some secondary products. To verify this hypothesis, we prepared *o*-phenylene diselenin (**2a**), selenaindan (**9a**) and their phenyl-substituted analogs **2d** and **9d**.



The preparation of **2d** started with the reduction of 2,3-diphenylmaleic anhydride to 2,3-diphenylbut-2-ene-1,4-diol via 3,4-diphenyl-2(5H)-furanone as described by Urove and Welker (15). However, the reduction of 3,4-diphenyl-2(5H)-furanone to 2,3-diphenylbut-2-ene-1,4-diol was problematic and even after some modifications, only a 35% yield was achieved. The diol was easily brominated to (*Z*)-1,4-dibromo-2,3-diphenylbut-2-ene-1,4-diol (**15d**) with PBr_3 (15).

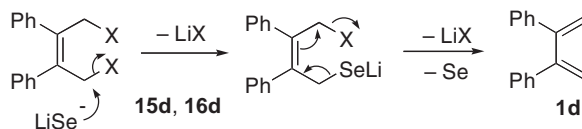
The attempted cyclization of dibromide **15d** with Li_2Se , readily prepared from the reaction of elemental selenium with 2.1 equivalents of Super-Hydride© in THF at 0°C (16), did not provide the expected monoselenide **9d**, but instead, diene **1d** formed in 65% yield (Scheme 7).



Scheme 7. Attempted cyclization of dibromide **15d**.

We anticipated that the substitution of the bromine atom with non-halide leaving groups such as mesylate would circumvent the elimination reactions from taking place. However, the addition of a THF solution of mesylate **16d** to a freshly prepared THF suspension of Li_2Se once again

did not afford the desired monoselenide **9d**; diene **1d** was the main component of the reaction mixture (Scheme 8).



Scheme 8. Attempted monodeselenation of **16d**.

The formation of diene **1d** was not entirely unexpected knowing the ability of selenides and tellurides to dehalogenate vicinal dihalides (*17*) and dimesylates (*18*) to give the corresponding olefins. The likely mechanism of dehalogenation of the 1,4-dibromo-2-butene derivative **15d** is shown in Scheme 8.

We were eventually able to prepare diselenin **2d** from 1,4-diselenocyanato-2,3-diphenylbut-2-ene (**18d**) when treated with sodium methoxide. Interestingly, the choice of solvent played an important role in this preparation. The use of methanol resulted in a significant (up to 60%) formation of the corresponding diene **1d** but with benzene this unfavorable side reaction was limited to ca. 20%. Thus, although the method was not completely optimized, we were able to isolate compound **2d** in 45% yield.

Recrystallization of the crude material from methylene chloride hexanes yielded well-formed crystals. A single-crystal X-ray crystallography provided an insight into the structure of the dihydrodiselenin **2** (Figure 4). To our knowledge, this is the first time a dihydrodiselenin has been characterized crystallographically. To gain better insight into the factors responsible for instability of **2**, we have compared them with independently prepared corresponding dihydrodithiin **20** (Figure 5).

There are two interesting aspects that emerge upon comparison of the structures in Figures 4 and 5. First, diselenin **2d** has an unusually small dihedral angle C–Se–Se–C, ca. 12° in comparison to a much bigger ca. 64° value observed for its sulfur analog **20**. Secondly, a ca. 3.5° value observed for the C2–C1–C4–C3 dihedral angle in **2d** is significantly bigger than an analogous value, ca. 0.47°, observed for compound **20**.

Additionally, the Se–Se bond (2.36 Å) is slightly longer than the average value observed for both linear and cyclic diselenides (Table 2) (*19*). The above data suggest an existence of a substantial strain in the molecule of dihydrodiselenin **2d**.

Our attempts at developing a novel synthetic route to the dihydrodiselenophene **9d** ring system (centered on a double nucleophilic displacement strategy) were unsuccessful; compound **9d** was

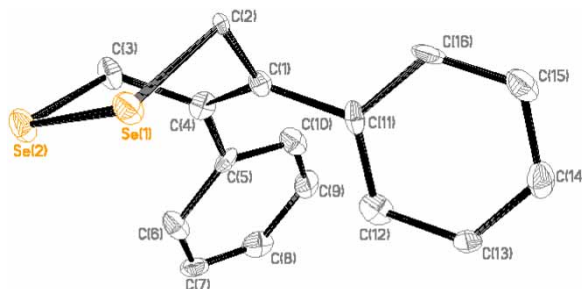


Figure 4. The X-ray structure of diselenin **2d**. Selected bond lengths (Å): Se1–Se2, 2.361(2); Se1–C2, 1.984(9); C1–C4, 1.35(1); C1–C2, 1.52(1); selected angles (°): C2–Se1–Se2, 94.7(2); C2–Se1–Se2–C3, 11.8(4); C2–C1–C4–C3, 3.5(1).

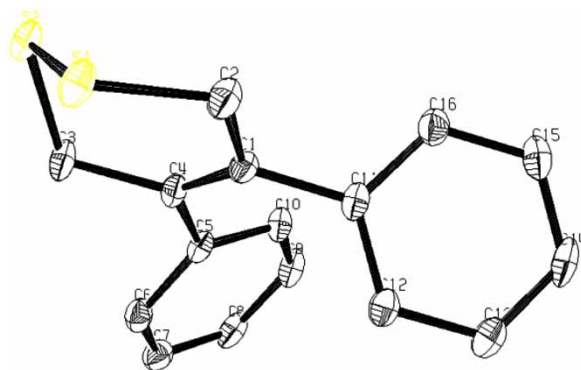
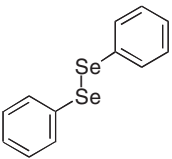
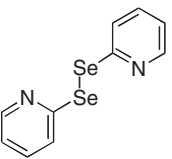
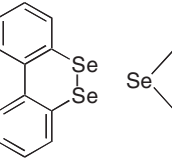
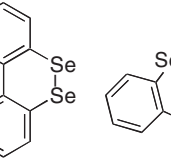
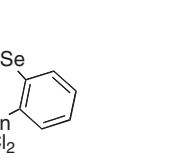


Figure 5. The X-ray structure of dithiin **20**. Selected bond lengths (Å): S1–S2, 2.039(1); S1–C2, 1.803(3); C1–C4, 1.341(4); C1–C2, 1.521(3); selected angles (°): C2–S1–S2, 97.5(1); C2–S1–S2–C3, 63.7(1); C2–C1–C4–C3, –0.5(4).

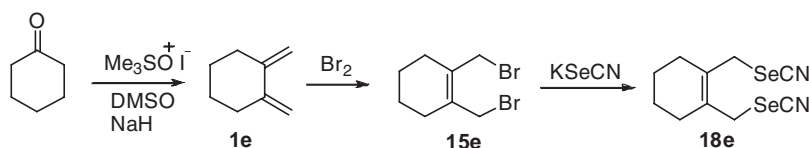
Table 2. The Se–Se bond lengths and dihedral angles for selected cyclic diselenides.

Diselenide					
Se–Se bond length (Å)	2.29 ^{20a}	2.30 ^{20b}	2.35 ^{20c}	2.32 ^{20c}	2.31 ^{20b}
C–Se–Se–C dihedral angle (°)	97	84.3	59.3	—	98.2

finally prepared from compound **17** following a useful procedure published by Nakayama *et al.* (20) (Scheme 7).

Another approach was chosen to prepare diselenin **2a** with 1,2-bis-selenocyanatomethylbenzene (**18a**) used as a substrate. Compound **18a** was synthesized from the corresponding diol via bromination with PBr₃ and finally a substitution with KSeCN.

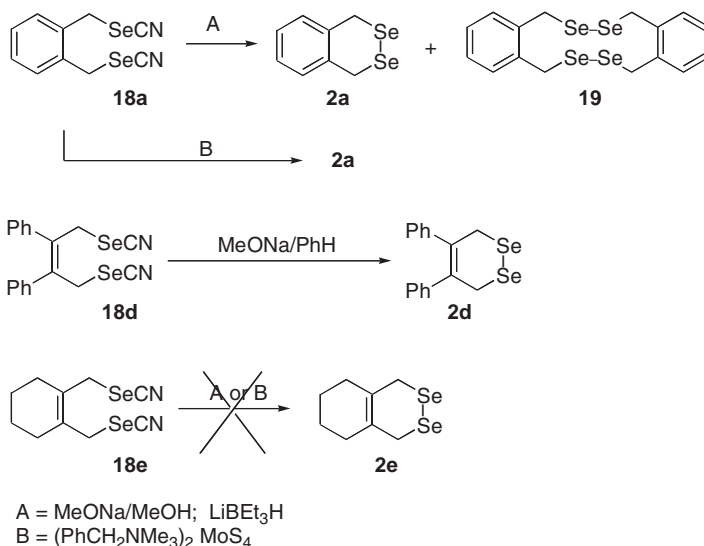
Compound **18e** was prepared in a similar sequence of reactions involving the bromination of diene **1e**, with the substitution of bromine in **15e** with the selenocyanate anion (Scheme 9). An interesting one-step conversion of ketones to dienes with trimethylsulfoxide iodide and sodium hydride approach was applied as reported by Yurchenko *et al.* (21). Although, diene **1e** was isolated in lower than the reported yield, the following conversions were almost quantitative.



Scheme 9. Preparation of selenocyanate **18e**.

Sato and coworkers (22a) reported the isolation of dimer **19** instead of the expected diselenin **2a**. In our hands, the cyclization of 1,2-benzene dimethylselenocyanate (**18a**) with sodium methoxide

in methanol and with Super-Hydride© followed by air oxidation produced an inseparable mixture of a compound with a ^1H NMR signal at 3.95 ppm and dimer **19** (Scheme 10).



Scheme 10. Attempted formation of **2e**.

A new methodology involving the coupling of selenocyanates using thiomolybdates to give diselenides (**23**) allowed us to prepare diselenin **2a**, although in modest yield (Scheme 10). Diselenin **2a** (aforementioned compound characterized by a singlet at 3.95 ppm) is an orange solid; it can be stored at room temperature.

Unfortunately, all attempts to prepare diselenin **2e** from selenocyanate **18e** using methods applied to prepare **2d** and **2a** were unsuccessful; complex mixtures were formed.

The preparation of 1,2-benzo[*c*]dihydroselenophene (**9a**) was accomplished without difficulty. 1,2-Bis-bromomethyl-benzene (**15a**) reacted easily with lithium selenide to give the desired product.

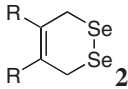
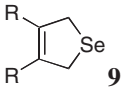
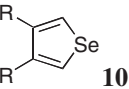




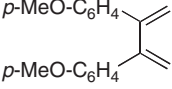
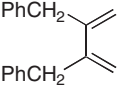
All of our selenium-containing compounds were characterized by ^{77}Se NMR. The values are given in Table 3. The differences in chemical shifts of diselenins (300–350 ppm), monoselenides (100–150 ppm) and selenophenes (550–600 ppm) warrant using ^{77}Se NMR as a diagnostic tool in the detection of other selenium species.

2.2. Elucidation of the mechanism of the selenium transfer

The thermal fragmentation of metallocene pentaselenides in the presence of dienes **1** was repeated using a range of solvents such as benzene, toluene and chlorobenzene, 1,2-dichlorobenzene and 1,2,4-trichlorobenzene. ^1H NMR analyses of the reaction mixtures carried out in those solvents showed no trace of the characteristic diselenide signal expected at ~ 3.90 ppm. Even dibenzylbutadiene requiring milder conditions for the selenium transfer gave negative results.

Aware of the inherent instability of the 1,2-diselenin-ring system as being incompatible with the rather harsh reaction conditions (refluxing at 180°C) involved in the thermal fragmentation of titanocene pentaselenide (**8**), we wished to find some other evidence that the elusive diselenins **2** form during the selenium transfer. In addition, we hoped to determine the likely path in which the diselenins disintegrated. Three paths, *i.e.* direct conversion to selenophene **10** involving a loss

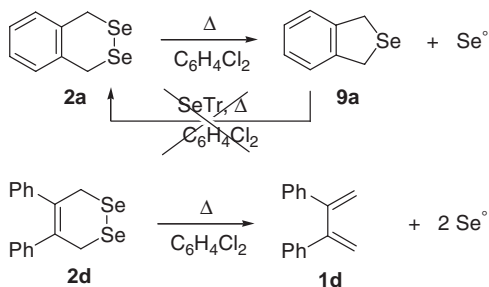
Table 3. ^{77}Se NMR shifts of selenium-transfer products.

Compound				
	1a	308.4	152.8	–
	1c	–	89.8	–
	1d	346.2	105.8	584.5
	1e	–	98.0	–
	1f	–	96.9	574.8
	1g	–	95	556.5

of a molecule of H_2Se from diselenin **2**, a ring contraction involving the extrusion of elemental selenium or a complete loss of selenium in a reverse Diels–Alder reaction to give diene **1** are reasonable.

Thus, independently prepared samples of diselenins **2d** and **2a** were refluxed in 1,2-dichlorobenzene. The NMR analysis of the reaction mixtures revealed that diselenin **2d** was converted to the corresponding diene **1d** immediately when reflux started.

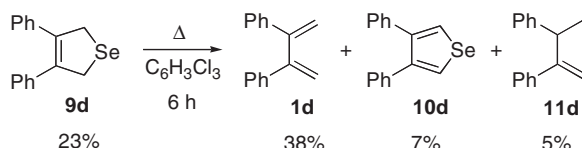
Interestingly, diselenin **2a** was much more stable and even after 1 h reflux, some of this compound was present in the solution although most of it converted to the corresponding 1,3-benzo[c]dihydroselenophene (**9a**) along with some unidentified products (Scheme 11). In the decomposition of **2d**, a rapid succession of colors was observed; the original orange color became

Scheme 11. Decomposition of **2d**.

brown and changed to yellow with the formation of black elemental selenium. The intermediary brown color likely corresponds to some selenium species formed in the reverse Diels–Alder reaction. The analogous reverse Diels–Alder reaction of dihydrodiselenin **2a** is not easily achieved as a destabilized diene would form. Thus, the alternative path involving the extrusion of one selenium atom resulting in the formation of **9a** is predominant. On the other hand, no trace of diselenin **2a** was observed upon treatment of **9a** with pentaselenide **8**. In fact, the opposite reaction occurs; the treatment of diselenin **2a** with pentaselenide **8** in refluxing dichlorobenzene results in a complete decomposition of **2a** in 30 min.

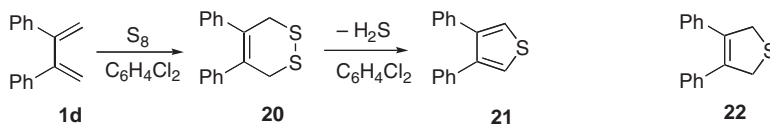
The observed behavior is consistent with the instability of diselenins and opens the possibility that diselenins might indeed have been formed as a result of the Se₂ trapping.

It was established that during the selenium transfer to dienes, the concentration of dihydroselelenophenes slowly decreases even further, concomitant with the formation of selenophenes. To learn more about this conversion, a separate experiment involving independently prepared 1,5-dihydro-3,4-diphenylselenophene (**9d**) was carried out in refluxing 1,2,4-trichlorobenzene (Scheme 12). Only 33% of the starting material remained after 3 h of reflux with the corresponding diene being the main product and ca. 5% of both selenophene **10d** and butene derivative **11d**. After an additional 3 h, only 23% of the initial dihydroselelenophene was left, with the diene at a steady level and concentrations of selenophene **10d** and 1-butene **11d** slightly increased. Apparently, dihydroselelenophene **9d** is not stable at high temperatures and this is why it formed in low yield if the selenium transfer was carried out in refluxing trichlorobenzene. Likely, the decomposition was accompanied by polymerization, decreasing the yield of monomeric species.



Scheme 12. Decomposition of selenophene **9d**.

The much higher thermal stability of dihydroselelenophene **9d** compared with that of the corresponding diselenin **2d** is surprising considering the results observed with sulfur transfer to dienes. Dihydrodithiin **20**, the sulfur analog of **2**, usually is trapped in a relatively high yield. It can be easily isolated and appears to be more stable. To verify if this stability would hold under the selenium-transfer conditions, sulfuration of diene **1d** was carried out under conditions used for selenium transfer. Thus, a solution of diene **1d** and elemental sulfur was refluxed in trichlorobenzene (Scheme 13).



Scheme 13. Reaction of **9d** with elemental sulfur.

Diene **1d** reacted completely after 2 h to form 58% of the corresponding thiophene **21** as well as 15% of 1-butene derivative **11d**. Sampling during the reaction revealed, however, that disulfur adduct **20** was at times the dominant species with only small amounts of the corresponding monosulfide adduct **22**.

3. Discussion

In this paper, we describe for the first time the generation and trapping of a diatomic selenium species. Although this result is exciting, there are numerous limitations characteristic of our approach to the selenium transfer. They apply not only to diselenins but to dihydroselenophenes as well (the best isolated yields below 30%).

In our attempts to optimize the selenium-transfer reaction, we have modified the reaction conditions using various SeTrs and dienes. We have studied the properties of the selenium-containing product as well. A rationale follows for the gathered observations.

Three sources of selenium, elemental selenium, titanocene pentaselenide (**8**) and zirconocene pentaselenides (**12**), were used. Both metallocene pentaselenides are much more soluble in organic solvents than elemental selenium. This advantage, however, disappears at high temperatures required for dienes to trap selenium; pentaselenides decompose rapidly before any efficient selenium transfer occurs. Indeed, when decomposing, the metallocene moieties dramatically enhance side reactions by providing a source of hydrogen. Only for *in situ*-generated 5,6-dimethylene-cyclohexa-1,3-diene (**1a**) requiring temperatures 80–130°C was this process negligible. On the other hand, the use of much less stable (expected to provide an easier access to diatomic selenium) zirconocene pentaselenide (**12**) was ineffective, likely caused by the fast decomposition of the SeTr.

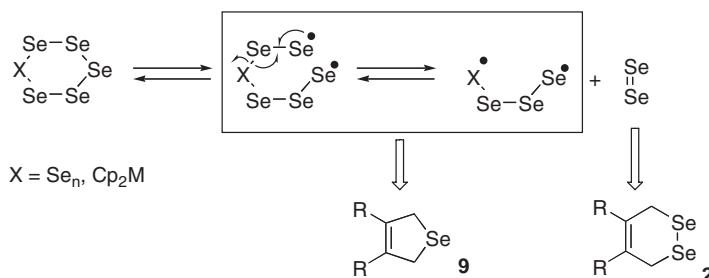
The low solubility of elemental selenium had the biggest impact on the selenium transfer yield at low temperatures (reaction with **1a**) where the results were much lower than those with metallocene pentaselenides. At high temperatures, the solubility of elemental selenium was sufficient to provide yields of selenium transfer higher than those observed with pentaselenide derivatives. This positive result was likely due to the prevalence of the steady concentration of an available selenium species during the course of the reaction (no decomposition leading to the disappearance of SeTr and side reactions).

Three groups of dienes were tested as selenium acceptors: 2,3-dimethyl- (**1c**) and 2,3-dibenzyl- (**1g**) butadienes (both with aliphatic substituents), 2,3-diphenylbutadiene (**1d**) and its *p*-methoxy derivative (**1f**). Finally, two cyclic butadienes were employed: 5,6-dimethylene-cyclohexa-1,3-diene (**1a**) and 1,2-dimethylene-cyclohexane (**1e**). Interestingly, the structural similarity between dienes, as between **1a** and **1e** had no impact on the result. Indeed, the volatility of the dienes and their reactivity seemed to control the outcome of the selenium transfer. Three non-volatile dienes, **1d**, **1f** and **1g** reacted in a very similar pattern, producing dihydroselenophenes, butenes and some selenophenes. *p*-Methoxy substitution of **1f** resulted only in a faster rate of polymerization when compared with **1d**. Results obtained with 2,3-dibenzylbutadiene (**1g**) did not resemble those with 2,3-dimethylbutadiene (**1c**) for which at most a 2% yield of monoselenide was observed and no other products formed (except for some polymeric species).

The only reasonable explanation for this lack of activity of **1c** might be its incompatibility with selenium-transfer conditions involving temperatures of 180°C and above causing the low-boiling diene **1c** to escape during reflux. A similar effect is probably operative in sulfur transfer where the results for **1c** were inferior to those for **1g**. This is an effect likely attributed to the high volatility of **1c** (2*i*, *j*). The identically low, 2% yield obtained with 1,2-dimethylene-cyclohexane (**1e**) was likely caused by its volatility as well (b.p. 124°C). In spite of similar volatility, 5,6-dimethylene-cyclohexa-1,3-diene (**1a**) gave the best yields of selenium transfer. This might be easily rationalized by its high reactivity. Indeed, diene **1a** was never isolated due to its low stability (it has to be generated *in situ*) and most likely reacts immediately with the selenium species under our conditions.

The use of diene **1a** allowed us to make an interesting observation. The yield and composition of its selenium-transfer products depended on the way its precursor was treated with the SeTrs. When the precursor was slowly added instead of refluxing together with the SeTrs, significantly

more diselenin **2a** formed at the expense of dihydroselenophene **9a**. The same effect was also observed with elemental selenium. The increase in the yield of **2a** might be easily explained assuming that the active diatomic selenium species forms from the SeTr at a relatively slow rate. Thus, the slow addition of the precursor to reflux with the SeTr allows for the Se₂ species to be replenished. Consequently, the formation of the monoselenium adduct **9a** might be independent of the formation of **2a** (Scheme 14). Once formed, however, **2a** decomposes to **9c** and other products.



Scheme 14. Mechanistic proposal for selenium transfer.

Various radical selenium species might contribute to the formation of **9** and **2** (via equilibration giving Se₂). The extent to which both processes occur would likely be difficult to measure due to the extrusion of selenium from **2** and its conversion to **9** and other products at elevated temperatures required for effective selenium transfer.

Low thermal stability of diselenins is a third factor (after the low reactivities of SeTrs and dienes) that thwarted our efforts to deliver a practical path to diselenins. Two diselenins, **2d** and **2a**, that we prepared decomposed very easily at elevated temperatures. Although Se–Se bonds themselves are relatively weak, the thermal instability of diselenin **2d** is likely created by its unusually low, ca. 12° C–Se–Se–C dihedral angle when compared with a much bigger ca. 64° angle in a relatively strain-free molecule of dihydrodithiin **20**. Therefore, it is not surprising that this arrangement destabilizes the molecule by unfavorable Se–Se electronic interactions (Figure 6) and facilitates the observed syn elimination.

Diselenin **2a** is more thermally stable than **2d** (it can survive 1–2 min at temperatures as high as 180°C). Additionally, its decomposition pattern is different – instead of a corresponding diene, dihydroselenophene **9a** forms. It is likely that the higher value of the dihedral angle rather than difficulties in the formation of diene **1a** help explain the result. In spite of a somewhat higher stability of **2a**, obviously there is an intrinsic strain in diselenins that we have studied. This feature is likely the responsible factor comparing with dihydrodithiin **20** (the sulfur analog of **1a**) that requires up to 2 h of reflux in dichlorobenzene to completely convert to a corresponding thiophene **21**.

In an attempt to rationalize the formation of various products during the selenium transfer, a path involving diselenins is proposed (Scheme 15).

Scheme 15 takes into account the instability of diselenins and rationalizes the slow formation of dihydroselenophenes as a result of the low concentration of diselenin **2**. There are two other paths predicting a decrease in the concentration of dihydroselenophene **9**. First, it is depleted by a

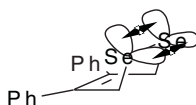
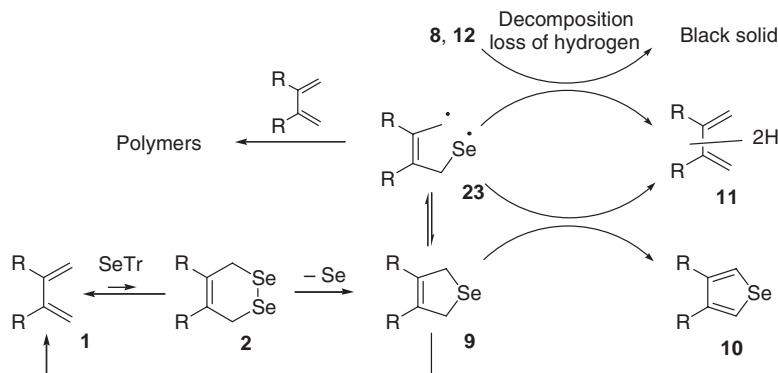


Figure 6. Strain in 4,5-diphenyl-3,6-dihydrodiselenin (**2d**).



Scheme 15. Proposed pathways for the decomposition of **2**.

conversion to the corresponding diene. Another path decreasing the concentration of **9** proceeds via a cleavage of the C–Se bond. The diradical species **23** formed this way might dehydrogenate dihydroselenophene **9** to give selenophene **10** and butenes **11**. It is also likely that the intermediacy of **23** could account for polymerization, decreasing the yield of the products.

In the presence of metallocene pentaselenides, another possibility exists. When thermally fragmented, metallocene pentaselenides appear to deliver not only an active selenium species (possibly Se_2) but also undergo some structural changes converting to a black solid and providing an easily accessible hydrogen source in the process. Hydrogen is trapped by diradical **23** being in equilibrium with dihydroselenophene **9**. Consequently, the formation of butenes **11** might inhibit any effective selenium transfer to dienes, which is observed (Figure 3). This process, although interesting, prevented us from being able to increase the yields of **9**. Indeed, metallocene pentaselenides act as quite efficient hydrogenating reagents regioselectively delivering hydrogen to give mainly kinetically controlled 1,2-addition products.

4. Conclusion

For the first time, diatomic selenium transfer to dienes has been observed. Although the yields of diselenium adduct are low, our detailed study defining the required conditions for the efficient selenium-transfer systems should help develop a new selenium-transfer methodology. The selenium transfer to dienes under our conditions is currently the simplest and most efficient path to dihydroselenophenes.

We have proposed a detailed mechanism accounting for the products and the side products as well as rationalizing the decomposition of SeTrs. It still remains unclear as to the exact nature of the selenium-transfer species as radical entities are very reasonable intermediates in this chemistry. Diene **1a** delivered an apparent Se_2 moiety, although it is possible that a triplet species is responsible. We are hopeful to discover an improved selenium-transfer reagent system to work efficiently at lower temperatures so the isolation of diselenium adducts might routinely be accomplished.

5. Experimental section

5.1. Preparation of 1,2-benzene-3,6-dihydrodiselenin (**2a**)

A solution of 1,2-bis(selenocyanatomethyl)benzene (**18a**, 50 mg, 0.16 mmol) in 0.5 ml of DMF was added to a suspension of benzyltrimethylammonium thiomolybdate $(\text{PhCH}_2\text{NMe}_3)_2\text{MoS}_4$

(180 mg, 0.34 mmol) in 1 ml of DMF. Stirring was continued for 10 min. Then, 5 ml of water was added and the suspension was extracted six times with 2 ml portions of hexanes. The combined extracts were dried using the rotary evaporator and crystallized from hexanes to give 6 mg (0.023 mmol, 14% yield) of an orange solid. Decomp. 92–95°C (change of color from orange to yellow), m.p. 115–128°C. ^1H NMR (CDCl_3) δ 3.95 (s, 4H), 7.29 (m, 4H). ^{13}C NMR (CDCl_3) δ 24.3, 127.8, 128.2, 137.1 ppm. ^{77}Se NMR (CDCl_3) δ 308 ppm. EI-MS: m/z (%): 264 (41, $[\text{M}]^+$). HRMS calcd. for $\text{C}_8\text{H}_8^{80}\text{Se}_2$: 263.89564; found: 263.89569.

5.2. Preparation of 4,5-diphenyl-3,6-dihydrodiselenin (2d)

(*Z*)-1,4-Diselenocyanato-2,3-diphenyl-2-butene (**18d**, 21 mg, 0.5 mmol) was dissolved upon heating in 50 ml of benzene and the solution was cooled to room temperature under nitrogen. Then, a solution of sodium methoxide in methanol (0.5 mmol, 25%) diluted in 10 ml of methanol was added via a syringe. The solution was stirred for 3 h. The solvent was removed, and the residue was extracted with methylene chloride and filtered. Methylene chloride was almost completely removed and methanol was added to the residue. The precipitate was filtered and washed with methanol to give 7 mg (1.92E-5 mol, 38% yield) of orange solid **2d**. Compound **2d** tends to decompose at room temperature but is stable when stored in the freezer. M.p. (decomp.) 85–88°C. ^1H NMR (CDCl_3): δ 3.78 (s, 4H), 7.08–7.13 (m, 10H) ppm. ^{13}C NMR (CDCl_3): δ 28.0, 126.8, 127.9, 129.4, 138.0, 140.8 ppm. EI-MS (no heating, ion source at 80°C) m/z (%): 364 (0.8, $[\text{M}]^+$), 284 (3, $[\text{M}-\text{H}_2\text{Se}]^+$), 206 (100, $[\text{M}-2\text{Se}]^+$). HRMS calcd for $\text{C}_{16}\text{H}_{14}^{78}\text{Se}^{80}\text{Se}$: 363.94338; found: 363.94406.

5.3. Reaction of 1,4-dihydro-benzo[d][1,2]oxathiine 3-oxide (13) with SeTrs: reflux

Sultine **13** (0.1 mmol, 17 mg) was refluxed with an appropriate SeTr in 1 mL of an appropriate solvent. The following quantities of SeTrs were used: 0.12 mmol (69 mg) of **8**; 0.12 mmol (74 mg) of **12** and 0.4 mmol (32 mg) of elemental selenium. The reaction mixtures were analyzed by NMR. The identities of the products **2a** and **9a** were determined by comparisons with separately prepared samples. Yields were determined using bibenzyl as the internal standard.

5.4. Reaction of 1,4-dihydro-benzo[d][1,2]oxathiine 3-oxide (13) with SeTrs: addition and reflux

A solution of compound **13** in 1 ml of PhCl was added over a 5 min period to a refluxed solution of the SeTr (**8**, **12** or elemental selenium) in an appropriate solvent. Once completed, the reaction mixture was additionally refluxed for 1 min and analyzed by ^1H NMR. The identities of the products **2a** and **9a** were determined by a comparison with separately prepared samples. Yields were determined using bibenzyl as the internal standard.

5.5. Reaction of 1,3-dihydro-benzo[c]thiophene 2,2-dioxide (14) with titanocene pentaselenide (8)

Compound **14**, 50 mg (0.3 mmol) and 170 mg (0.37 mmol) of pentaselenide **8** and 4 ml of dichlorobenzene were placed in a 10 ml pressure-resistant glass container. This mixture was then placed in a microwave oven and irradiated with 100–140 W power applied to maintain the temperature 250°C. A sample collected after 10 min and analyzed by ^1H NMR indicated that 20% of dihydro-selenophene **9a** formed.

5.6. Preparative reactions of dienes with SeTrs

A reaction mixture containing one of the SeTrs (elemental selenium (126 mg, 1.6 mmol, not resulting in a fully homogeneous solution) or titanocene pentaselenide (**8**, 58 mg, 0.1 mmol)) and diene (0.4 mmol) in either 1,2,4-trichlorobenzene or 1,2-dichlorobenzene (1 ml) was refluxed for the required time. After cooling, the solution was removed by decantation from solid residues. The residue was additionally washed with a small amount of benzene and the washings were combined with the rest of the liquid. The components of the crude reaction mixture (containing selenophene, butenes and dihydro-selenophenes) were purified by column chromatography without removing the solvent using 0–2% ethyl acetate in hexanes as an eluent. The given yields refer to the amounts of products obtained after chromatography (two chromatographies in the case of selenophenes and butenes due to their similar retention factors). Analytical samples of solid dihydro-selenophenes were obtained by recrystallization from hexanes with activated carbon to remove polymeric species. Selenophenes and solid butenes were recrystallized from hexanes.

5.7. 5,7,1,3-dihydrobenzo[*c*]selenophene (**9a**)

This compound was prepared by a literature method (24).

5.8. 2,5-Dihydro-3,4-dimethylselenophene (**9c**)

Reaction time: 300 min; solvent: C₆H₃Cl₃; SeTr: Se. A five-fold excess of diene **1c** was used. Pungent yellowish oil. Yield 3 mg (0.02 mmol, 2%). ¹H NMR (CDCl₃) δ 1.64 (s, 6H); 3.67 (s, 4H) ppm. ¹³C NMR (CDCl₃) δ g16.1, 35.5, 130.1 ppm. ⁷⁷Se NMR (CDCl₃): δ 89.8 ppm. HRMS calcd. for C₆H₁₀⁷⁶Se: 157.99746; found: 157.99630.

5.9. 2,5-Dihydro-3,4-diphenylselenophene (**9d**)

Reaction time: 90 min; solvent: C₆H₃Cl₃; SeTr: Se. Yield 31 mg (1.1 mmol, 27%). White solid, m.p. 121–122°C. ¹H NMR (CDCl₃): δ 4.27 (s, 4H); 7.21–7.02 (m, 10H) ppm. ¹³C NMR (50 MHz, CDCl₃): δ 35.2, 127.1, 128.2, 128.7, 137.6, 138.1 ppm. ⁷⁷Se NMR (CDCl₃): δ 105.8 ppm. MS (EI) *m/z* (%): 286 (46). HRMS calcd. for C₁₆H₁₄⁸⁰Se: 286.02607; found: 286.02546.

5.10. 1,3,4,5,6,7-Hexahydro-benzo[*c*]selenophene (**9e**)

Reaction time: 180 min; solvent: C₆H₄Cl₂; SeTr: Se. Pungent yellowish oil, yield 4 mg (0.021 mmol, 5%). ¹H NMR (CDCl₃): δ 1.9 (m, 4H), 2.26 (m, 4H); 3.81 (s, 4H) ppm. ¹³C NMR δ g22.7, 27.7, 34.2, 133.0 ppm. ⁷⁷Se NMR (CDCl₃): δ 98 ppm. HRMS calcd. for C₈H₁₂⁸⁰Se: 188.01042; found: 188.00992.

5.11. 3,4-Bis-(4-methoxy-phenyl)-2,5-dihydro-selenophene (**9f**)

Reaction time: 60 min; solvent: C₆H₃Cl₃; SeTr: Se. Yellow solid, yield 18 mg (0.052 mmol, 12%); m.p. 141–142°C. ¹H NMR (CDCl₃): δ 3.74 (s, 6H), 4.21 (s, 4H), 6.68 (d, 4H, *J*_{H–H} = 9 Hz), 6.99 (d, 4H, *J*_{H–H} = 9 Hz). ¹³C NMR (CDCl₃): δ 35.1, 55.1, 113.6, 129.9, 130.7, 136.0, 158.4 ppm.

^{77}Se NMR (CDCl_3): δ 96.9 ppm. EI-MS m/z (%): 346, (92, $[\text{M}]^+$), 265 (100, $[\text{M}-\text{SeH}]^+$); HRMS calcd. for $\text{C}_8\text{H}_{18}\text{O}_2^{80}\text{Se}$: 346.04634; found: 346.04720.

5.12. 3,4-Dibenzyl-2,5-dihydro-selenophene (9g)

Reaction time: 120 min; solvent: $\text{C}_6\text{H}_3\text{Cl}_3$; SeTr: Se. Oil, yield 30 mg (0.052 mmol, 24%). ^1H NMR (CDCl_3): δ 3.61 (s, 4H), 3.73 (s, 4H), 7.15–7.45 (m, 10H) ppm. ^{13}C NMR (CDCl_3): δ 33.4, 36.7, 126.3, 128.4, 128.5, 135.1, 138.9 ppm. ^{77}Se NMR (CDCl_3): δ 95 ppm. HRMS: Calc. for $\text{C}_{16}\text{H}_{12}^{77}\text{Se}$ 311.06505; found: 311.06520

5.13. 3,4-Diphenylselenophene (10d)

Reaction time: 48 h; solvent: $\text{C}_6\text{H}_3\text{Cl}_3$; SeTr: Se. White solid, yield 22 mg (0.077 mmol, 19%); m.p. 106–10°C (lit. 109.5–110.5) (12). ^1H NMR (CDCl_3): δ 7.94 (s, 2H), 7.24–7.11 (m, 10H) ppm. ^{13}C NMR (CDCl_3): δ 126.8, 128.0, 128.8, 129.1, 138.2, 144.5 ppm. ^{77}Se NMR (51 MHz, CDCl_3): δ 584.5 ppm. EI-MS m/z (%): 284 (100, $[\text{M}]^+$), 202 (47, $[\text{M}-\text{H}_2\text{Se}]^+$), 189 (9, $[\text{M}-\text{CH}_2-\text{H}_2\text{Se}]^+$). HRMS calcd. for $\text{C}_{16}\text{H}_{12}^{81}\text{Se}$: 285.01814; found: 285.01825.

5.14. 3,4-Bis-(4-methoxy-phenyl)-selenophene (10f)

Reaction time: 24 h; solvent: $\text{C}_6\text{H}_3\text{Cl}_3$; SeTr: Se. White solid; yield 19 mg (0.056 mmol, 14%); mp. 124–125°C. ^1H NMR (CDCl_3): δ 3.78 (s, 6H), 6.76 (d, 4H), 7.06 (d, 4H), 7.84 (s, 2H) ppm. ^{13}C NMR (CDCl_3): δ 55.3, 113.3, 127.5, 130.0, 130.7, 143.8, 158.2 ppm. ^{77}Se NMR (CDCl_3): δ 574.8 ppm. EI-MS m/z (%): 344, (100, $[\text{M}]^+$), 329 (8, $[\text{M}-\text{CH}_3]^+$); HRMS calcd. for $\text{C}_{18}\text{H}_{16}\text{O}_2^{80}\text{Se}$: 344.03155; found: 344.03055.

5.15. 3,4-Dibenzyl-selenophene (10g)

Reaction time: 48 h; solvent: $\text{C}_6\text{H}_3\text{Cl}_3$; SeTr: Se. White solid, yield 19 mg (0.6 mmol, 15%); m.p. 60–61°C. ^1H NMR (CDCl_3): δ 3.76 (s, 4H), 7.10–7.30 (m, 10H), 7.42 (s, 2H). ^{13}C NMR (CDCl_3): δ 37.1, 126.1, 127.0, 128.4, 128.8, 139.7, 142.5 ppm. ^{77}Se NMR (CDCl_3) δ 556.5 ppm. HRMS calcd. for $\text{C}_{18}\text{H}_{14}^{80}\text{Se}$: 313.04950; found: 313.04955.

5.16. Reactions of dienes with SeTrs in the presence of the internal standard

A reaction mixture containing one of the SeTrs, diene 1 (0.2 mmol) and bibenzyl as the internal standard in 0.5 ml of a solvent was stirred under reflux. Elemental selenium, titanocene pentaselenide (**8**) and zirconocene pentaselenide (**12**) were used as SeTrs in required amounts. The reaction mixture was sampled at regular intervals through a special port at the top of the condenser to maintain an inert atmosphere in the flask. The progress of the reaction was evaluated by ^1H NMR.

5.17. Decomposition of dihydrodiselenins 2a and 2d

A solution of 0.02 mmol of dihydrodiselenin (7 mg of **2d**; 5 mg of **2a**) was refluxed in 0.5 ml of 1,2-dichlorobenzene with 5 mg (0.027 mmol) bibenzyl as an internal standard added. Small samples were analyzed by NMR (CDCl_3) without the removal of solvent.

5.18. Decomposition of dihydroselenophene **9d**

A solution of 11 mg (0.04 mmol) of dihydroselenophene **9d** was refluxed in 0.5 ml of 1,2,4-trichlorobenzene with 7 mg (0.04 mmol) bibenzyl as an internal standard added. Small samples were analyzed by NMR (CDCl₃) without the removal of solvent.

6. Supporting Information Available

¹H NMR, ¹³C NMR and ⁷⁷Se NMR spectra for selected compounds.

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Notes

1. For a more complete list see (2k).
2. The spin states of Se₂ have been theoretically established with the singlet state lower than the triplet by a range of 11.5–16 kcal/mol: see National Institute of Standards and Technology (NSIT), Gaithersburg, MD, 20899–1070. URL: <http://cccbdb.nist.gov/stgap2.asp?casno=12185170&charge=0> (accessed July 20, 2010).
3. For other selenophene-related references see (8c).
4. We have used a microwave oven applying conditions described by Illescas *et al.* (14).

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