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Palladium and platinum catalyzed hydroselenation of alkynes: Se–H vs Se–Se addition to C≡C bond

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Abstract

A mechanistic study of the hydroselenation of alkynes catalyzed by $Pd(PPh_3)_4$ and $Pt(PPh_3)_4$ has shown that the palladium complex gives products of both Se–H and Se–Se bond addition to the triple bond of alkynes, while the platinum complex selectively catalyzes Se–H bond addition. The key intermediate of PhSeH addition to the metal center, namely $Pt(H)(SePh)(PPh_3)_2$, was detected by ^{1}H-NMR spectroscopy. The analogous palladium complex rapidly decomposes with evolution of molecular hydrogen. A convenient method was developed for the preparation of Markovnikov hydroselenation products $H_2C{=}C(SePh)R$, and the scope of this reaction was investigated. The first X-ray structure of the Markovnikov product $H_2C{=}C(SePh)CH_2N^+HMe_2{\cdot}HOOC{-}COO^-$ is reported.

Keywords: Hydroselenation; Vinyl selenide; Platinum complex; Palladium complex; Catalytic reaction; ^{77}Se-NMR

1. Introduction

The transition-metal-catalyzed addition of E–E and E–H bonds to alkynes is an important method of organic synthesis [1–4]. It successfully serves as an initial step in the catalytic heterofunctionalization of organic compounds, highly valuable for the development of various carbon-element frameworks [1]. Vinyl selenides are in demand in both the synthetic organic chemistry [5–8] and material science [9,10].

However, the mechanism of these catalytic reactions is not fully understood and deserves further detailed studies. Much attention has been paid to develop appropriate methodology of S–H [3,11–13] and S–S [1,4,14] addition reactions to alkynes. However, the addition of Se–Se [14,15] and, especially, Se–H [16,17] bonds to alkynes is significantly less studied. In many addition reactions of this type either palladium or platinum complexes are involved. The yields and selectivity of the catalytic processes are dependent on metal and very often are rather difficult to rationalyze [1–17].

Our recent study on the addition of PhSeSePh to C≡C bond has shown that the similar $Pd(PPh_3)_4$ and $Pt(PPh_3)_4$ complexes lead to different intermediates in the catalytic cycle [15]. Palladium catalyzed transformation involves dinuclear complexes (**2**, **3**). In contrast, platinum complexes (**5**, **6**) are mononuclear, and only the unstable *cis*-isomer (**5**) exhibits the desired activity [15] as shown in Scheme 1 (PPh_3 ligand dissociation/association is omitted in the schemes for simplicity reasons). Under reaction conditions platinum complexes quickly lose the catalytic activity due to the isomerization **5**→**6**. Dinuclear chalcogenide complexes of palladium and mononuclear complexes of platinum were also observed in stoichiometric E–E addition and ligand substitution reactions [18–25].

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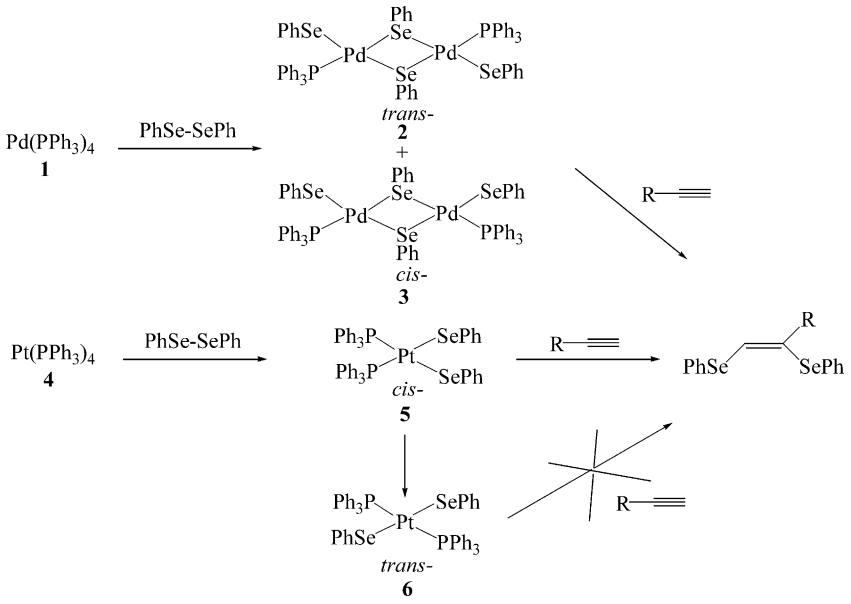


Scheme 1.

Therefore, we decided to investigate platinum and palladium catalyzed addition of PhSeH to alkynes, and to compare the catalytic activity of Pt vs Pd complexes and the mechanism of Se–H vs Se–Se bond addition.

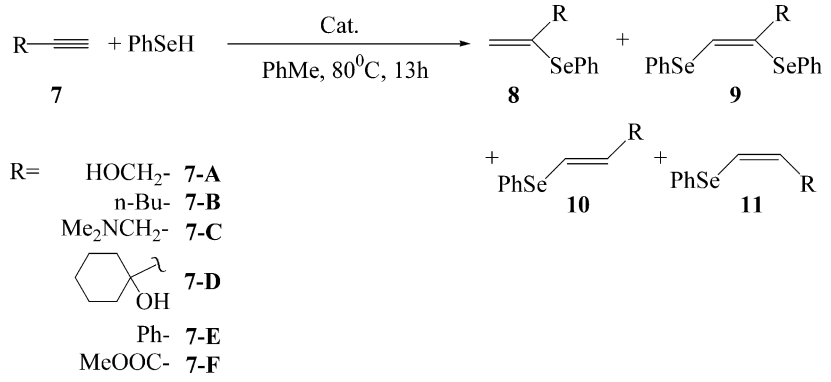
In the present article we report the mechanistic study of transition metal catalyzed PhSeH addition to alkynes. Both Pd- and Pt-catalyzed reactions are described.

2. Results and discussion

Palladium catalyzed addition of PhSH and PhSeH to terminal alkynes is known to occur according to the Markovnikov rule [11–17]. In some cases anti-Markovnikov by-products of *cis*- or *trans*- geometry may be formed as a result of non-catalytic side-reactions. In our study PhSeH addition leads to Markovnikov product (**8**), except for activated alkynes with R = Ph, COOMe (Scheme 2). Performing the reaction without catalyst clearly showed that anti-Markovnikov products (**10**, **11**) are formed in a non-catalytic addition (Table 1). For activated alkynes the side reaction leading to **10** and **11** is fast compared to catalytic transformation and we were unable to obtain Markovnikov products in a good yield (Table 1, No. 5, 6). In the other cases (**7A**–**7D**) in palladium catalyzed reaction both the Markovnikov product **8** and bis-selenide **9** were detected. The structures of the products were determined using 2D ^{1}H-^{77}Se HMQC, NOESY and LR-COSY NMR experiments. The use of platinum catalyst with the same set of alkynes (**7A**–**7D**) leads to the formation of **8** and Ph_2Se_2 (Table 1).

The most interesting feature of the studied system is the presence of both mono- and bis-seleno substituted products (**8** and **9**, respectively) in comparable yields for palladium catalyzed transformation while with platinum catalyst the reaction is highly selective and yields only **8** (Table 1, No. 1–4).

To clarify the reaction mechanism we have undertaken ^{31}P- and ^{1}H-NMR study of the $Pd(PPh_3)_4$–PhSeH



Scheme 2.

Table 1
The yields [a] (in %) of PhSeH addition reaction to alkynes under various conditions

No	Alkyne	$Pd(PPh_3)_4$ catalyzed **8**:**9**:**10**:**11**	$Pt(PPh_3)_4$ catalyzed [b] **8**:**9**:**10**:**11**	Non-catalyzed **8**:**9**:**10**:**11**
1	**7A**	20:36:0:0	60:0:0:0	0:0:0:0
2	**7B**	49:25:0:0	60:0:0:0	0:0:0:0
3	**7C**	42:42:0:0	55:0:0:0	0:0:0:0
4	**7D**	40:40:0:0	51:0:0:0	0:0:0:0
5	**7E**	19:0:19:62	21:0:13:62	0:0:17:63
6	**7F**	0:15 [c]:18:67	0:3 [c]:10:70	0:0:7:73

Heated at 80 °C for 13 h in toluene solutions, see Section 4 for details.
[a] Determined by NMR spectroscopy and calculated according to PhSeH conversion.
[b] Ph_2Se_2 is also obtained in 20–25% yield.
[c] Mixture of *E*/*Z* isomers see Ref. [15] for details.

system in benzene-d_6 at room temperature. $^{31}P\{^1H\}$-NMR spectrum showed $\delta = 28.2$ and 26.8 ppm peaks with the relative ratio of about 3:1, which correspond to *trans*- and *cis*-isomers of dinuclear complex (**2**, **3**) [15]. The other signals in the spectrum were: 25.0 ppm ($OPPh_3$), 22.3 ppm and −4.6 ppm (PPh_3). Thus, in reaction of PhSeH with $Pd(PPh_3)_4$ the same intermediate complexes are formed as in the oxidative addition of PhSeSePh to $Pd(PPh_3)_4$. Since we have shown that dinuclear complexes (**2**, **3**) catalyze the addition of diphenyl diselenide to alkynes [15], this observation explains why product **9** is formed under the catalytic conditions.

Upon the addition of palladium complex colorless PhSeH solution rapidly darkened and gas evolution was observed. In ^{1}H-NMR spectrum the signal at $\delta = 4.5$ ppm corresponding to H_2 dissolved in benzene was detected (Fig. 1A, literature data [26]: $\delta \approx 4.5$ ppm in toluene-d_8). The hydrogen signal disappears after purging the solution with argon in NMR tube (Fig. 1B). An additional check has been performed with the authentic sample of H_2 dissolved in benzene-d_6 (Fig. 1C).

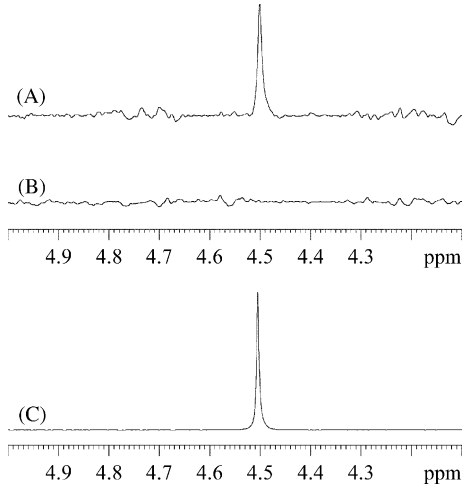


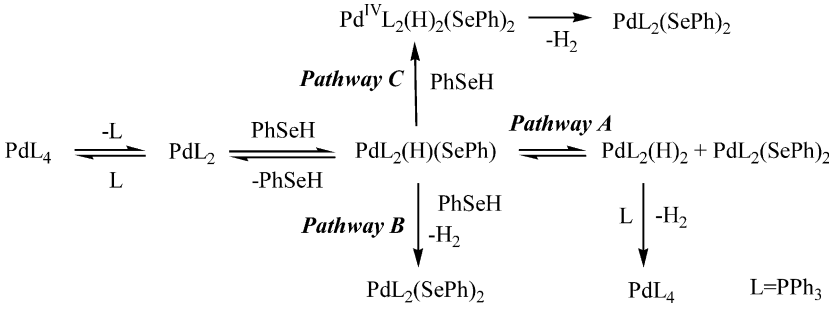
Fig. 1. (A) ^{1}H-NMR spectrum of hydrogen in reaction mixture (benzene-d_6); (B) ^{1}H-NMR spectrum of the reaction mixture after purging with argon; (C) ^{1}H-NMR spectrum of authentic hydrogen sample (benzene-d_6).

We suggest that PhSeH undergoes oxidative addition to Pd^0 and molecular hydrogen is formed as a result of $Pd(H)(SePh)(PPh_3)_2$ decomposition (Pathway A, Scheme 3). The other possible pathway of hydrogen formation may involve a direct reaction of the above complex with PhSeH (Pathway B) or oxidative addition of the second phenylselenol molecule and reductive elimination from the Pd^{IV} complex (Pathway C). It was shown earlier that mononuclear palladium diselenides are subject of fast dimerization to form dinuclear [19,21,22]. In agreement with this observation $Pd(PPh_3)_2(SePh)_2$ gives dinuclear complexes **2** and **3**, both detected with ^{31}P-NMR spectroscopy.

The catalytic E–H bond addition to alkynes can proceed via the following sequence: (i) oxidative addition of E–H to Pd^0 giving **12**, (ii) alkyne insertion leading to σ-vinyl derivative **13** and (iii) releasing the final product **8** after the C–H reductive elimination stage (Scheme 4). It should be noted that alkyne insertion occurs only into the Pd–Se bond, otherwise anti-Markovnikov products should be observed. Under catalytic conditions intermediate **12** can give the dinuclear complexes (**2**, **3**). The dinuclear complexes are known to catalyze PhSeSePh addition to alkynes [15], through the alkyne insertion (**14**) and C–Se reductive elimination giving **9**. Reductive elimination releases Pd^0 complex, and the process is most likely accompanied by the dissociation of dinuclear derivative **14**. Another mechanism of Markovnikov product (**8**) formation involves trapping of the intermediate **14** with acid (PhSeH). Trapping with PhSeH does not change palladium oxidation state and the corresponding dinuclear derivatives (**2**, **3**) are formed from **14**.

In fact, three catalytic processes may take place in the studied system: one pathway to accomplish a formal PhSeSePh addition to the triple bond leading to **9**, and two other pathways to achieve PhSeH addition giving **8**.

To clarify the Markovnikov product formation mechanism we have performed additional experiments. A



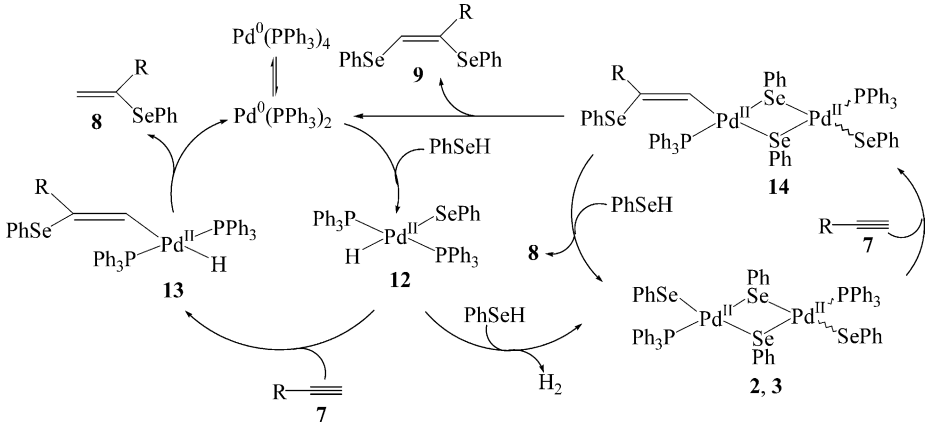
Scheme 3.

mixture of complexes **2** and **3** has been prepared in benzene-d_6 by the oxidative addition reaction of Ph_2Se_2 to Pd^0 (15 min, 80 °C). Alkyne ($HC{\equiv}CCH_2CH_2OH$) and acid (CF_3COOH) were added and the mixture was heated at 80 °C for 3 h. ^1H- and ^1H-^{77}Se HMQC NMR analysis of the products has detected a mixture of **8** and **9** in 31 and 15% yields, respectively, calculated based on initial Pd^0. If the same reaction is performed in the absence of acid only **9** is obtained in 50% yield. Therefore, the experiments confirm that **8** can be obtained upon trapping complex **14** with acid. Since hydride complex **12** was not detected and complexes **2**, **3** are immediately formed, trapping **14** with PhSeH could be the dominating pathway of hydroselenation of alkynes catalyzed by palladium complexes. This finding is in agreement with earlier study [16], suggesting that phenylselenol addition to alkynes involves the formation of palladium complex with σ-vinyl ligand (**14**) followed by reaction with PhSeH. However, our results show that the Markovnikov product **8** is not the only one [16]. Besides trapping with PhSeH, the intermediate complex **14** can undergo reductive elimination leading to bis-seleno substituted compound **9**.

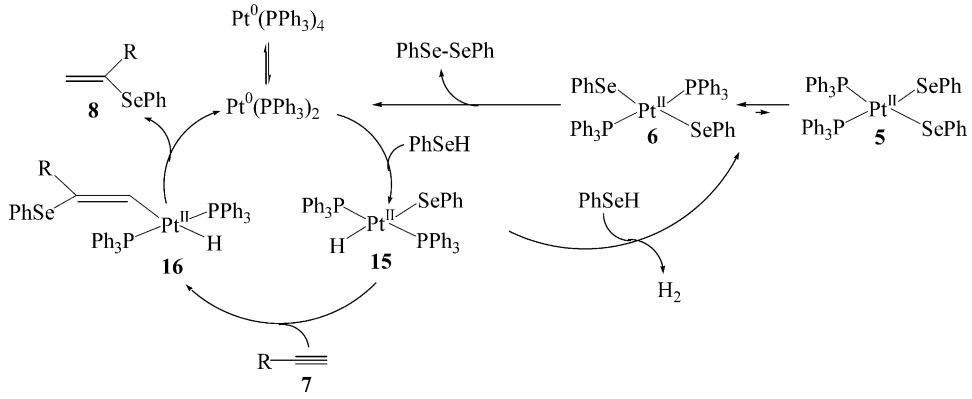
Recently, we have shown that $Pt(PPh_3)_4$ does not catalyze the addition of PhSeSePh to alkynes contrary to palladium [15]. Surprisingly, $Pt(PPh_3)_4$ was found to serve as efficient catalyst in PhSeH addition reaction, which results in the formation of a single Markovnikov product **8** (Table 1). Comparing $Pd(PPh_3)_4$ and $Pt(PPh_3)_4$ one may clearly see that the latter is superior to provide better selectivity of the process and higher yield. In our experience the mixture of **8** and **9** is rather difficult to separate. Therefore, the less selective palladium catalyzed reaction should be considered as inferior from practical point of view. Since no by-products are formed in the platinum catalyzed transformation (except Ph_2Se_2), the isolation procedure can be significantly simplified. In addition, platinum catalyzed reaction is not sensitive to Ph_2Se_2 impurities in PhSeH, which may be present due to easy oxidation of the latter by air.

The key intermediate of PhSeH oxidative addition reaction to Pt^0 has been detected by ^1H-NMR spectroscopy (**15**, Scheme 5). The singlet at $\delta = -8.77$ ppm with platinum and selenium satellites ($J_{Pt-H} = 999.8$ Hz, $J_{Se-H} = 44.1$ Hz) clearly confirms the presence of hydride proton bonded to the metal (Fig. 2). Since $^2J_{P-H}$ coupling is not observed, while $^2J_{Se-H}$ coupling is present, most likely there is no phosphine ligand in *trans*- position to hydrogen and we can conclude that **15** is *trans*-[Pt(H)(SePh)$(PPh_3)_2$]. This finding agrees with earlier studies of oxidative addition of thiols and selenols to low-valent transition metal complexes [27,28].

$^{31}P\{^1H\}$-NMR monitoring of the PhSeH reaction with $Pt(PPh_3)_4$ in benzene-d_6 at room temperature has shown the major resonances: 20.8 ppm with ^{195}Pt



Scheme 4.



Scheme 5.

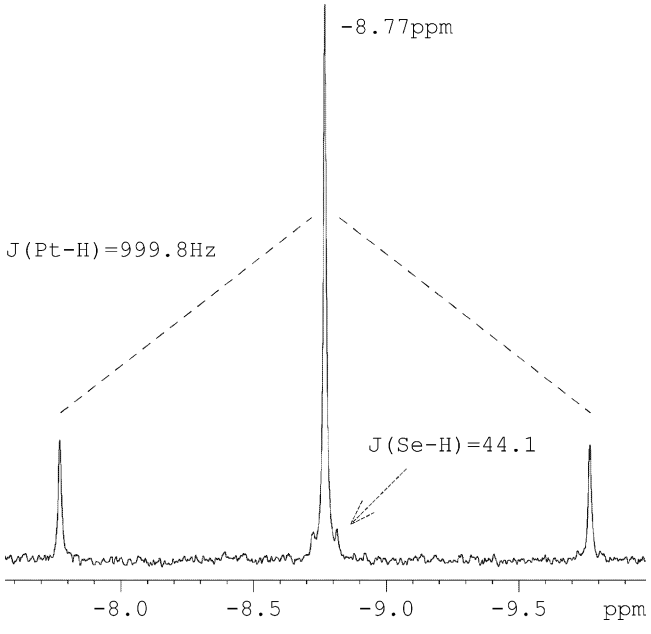


Fig. 2. ^{1}H-NMR spectrum of hydride proton region of **15** (toluene-d_8).

satellites $J_{Pt-P} = 2842$ Hz, 18.5 ppm with ^{195}Pt satellites $J_{Pt-P} = 2966$ Hz, which correspond to *trans*-[Pt(SePh)$_2$(PPh$_3$)$_2$] (**6**) and *cis*-[Pt(SePh)$_2$(PPh$_3$)$_2$] (**5**), respectively, [15] 25.0 ppm (OPPh$_3$) and −4.6 ppm (PPh$_3$). The other minor resonances in the spectrum are: 20.8, 23.7, 30.6 ppm. One of the minor resonances may correspond to the hydride complex **15**. It should be noted that analogous palladium complex (**12**) was not detected under the similar conditions. The most likely reason is a higher reactivity of **12** compared to **15**. At room temperature **5** slowly isomerizes to **6**.

For platinum complexes we can suggest an analogous mechanism as for the palladium complexes discussed above. Reaction of Pt^0 with two molecules of PhSeH leads to the same metal complexes (**5**, **6**) as reaction of Pt^0 with PhSeSePh (Scheme 5). However, at 80 °C *cis*-[Pt(SePh)$_2$(PPh$_3$)$_2$] (**5**) very rapidly isomerizes to *trans*-[Pt(SePh)$_2$(PPh$_3$)$_2$] (**6**) (Scheme 1) [15], thus avoiding bisselenide **9** formation under catalytic conditions. Indeed, in ^{31}P{^{1}H}-NMR spectra of the catalytic reaction mixture after heating at 80 °C only the signals corresponding to the *trans*-isomer were detected. Most likely there is a competition of PhSeSePh and PhSeH oxidative addition to zero valent metal. The product is formed by trapping of **15** with alkyne. During the catalytic reaction Ph_2Se_2 accumulates due to the decomposition of hydride complex, and this process may lower the overall yield of **8**. The presence of Ph_2Se_2 in the reaction mixture was unambiguously confirmed by ^{1}H-^{77}Se HMQC experiment. The final yield of diphenyl diselenide is 20–25% based on initial PhSeH (Table 1). For preparative purposes PhSeSePh can be easily separated and recycled to PhSeH (for the PhSeH synthesis from Ph_2Se_2 see [8,29]).

To confirm the reaction mechanism *trans*-[Pt(SePh)$_2$(PPh$_3$)$_2$] (**6**) was prepared and used as a catalyst in PhSeH addition to **7B**. The same 60% yield of **8B** was obtained as in the Pt(PPh$_3$)$_4$ catalyzed reaction (Table 1).

To clarify the mechanism of Markovnikov product formation an additional experiment has been performed, similar to palladium system discussed above. After Ph_2Se_2 reaction with Pt^0 (15 min, 80 °C in benzene-d_6) the addition of alkyne (HC≡CCH$_2$CH$_2$OH) and acid (CF$_3$COOH) gave no product. Only the traces of **8** (yield ~0.5% based on initial Pt^0) were detected after 3 h at 80 °C. These observation rules out the pathways involving trapping of platinum σ-vinyl intermediate with acid, in contrast to the palladium catalyzed reaction.

The X-ray quality single crystals were obtained for the oxalic acid salt of **8C**. The molecular structure of the compound is shown in Fig. 3, main geometry parameters are summarized in Table 2. Two slightly different conformations were found in the crystal (see torsion angles in Table 2). The molecule possess typical geometry expected for Markovnikov product with the vinyl group C=C bond lengths of 1.322(8) and 1.330(8) Å. The C–Se bond lengths are of 1.917(6) and 1.918(6) Å. The hydrogen bonds involving carboxylic oxygen

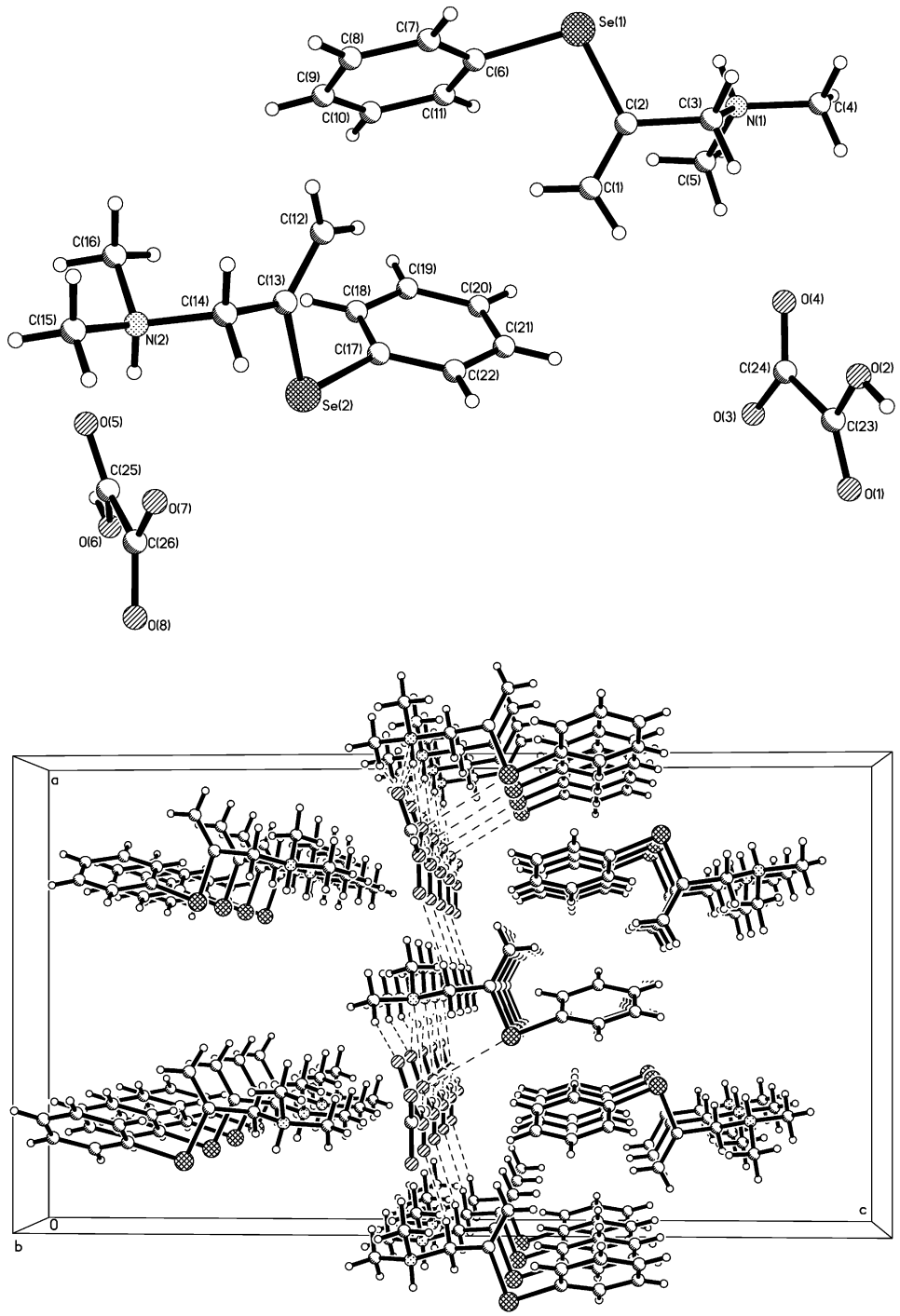


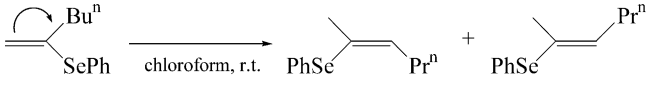
Fig. 3. Molecular structure and crystal packing for $H_2C{=}C(SePh)CH_2N^+HMe_2{\cdot}HOOC{-}COO^-$ (**8C**·HOOC–COOH).

atoms were found in the studied molecule, N(2)–H(2)···O(5) = 2.098 Å and N(2)–H(2)···O(7) = 2.155 Å (N(1)–H(1)···O(3) = 2.134 Å and N(1)–H(1)···O(1) = 2.137 Å). To the best of our knowledge this is the first X-ray structure of organic molecule with $H_2C{=}C{-}Se{-}$ fragment. A very interesting feature of **8C** is the presence of noncovalent Se···O interaction in the crystal, Se(2)–O(5) = 3.741 Å and Se(2)–O(7) = 3.385 Å. It was suggested recently that noncovalent Se···O interactions are responsible for modulation of biological activity of selenium compounds [30].

A very interesting rearrangement of the terminal vinylselenide **8B** has been observed in chloroform solution (Scheme 6). The 50% conversion of **8B** was achieved after ~24 h and the reaction was almost complete after a week with the final ratio **16B**:**17B** ≈ 1.4:1.0. Heterosubstituted vinyl selenides containing α-hydrogen atoms (**8A**, **8C**) under similar conditions do

Table 2
Selected geometry parameters for **8C**: bond lengths (in Å), bond angles and torsion angles (°)

Parameter	Value	Parameter	Value	Parameter	Value
Bond lengths		*Bond angles*		*Torsion angles*	
Se(1)–C(2)	1.918(6)	C(2)–Se(1)–C(6)	99.9(2)	C(1)–C(2)–C(3)–N(1)	113.22(0.67)
Se(1)–C(6)	1.921(6)	C(13)–Se(2)–C(17)	100.4(3)	C(2)–C(3)–N(1)–C(4)	−179.45(0.50)
Se(2)–C(13)	1.917(6)	C(3)–N(1)–C(4)	110.4(5)	C(2)–C(3)–N(1)–C(5)	−54.49(0.62)
Se(2)–C(17)	1.918(7)	C(3)–N(1)–C(5)	111.9(5)	C(1)–C(2)–Se(1)–C(6)	−3.50(0.64)
O(1)–C(23)	1.193(7)	C(4)–N(1)–C(5)	111.6(5)	C(3)–C(2)–Se(1)–C(6)	176.92(0.43)
O(2)–C(23)	1.321(7)	C(15)–N(2)–C(16)	111.0(5)	C(12)–C(13)–Se(2)–C(17)	0.91(0.64)
O(3)–C(24)	1.277(7)	C(15)–N(2)–C(14)	109.1(5)	C(14)–C(13)–Se(2)–C(17)	−176.72(0.47)
O(4)–C(24)	1.203(7)	C(16)–N(2)–C(14)	111.1(5)	C(12)–C(13)–C(14)–N(2)	111.48(0.69)
O(5)–C(25)	1.199(7)	C(1)–C(2)–C(3)	121.4(6)	C(13)–C(14)–N(2)–C(15)	−176.29(0.55)
O(6)–C(25)	1.313(7)	C(1)–C(2)–Se(1)	125.7(5)	C(13)–C(14)–N(2)–C(16)	−53.59(0.66)
O(7)–C(26)	1.265(6)	C(3)–C(2)–Se(1)	112.9(4)		
O(8)–C(26)	1.250(7)	N(1)–C(3)–C(2)	113.7(5)		
N(1)–C(3)	1.490(7)	C(11)–C(6)–C(7)	120.2(6)		
N(1)–C(4)	1.498(8)	C(11)–C(6)–Se(1)	121.5(5)		
N(1)–C(5)	1.500(7)	C(7)–C(6)–Se(1)	118.3(5)		
N(2)–C(15)	1.486(9)	C(6)–C(7)–C(8)	118.7(6)		
N(2)–C(16)	1.492(7)	C(9)–C(8)–C(7)	121.3(7)		
N(2)–C(14)	1.509(8)	C(8)–C(9)–C(10)	119.1(7)		
C(1)–C(2)	1.322(8)	C(9)–C(10)–C(11)	120.4(6)		
C(2)–C(3)	1.501(9)	C(6)–C(11)–C(10)	120.3(7)		
C(6)–C(11)	1.350(9)	C(12)–C(13)–C(14)	120.8(6)		
C(6)–C(7)	1.383(9)	C(12)–C(13)–Se(2)	124.3(5)		
C(7)–C(8)	1.393(9)	C(14)–C(13)–Se(2)	114.9(4)		
C(8)–C(9)	1.351(10)	C(13)–C(14)–N(2)	113.6(5)		
C(9)–C(10)	1.373(11)	C(22)–C(17)–C(18)	118.8(7)		
C(10)–C(11)	1.386(10)	C(22)–C(17)–Se(2)	120.0(5)		
C(12)–C(13)	1.330(8)	C(18)–C(17)–Se(2)	121.1(5)		
C(13)–C(14)	1.479(9)	C(19)–C(18)–C(17)	119.5(7)		
C(17)–C(22)	1.373(8)	C(18)–C(19)–C(20)	120.7(7)		
C(17)–C(18)	1.401(9)	C(21)–C(20)–C(19)	120.4(8)		
C(18)–C(19)	1.359(10)	C(20)–C(21)–C(22)	119.3(7)		
C(19)–C(20)	1.375(12)	C(21)–C(22)–C(17)	121.2(7)		
C(20)–C(21)	1.366(11)	O(1)–C(23)–O(2)	124.8(6)		
C(21)–C(22)	1.372(9)	O(1)–C(23)–C(24)	122.0(6)		
C(23)–C(24)	1.541(8)	O(2)–C(23)–C(24)	113.2(5)		
C(25)–C(26)	1.541(8)	O(4)–C(24)–O(3)	127.6(5)		
		O(4)–C(24)–C(23)	119.7(6)		
		O(3)–C(24)–C(23)	112.7(5)		
		O(5)–C(25)–O(6)	124.4(6)		
		O(5)–C(25)–C(26)	122.0(6)		
		O(6)–C(25)–C(26)	113.6(5)		
		O(8)–C(26)–O(7)	126.1(6)		
		O(8)–C(26)–C(25)	119.5(5)		
		O(7)–C(26)–C(25)	114.4(5)		



8-B **16-B** (*Z*-) **17-B** (*E*-)

Scheme 6.

not undergo the isomerization. In the case of PhSH addition to alkynes double bond migration has been observed under palladium catalyzed conditions [13], again only for the acetylenic hydrocarbons without heteroatomic substituents. The present study shows that for the isomerization of vinyl selenide **8B** transition metal complexes are not required. This side reaction may lower the overall selectivity of the PhSeH addition to hexyne-1 (**7B**) leading to the mixture of isomers.

The theoretical calculations at the B3LYP/Lanl2dz level were performed to predict relative stability of the isomers. On the ΔH energy surface both **16B** and **17B** are more stable compared to **8B** by 3.0 and 2.4 kcal mol^{-1}, respectively. Therefore, the isomerization is thermodynamically driven, while **8B** is the kinetic product.

3. Conclusions

We have shown that $Pd(PPh_3)_4$ catalyzed PhSeH addition to alkynes leads to the mixture of mono- and bis-seleno substituted products **8** and **9**, whereas $Pt(PPh_3)_4$ provides better selectivity and yield resulting in Markovnikov product only (**8**). In both cases palladium and platinum diselenide derivatives (**2**, **3** and **5**, **6**) can be formed from M^0 and PhSeH. However, Se–Se addition to alkynes does not take place in the presence of platinum complex and PhSeSePh is released instead. In contrast, palladium complexes catalyze Se–Se addition to the C≡C bond leading to the mixture of products. The C–H bond formation in palladium catalyzed transformation most likely is an intermolecular trapping of σ-vinyl intermediate **14** with PhSeH, in contrast to intramolecular reductive elimination occurring when platinum catalyst is used.

The earlier studies on Markovnikov S–H and Se–H addition reactions were concentrated on palladium complexes, while the present work suggests that platinum complexes are superior, particularly in where it concerns the selectivity. Low overall selectivity of PhSeH addition to activated alkynes and acetylenic hydrocarbons may be observed due to side reactions of non-catalyzed addition and double bond isomerization, respectively.

4. Experimental

4.1. General

Unless otherwise stated, synthetic work was carried out under argon atmosphere. The reagents, namely $Pd(PPh_3)_4$ (Aldrich), $Pt(PPh_3)_4$ (Acros), Ph_2Se_2 (Acros), PhSeH (Acros), alkynes (Acros and Fluka) were checked with NMR and used as supplied.

4.2. NMR spectroscopy

All NMR measurements were performed using a three channel Bruker DRX500 spectrometer operating at 500.1, 202.5, 125.8 and 95.4 MHz for ^1H, ^{31}P, ^{13}C and ^{77}Se nuclei, respectively. The spectra were processed on a Silicon Graphics workstation using XWINMR 3.0 software package. All 2D spectra were recorded using inverse triple resonance probehead with active shielded Z-gradient coil. ^1H and ^{13}C chemical shifts are reported relative to the corresponding solvent signals used as internal reference, external 85% H_3PO_4/H_2O ($\delta = 0.0$ ppm) used for ^{31}P and $Ph_2Se_2/CDCl_3$ ($\delta = 463.0$ ppm) for ^{77}Se [31].

4.2.1. 2D ^1H-^{77}Se HMQC NMR experiment

The spectrum was collected with ^1H and ^{77}Se 90° pulses of 12.5 and 16.0 μs, respectively, a relaxation delay of 2s, $\Delta = (2 \cdot J_{H-Se})^{-1} = 250$ ms (optimized for long range coupling constant of 2 Hz), a 0.25 s acquisition time and 4500 and 25 000 Hz spectral windows for the ^1H(F2) and ^{77}Se(F1) dimensions correspondingly. Four or eight transients were averaged for each of 256 increments on t_1. The data was zero filled to 2048×2048 matrix and processed with QSINE(SSB = 2) window function for both F2 and F1 dimensions. The 1 ms sine shaped pulse field gradient pulses with the ratio 50.0:30.0:35.3 (%) followed with 100 μs recovery delay were applied.

4.2.2. 2D NOESY NMR experiment

The spectra were recorded using bipolar gradient pulse sequence: 90-t_1-90-τ_{mix}/2–G1–180–G2-τ_{mix}/2–90–acq, with $\tau_{mix} = 1$–2 s, and 40.0, −40.0 (%) field gradient pulses for G1 and G2, respectively. The further details as described earlier [32].

The rest of NMR experiments were performed using pulse sequences supplied by hardware manufacturer.

4.3. Detecting H_2 with ^1H-NMR

At room temperature (r.t.) PhSeH (15.7 mg, 1×10^{-4} mol) was dissolved in 0.5 ml of C_6D_6 and placed in NMR tube. $Pd(PPh_3)_4$ (57.8 mg, 5×10^{-5} mol) was added to the solution immediately changing its' color to dark. Gas evolution occurs for the time period over 10–15 min. ^1H-NMR spectra indicate appearing of H_2 peak at 4.5 ppm, which vanishes after purging the solution with argon. Authentic H_2 sample was prepared by purging hydrogen from balloon through the C_6D_6 and $\delta = 4.5$ ppm was the only new peak appeared.

4.4. Trapping with acid (M = Pd, Pt)

Ph_2Se_2 (9.4 mg, 3×10^{-5} mol) and $M(PPh_3)_4$ (2×10^{-5} mol) were dissolved in 0.5 ml of C_6D_6 and the mixture was heated at 80 °C for 15 min. The $^{31}P\{^1H\}$-NMR spectrum was recorded to insure corresponding oxidative addition products formation. The alkyne HC≡C–CH_2CH_2OH (2.8 mg, 4×10^{-5} mol) and the acid CF_3COOH (4.6 mg, 4×10^{-5} mol) were added and the solution was heated at 80 °C for 3 h.

4.5. Detecting complex Pt(H)(SePh)(PPh_3)$_2$ with NMR spectroscopy

At r.t. PhSeH (7.9 mg, 5×10^{-5} mol) was dissolved in 0.5 ml of C_6D_6 and $Pt(PPh_3)_4$ (62.2 mg, 5×10^{-5} mol) was added to the solution changing its' color to orange. NMR monitoring has shown that the hydride resonance

($\delta = -8.77$ ppm) slowly decrease in intensity upon vanishing after several hours.

4.6. General synthetic procedure for **8A–8D**

Phenylselenol (157 mg, 1×10^{-3} mol) was dissolved in 0.5 ml of toluene giving clear solution. $Pt(PPh_3)_4$ or $Pd(PPh_3)_4$ (3 mol.%) was dissolved in the solution changing the color to orange or dark brown in the former and latter cases, respectively. The alkyne (1.5×10^{-3} mol) was added to the solution and reaction mixture was heated for 13 h at 80 °C in a sealed tube. After completing the reaction the solvent was removed on rotor evaporator and the product extracted with 2.0 ml of $CHCl_3$. The product was further purified with chromatography on silica.

Structure elucidation of the products was made utilizing 2D NOESY, LR-COSY, ^{1}H-^{13}C HSQC, ^{1}H-^{13}C HMBC, ^{1}H-^{77}Se HMQC NMR experiments.

4.6.1. $H_2C{=}C(SePh){-}CH_2OH$ (**8A**)

Yellow oil; ^{1}H-NMR (500 MHz; $CDCl_3$; δ, ppm): 7.55 (m, 2H, Ph), 7.30 (m, 3H, Ph), 5.89 (br.s, 1H, HC=), 5.44 (s, 1H, HC=), 4.19 (br.s, 2H, $-CH_2-$). $^{13}C\{^1H\}$ (126 MHz; $CDCl_3$; δ, ppm): 152.8, 141.4, 133.9, 129.3, 127.8, 118.4 ($H_2C=$), 66.4(CH_2). ^{77}Se (95 MHz; $CDCl_3$; δ, ppm): 385.6. Anal. Calc. for $C_9H_{10}OSe$: C, 50.72; H, 4.73; Se 37.05. Found: C, 50.96; H, 4.67; Se, 36.67%. Mass spectrum (EI), *m/e* 214 [M^+, 15].

4.6.2. $H_2C{=}C(SePh){-}^{\alpha}CH_2{-}^{\beta}CH_2{-}^{\gamma}CH_2{-}^{\delta}CH_3$ (**8B**)

White oil; ^{1}H-NMR (500 MHz; $CDCl_3$; δ, ppm; J, Hz): 7.56 (m, 2H, Ph), 7.30 (m, 3H, Ph), 5.50 (br.s, 1H, HC=), 5.12 (s, 1H, HC=), 2.30 (br.t, 2H, $J = 7.4$, $-^{\alpha}CH_2-$), 1.53 (tt, 2H, $J_1 = 7.4$, $J_2 = 7.5$, $-^{\beta}CH_2-$), 1.32 (tq, 2H, $J_1 = 7.5$, $J_2 = 7.4$, $-^{\gamma}CH_2-$), 0.90 (t, 3H, $J = 7.4$, $-^{\delta}CH_3$). ^{77}Se (95 MHz; $CDCl_3$; δ, ppm): 423.5. Mass spectrum (EI), *m/e* 240 [M^+, 10].

4.6.3. $H_2C{=}C(SePh){-}CH_2{-}NMe_2$ (**8C**)$\cdot HOOC{-}COOH$

White solid. After completing the reaction and removing the solvent and unreacted alkyne on rotor evaporator the crude was dissolved in 3 ml of toluene. The THF solution of HOOC–COOH (1.5×10^{-3} mol in 2 ml) was added resulting in immediate white precipitate formation. The solid was washed with toluene, THF, extracted with 4 ml of methanol and dried in vacuum.

^{1}H-NMR (500 MHz; CD_3OD; δ, ppm;): 7.60 (m, 2H, Ph), 7.40 (m, 3H, Ph), 6.07 (br.s, 1H, HC=), 5.59 (s, 1H, HC=), 3.92 (br.s, 2H, CH_2), 2.89 (s, 6H, CH_3). $^{13}C\{^1H\}$ (126 MHz; CD_3OD; δ, ppm): 165.9 (C=O), 136.1, 133.1, 131.1, 130.2, 128.2, 127.9 ($H_2C=$), 63.2 ($-CH_2-$), 43.4 ($-CH_3$). Anal. Calc. for $C_{13}H_{17}NO_4Se$: C, 47.28; H, 5.19; N, 4.24; Se, 23.91. Found: C, 47.20; H, 5.15; N, 4.04; Se, 23.99%. Mass spectrum (EI), *m/e* 241 [$M^+ -$HOOC–COOH, 15].

4.6.4. $H_2C{=}C(SePh){-}C_6H_{10}(OH)$ (**8D**)

Yellow oil; ^{1}H-NMR (500 MHz; $CDCl_3$; δ, ppm): 7.58 (m, 2H, Ph), 7.30 (m, 3H, Ph), 5.76 (s, 1H, HC=), 5.00 (s, 1H, HC=), 1.85–1.55 (m, 9H, $-C_6H_{10}-$), 1.24 (m, 1H, $-C_6H_{10}-$). $^{13}C\{^1H\}$ (126 MHz; $CDCl_3$; δ, ppm): 153.9, 141.6, 135.0, 129.3, 127.9, 114.3 ($H_2C=$), 75.1 ($-C(OH)-$), 37.1(CH_2), 25.5 (CH_2), 22.0 (CH_2). ^{77}Se (95 MHz; $CDCl_3$; δ, ppm): 376.2. Anal. Calc. for $C_{14}H_8OSe$: C, 59.79; H, 5.69; Se 28.07. Found: C, 59.56; H, 6.01; Se, 28.37%. Mass spectrum (EI), *m/e* 282 [M^+, 20].

4.7. Isomerization of **8B** to **16B** and **17B**

After purification on silica **8B** was placed in NMR tube with 0.5 ml of $CDCl_3$ and kept at the r.t. NMR spectra were taken daily to follow isomerization reaction. Half conversion was observed after 24 h, about 97% conversion was achieved after 7 days. The same ratio **16B**:**17B** $\approx$ 1.4:1.0 was observed during the isomerization process as determined with ^{1}H-NMR. Removing chloroform on rotary evaporator gives mixture of **16B** and **17B** with no other by-products formed. The same set of 2D NMR methods was utilized in structure determination as described in Section 4.6.

4.7.1. Z-$H_3C{-}HC{=}C(SePh){-}^{\alpha}CH_2{-}^{\beta}CH_2{-}^{\gamma}CH_3$ (**16B**)

White oil; ^{1}H-NMR (500 MHz; C_6D_6; δ, ppm; J, Hz): 7.45 (m, 2H, Ph), 6.97 (m, 3H, Ph), 5.64 (br.t, 1H, $J =$ 7.1, HC=), 2.30 (dt, 2H, $J_1 = 7.1$, $J_2 = 7.3$, $-^{\alpha}CH_2-$), 1.98 (br.s, 3H, CH_3), 1.36 (tq, 2H, $J_1 = 7.3$, $J_2 = 7.3$, $-^{\beta}CH_2-$), 0.87 (t, 3H, $J = 7.3$, $-^{\gamma}CH_3$). $^{13}C\{^1H\}$ (126 MHz; C_6D_6; δ, ppm): 134.9 (=CH–), 133.4, 130.3, 126.9, 129.2, 128.3, 34.3 ($-^{\alpha}CH_2-$), 26.8 (CH_3-), 22.9 ($-^{\beta}CH_2-$), 14.1 ($-^{\gamma}CH_3$). ^{77}Se (95 MHz; C_6D_6; δ, ppm): 363.8. Anal. Calc. for $C_{11}H_{16}Se$: C, 60.25; H, 6.74; Se 33.01. Found (E/Z mixture): C, 60.22; H, 6.79; Se, 33.10%. Mass spectrum (EI), *m/e* 240 [M^+, 10].

4.7.2. E-$H_3C{-}HC{=}C(SePh){-}^{\alpha}CH_2{-}^{\beta}CH_2{-}^{\gamma}CH_3$ (**17B**)

White oil; ^{1}H-NMR (500 MHz; C_6D_6; δ, ppm; J, Hz): 7.51 (m, 2H, Ph), 7.01 (m, 3H, Ph), 6.02 (br.t, 1H, $J =$ 7.4, HC=), 1.92 (br.s, 3H, CH_3), 1.87 (dt, 2H, $J_1 = 7.4$, $J_2 = 7.3$, $-^{\alpha}CH_2-$), 1.23 (tq, 2H, $J_1 = 7.3$, $J_2 = 7.3$, $-^{\beta}CH_2-$), 0.78 (t, 3H, $J = 7.3$, $-^{\gamma}CH_3$). $^{13}C\{^1H\}$ (126 MHz; C_6D_6; δ, ppm): 137.4 (=CH–), 133.1, 131.1, 129.4, 128.2, 126.7, 31.7 ($-^{\alpha}CH_2-$), 22.4 ($-^{\beta}CH_2-$), 20.4 (CH_3-), 13.9 ($-^{\gamma}CH_3$). ^{77}Se (95 MHz; C_6D_6; δ, ppm): 471.6. Anal. Calc. for $C_{11}H_{16}Se$: C, 60.25; H, 6.74; Se,

33.01. Found (*E*/*Z* mixture): C, 60.22; H, 6.79; Se, 33.10%. Mass spectrum (EI), *m*/*e* 240 [M^+, 10].

4.8. Crystal structure determination

Single crystals of **8C·HOOC–COOH** were obtained by slow evaporation of methanol solution. The samples were mounted in air on glass fiber using 5 min epoxy resin. The X-ray intensity data sets were collected on a Bruker AXS SMART 1000 diffractometer equipped with a CCD detector (graphite monochromator, 230(2) K, ω scanning technique, scan step was 0.3°, frames were exposed for 30 s) using a standard procedure [33]. The semiempirical absorption correction was applied [34]. The crystallographic parameters and selected details of the refinement of structures are given in Table 3. The structures were solved by direct and Fourier techniques, and refined by full-matrix least-squares method with anisotropic thermal parameters for all non-hydrogen atoms. The positions of the hydrogen atoms of the phenyl, methyl and methylene substituents were calculated geometrically and refined using the riding model. The positions of the other hydrogen atoms were found from the difference Fourier map. All calculations were carried out with the use of the SHELEX-97 program package [35]. The main geometric parameters are given in Table 2.

Table 3
Data collection and processing parameters for the compounds **8C**·HOOC–COOH

Parameter	Value
Empirical formula	$C_{13}H_{17}NO_4Se$
Formula weight	330.24
Temperature (K)	230(2)
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	*Pca*2(1)
Unit cell dimensions	
a (Å)	16.525(4)
b (Å)	5.6633(13)
c (Å)	30.171(6)
α (°)	90
β (°)	90
γ (°)	90
Volume (A^3)	2823.6(11)
Z	8
Calculated density (Mg m^{-3})	1.554
Absorption coefficient (mm^{-1})	2.669
F(0 0 0)	1344
Crystal size (mm)	0.02 × 0.03 × 0.15
θ Range for data collection (°)	2.46–30.07
Index ranges	$-23 \le h \le 23$, $-3 \le k \le 7$, $-33 \le l \le 42$
Reflections collected/unique	11 056/5845 [$R_{int} = 0.0481$]
Completeness to $2\theta = 30.05$	60.2%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	5845/1/349
Goodness-of-fit on F^2	1.001
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0453$, $wR_2 = 0.0915$
R indices (all data)	$R_1 = 0.0686$, $wR_2 = 0.0955$
Absolute structure parameter	0.288(14)
Largest difference peak and hole (e A^{-3})	1.785 and −0.400

4.9. Theoretical calculations

B3LYP hybrid density functional method and Lanl2dz ECP basis set were employed as implemented in GAUSSIAN-98 package [36]. Normal coordinate analysis was performed to verify stationary points (no imaginary frequencies) and to calculate ΔH energies. The other calculation details are as described earlier [37].

5. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 205605. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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