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Mechanistic Investigation and New Catalyst Design in Palladium- and Platinum-Catalyzed Se−Se Bond Addition to Alkynes

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The present study explains the different catalytic activities of platinum and palladium in Se−Se addition reactions with alkynes. Under the catalytic conditions *cis*-$[Pt(SePh)_2(PPh_3)_2]$ undergoes fast isomerization to the trans isomer, which does not react with alkynes. Palladium complexes maintain their catalytic activity, due to the formation of the dinuclear structure $[Pd_2(SePh)_4(PPh_3)_2]$. It was shown that the palladium intermediate involved in the catalytic cycle can be prepared directly in the reaction mixture starting from the simple $[PdCl_2(PPh_3)_2]$ precursor, thus allowing replacement for the traditional $Pd(PPh_3)_4$ catalyst. X-ray analysis shows that the products of Se−Se addition reactions with alkynes possess the necessary geometry parameters for coordination as bidentate ligands.

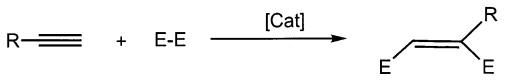
1. Introduction

Transition-metal-catalyzed element−element (E−E) addition to alkynes represents an efficient single-step way to form two C_{sp^2}−E bonds in a stereoselective manner.[1] The process can be performed with 100% atom efficiency, since no waste materials are formed. Stereoselectivity of the catalytic cycle is very high, and in the majority of cases E−E addition proceeds in a syn manner (Scheme 1), but in some cases a mixture of *E* and *Z* isomers may be obtained due to parallel noncatalytic addition or isomerization.[1]

One of the very well-known examples is Pd(0)-catalyzed S−S and Se−Se bond addition to alkynes developed by Ogawa, Sonoda, et al.[2] With 5 mol % of catalyst S−S addition to 1-octyne resulted in 77% and 21% yields for $Pd(PPh_3)_4$- and $Pt(PPh_3)_4$-catalyzed transformations, respectively. The catalytic process leads to the expected *Z* isomers,[2] with a few exceptions of *E*/*Z* mixtures obtained due to noncatalytic thermal addition.[2] The latter reaction is known to proceed according to either free radical[3,4] or nucleophilic[5] mechanisms.

The products of E−E (E = S, Se) addition reactions are of high practical interest. Alkenyl selenides (E = Se) have found important application in synthetic organic chemistry.[6−9] Bis-selenium-substituted derivatives of *Z* stereochemistry were shown to coordinate to transition metals as chelate ligands, forming stable complexes.[10−13] The latter and related compounds are in demand in materials science as precursors of semiconducting[14] and advanced optical materials.[15]

Scheme 1. General Scheme of E−E Addition Reactions with Alkynes



E-E = S-S, Se-Se, B-B, Sn-Sn, Si-Si, etc.

The generally accepted mechanism of transition-metal-catalyzed E−E bond addition to alkynes (Scheme 2) is believed to be roughly the same for a wide range of elements involved (E = S, Se, B, Sn, Si, Ge, etc.)[1,2] to include the following steps: (1) E−E oxidative addition to the metal center (step i), (2) alkyne coordination to a π-complex (step ii), (3) intramolecular insertion (step iii), and (4) reductive elimination leading to carbon−element

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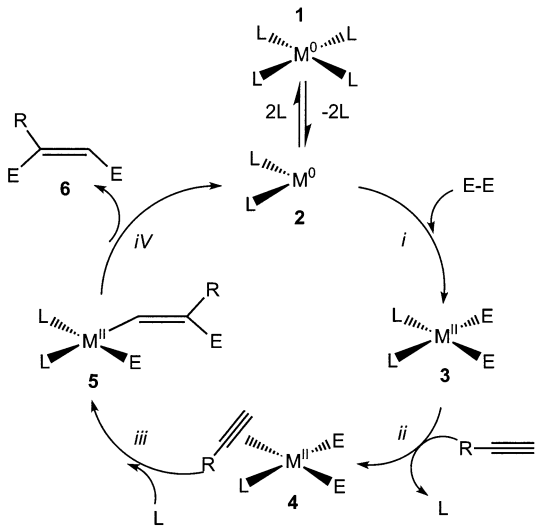
Scheme 2. Proposed Mechanism of Catalytic E−E Addition Reactions



(C−E) bond formation (step iv). However, the actual realization of this scheme is substantially element and catalyst dependent. For example, the origins of different chalcogenide reactivities cannot be resolved at the moment.[1,2] The metal dependence is rather difficult to rationalize. For example, both B−B and S−S (Se−Se) addition reactions are believed to take place within similar mechanisms (Scheme 2). However, for the former case Pt(0) was found to be the best catalyst and Pd(0) was inactive,[16] while in the latter case Pd(0) was superior to Pt(0).[2]

Attempts to clarify the situation by considering the properties of catalytic cycle intermediates (**3**) again bring up several puzzling questions. Stoichiometric reactions of E−E (E = S, Se, Te) oxidative additions to Pd(0) result in the isolation of dinuclear $[Pd_2E_4L_2]$ complexes,[17−21] while the same process for Pt(0) leads mainly to the isolation of *trans*-$[PtL_2E_2]$ derivatives[18,22−24] with a small amount of corresponding dinuclear compounds.[18] The generally accepted mechanism of the catalytic cycle assumes *cis*-$[ML_2E_2]$ (**3**) formation after an oxidative addition reaction (step i, Scheme 2).

We decided to perform a detailed mechanistic investigation to understand the role of mono- and dinuclear metal complexes and to rationalize dramatic differences in catalytic activity between platinum and palladium. Homogeneous $Pd(PPh_3)_4$- and $Pt(PPh_3)_4$-catalyzed Se−Se addition reactions were chosen as models for the study. In addition to the great synthetic importance of selenium compounds, ^{77}Se NMR through inverse detected HMQC experiments allows rather easy structure and stereochemistry determination.

In addition, a new efficient catalytic system has been developed to be utilized under simplified reaction conditions on the basis of easily available transition-metal complexes.

2. Results

The stoichiometric reaction between $Pd(PPh_3)_4$ and Ph_2Se_2 in toluene-d_8 resulted in the appearance of three $^{31}P\{^1H\}$ resonances at δ 28.2, 26.9, and −4.8 ppm within 10−20 min at room temperature. The first two resonances can be assigned to cis and trans isomers of $[Pd_2(SePh)_4(PPh_3)_2]$ (**8** and **9**; Scheme 3), for which NMR data and X-ray structures have been reported;[20] the last signal can be attributed to PPh_3.

The same products have been observed while performing the reaction under catalytic conditions in toluene-d_8 at 80 °C. The addition of alkynes to the mixture of **8** and **9** leads to the (*Z*)-alkenyl diselenides **6** (Scheme 3). Reactions with alkynes were slow at lower temperatures: i.e., 5% conversion of propargyl alcohol to **6b** was detected after 2 h at 30 °C. Heating at 80 °C leads to quantitative formation of **6a** and **6b** after ca. 2 h.

The ^{31}P NMR monitoring of the 1:1 mixture of Ph_2Se_2 and $Pt(PPh_3)_4$ resulted in detection of *trans*-$[Pt(PPh_3)_2(SePh)_2]$ (**12**), according to published NMR data (δ 20.3 ppm, $J(Pt-P) = 2841.6$ Hz),[23] and PPh_3 (−4.8 ppm) as final products of Se−Se oxidative addition reactions in toluene-d_8 at 80 °C. No product formation was observed upon alkyne addition to this complex at both room temperature and 80 °C. When the oxidative addition process was performed at room temperature directly in the NMR tube, signals corresponding to *cis*-$[Pt(PPh_3)_2(SePh)_2]$ (**11**) were detected ($^{31}P\{^1H\}$ 18.7 ppm, $J(Pt-P) = 2966.3$ Hz), the intensity of which decrease upon staying in solution, with a simultaneous increase in the intensity of the resonances for the trans isomer **12**. A 1:1 mixture of cis and trans isomers has been obtained within 1 h at 30 °C, and quantitative conversion is achieved after several hours. Performing the reaction of Ph_2Se_2 with $Pt(PPh_3)_4$ followed by immediate addition of the alkyne resulted in the product formation (Scheme 3).

Therefore, we may postulate that the cis complex **11** is formed first after the oxidative addition reaction and is involved in the product formation, while the trans derivative **12** results from the isomerization process and is inactive toward alkynes.

We have found that the isomerization reaction becomes slow at −5 °C. At this temperature complex **11** can be isolated, and we were able to obtain single crystals. The molecular structure of **11** is shown in Figure 1, and selected geometry parameters are given in Table 1. X-ray analysis unambiguously confirmed the proposed structure of this important intermediate complex.

$^{31}P\{^1H\}$ NMR monitoring of a catalytic reaction with 3 mol % of the catalyst in toluene-d_8 at 80 °C has shown the presence of the same 28.2 and 26.9 ppm resonances (**8** and **9**) and PPh_3 (−4.8 ppm). In the case of platinum,

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Scheme 3. Stoichiometric Se−Se Oxidative Addition and Alkyne Insertion Reactions

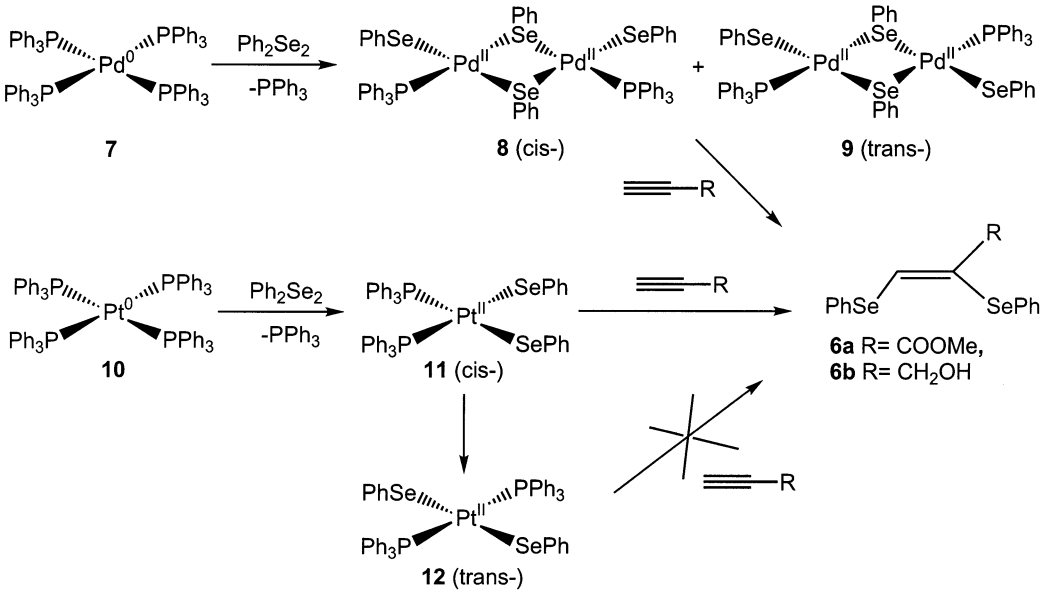


Table 1. Selected Bond Lengths (Å) and Angles (deg) for 11

Pt(1)−P(1)	2.310(2)	P(1)−C(13)	1.836(8)
Pt(1)−P(2)	2.3111(19)	P(1)−C(19)	1.844(8)
Pt(1)−Se(2)	2.4604(10)	P(1)−C(25)	1.853(7)
Pt(1)−Se(1)	2.4970(9)	P(2)−C(31)	1.811(7)
Se(1)−C(1)	1.916(8)	P(2)−C(43)	1.830(8)
Se(2)−C(7)	1.937(8)	P(2)−C(37)	1.839(8)
P(1)−Pt(1)−P(2)	97.31(7)	C(7)−Se(2)−Pt(1)	113.1(2)
P(1)−Pt(1)−Se(2)	173.52(6)	C(13)−P(1)−Pt(1)	122.1(3)
P(2)−Pt(1)−Se(2)	85.75(6)	C(19)−P(1)−Pt(1)	106.7(3)
P(1)−Pt(1)−Se(1)	82.25(5)	C(25)−P(1)−Pt(1)	114.5(3)
P(2)−Pt(1)−Se(1)	175.04(6)	C(31)−P(2)−Pt(1)	112.1(3)
Se(2)−Pt(1)−Se(1)	95.19(3)	C(43)−P(2)−Pt(1)	111.8(2)
C(1)−Se(1)−Pt(1)	106.8(2)	C(37)−P(2)−Pt(1)	120.2(2)

$^{31}P\{^{1}H\}$ NMR monitoring of a toluene-d_8 solution at 80 °C showed the presence of PPh_3 (−4.8 ppm) and a 20.3 ppm resonance with ^{195}Pt satellites (J(Pt−P) = 2841.6 Hz), which corresponds to **12**.

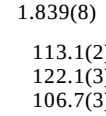
As shown in Table 2, $Pd(PPh_3)_4$ has been found as much more efficient catalyst—100% and 41% yields for alkyne with R = COOMe, CH_2OH, respectively, after 5 h, while $Pt(PPh_3)_4$ is inactive (entries 1−4). Similar relative catalyst activity was observed for Ph_2S_2 addition to octyne-1.[2]

Kinetic measurements in the initial concentration region in the range of (0.5− 6.2) × 10^{-4} M (0.09−0.36 mol %) catalyst concentration were performed for the Ph_2Se_2 addition reaction with propargyl alcohol at 80 °C.[25] A linear dependence of observed first-order rate constants vs initial [$Pd_2(SePh)_4(PPh_3)_2$] concentration has been found.

For the further catalytic reaction study, we decided to check whether the activity of palladium selenide complexes might depend on the way they are prepared. The catalytic reaction intermediates [$Pd_2(SePh)_4(PPh_3)_2$] (**8** and **9**) were synthesized from $PdCl_2(PPh_3)_2$ through chloride ligand substitution with [$PhSe^-$] obtained in situ by reduction of Ph_2Se_2 with $NaBH_4$. A pyridine solution of $NaBH_4$ was found to be the best for an in situ ligand exchange reaction, though fresh solutions of $NaBH_4$ in MeOH or EtOH may also be used.

(25) For details of kinetic measurements, see the Supporting Information.

Table 2. Ph_2Se_2 Addition to Alkynes Catalyzed by Transition-Metal Complexes[a]

	Catalyst	Alkyne	Product(s)	Yield[b], %	Z/E
1	$Pd(PPh_3)_4$	HC≡C-COOMe	**6a**	100	1.4/1.0
2	$Pd(PPh_3)_4$	HC≡C-CH_2OH	**6b**	41[d]	1.0/0.0
3	$Pt(PPh_3)_4$	HC≡C-COOMe	**6a**	9[e]	1.0/1.7
4	$Pt(PPh_3)_4$	HC≡C-CH_2OH	**6b**	0[e]	-
5	$Pd(PPh_3)_2Cl_2$[c]	HC≡C-COOMe	**6a**	100	1.4/1.0
6	$Pd(PPh_3)_2Cl_2$[c]	HC≡C-CH_2OH	**6b**	46[d]	1.0/0.0
7	$Pd(PPh_3)_2Cl_2$[c]		**6c**	20[d]	1.0/0.0
8	$Pd(PPh_3)_2Cl_2$[c]	HC≡C-CH_2-NMe_2	**6d**	19[d]	1.0/0.0
9	$Pd(DPPB)Cl_2$[c]	HC≡C-CH_2OH	**6b**	17	1.0/0.0
10	$Pd(PCy_3)_2Cl_2$[c]	HC≡C-CH_2OH	**6b**	8	1.0/0.0
11	$Pd(DPPE)Cl_2$[c]	HC≡C-CH_2OH	**6b**	5	1.0/0.0
12	$Pd(CH_3CN)_2Cl_2$[c]	HC≡C-CH_2OH	**6b**	0	-
13	$Pd(PPh_3)_2Cl_2$[c,f]	HC≡C-CH_2OH	**6b**	46[d]	1.0/0.0
14	$Pd(PPh_3)_2Cl_2$[c,f]	HC≡C-COOMe	**6a**	100	1.4/1.0

[a] Unless otherwise stated, the reactions were performed as described in the Experimental Section. [b] Determined by NMR after 5 h. [c] Treated with $NaBH_4$/Py; see the Experimental Section. [d] Final yields of 60% were obtained after reaction time of 15−20 h. [e] Increasing the reaction time to 15 h does not increase the yield. [f] Regular conditions were used without treatment under argon.

A $^{31}P\{^{1}H\}$ NMR spectrum of the reaction mixture after $NaBH_4$/pyridine addition indicated the presence of 28.2 and 26.9 ppm resonances, thus confirming that the same palladium complexes have been formed as were found in the Ph_2Se_2 addition to $Pd(PPh_3)_4$.

Our results show that $PdCl_2(PPh_3)_2$ neither catalyzes Se−Se addition reactions with alkynes nor catalyzes S−S addition, as has been reported earlier.[2] However, adding a small amount of $NaBH_4$ directly to the reaction mixture, which already contains Ph_2Se_2, initiates the catalytic process (Table 2, entries 5−8). The yield and stereoselectivity are the same as those observed for $Pd(PPh_3)_4$ (Table 2).

A ligand dependence study (L = PPh_3, PCy_3, DPPE, DPPB, CH_3CN) has shown that the triphenylphosphine ligand is the best choice for the catalytic synthesis of (*Z*)-alkenyl diselenides (Table 2, entries 6, 9−12). Introducing chelate ligands leads to a mononuclear palladium(II) diselenide complex with cis geometry, as

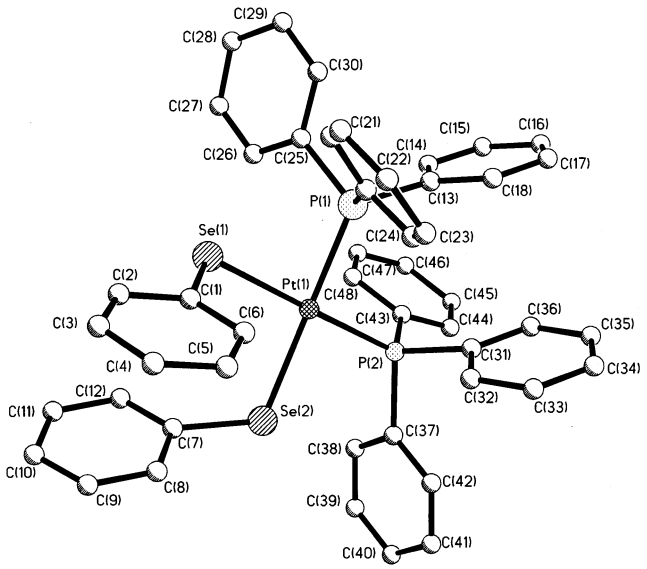


Figure 1. Structure of *cis*-[$Pt(SePh)_2(PPh_3)_2$] (**11**).

confirmed by the X-ray structure of [$Pd(SePh)_2$(DPPE)].[26] However, the complex was quite inactive in the catalytic reaction (Table 2, entry 11). To check the results, we have synthesized [$Pd(SePh)_2$(DPPE)] according to literature methods[26] and performed a stoichiometric reaction with HC≡CCOOMe. ^{1}H NMR monitoring over 3 h of a toluene solution at 80 °C has indicated only traces of the product, while $^{31}P\{^1H\}$ resonances of the palladium complex remained unchanged. The result suggests that mononuclear palladium complexes are less active toward alkynes. The better donor ligand tricyclohexylphosphine (PCy_3) does not increase the catalytic activity of the palladium complex (Table 2, entry 10).

With an alkyne bearing an electron-acceptor substituent (Table 2, entry 5), a higher yield has been observed, though a mixture of *E* and *Z* isomers is formed. The formation of two isomers in the case of methyl propiolate (entry 5) and a single isomer in the case of other alkynes (entries 6−8) has been clearly detected using ^{1}H−^{77}Se HMQC experiments. The assignment of stereochemistry for all products was performed according to NOESY data and verified by X-ray structure (see below).

It was very interesting to note that the developed catalytic system can be employed under regular experimental conditions in air (Table 2, entries 13 and 14), in contrast to $Pd(PPh_3)_4$- and $Pt(PPh_3)_4$-catalyzed reactions, which usually are performed under an inert atmosphere.

Although (*Z*)-alkenyl diselenides have been long considered as possible chelate ligands, to the best of our knowledge the X-ray structures of these ligands have not yet been reported. All of the products of Se−Se addition synthesized in the present work and by others[2] are oils. X-ray-quality single crystals were obtained for alkenyl diselenide **6** (R = CH_2NMe_2) by converting it into the salt. The structure is shown in Figure 2, and corresponding geometry parameters are given in Table 3.

The alkene unit possesses the typical geometry for sp^2-hybridized atoms (Figure 2), with a C=C distance

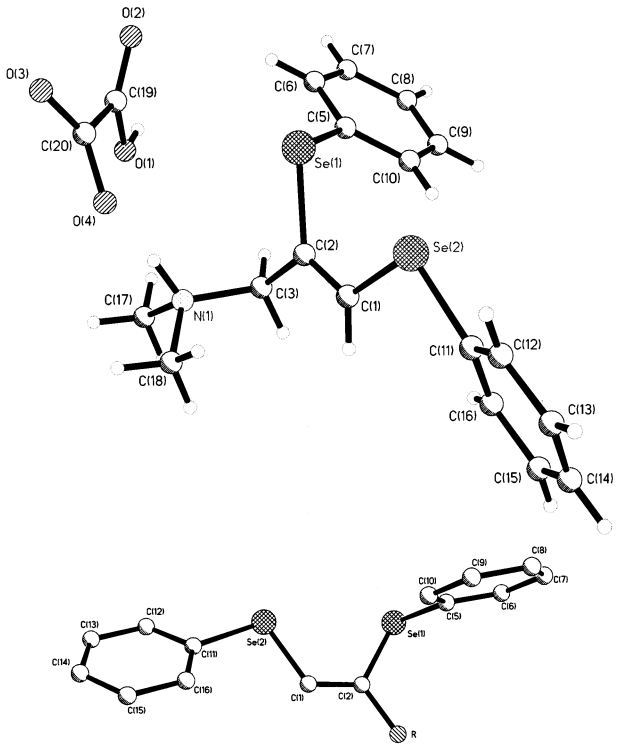


Figure 2. Structure of (*Z*)-(SePh)CH=C(SePh)CH_2N-Me_2*HOOCCOOH (**6e**).

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 6e

Se(1)−C(2)	1.915(5)	N(1)−C(3)	1.486(5)
Se(1)−C(5)	1.923(5)	N(1)−C(18)	1.494(5)
Se(2)−C(1)	1.879(5)	N(1)−C(17)	1.497(6)
Se(2)−C(11)	1.914(5)	C(1)−C(2)	1.326(6)
O(1)−C(19)	1.303(5)	C(2)−C(3)	1.493(6)
O(2)−C(19)	1.208(5)	C(5)−C(6)	1.372(7)
O(3)−C(20)	1.226(5)	C(19)−C(20)	1.529(6)
O(4)−C(20)	1.265(5)		
C(2)−Se(1)−C(5)	96.3(2)	C(6)−C(5)−Se(1)	119.5(4)
C(1)−Se(2)−C(11)	99.9(2)	C(10)−C(5)−Se(1)	120.1(4)
C(3)−N(1)−C(18)	111.5(3)	C(16)−C(11)−Se(2)	123.7(4)
C(3)−N(1)−C(17)	111.3(4)	C(12)−C(11)−Se(2)	116.5(4)
C(18)−N(1)−C(17)	110.3(4)	O(2)−C(19)−O(1)	125.3(5)
C(2)−C(1)−Se(2)	122.8(4)	O(2)−C(19)−C(20)	121.3(4)
C(1)−C(2)−C(3)	122.5(4)	O(1)−C(19)−C(20)	113.3(4)
C(1)−C(2)−Se(1)	120.0(4)	O(3)−C(20)−O(4)	126.7(4)
C(3)−C(2)−Se(1)	117.4(3)	O(3)−C(20)−C(19)	116.9(4)
N(1)−C(3)−C(2)	113.8(4)	O(4)−C(20)−C(19)	116.4(4)
C(6)−C(5)−C(10)	120.4(5)		

of 1.326 Å and an Se−C=C−Se dihedral angle of only 0.9°. Bond angles (C−C−Se) are also close to the expected 120° values. Most likely, (*Z*)-alkenyl diselenides are not subject to internal steric strain due to cis-positioned PhSe groups.

Two selenium atoms are located at distances of 1.879 and 1.915 Å from the C1 and C2 vinyl atoms, respectively. None of the phenyl rings shield selenium lone pairs from external coordination, nor do they cause large steric hindrance in accessing them (C2−Se1−C5 = 96.3°, C1−Se2−C11 = 99.9°).

3. Discussion

On the basis of the mechanistic study described above, we can explain the difference in catalytic activity

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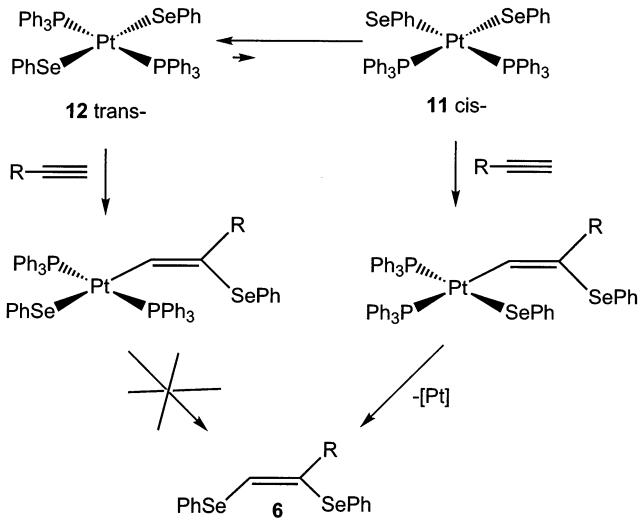
Scheme 4. Alkyne Insertion and C−E Reductive Elimination in Platinum Complexes



between platinum and palladium in Se−Se addition reactions with alkynes. Under experimental conditions complex **11** undergoes irreversible isomerization to the trans derivative **12**. While the former complex reacts with alkynes, leading to Se−Se addition products, the latter complex does not show any catalytic activity. Most likely, product formation is blocked at the C−E reductive elimination stage in trans derivatives of Pt^{II} (Scheme 4). The driving force for the isomerization reaction can be either the decrease of steric strain between bulky phosphine ligands or the trans effect.

The question concerning the active form of the palladium complex in the studied catalytic reaction is also rather difficult. The main differences between the platinum and palladium selenide complexes originate from the ability of the latter to form dimeric species, while the former are present in the mononuclear state only. In our study dinuclear palladium complexes were detected in both stoichiometric and catalytic reactions.

Indeed, both dinuclear complexes **8** and **9** have cis-oriented Se−Pd−Se units, which is needed for product formation. The first-order rate constant dependence vs initial palladium dimer concentration agrees with a mechanism involving dinuclear complexes in the catalytic cycle (Scheme 5). On the other hand, this does not exclude the pathway involving a mononuclear palladium derivative, if after dissociation only one mononuclear complex reacts with alkyne. In this case, again, mononuclear palladium derivatives with cis geometry can be obtained from dinuclear complexes (Scheme 6). The study clearly shows that it is the dinuclear complex formation that changes the reactivity of palladium complexes in the catalytic process.

The relative reactivities of various alkyne molecules have been estimated from the reactions stopped after the short time of 5 h (Table 2, entries 5−8). Activated alkyne (HC≡CCOOMe) is the most reactive toward Ph_2Se_2, while alkynes with electron donor substituents showed lower yields. Increasing the steric strain in the alkyne molecule (cf. entries 6 and 7) decreases the yield as well. After a longer reaction time of 15−20 h 60% yields of the Se−Se addition products are obtained.

As indicated by earlier experimental[1,27,28] and theoretical[16,29,30] studies, alkyne insertion (Scheme 1, step ii) into the M−X bond (X = C, B, S, halogens, etc.) is highly stereoselective and leads to *Z* adducts. In the studied reactions (*Z*)-alkenyl diselenides are exclusively formed (Table 2), except for methyl propiolate, where the *E* isomer is a byproduct.

It would be interesting to compare the results of the present study with B−B addition to alkynes, which has been very well experimentally and theoretically studied.[16] The complexes resulting from Se−Se oxidative addition reactions with zerovalent metals are stable for both platinum and palladium, in contrast to B−B bond activation on palladium, where $[PdB_2L_2]$ compounds were found to be unstable.[16] The product of Se−Se oxidative addition to Pt^0 is stable; however, it undergoes further isomerization. The present study clearly indicates that not only the relative thermodynamic stability of the oxidative addition intermediates but also the stereochemistry are the crucial factors responsible for the catalytic activity.

Direct synthesis of palladium selenide complexes from easily available precursors opens up wide opportunities for new catalyst design, since various ligands may be easily tested in the catalytic reaction. Moreover, the synthetic procedure does not require an inert atmosphere. The results can be rationalized by taking into account that both the initial catalyst and palladium(II) selenide are air stable and the lifetime of the Pd^0 intermediate is rather short, since the oxidative addition reaction proceeds easily and catalytic conditions imply significant excess of Ph_2Se_2 over Pd(0).

Structural studies of (*Z*)-alkenyl diselenides confirm the favorable geometry for possible application as chelate ligands (Figure 2, side view). The observed Se···Se distance of 3.303 Å is very close to the P···P distance of 3.279 Å in *cis*-$Ph_2PCH{=}CHPPh_2$,[31] which is a well-established ligand in transition-metal chemistry.

4. Experimental Section

4.1. General Considerations. Unless otherwise stated, synthetic work was carried out under an argon atmosphere. Solvents were purged with argon before use. The $Pd(PR_3)_2Cl_2$ complexes were prepared according to published procedures.[32] Other reagents, namely $Pd(PPh_3)_4$ (Aldrich), $Pt(PPh_3)_4$ (Acros), Ph_2Se_2 (Acros), and alkynes (Acros and Lancaster), were checked by 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 the XWINMR 3.0 software package. All 2D spectra were recorded using an inverse triple-resonance probehead with active shielded Z-gradient coil. ^1H and ^{13}C chemical shifts are reported relative to the corre-

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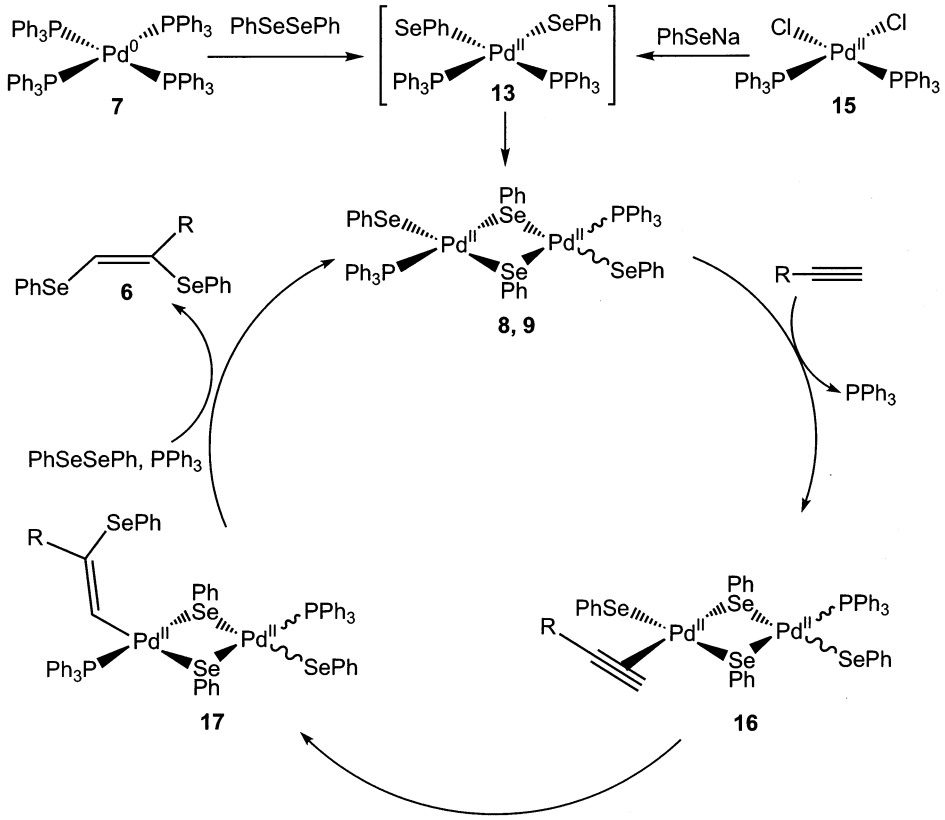
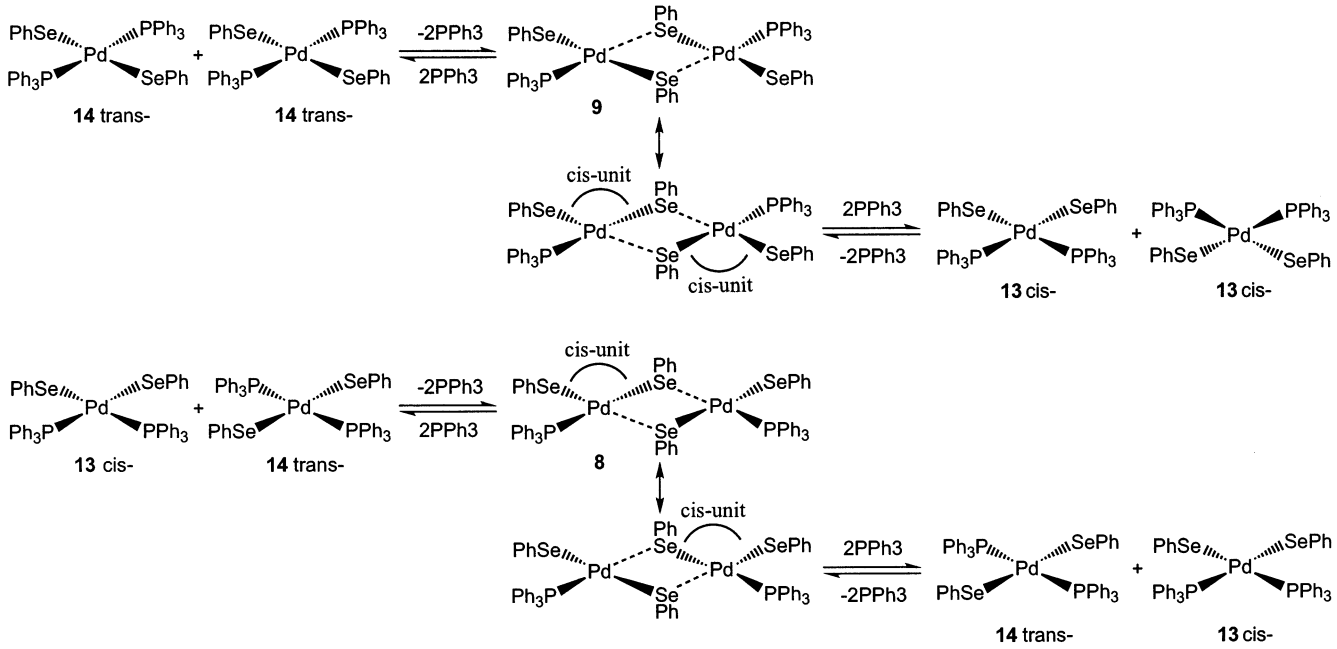
Scheme 5. Proposed Mechanism of Catalytic E−E Addition Reactions Involving Dinuclear Complexes



Scheme 6. Proposed Mechanism of the Isomerization Reactions



sponding solvent signals used as internal reference; external 85% H_3PO_4/H_2O (δ 0.0 ppm) was used for ^{31}P and $Ph_2Se_2/CDCl_3$ (δ 463.0 ppm) for ^{77}Se.[33]

(i) 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, with a relaxation delay of 2 s, $\Delta = (2J_{H-Se})^{-1} =$ 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 corresponding ^1H(F2) and ^{77}Se(F1) dimensions. Four or eight transients were averaged for each of 256 increments on t_1. The data were zero-filled to a 2048 × 2048 matrix and processed with a 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.

(ii) 2D NOESY NMR Experiment. The spectra were recorded using the bipolar gradient pulse sequence 90−t_1−

(33) Duddeck, H. Sulfur, Selenium, & Tellurium NMR. In *Encyclopedia of Nuclear Magnetic Resonance*; Grant, D. M., Harris, R. K., Eds.; Wiley: Chichester, U.K., 1996; Vol. 7, pp 4623−4636.

$90-\tau_{mix}/2-G1-180-G2-\tau_{mix}/2-90-acq$, with $\tau_{mix} = 1-2$ s and 40.0, −40.0 (%) field gradient pulses for G1 and G2, respectively. Further details are as described earlier.[34]

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

4.3. NMR Monitoring of Stoichiometric Reactions. (i) Oxidative Addition. Ph_2Se_2 (5.4 mg, 1.7×10^{-5} mol) was dissolved in 0.5 mL of toluene-d_8, and $Pd(PPh_3)_4$ (20 mg, 1.7×10^{-5} mol) was added to the solution. ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded every 15 min. The measurements were performed at both 80 °C and room temperature. The same procedure was used in the case of $Pt(PPh_3)_4$ (21 mg, 1.7×10^{-5} mol).

(ii) Alkyne Insertion. Following the oxidative addition reaction above, a 2-fold excess of alkyne was added to the solution and the NMR tube was placed into an external water bath at 80 °C. After the mixture was cooled to room temperature, ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded every 30 min over 4 h.

4.4. NMR Monitoring of Catalytic Reactions. Exactly the same catalytic conditions were implied as described below for synthetic procedure, except toluene-d_8 was used as the solvent and the reaction was performed in an NMR tube. For $Pd(PPh_3)_4$- and $Pt(PPh_3)_4$-catalyzed reactions, two kinds of measurements were done with 3 and 10 mol % of catalyst to ensure a good signal-to-noise ratio in the spectrum. In both cases the same setd of resonances in $^{31}P\{^1H\}$ spectra were obtained.

4.5. General Synthetic Procedure. (i) $Pd(PPh_3)_4$- and $Pt(PPh_3)_4$-Catalyzed Reactions. Diphenyl diselenide (61.6 mg, 2.0×10^{-4} mol) was dissolved in 0.5 mL of toluene, giving a clear yellow solution. Tetrakis(triphenylphosphine)palladium (7.0 mg, 6.1×10^{-6} mol) was dissolved in the solution, changing the color to dark brown, followed by addition of alkyne (3.0×10^{-4} mol). The reaction mixture was heated for 15−20 h at 80 °C. The $Pt(PPh_3)_4$-catalyzed process was performed in a similar manner.

(ii) $PdCl_2(PPh_3)_2$-Catalyzed Reaction. A pyridine solution (1.0 mL) of $NaBH_4$ (10.5 mg, 2.8×10^{-4} mol) was prepared separately and stored (freshly prepared ethanol and methanol solutions can also be used).

Diphenyl diselenide (61.6 mg, 2.0×10^{-4} mol) was dissolved in 0.5 mL of toluene, giving a clear yellow solution. The palladium complex $PdCl_2(PPh_3)_2$ (4.3 mg, 6.1×10^{-6} mol) was added to the solution. A solution of $NaBH_4$ (3×15 μL, 1.3×10^{-5} mol) was added to the suspension over 5 min with stirring until the yellow $PdCl_2(PPh_3)_2$ was dissolved, giving a clear brown solution. Alkyne (3.0×10^{-4} mol) was added to the reaction mixture, followed by heating for 20 h at 80 °C.

With the alkynes having electron-withdrawing groups, a side reaction of $PhSe^-$ nucleophile attack at the triple bond may take place. To avoid byproduct formation, the catalyst solution in toluene should be washed with 5 mL of water prior to alkyne addition.

(iii) Product Separation and Structure Determination. After catalytic reaction was complete, the solvent was removed on a rotary evaporator. The product was purified using column chromatography on silica gel with the following eluents: **6a**, 1/2 hexane/$CHCl_3$; **6b**, 3/1 hexane/ethyl acetate; **6c**, 5/1 hexane/ethyl acetate; **6d**, chloroform. Then the product was dried under vacuum.

In each case the stereochemistry was determined using 2D NOESY NMR experiments. ^1H signal assignment confirmed with 2D COSYLR method, ^{13}C signal assignment performed upon analyzing ^1H-^{13}C HMQC and ^1H-^{13}C HMBC spectra. ^{77}Se chemical shifts were determined utilizing ^1H-^{77}Se HMQC pulse sequence.

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(*Z*,*E*)-HC(SePh)=C(SePh)COOMe (6a). *Z* isomer: yellow oil; ^1H NMR (500 MHz; $CDCl_3$; δ, ppm) 8.92 (s, 1H, HC=), 7.62 (m, 2H, Ph), 7.51 (m, 2H, Ph), 7.38 (m, 3H, Ph), 7.29 (m, 3H, Ph), 3.71 (s, 3H, OMe); $^{13}C\{^1H\}$ NMR (126 MHz; CD_3OD; δ, ppm) 164.0 (C=O), 158.7 (HC=), 133.6, 131.5, 129.9, 129.8, 129.6, 129.2, 128.6, 127.2, 120.2 (=C−), 52.7 (OMe); ^{77}Se NMR (95 MHz; $CDCl_3$; δ, ppm) 356.7, 462.9; mass spectrum (EI) *m/e* 398 (M^+, 30). Anal. Calcd for $C_{16}H_{14}O_2Se_2$: C, 48.50; H, 3.56; Se, 39.86. Found: C, 48.25; H, 3.65; Se, 39.82. *E* isomer: yellow oil; ^1H NMR (500 MHz; $CDCl_3$; δ, ppm) 7.92 (s, 1H, HC=), 7.49 (m, 4H, Ph), 7.32 (m, 6H, Ph), 3.83 (s, 3H, OMe); $^{13}C\{^1H\}$ NMR (126 MHz; CD_3OD; δ, ppm) 166.5 (C=O), 151.8 (HC=), 132.9, 132.8, 132.7, 130.2, 129.4, 129.3, 128.2, 127.7, 114.4 (=C−), 52.8 (OMe); ^{77}Se NMR (95 MHz; $CDCl_3$; δ, ppm) 435.1, 535.5; mass spectrum (EI) *m/e* 398 (M^+, 30). Anal. Calcd for $C_{16}H_{14}O_2Se_2$: C, 48.50; H, 3.56; Se, 39.86. Found: C, 48.11; H, 3.75; Se, 40.13.

(*Z*)-HC(SePh)=C(SePh)CH_2OH (6b): yellow oil; ^1H NMR (500 MHz; $CDCl_3$; δ, ppm) 7.60 (m, 2H, Ph), 7.56 (m, 2H, Ph), 7.41 (s, 1H, HC=), 7.31 (m, 6H, Ph), 4.17 (s, 2H, $-CH_2-$); $^{13}C\{^1H\}$ NMR (126 MHz; $CDCl_3$; δ, ppm) 133.5 (HC=), 133.2, 132.4, 132.1 (=C−), 130.3, 129.4, 129.3, 128.6, 127.8, 127.5, 67.5 (CH_2); ^{77}Se NMR (95 MHz; $CDCl_3$; δ, ppm) 405.1, 341.5; mass spectrum (EI) *m/e* 370 (M^+, 15). Anal. Calcd for $C_{15}H_{14}OSe_2$: C, 48.93; H, 3.83; Se 42.89. Found: C, 49.27; H, 3.97; Se, 42.53.

HC(SePh)=C(SePh)C_6H_{10}(OH) (6c): yellow oil; ^1H NMR (500 MHz; $CDCl_3$; δ, ppm) 7.66 (s, 1H, HC=), 7.57 (m, 2H, Ph), 7.52 (m, 2H, Ph), 7.30 (m, 6H, Ph), 1.75 (m, 4H, α-CH_2), 1.66 (m, 2H, β-CH_2), 1.65 (m, 1H, γ-CH_2), 1.59 (m, 2H, β-CH_2), 1.19 (m, 1H, γ-CH_2); $^{13}C\{^1H\}$ NMR (126 MHz; $CDCl_3$; δ, ppm) 139.9 (=C−), 137.2 (HC=), 133.2, 130.9, 130.5, 129.8, 129.3, 129.2, 127.7, 126.4, 76.3 (C−OH), 36.7 (α-CH_2), 25.3 (γ-CH_2), 21.9 (β-CH_2); ^{77}Se NMR (95 MHz; $CDCl_3$; δ, ppm) 417.4, 317.8; mass spectrum (EI) *m/e* 438 (M^+, 15). Anal. Calcd for $C_{20}H_{22}OSe_2$: C, 55.06; H, 5.08; Se, 36.19. Found: C, 55.35; H, 5.18; Se, 35.93.

(*Z*)-HC(SePh)=C(SePh)CH_2NMe_2 (6d): yellow oil; ^1H NMR (500 MHz; $CDCl_3$; δ, ppm) 7.59 (m, 4H, Ph), 7.31 (m, 6H, Ph), 7.28 (s, 1H, HC=), 3.04 (s, 2H, $-CH_2-$), 2.22 (s, 6H, $-CH_3$); $^{13}C\{^1H\}$ NMR (126 MHz; $CDCl_3$; δ, ppm) 133.0 (HC=), 132.9, 132.8, 131.2, (=C−), 130.9, 129.4, 129.3, 129.1, 127.5, 127.2, 67.3 (CH_2), 45.0 (CH_3); ^{77}Se NMR (95 MHz; $CDCl_3$; δ, ppm) 403.0, 378.4; mass spectrum (EI) *m/e* 397 (M^+, 10). Anal. Calcd for $C_{17}H_{19}NSe_2$: C, 51.66; H, 4.85; N, 3.54; Se, 39.95. Found: C, 51.46; H, 4.73; N, 3.61; Se, 40.24.

Synthesis of (*Z*)-HC(SePh)=C(SePh)CH_2NMe_2*HOOCCOOH (6e) for X-ray Structure Determination. After the catalytic reaction was complete, the solvent was removed on rotary evaporator. The resulting dark brown solid was dissolved in acetone, followed by the addition of an acetone solution of HOOCCOOH in 1:1 molar ratio. The obtained white precipitate was washed three times with cold acetone and dried under vacuum. **6e**: white solid; ^1H NMR (500 MHz; CD_3OD; δ, ppm; *J*, Hz) 7.99 (s, 1H, *J*(H−Se) = 12.4, HC=), 7.62 (m, 2H, Ph), 7.55 (m, 2H, Ph), 7.36 (m, 6H, Ph), 3.87 (s, 2H, $-CH_2-$), 2.82 (s, 6H, CH_3-); $^{13}C\{^1H\}$ NMR (126 MHz; CD_3OD; δ, ppm) 166.6 (C=O), 149.3 (HC=), 134.4, 133.5, 131.0, 130.8, 129.5, 129.4, 130.76, 129.1, 120.6 (−C=), 64.3 ($-CH_2-$), 43.2 ($-CH_3$); ^{77}Se NMR (95 MHz; CD_3OD; δ, ppm) 435.6, 364.2; mass spectrum (EI) *m/e* 397 (M^+ − HOOC − COOH, 20). Anal. Calcd for $C_{19}H_{21}NO_4Se_2$: C, 47.02; H, 4.36; N, 2.89; Se 32.54. Found: C, 47.45; H, 4.57; N, 2.89; Se, 32.76.

4.6. Crystal Structure Determination. (i) Preparing Single Crystals of *cis*-$[Pt(PPh_3)_2(SePh)_2]$. Ph_2Se_2 (5.4 mg, 1.7×10^{-5} mol) and $Pt(PPh_3)_4$ (21 mg, 1.7×10^{-5} mol) were quickly dissolved in 1.4 mL of C_6H_6/hexane (6/1) at room temperature and stirred for 1 min. The resulting mixture was stored at −5 °C. Light brown crystals were obtained upon slow solvent evaporation. The $^{31}P\{^1H\}$ NMR spectrum (18.7 ppm,

Table 4. Data Collection and Processing Parameters for Compounds 6e and 11

	6e	11
empirical formula	$C_{19}H_{21}NO_4Se_2$	$C_{54}H_{46}P_2PtSe_2$
fw	485.29	1109.86
temp, K	503(2)	293(2)
wavelength, Å	0.710 73	0.710 73
cryst syst, space group	monoclinic, $P2_1/n$	triclinic, $P\bar{1}$
a, Å	8.4187(19)	9.3314(17)
b, Å	10.486(3)	14.310(3)
c, Å	22.815(5)	17.952(3)
α, deg	90	80.177(4)
β, deg	95.124(5)	83.308(4)
γ, deg	90	73.687(4)
V, Å^3	2006.0(8)	2261.0(7)
Z; calcd density, Mg m^{-3}	4; 1.607	2; 1.630
abs coeff, mm^{-1}	3.709	4.820
F(000)	968	1092
θ range for data collecn, deg	1.79−30.05	1.15−30.04
index ranges	$-10 \le h \le 11$, $-14 \le k \le 5$, $-31 \le l \le 26$	$-13 \le h \le 12$, $-20 \le k \le 19$, $-25 \le l \le 14$
no. of rflns collected/unique	6982/3714 (R(int) = 0.0396)	10 562/9508 (R(int) = 0.0436)
completeness to $2\theta = 30.05°$, %	60.2	71.9
Refinement method	full-matrix least squares on F^2	full-matrix least squares on F^2
no. of data/restraints/params	3714/0/243	9508/0/532
goodness of fit on F^2	0.989	1.006
final R indices ($I > 2\sigma(I)$)	R1 = 0.0459, wR2 = 0.0849	R1 = 0.0521, wR2 = 0.1096
R indices (all data)	R1 = 0.0710, wR2 = 0.0896	R1 = 0.0671, wR2 = 0.1245
largest diff peak and hole, e Å^{-3}	0.888 and −0.497	2.870 and −1.701

J(Pt−P) = 2966.3 Hz) of the crystallized product confirmed the presence of the cis isomer.

(ii) Preparing Single Crystals of (*Z*)-(SePh)CH=C-(SePh)CH$_2$NMe$_2$*HOOCCOOH (6e). The salt (20 mg) was dissolved in 0.6 mL of methanol. The solution was placed into an NMR tube and capped with 0.2 mL of hexane. Slow evaporation at +5 °C gave light yellow crystals. the ^{1}H NMR spectrum has shown that the resonances of the crystallized product do not change as compared to those of the parent compound.

The samples were mounted in air on a glass fiber using 5 min epoxy resin. The X-ray intensity data sets for **6e** and **11**[35] were collected on a Bruker AXS SMART 1000 diffractometer equipped with a CCD detector (graphite monochromator, 123(2) K, ω-scanning technique, scan step 0.3°, frames exposed for 30 s) using a standard procedure.[36] A semiempirical absorption correction was applied.[37] The crystallographic parameters and selected details of the refinement of structures are given in Table 4. The structures were solved by direct and Fourier techniques and refined by full-matrix least-squares methods with anisotropic thermal parameters for all non-hydrogen atoms. The positions of the hydrogen atoms of the phenyl, methyl, and methylene substituents in **6e** and **11** 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 SHELEX97 program package.[38] The main geometric parameters for **6e** and **11** are given in Tables 1 and 3, respectively.

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Supporting Information Available: Text and figures giving details of kinetic measurements and tables giving X-ray structure determination data for **6e** and **11** (Tables S1−S10). This material is available free of charge via the Internet at http://pubs.acs.org.

OM0205391

(35) For the structure of **11** determined at 120 K, see ref 24.

(36) SMART (control) and SAINT (integration) software, version 5.0; Bruker AXS Inc., Madison, WI, 1997.

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