576 Russian Chemical Bulletin, International Edition, Vol. 54, No. 3, pp. 576—587, March, 2005

Palladium-catalyzed activation of E—E and C—E bonds in diaryl dichalcogenides (E = S, Se) under microwave irradiation conditions

V. P. Ananikov,[a]* N. V. Orlov,[a] and I. P. Beletskaya[b]*

[a]N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences,
47 Leninsky prosp., 119991 Moscow, Russian Federation.
Fax: +7 (095) 135 5328. E-mail: val@ioc.ac.ru
[b]Department of Chemistry, M. V. Lomonosov Moscow State University,
Leninskie Gory, 119899 Moscow, Russian Federation.
Fax: +7 (095) 939 3618. E-mail: beletska@org.chem.msu.ru

The first example of palladium-catalyzed stereoselective addition of diphenyl disulfide and diphenyl diselenide to the triple bond of terminal alkynes under microwave irradiation conditions is described. It was found that both the element—element (E—E) and carbon—element bonds can be activated in the catalytic system studied. The products of both reactions were isolated in quantitative yields. According to quantum-chemical calculations, the reaction mechanism involves the oxidative addition of the E—E bond to Pd^0. Depending on the microwave power and reaction conditions, the next stage is either the reaction with alkyne or the carbon—element bond activation. The product of the oxidative addition of Ph_2Se_2 to Pd^0, namely, dinuclear complex $[Pd_2(SePh)_4(PPh_3)_2]$, was detected by $^{31}P\{^1H\}$ NMR spectroscopy directly in the Ph_2Se_2/PPh_3 melt formed under microwave irradiation conditions.

Key words: palladium complexes, catalysis, microwave irradiation, diaryl dichalcogenides, element—element bond activation, carbon—element bond activation, alkynes, vinyl sulfides, vinyl selenides, quantum-chemical calculations.

The development of cheap and environmentally friendly methods of synthesis is the leading trend in modern metal complex catalysis. One of the most promising methods for solving these problems is to carry out catalytic reactions in the absence of a solvent under microwave irradiation conditions.[1—6] Recently, we have performed the addition of diaryl dichalcogenides to alkynes in Ar_2E_2/PPh_3 melt under solvent-free conditions; the process was catalyzed by palladium complexes.[7,8] Conducting a reaction under solvent-free conditions offers such advantages as shortening of reaction time, high stability of the catalyst and possibility of its recycling, and significant simplification of the isolation and purification of the reaction product.[7,8]

In the present work, we report palladium-catalyzed addition of diaryl dichalcogenides Ar_2E_2 (E = S (**1a**), Se (**1b**)) to alkynes R—C≡CH (**2a—d**) in melt under microwave irradiation conditions. Activation of not only the E—E but also the E—C bond in the systems under study was revealed.

Palladium-catalyzed addition of Ar_2E_2 to alkynes allows a highly stereoselective formation of two new C—E bonds in a single reaction step.[9—12] The catalytic cycle begins with the oxidative addition of ArE—EAr to the metal to give a $Pd(EAr)_2(PPh_3)_2$ complex, which then undergoes dimerization into a dinuclear complex $Pd_2(EAr)_4(PPh_3)_2$. The structures of the dinuclear complexes were established by X-ray analysis[13—16] and their identification under the catalytic reaction conditions was done by NMR spectroscopy.[7,8,11,12] Achievement of a nearly 100% yield of the reaction product, *Z*-(ArE)HC=C(ArE)R, requires an excess of the ligand (PPh_3/[Pd] > 6), which precludes polymerization of the catalyst and formation of insoluble palladium-containing polymer $[Pd(EAr)_2]_n$ inactive in this reaction.[9,10] Studies of the catalytic reaction in solution revealed no E—C bond cleavage under the action of palladium complexes.

Experimental

NMR spectra were recorded on a Bruker DRX-500 spectrometer operating at 500.1, 202.5, 125.8, and 95.4 MHz for ^1H, ^{31}P, ^{13}C and, ^{77}Se nuclei, respectively. All measurements were carried out at room temperature. ^1H and ^{13}C NMR chemical shifts are reported relative to the corresponding solvent signals used as internal references; external references for heteronuclear experiments were 85% H_3PO_4/H_2O ($\delta(^{31}P)$ 0.0) and $Se_2Ph_2/CDCl_3$ ($\delta(^{77}Se)$ 463.0).

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 3, pp. 569—580, March, 2005.

To carry out reactions under microwave irradiation conditions, a domestic microwave oven was used, with a 100% power corresponding to 900 W.

Catalytic addition of diaryl dichalcogenides to alkynes (synthesis of compounds 3a—h). A mixture of Ar_2E_2 (0.5 mmol) and PPh_3 (0.1 mmol for E = S and 0.2 mmol for E = Se) in a tube was heated in the microwave oven at a power of 450 W until the formation of a homogeneous melt. Then, 0.01 mmol of $Pd(OAc)_2$ (2 mol.%) was added to the melt and the mixture was shaken until complete dissolution of the salt and formation of a homogeneous dark brown melt. Alkyne (0.75 mmol) was added to the melt and the reaction mixture was placed in the microwave oven. The reaction was carried out in a tube with a screw cup at a microwave power of 450 W for 15 min (E = S) and at 180 W for 100 min (E = Se). After completion of the reaction, the non-consumed alkyne was distilled off on a rotary evaporator. Chloroform (5 mL) was added to the mixture obtained and pre-adsorption on L40/100 silica gel was carried out. The product was purified by flash chromatography on L5/40 silica gel (with a hexane—chloroform mixture as an eluent) and dried *in vacuo*. The product yields are listed in Table 1. The structures of the products were established by ^1H, ^{13}C, and ^{77}Se NMR spectroscopy based on the published data.[7—12] The stereochemistry of the products was established by 2D NOESY and COSY-LR NMR spectroscopy.

Catalytic reactions of diaryl dichalcogenides with triaryl(trialkyl)phosphines, triaryl(trialkyl) phosphites, and bidentate phosphines. A mixture of Ar_2E_2 (0.5 mmol) and PR'_3 (0.5 mmol) in a tube was heated in the microwave oven at a power of 450 W until the formation of a homogeneous melt. Then, 0.01 mmol of $Pd(OAc)_2$ (2 mol.%) was added to the melt and the mixture was shaken until complete dissolution of the salt and formation of a homogeneous dark brown melt. The reaction was conducted in a tube with a screw cup at a microwave power in the range 450—900 W for 5 to 15 min. The structures of products obtained were established by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. The product yields are listed in Table 2.

Table 1. Yields in addition reactions of diphenyl disulfide (**1a**) and diphenyl diselenide (**1b**) to alkynes R—C≡CH (**2a—d**)*

Entry	Ph_2E_2	Alkyne	R	Product	Yield** (%)
1	**1a**	**2a**	n-C_5H_{11}	**3a**	99 (85)
2	**1b**	**2a**	n-C_5H_{11}	**3b**	99 (86)
3	**1a**	**2b**	$(CH_2)_2OH$	**3c**	99 (82)
4	**1b**	**2b**	$(CH_2)_2OH$	**3d**	99 (85)
5	**1a**	**2c**	CH_2OMe	**3e**	99 (92)
6	**1b**	**2c**	CH_2OMe	**3f**	99 (97)
7	**1a**	**2d**	CH_2NMe_2	**3g**	97 (80)
8	**1b**	**2d**	CH_2NMe_2	**3h**	96 (79)

* The reaction was carried out in a hermetically closed tube containing 0.5 mmol of Ph_2E_2, 0.75 mmol of alkyne, 2 mol.% of $Pd(OAc)_2$, and PPh_3 (20 mol.% for E = S and 40 mol.% for E = Se) at a microwave power of 180 W for 100 min for the diphenyl diselenide addition and at 450 W for 15 min for the diphenyl disulfide addition.

** Determined by NMR spectroscopy with respect to the initial amount of Ph_2E_2; the isolated yield is given in parentheses (see Experimental).

Table 2. Reactions of diphenyl disulfide (**1a**) and diphenyl diselenide (**1b**) with phosphorus-containing compounds **4** under microwave irradiation conditions[a]

Entry	Ph_2E_2	**4**	Yield[b] (%)	
			5	**6**
1	**1b**	PPh_3	**5b**, 10	**6b**, 10
2	**1a**	PPh_3	**5a**, 5	**6a**, 5
3	**1b**	PPh_3	**5b**, 96 (92)	**6b**, 96 (94)
4	**1a**	PPh_3	**5a**, 53	**6a**, 53
5	**1b**	PBu_3	**5c**, 66	**6b**, 66
6	**1b**	$P(OBu^n)_3$	**5d**, 23	**6b**, 23
7	**1b**	$P(OPh)_3$	**5e**, 86	**6b**, 86
8	**1b**	DPPE	**5f**, 97	**6b**, 97[c]
9	**1b**	DPPB	**5g**, 96	**6b**, 97[c]

[a] The reaction was carried out in a tube with a screw cup containing 0.5 mmol of Ph_2E_2 and 0.5 mmol of PR'_3 at a microwave power of 900 W for 15 min. Entries *1* and *2* were performed without catalyst and entries *3—9* were performed with 2 mol.% $Pd(OAc)_2$ as a catalyst.

[b] Determined by NMR spectroscopy with respect to the initial amount of Ph_2E_2; the isolated yield is given in parentheses (see Experimental).

[c] A mixture of monoselenide and diselenide of the bidentate phosphine.

Isolation of Ph_2Se and $Se{=}PPh_3$. After completion of the reactions (see above), chloroform (5 mL) was added to the melt and pre-adsorption on L40/100 silica gel was carried out. Products were purified by flash chromatography on L5/40 silica gel (with a hexane—ethyl acetate mixture as eluent) and dried *in vacuo*. The structures of the products were established by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. The yields were 94% (Ph_2Se) and 92% ($Se{=}PPh_3$).

Calculation Procedure

Geometry optimization and energy calculations were performed using the B3LYP hybrid potential[17—19] and the Lanl2dz basis set[20—23] augmented with polarization d-functions for the C, P, S, and Se atoms.[24,25] The character of the stationary points located was checked by calculating the eigenvalues of the Hessian matrix (intermediates were characterized by real frequencies and transition states were characterized by one imaginary frequency). The character of the most important transition states was verified by the IRC calculations. The thermodynamic functions were calculated according to the "harmonic oscillator—rigid rotator" model. All calculations were performed using the GAUSSIAN-03 suite of programs.[26] The molecular structures and vibrations were visualized using the MOLDEN graphic package.[27]

To reduce the computational cost, calculations were performed for a number of model reactions in which the phosphine ligand is simulated by the PH_3 group and the phenyl substituents are simulated by Me groups. Earlier, numerous quantum-chemical studies of various catalytic reactions showed[28—30] that such model systems provide a correct qualitative description of major trends.

The catalytic cycle involving mononuclear and dinuclear palladium complexes was calculated for reactions (1) and (2), respectively:

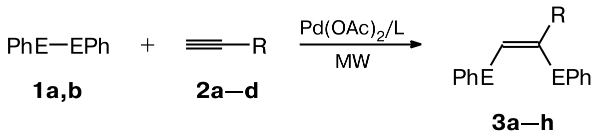
$$\mathrm{PH_3 + MeSeSeMe + Pd(SeMe)_2(PH_3)_2 \longrightarrow}$$
$$\mathrm{\longrightarrow Se{=}PH_3 + MeSeMe + Pd(SeMe)_2(PH_3)_2,} \quad (1)$$

$$\mathrm{PH_3 + MeSeSeMe + Pd_2(SeMe)_4(PH_3)_2 \longrightarrow}$$
$$\mathrm{\longrightarrow Se{=}PH_3 + MeSeMe + Pd_2(SeMe)_4(PH_3)_2.} \quad (2)$$

Results and Discussion

Microwave-assisted addition of diaryl dichalcogenides **1** to alkynes **2** was studied taking the model reactions of diphenyl disulfide (**1a**) and diphenyl diselenide (**1b**) with hept-1-yne ($R = C_5H_{11}$). The reactions were conducted under solvent-free conditions in the presence of $Pd(OAc)_2$ (2 mol.%) and triphenylphosphine (20—40 mol.%) as a ligand (Scheme 1).

Scheme 1



E = S (**1a**, **3a,c,e,g**), Se (**1b**, **3b,d,f,h**);
R = *n*-C_5H_{11} (**2a**, **3a,b**), CH_2CH_2OH (**2b**, **3c,d**), CH_2OMe (**2c**, **3e,f**), CH_2NMe_2 (**2d**, **3g,h**);
L = PPh_3, $P(OBu^n)_3$, $P(OPh)_3$ *etc.*

Microwave heating leads to formation of a dark brown melt. In the absence of palladium complexes, no reaction occurs (Table 3, entries *1* and *2*). According to ^1H NMR spectroscopic data, the addition of Ph_2S_2 proceeds with an almost 100% yield (see Table 3, entry *3*), in contrast to the addition of Ph_2Se_2 where the product yield was only 40% (see Table 3, entry *4*). In the reaction with compound **1a**, the melt remains homogeneous. The reaction with compound **1b** is accompanied by the formation of a dark brown residue of $[Pd(SePh)_2]_n$ polymer, which indicates a deficiency of the ligand. An increase in the amount of triphenylphosphine leads to an increase in the yield of compound **3b** to 85%, which, however, does not reach a quantitative level (see Table 3, entry *5*). $^{31}P\{^1H\}$ and ^1H NMR analyses of the reaction mixture revealed a transformation of PPh_3 into $Se{=}PPh_3$ (see Table 3, entries *4* and *5*) and the formation of Ph_2Se in a $Ph_2Se : Se{=}PPh_3$ ratio of 1 : 1 (entries *4* and *5*).

Table 3. Addition of diphenyl disulfide (**1a**) and diphenyl diselenide (**1b**) to hept-1-yne under microwave irradiation conditions*

Entry	Ph_2E_2	Catalyst (mol.%)	Product	Yield** (%)	
				3	$E{=}PPh_3$
1	**1a**	PPh_3 (20)	—	0	0
2	**1b**	PPh_3 (40)	—	0	0
3	**1a**	$Pd(OAc)_2$ (2), PPh_3 (20)	**3a**	98	1 (5)
4	**1b**	$Pd(OAc)_2$ (2), PPh_3 (20)	**3b**	40	9 (45)
5	**1b**	$Pd(OAc)_2$ (2), PPh_3 (40)	**3b**	85	15 (37)

* The reaction was conducted in a tube with a screw cup containing 0.5 mmol of Ph_2E_2 and 0.75 mmol of hept-1-yne at a microwave power 900 W for 5 min.

** Determined by NMR spectroscopy with respect to the initial amount of Ph_2E_2; the conversion of PPh_3 calculated with respect to the initial amount of ligand is given in parentheses.

Thus, the microwave-assisted addition of dichalcogenides to alkynes (see Scheme 1) is accompanied by a side reaction of Ph_2E_2 (**1**) with PPh_3 (**4**) resulting in $E{=}PPh_3$ (**5**) (Scheme 2). A specific feature of the side reaction is the cleavage of the E—C bond, which has not earlier been observed in the thermal reactions where only palladium-catalyzed activation of the E—E bond occurred (see Scheme 1). The side reaction is catalyzed by palladium complexes (*cf.* entries *2* and *5* in Table 3), being much more characteristic of compound **1b** (*cf.* entries *3* and *4* in Table 3). In the addition of Ph_2Se_2 to hept-1-yne, nearly 40% of the ligand added is converted into $Se{=}PPh_3$ (see Table 3, entries *4* and *5*). A dramatic decrease in the yield of the product **3b** in the presence of a small excess of PPh_3 (see Table 3, entry *4*) is due to the fact that a decrease in the amount of ligand is followed by fast deactivation of the catalyst owing to formation of an insoluble polymer, $[Pd(SePh)_2]_n$.

Scheme 2

$$\underset{\mathbf{1a,b}}{\mathrm{PhE{-}EPh}} + \underset{\mathbf{4}}{\mathrm{PR'_3}} \xrightarrow[\mathrm{MW}]{\mathrm{[Pd]}} \underset{\mathbf{5}}{\mathrm{E{=}PR'_3}} + \underset{\mathbf{6a,b}}{\mathrm{PhEPh}}$$

The side reaction was studied under alkyne-free conditions using a large number of phosphorus-containing compounds (see Scheme 2 and Table 2). Products **5** and **6** are formed in high yields only in the presence of catalytic amounts of palladium complexes (see Table 2, *cf.* entries *1*, *2* and *3*, *4*). Compound **1b** is converted into diphenyl selenide **6b** in quantitative yield (see Table 2, entry *3*). Diphenyl disulfide (**1a**) is much less reactive (see Table 2, entry *4*). Compound **1b** reacts with tributylphosphine, tributyl phosphite, and triphenyl phosphite (see Table 2, entries *5*—*7*) under microwave irradiation conditions. The low yield of compound **5** in the reaction with tributyl phosphite is due to a noncatalytic side reaction similar to the Arbuzov rearrangement, which was confirmed by

^{31}P NMR spectroscopy (see Table 2, entry *6*). Compound **1b** also reacts with chelate-forming phosphines, namely, bis(diphenylphosphino)ethane (DPPE) and bis(diphenylphosphino)butane (DPPB) (see Table 2, entries *8* and *9*).

Microwave-assisted catalytic reactions of phosphines with diaryl dichalcogenides can be used for synthetic purposes to obtain products **5** and **6**. Both products, Ph_2Se and $Se{=}PPh_3$, were isolated by flash chromatography in 92 and 94% yields, respectively (see Table 2, entry *3*).

As expected, the yields of product **3b** in the catalytic addition of Ph_2Se_2 to hept-1-yne (see Scheme 1) carried out with different ligands were far from 100% (78% with $L = P(OBu^n)_3$, 53% with $L = P(OPh)_3$, and only trace amounts of product **3b** were detected in the reaction with the chelate-forming ligand, DPPE). Similar results were obtained in studies of conventional thermal reactions in toluene and benzene with chelate-forming ligands.[7—12]

By varying the microwave power, we succeeded in preparing product **3b** in virtually 100% yield (Table 4). A decrease in the microwave power causes slowing down of the side reaction of PPh_3 with Ph_2Se_2, which leads to a decrease in the yields of compounds **5b** and **6b** and to an increase in the yield of product **3b** (see Table 4, entries *4*—*6*). In particular, at a microwave power of 180 W the reaction proceeds with a nearly 100% yield (Table 4, entry *6*). As the microwave power decreases, the catalytic reaction also slows down, which requires an increase in the reaction time to 100 min.

The yield of product **3a** in the catalytic reaction of Ph_2S_2 with hept-1-yne is independent of microwave power (see Table 4, entries *1*—*3*), because in this case the side reaction (ligand conversion) proceeds much more slowly. The catalytic reaction is completed in 5 min and provides an almost 100% yield of product **3a** (see Table 4).

Table 4. Effect of microwave power on product yields in the addition reactions of diphenyl disulfide (**1a**) and diphenyl diselenide (**1b**) to hept-1-yne*

Entry	Ph_2E_2	Power /W	*t*/min	Yield** (%)		
				3	5	6
1	**1a**	900	5	98	1	1
2	**1a**	450	10	97	0	0
3	**1a**	180	100	99	0	0
4	**1b**	900	5	39	10	10
5	**1b**	450	10	68	14	14
6	**1b**	180	100	99	1	1

* Reactions were carried out in a tube with a screw cup containing 0.5 mmol of Ph_2E_2, 0.75 mmol of hept-1-yne, 2 mol.% $Pd(OAc)_2$, and 20 mol.% of PPh_3.

** Determined by NMR spectroscopy with respect to the initial amount of Ph_2E_2.

When carried out under optimized conditions, the additions of diphenyl diselenide and diphenyl disulfide to various alkynes at 180 and 450 W, respectively, gave nearly 100% yields of the corresponding products (see Table 1) with high stereoselectivity ($Z/E > 97/3$). The configuration of the double bond in the reaction products was established by the 2D COSY-LR and NOESY NMR methods. The yields of the reaction products isolated by flash chromatography were 79—97%. The addition of diphenyl disulfide to alkynes can be performed at a microwave power of 900 W for 5 min and at 180 W for 100 min.

In spite of the longer reaction time, the lower microwave power is more preferable because of the higher stereoselectivity of the reaction achieved in this case. High microwave power and long heating time lead to the formation of the *E*-isomer of the product (up to 10—20%) due to the double bond isomerization or noncatalytic addition of diaryl dichalcogenides to alkynes by a radical mechanism.

In order to compare conventional heating and microwave-assisted heating, we additionally studied the reactions of PPh_3 with compounds **1a,b** (see Scheme 2) in a thermostated oil bath with magnetic stirring. The noncatalytic reaction does not proceed in toluene upon heating and in melt under solvent-free conditions (Table 5, entries *1*—*3*). The addition of palladium acetate (2 mol.%) followed by heating of the melt at 140 °C for 30 min leads to a 85% yield of the reaction product of **1b** and PPh_3; further heating of the melt leads to a virtually quantitative yield of the products (see Table 5, entries *6* and *7*). The half-conversion time determined from kinetic measurements was 17 min. At temperatures below 140 °C, the product yields were very low (see Table 5, entries *4* and *5*).

Table 5. Reactions of diphenyl disulfide (**1a**) and diphenyl diselenide (**1b**) with triphenylphosphine under conventional heating conditions*

Entry	Ph_2E_2	Solvent	*T*/°C	*t*/min	$Pd(OAc)_2$ (mol.%)	Yield** (%)	
						5	6
1	**1b**	Toluene	100	120	—	0	0
2	**1b**	—	100	120	—	0	0
3	**1b**	—	140	180	—	2	2
4	**1b**	Toluene	100	120	2	11	11
5	**1b**	—	100	120	2	4	4
6	**1b**	—	140	30	2	85	85
7	**1b**	—	140	60	2	94	94
8	**1a**	—	140	30	2	0	0

* Reactions were carried out in a tube with a screw cup containing 0.5 mmol of Ph_2E_2 and 0.5 mmol of PR'_3. The tubes were placed in a thermostatted oil bath with magnetic stirring.

** Determined by NMR spectroscopy with respect to the initial amount of Ph_2E_2.

No reaction of disulfide **1a** with PPh_3 occurred even at 140 °C (see Table 5, entry *8*). Thus, microwave heating allows the temperatures above 140 °C to be achieved rapidly, which substantially accelerates the formation of products **5** and **6** (*cf.* Tables 2 and 5).

In previous studies[13—16] of the mechanism of conventional thermal reaction it was established that the oxidative addition of compounds Ph_2E_2 (E = S, Se) to Pd^0/PPh_3 results in complexes $[Pd(EPh)_2(PPh_3)_2]$, which can undergo dimerization into $[Pd_2(EPh)_4(PPh_3)_2]$ dinuclear complexes under the reaction conditions. Recently,[7,8] we have shown that dinuclear complexes are also formed in a melt under solvent-free conditions. To establish the structure of the intermediates formed under microwave irradiation conditions, we performed a special NMR study. A Ph_2Se_2/PPh_3 mixture was melted by exposure to microwave irradiation directly in the NMR tube, $Pd(OAc)_2$ was added to the melt, and the mixture was heated in the microwave oven (450 W) for 2 min. The $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture exhibited the signals at δ 34.7, 27.0, 25.6, 24.6, 21.2, 16.7, and –4.6. The signals at δ 34.7, 24.6, and –4.6 correspond to $Se{=}PPh_3$, $O{=}PPh_3$, and PPh_3, respectively. The signals at δ 27.0 and 25.6 can be assigned to dinuclear complexes, *trans*-$[Pd_2(SePh)_4(PPh_3)_2]$ and *cis*-$[Pd_2(SePh)_4(PPh_3)_2]$, respectively. The structures of related complexes were established[13—16] by X-ray analysis and NMR spectroscopy. The signals at δ 21.2 and 16.7 can be attributed to mononuclear complexes, *trans*-$[Pd(SePh)_2(PPh_3)_2]$ and *cis*-$[Pd(SePh)_2(PPh_3)_2]$, respectively, but unambiguous proof of the structures of these complexes based on the ^{31}P NMR spectrum is impossible. Thus, our $^{31}P\{^1H\}$ NMR study revealed the formation of the same intermediate dinuclear complexes in melt under microwave irradiation conditions as those formed in conventional thermal reactions.[7,8]

A commonly accepted mechanism of the element—element bond activation in palladium-catalyzed addition to alkynes begins with oxidative addition of the E—E bond to Pd^0. It is logical to assume that activation of the C—E bond also involves the oxidative addition to Pd^0. To clarify the issue, we carried out a density functional quantum-chemical study of the reaction of Me_2Se_2 with PH_3 (see Scheme 2) with the B3LYP density functional method and the Lanl2dz(d) basis set (the model system was described in the Experimental).

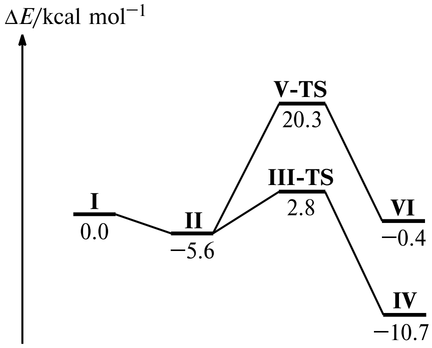
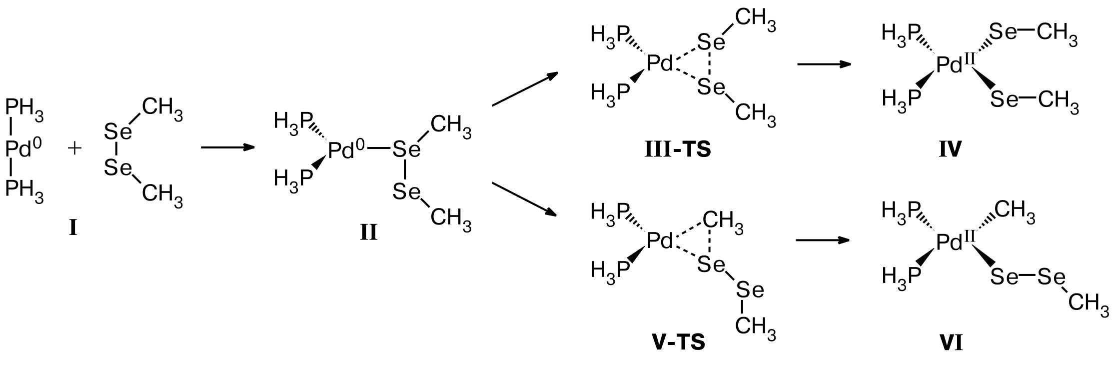


Fig. 1. Potential energy surface calculated for the oxidative addition reaction of Se—Se and Se—C bonds to palladium complexes.

Quantum-chemical calculations showed that both oxidative addition reactions begin with pre-coordination of the diselenide to the palladium atom (Scheme 3, Fig. 1 and 2) and formation of intermediate **II**. Both reactions have three-center transition states, **III-TS** and **V-TS**, in which two new bonds with the metal atom are formed simultaneously with cleavage of the Se—Se or C—Se bond (see Fig. 1). The transition state **V-TS** was more "late" in character compared to **III-TS**, as is evident from the Pd—Se bond lengths equal to 2.431 and 2.538 Å, respectively (see Fig. 2). The calculated geometric parameters are in good agreement with the energy characteristics. The oxidative addition of the Se—Se bond to the palladium complex (**II** → **III-TS** → **IV**) is characterized by an activation barrier, $\Delta E^{\neq}$, of 8.4 kcal mol^{-1} and an energy gain, ΔE, of –5.1 kcal mol^{-1}. The oxidative addition of the C—Se bond to the palladium complex (**II** → **V-TS** → **VI**) is characterized by a much higher activation barrier $\Delta E^{\neq} = 25.9$ kcal mol^{-1} and energy loss $\Delta E = 5.2$ kcal mol^{-1}.

Scheme 3



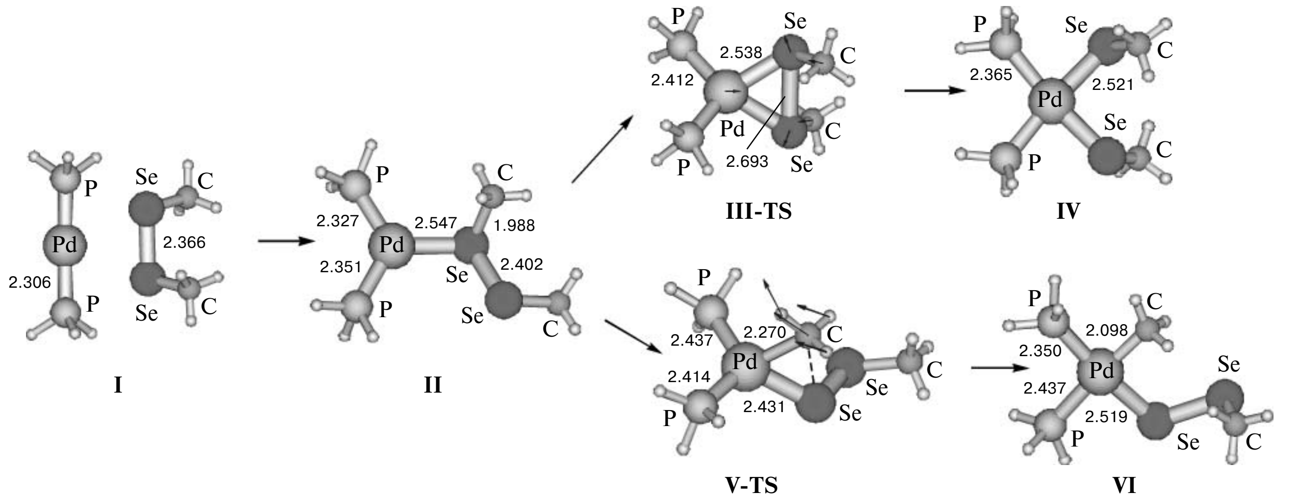


Fig. 2. Molecular structures of compounds **I**—**VI** optimized by the B3LYP/Lanl2dz(d) method.

The reaction products, namely, complexes **IV** and **VI**, have a square planar structure (see Fig. 2) typical of Pd^{II}. Complex **IV** is 10.3 kcal mol^{-1} more stable than complex **VI**.

In this case, the oxidative addition of the C—Se bond can be considered as hardly probable compared to the oxidative addition of the Se—Se bond. This means that cleavage of the selenium—carbon bond and formation of a new selenium—phosphorus bond occurs in the next reaction step and involves palladium(II) chalcogenide complexes.

A comparison of the Pd—P bond lengths in *trans*-position relative to the Me group and $SeCH_3$ fragments (see Fig. 2) gives the following order of the *trans* influence of the ligands is as follows: $CH_3 > SeCH_3$.

In recent studies[13—16] of the oxidative addition reaction in solution, it was shown that the initially formed complex $Pd(EAr)_2L_2$ undergoes dimerization into a dinuclear complex $Pd_2(EAr)_4L_2$. Therefore, in order to clarify the reaction mechanism, we performed quantum-chemical calculations of both complexes, *viz.*, mononuclear $Pd(SeCH_3)_2(PH_3)_2$, and dinuclear $Pd_2(SeCH_3)_4(PH_3)_2$.

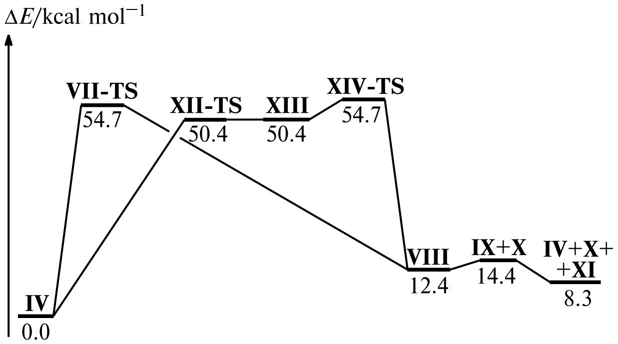
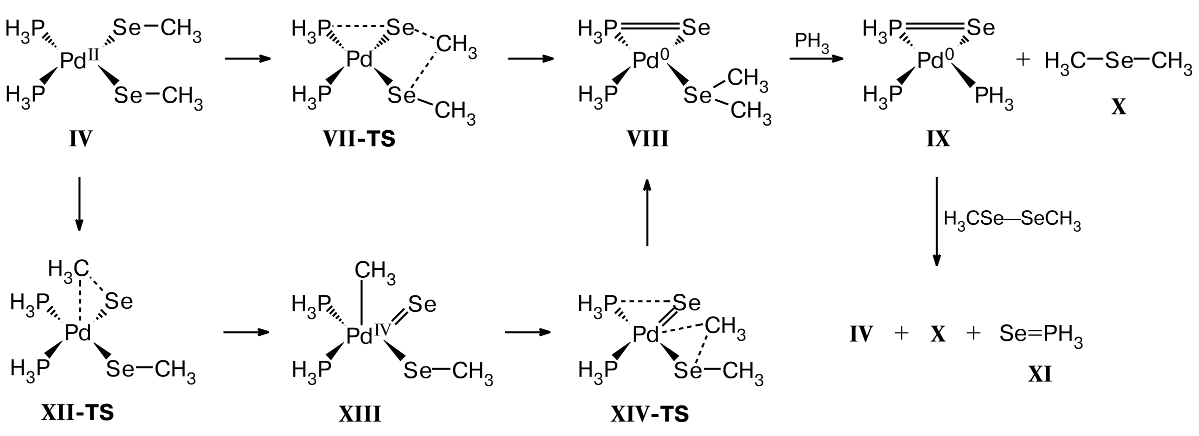


Fig. 3. Potential energy surface of 1,3- and 1,2-shifts of the Me group involving mononuclear palladium complexes.

The calculated pathways of formation of compounds $SeMe_2$ (**X**) and $Se=PH_3$ (**XI**) involving mononuclear palladium complexes are shown in Scheme 4 and in Fig. 3.

Scheme 4



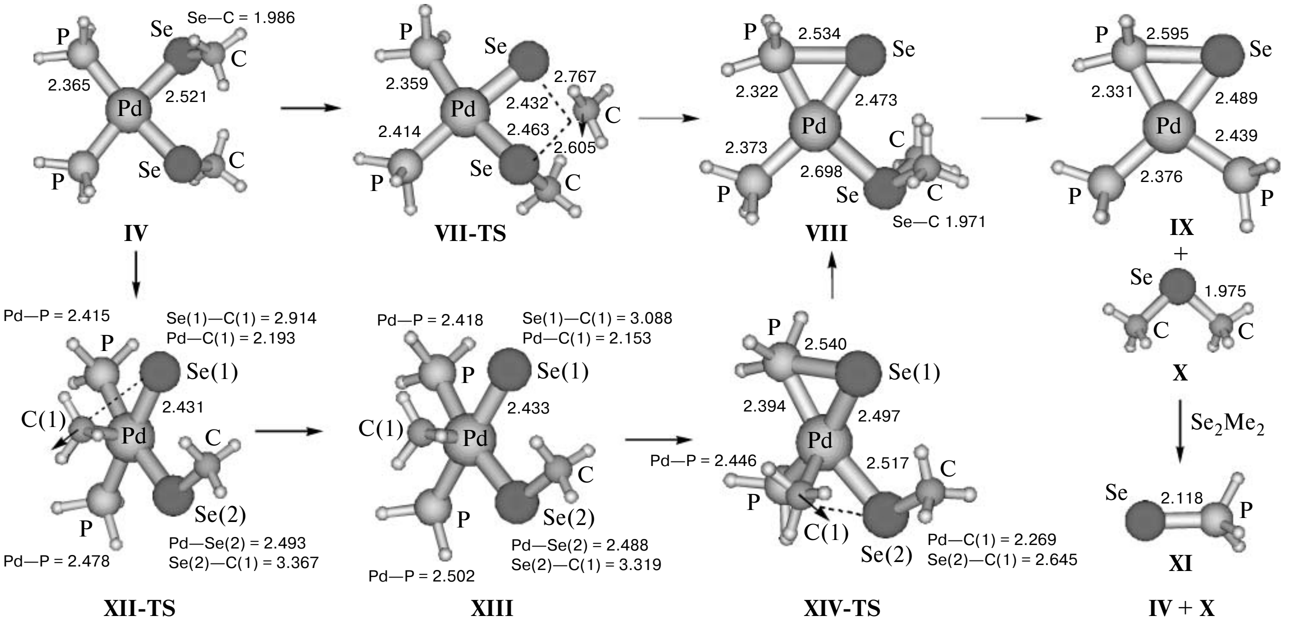


Fig. 4. Molecular structures of compounds **VII-TS**—**XI** optimized by the B3LYP/Lanl2dz(d) method.

The optimized molecular structures are presented in Fig. 4. We calculated this transformation assuming two different routes. One of them involves 1,3-transfer of Me group *via* transition state **VII-TS** in which the lengths of the broken and newly formed C—Se bonds are 2.767 and 2.605 Å, respectively (see Fig. 4). Motion along the reaction coordinate toward product **VIII** is accompanied by the formation of new carbon—selenium and phosphorus—selenium bonds, the oxidation state of the metal being decreased from Pd^{II} to Pd^0 (see Scheme 4). Ligand substitution in **VIII** leads to formation of complex **IX**. The catalytic cycle is completed after dissociation of **XI** and oxidative addition of the diselenide to $Pd(PH_3)_2$.

An alternative reaction pathway involves two consecutive 1,2-shifts of the Me group *via* transition states **XII-TS** and **XIV-TS** (see Scheme 4) with the lengths of the broken and newly formed C—Se bonds of 2.914 and 2.645 Å, respectively (see Fig. 4). In this case, the C—Se bond activation involves the oxidative addition resulting in a five-coordinate complex of Pd^{IV} (compound **XIII**). Shortening of the Pd=Se(1) bond to 2.433 Å compared to the Pd—Se(2) bond (2.488 Å) is evidence for the formation of a multiple palladium—selenium bond (see Fig. 4). Complex **XIII** cannot be considered as a stable intermediate owing to very low barrier to the reverse reaction **XIII** → **XII-TS** → **IV** (the energies of **XIII** and **XII-TS** are 50.37 and 50.44 kcal mol^{-1}, respectively). The barriers to reaction involving **VII-TS** and **XIV-TS** are 54.7 kcal mol^{-1}. Thus, for mononuclear palladium complexes both pathways (1,3-shift or two consecutive 1,2-shifts) can make equal contributions to the formation of the reaction product.

According to our calculations, activation of the carbon—chalcogen bond in dinuclear palladium complexes can also be a multipath process and follow alternative routes involving 1,3- and 1,2-shifts of the Me groups. Consider transfer of a Me group by a 1,3-shift (Scheme 5, Fig. 5 and 6). In dinuclear complex **XV**, the process can involve transfer of a Me group (1) from the bridging to the terminal selenium atom (**XV** → **XVI-TS** → **XVII**), (2) from the terminal to the bridging selenium atom (**XV** → **XVIII-TS** → **XIX**), and (3) between the bridging selenium atoms (**XV** → **XX-TS** → **XXI**). The calculated activation energies for the first and second reactions are 51.4 and 63.5 kcal mol^{-1}, respectively. We failed to locate the transition state **XX-TS**, because in this case geometry optimization led to the transition state of the 1,2-shift of the Me group (see below). It is noteworthy that the inter-

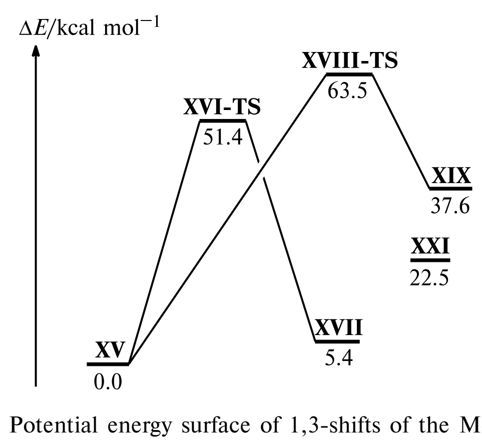
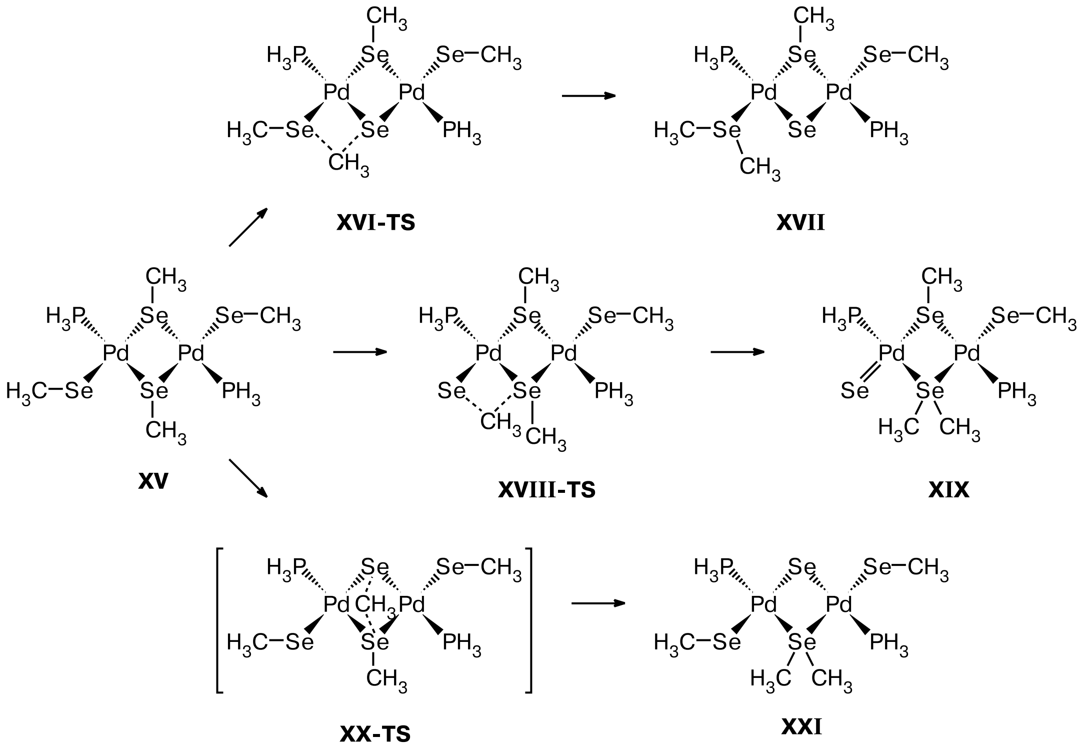


Fig. 5. Potential energy surface of 1,3-shifts of the Me group involving dinuclear palladium complexes.

Scheme 5



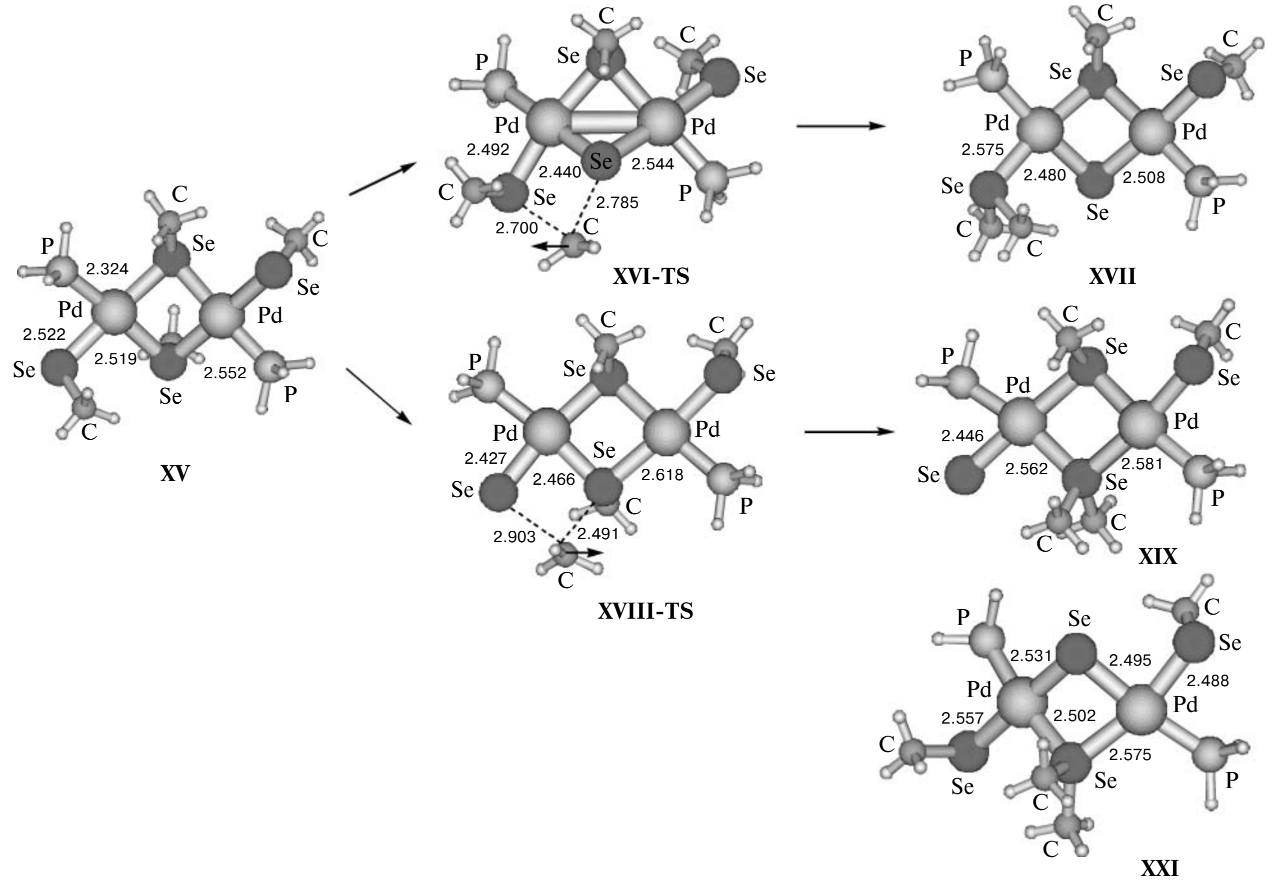
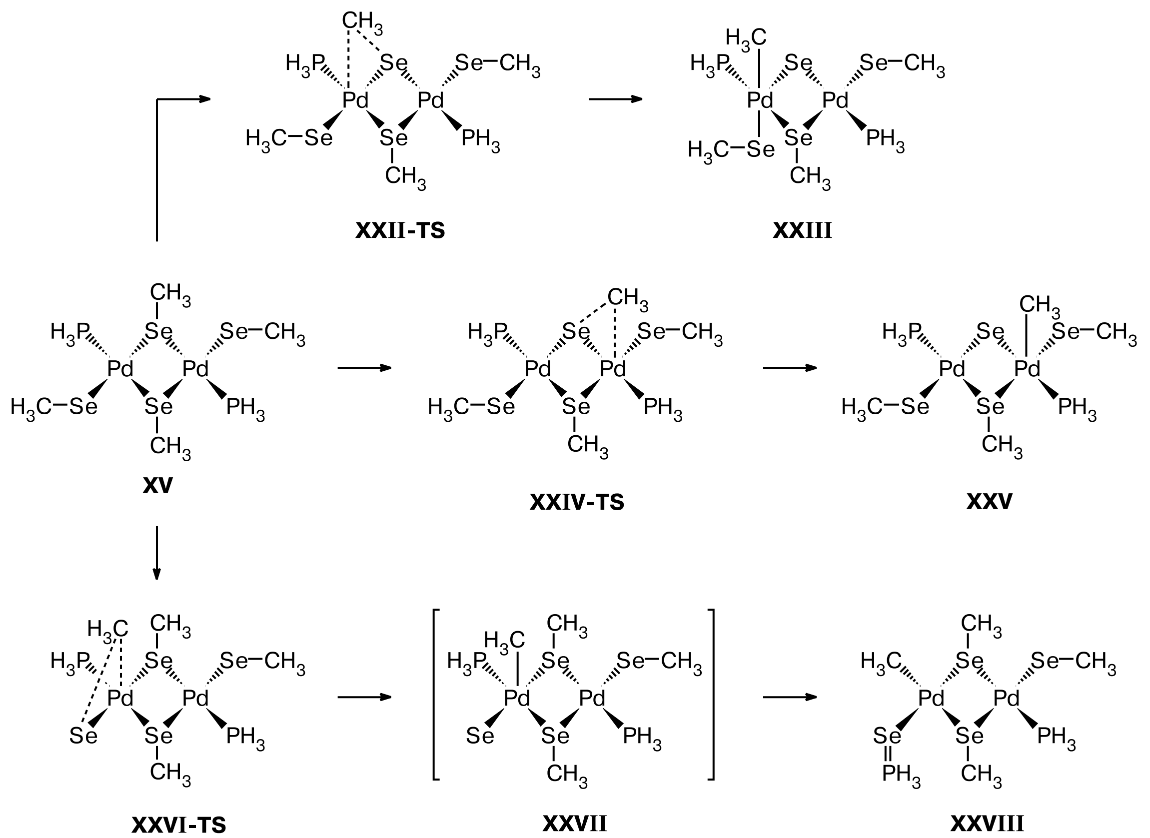


Fig. 6. Molecular structures of compounds **XV**—**XXI** optimized by the B3LYP/Lanl2dz(d) method.

Scheme 6



mediate complex with the bridging Se ligand (**XXI**) is 15 kcal mol^{-1} more stable then the complex with the terminal Se ligand (**XIX**).

A comparison of the lengths of the cleaved and newly formed C—Se bonds in **XVI-TS** (2.785 and 2.700 Å, respectively) and **XVIII-TS** (2.903 and 2.491 Å, respectively) suggests that the transition state **XVIII-TS** is more "late" than **XVI-TS** (see Fig. 6). This is in excellent agreement with the higher activation energy obtained for **XVIII-TS** (see Scheme 5 and Fig. 5). The bonds between palladium atoms and the bridging Se ligand in **XVII** (2.480 and 2.508 Å; see Fig. 6) are shorter than the corresponding bonds for the SeMe ligand in **XV** (2.519 and 2.552 Å; see Fig. 6) but longer than the Pd=Se bond in **XIII** (2.433 Å; see Fig. 4). The lengths of the bonds between palladium atoms and the $SeMe_2$ bridging ligand in **XIX** (2.562 and 2.581 Å; see Fig. 6) are intermediate between the lengths of the bonds of the SeMe bridging ligand in **XV** (2.519 and 2.552 Å; see Fig. 6) and the Pd—$SeMe_2$ bond length in **VIII** (2.698 Å; see Fig. 4). This is an indication of electron density delocalization on the palladium atoms in the dinuclear complexes **XVII** and **XIX**.

Three different transition states were located in quantum-chemical calculations of 1,2-shifts of the Me groups in the dinuclear palladium complexes (Scheme 6; Figs 7 and 8). Two transition states, **XXII-TS** and **XXIV-TS**, correspond to the Me group transfer from the bridging selenium atom to the palladium atom and one transition state, **XXVI-TS**, corresponds to the Me group transfer from the terminal selenium atom to the Pd atom. In the last-mentioned case, the motion along the reaction coordinate is accompanied by formation of a selenium—phosphorus bond, which results in complex **XXVIII**. A similar

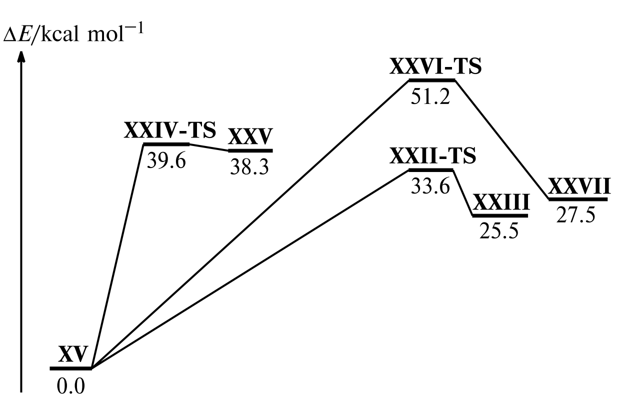


Fig. 7. Potential energy surface of 1,2-shifts of the Me group involving dinuclear palladium complexes.

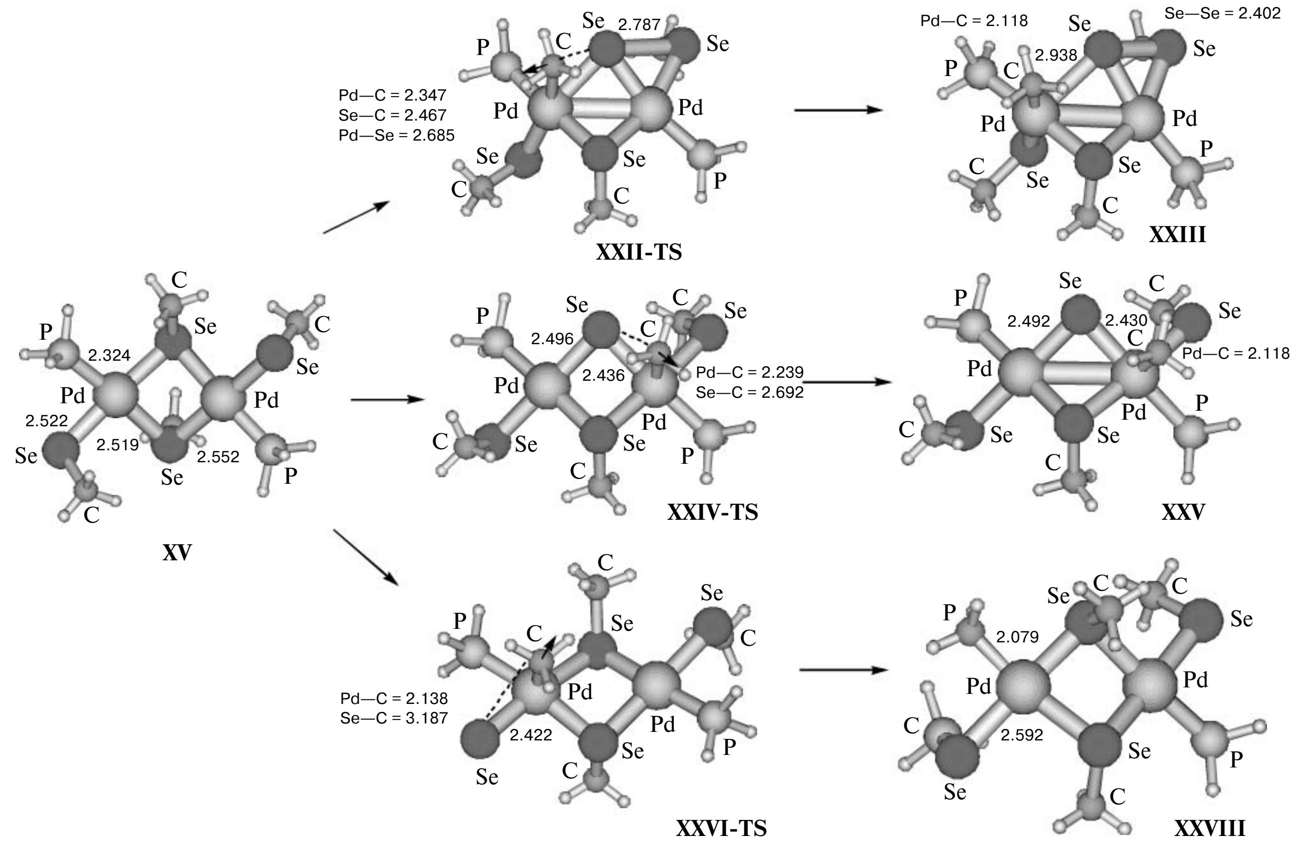


Fig. 8. Molecular structures of compounds **XXII-TS**—**XXVIII** optimized by the B3LYP/Lanl2dz(d) method.

process was also found for mononuclear palladium complexes (see above). The reaction leading to intermediate **XXV** is hardly probable due to the lower barrier to the reverse reaction (**XXV** → **XXIV-TS** → **XV**). It is noteworthy that the calculated activation barrier to cleavage of the Se—C bond *via* transition state **XXII-TS** is only 33.6 kcal mol^{-1}.

Among the three transition states of 1,2-shifts of the Me group in dinuclear complexes, the geometry of transition state **XXVI-TS** has the strongest similarity to that of the transition state **XII-TS** in the mononuclear complex (see Figs 2 and 8). These transition states are characterized by similar activation barriers (51.2 and 50.4 kcal mol^{-1}, respectively). It is noteworthy that in both cases we deal with the Me group shift from the terminal SeMe ligand to the palladium atom. The activation barriers to the cleavage of the selenium—carbon bond calculated for the Me group shift from the bridging SeMe ligand to the palladium atom are lower (33.6 and 39.6 kcal mol^{-1}; see Fig. 7). Thus, here we deal with a pronounced stabilization effect, which takes place in dinuclear palladium complexes.

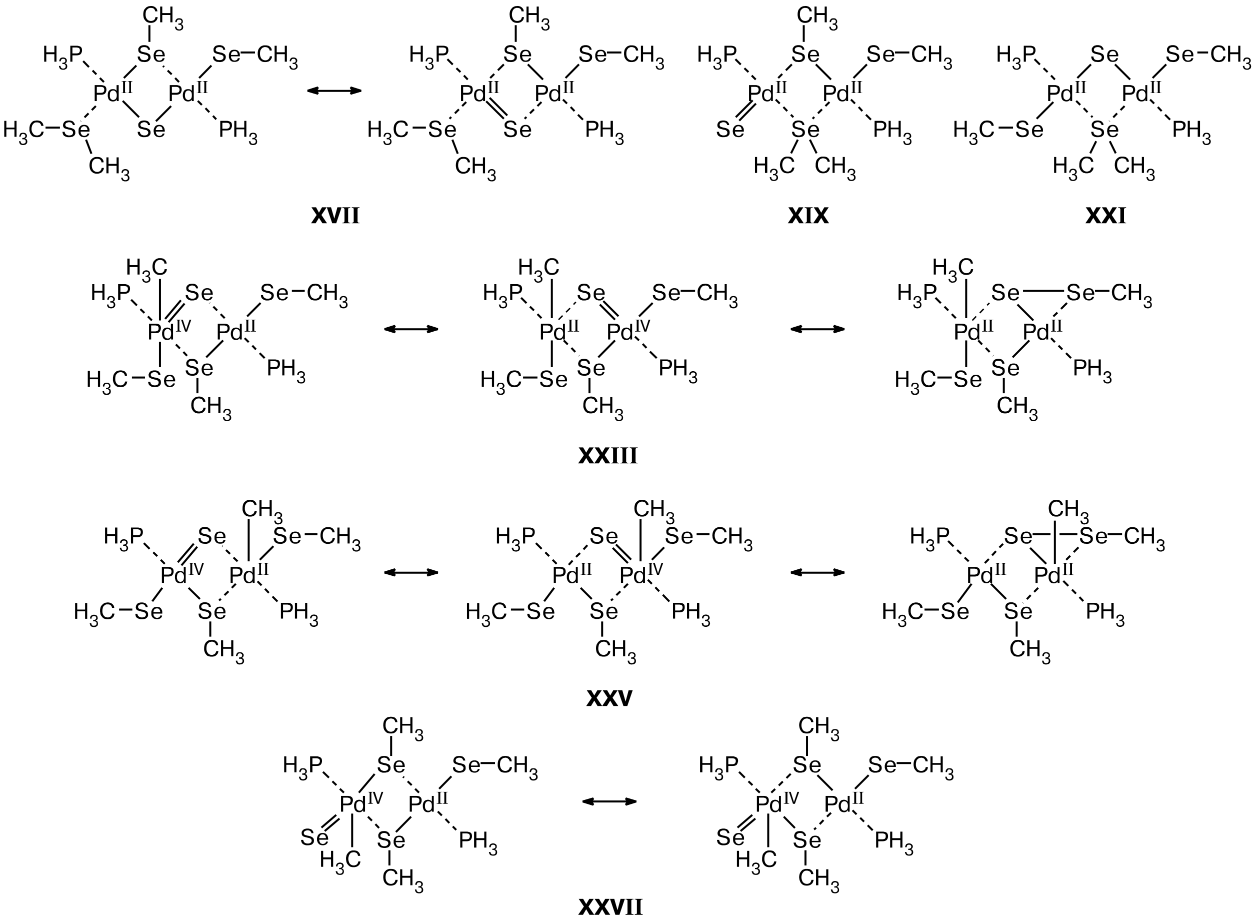
The relative stabilities of the intermediates **XVII**, **XIX**, **XXI**, **XXIII**, and **XXV** (see Schemes 5 and 6 and Figs 5 and 7) vary over a wide range (5—38 kcal mol^{-1}). Except for the systems **XIX** and **XXI**, the structures of these metal complexes can be described in terms of various resonance structures (Scheme 7). The highest relative stability is characteristic of the intermediates which (1) contain no terminal Se ligands, (2) contain no bridging $SeMe_2$ ligands, and (3) contain a minimum number of the resonance structures with Pd^{IV}. Combination of these three features gives the following series of the relative stability of metal complexes: **XVII** > **XXI**, **XXIII** > **XIX**, **XXV** (see Schemes 5 and 6 and Figs 5 and 7).

Based on the geometric parameters, the resonance structure with two Pd^{II} atoms contributes largely to the stabilization of complex **XXIII**. The Se—Se bond in complex **XXIII** (see Fig. 8) is only slightly longer than in free diselenide (2.402 Å *vs*. 2.366 Å), being equal to the bond length of coordinated diselenide in intermediate **II** (see Fig. 2).

Thus, additional stabilization of intermediates of the Se—C bond activation reaction in dinuclear palladium complexes is possible owing to electron density delocalization over the bridging ligands and to contribution of different resonance structures, which is impossible in the case of mononuclear complexes.

Geometry optimization of the transition state of the reaction of selenium—phosphorus bond formation involv-

Scheme 7



Note. Donor-acceptor bonds are denoted by dashed lines.

ing *cis*-arranged Se and PH_3 ligands in complexes **XVII**, **XIX**, **XXI**, **XXIII**, **XXV** led to compound **XI**. A similar reaction was discussed above for mononuclear complexes. Therefore, the reactions of dinuclear palladium complexes also result in products **X** and **XI**.

The results obtained in our calculations revealed the possibility of Se—C bond activation in both mononuclear and dinuclear palladium complexes. The lowest activation barrier was obtained for the C—Se bond cleavage *via* transition state **XXII-TS** ($\Delta E^{\neq}$ = 33.6 kcal mol^{-1}) in dinuclear complexes. This is consistent with modern concepts of involvement of such complexes in the reactions with alkynes in this system and is in agreement with the available experimental data.

The results of quantum-chemical calculations were discussed in terms of ΔE (see Schemes 3—6 and Figs 1, 3, 5, and 7). The results of calculations of the potential energy surface ΔH are listed in Table 6. It was found that the ΔE and ΔH values differ only slightly from one another, which confirms reliability of conclusions drawn.

Table 6. Relative energies of stationary points **I**—**XXVIII** obtained from B3LYP/Lanl2dz(d) calculations*

Stationary points	ΔE	ΔH	Stationary points	ΔE	ΔH
I	0.0	0.0	**XV**	0.0	0.0
II	−5.6	−4.6	**XVI-TS**	51.4	49.8
III-TS	2.8	3.0	**XVII**	5.4	5.3
IV	−10.7	−9.1	**XVIII-TS**	63.5	62.1
V-TS	20.3	19.7	**XIX**	37.6	37.7
VI	−0.4	0.5	**XXI**	22.5	22.4
VII-TS	54.7	53.4	**XXII-TS**	33.6	32.0
VIII	12.4	12.7	**XXIII**	25.5	24.6
IX + **X**	14.4	15.0	**XXIV-TS**	39.6	38.2
IV + **XI** + **X**	8.3	9.6	**XXV**	38.3	37.6
XII-TS	50.4	49.0	**XXVI-TS**	51.2	50.1
XIII	50.4	49.5	**XXVIII**	27.5	27.1
XIV-TS	54.7	53.2			

* The energies of the stationary points **II**—**XIV-TS** were calculated relative to the energy of the stationary point **I** and the energies of the stationary points **XVI-TS**—**XXVIII** were calculated relative to the energy of the stationary point **XV**.

* * *

Thus, in the present work we realized for the first time a catalytic element—element bond activation followed by the addition to alkynes under microwave irratiation conditions. It was shown that the reaction in Ph_2S_2/PPh_3 melt proceeds as palladium-catalyzed stereoselective addition of diphenyl disulfide to the triple bond, resulting in nearly 100% yields of *Z*-(PhS)HC=C(SPh)R. The reaction involving diphenyl diselenide depends on the microwave power. At low microwave power, a palladium-catalyzed stereoselective synthesis of *Z*-(PhSe)HC=C(SePh)R similar to the reaction involving diphenyl disulfide proceeds in the Ph_2Se_2/PPh_3 melt. At a higher microwave power, a previously unknown catalytic reaction of diphenyl diselenide with triphenylphosphine resulting in $Se=PPh_3$ and Ph_2Se proceeds in the system under study. A similar chemical transformation is also characteristic of other phosphine and phosphite ligands.

Oxidative addition of Ph_2Se_2 to Pd^0 in Ph_2Se_2/PPh_3 melt under microwave irradiation conditions results in $[Pd_2(SePh)_4(PPh_3)_2]$ dinuclear complexes detected by $^{31}P\{^1H\}$ NMR spectroscopy.

According to the results of quantum-chemical calculations, both mononuclear and dinuclear palladium complexes can catalyze the Se—C bond cleavage reaction. The reactions involving dinuclear complexes can proceed with smaller energy requirements, which is due to stabilization of the bridging selenium ligands.

This work was financially supported by the Russian Federation Presidential Foundation (Grant for Young Scientists MD-2384.2004.3), the Russian Foundation for Basic Research (Project No. 04-03-32501), and the Chemistry and Materials Science Division of the Russian Academy of Sciences (in the framework of the Program No. 1 "Theoretical and experimental investigations of the nature of chemical bonding and mechanisms of the most important chemical reactions and processes").

References

1. M. Larhed, C. Moberg, and A. Hallberg, *Acc. Chem. Res.*, 2002, **35**, 717.
2. K. Tanaka and F. Toda, *Chem. Rev.*, 2000, **100**, 1025.
3. R. S. Varma, *Pure Appl. Chem.*, 2001, **73**, 193.
4. J. O. Metzger, *Angew. Chem., Int. Ed. Engl.*, 1998, **37**, 2975.
5. A. Loupy, A. Petit, J. Hamelin, F. Texier-Boullet, P. Jacquault, and D. Mathe, *Synthesis*, 1998, 1213.
6. I. V. Tselinskii, A. A. Astrat´ev, and A. S. Brykov, *Zh. Obshch. Khim.*, 1996, **66**, 1699 [*Russ. J. Gen. Chem.*, 1996, **66** (Engl. Transl.)].
7. V. P. Ananikov and I. P. Beletskaya, *Org. Biomol. Chem.*, 2004, **2**, 284.
8. V. P. Ananikov and I. P. Beletskaya, *Izv. Akad. Nauk. Ser. Khim.*, 2004, 534 [*Russ. Chem. Bull., Int. Ed.*, 2004, **53**, 561].
9. H. Kuniyasu, A. Ogawa, S.-I. Miyazaki, I. Ryu, N. Kambe, and N. Sonoda, *J. Am. Chem. Soc.*, 1991, **113**, 9796.
10. A. Ogawa, *J. Organomet. Chem.*, 2000, **611**, 463.
11. V. P. Ananikov, M. A. Kabeshov, I. P. Beletskaya, G. G. Aleksandrov, and I. L. Eremenko, *J. Organomet. Chem.*, 2003, **687**, 451.
12. V. P. Ananikov, I. P. Beletskaya, G. G. Aleksandrov, and I. L. Eremenko, *Organometallics*, 2003, **22**, 1414.
13. R. Oilunkaniemi, R. S. Laitinen, and M. Ahlgren, *J. Organomet. Chem.*, 2001, **623**, 168.
14. R. Oilunkaniemi, R. S. Laitinen, and M. Ahlgren, *J. Organomet. Chem.*, 1999, **587**, 200.
15. I. Nakanishi, S. Tanaka, K. Matsumoto, and S. Ooi, *Acta Crystallogr., Sect. C.*, 1994, **50**, 58.
16. M. S. Hannu-Kuure, K. Paldán, R. Oilunkaniemi, R. S. Laitinen, and M. Ahlgren, *J. Organomet. Chem.*, 2003, **687**, 538.
17. A. D. Becke, *Phys. Rev. A*, 1988, **38**, 3098.
18. C. Lee, W. Yang, and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785.
19. A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648.
20. P. J. Hay and W. R. Wadt, *J. Chem. Phys.*, 1985, **82**, 270.
21. W. R. Wadt and P. J. Hay, *J. Chem. Phys.*, 1985, **82**, 284.
22. P. J. Hay and W. R. Wadt, *J. Chem. Phys.*, 1985, **82**, 299.
23. T. H. Dunning, Jr. and P. J. Hay, in *Modern Theoretical Chemistry*, Ed. H. F. Schaefer, III, Vol. **3**, Plenum, New York, 1976, 1.
24. R. Ditchfield, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, 1971, **54**, 724.
25. G. Orlova and J. D. Goddard, *J. Phys. Chem. A*, 1999, **103**, 6825.
26. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, *Gaussian 03, Rev. C. 1*, Gaussian, Inc., Pittsburgh (PA), 2003.
27. G. Schaftenaar and J. H. Noordik, *J. Comput.-Aided Mol. Des.*, 2000, **14**, 123.
28. A. Dedieu, *Chem. Rev.*, 2000, **100**, 543.
29. D. G. Musaev and K. Morokuma, *Top. Catal.*, 1999, **7**, 107.
30. N. Koga and K. Morokuma, *Chem. Rev.*, 1991, **91**, 823.

Received December 10, 2004;
in revised form February 16, 2005