New Catalytic System for S−S and Se−Se Bond Addition to Alkynes Based on Phosphite Ligands

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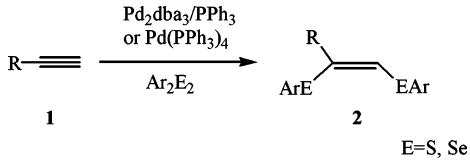
A new catalytic system for the Ar_2E_2 (E = S, Se) addition to terminal alkynes (HC≡C−R) has been developed to synthesize bis-element-substituted alkenes *Z*-H(ArE)C=C(EAr)R with high stereoselectivity and yields. Utilizing phosphite ligand $P(OiPr)_3$ allowed solving two major problems of this catalytic reaction: (1) prevent catalyst polymerization and (2) simplify product purification procedures. Key intermediates—*trans*-$[Pd(SPh)_2(P(OiPr)_3)_2]$ and *trans*-$[Pd_2(SPh)_4(P(OiPr)_3)_2]$—were synthesized by S−S oxidative addition reaction to Pd(0) and studied by X-ray analysis. The equilibrium between the mononuclear and dinuclear complexes in solution was established by ^{31}P NMR spectroscopy. In addition to the advantages in the synthetic procedure, the isolation of the stable palladium complexes with phosphite ligand made possible a detailed mechanistic study of the catalytic reaction.

1. Introduction

Transition metal catalyzed element−element bond addition to alkynes provides an efficient methodology for introducing two carbon−element bonds with high atom efficiency and selectivity.[1] The appropriate choice of catalyst and ligand are the key factors to achieve high efficiency and selectivity in the addition process. Very promising results were achieved using phosphite ligands $P(OR)_3$, which have several important advantages over traditionally utilized phosphines PR_3.[2]

The well-known reaction of palladium-catalyzed S−S and Se−Se bond addition to alkynes leads to *Z*-substituted alkenes **2** with excellent stereoselectivity (Scheme 1).[3] The products of the reaction, bis-sulfur- and bis-seleno-substituted alkenes (**2**), are of much importance for organic synthesis, for coordination chemistry as bidentante ligands, and for microelectronics as precursors of new optical materials.[4]

Scheme 1



An in-depth mechanistic study has shown that the catalytic reaction of S−S and Se−Se bond addition to alkynes involves intermediate dinuclear palladium complexes $[Pd_2(ArE)_4L_2]$.[5] Such complexes have been isolated after the oxidative addition of Ar_2E_2 to PdL_4 or substitution reaction of the chloride ligands in $PdCl_2L_2$ by ArE^-.[6] The choice of the ligand L was of crucial importance for performing the catalytic reaction. To achieve good yield in the catalytic reaction, an excess of triphenylphosphine ligand (L = PPh_3) was used;[5] otherwise rapid catalyst deactivation took place due to insoluble polymer $[Pd(ArE)_2]_n$ formation.[3b,7] In addition to the polymerization problem, an excess of PPh_3 in

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Table 1. Ligand Dependence Study in the Palladium-Catalyzed Ph_2S_2 Addition to 3-Butyn-1-ol[a]

entry	ligand	yield,[b] %
1	PPh_3	90
2	$P(p\text{-}FC_6H_4)_3$	88
3	PCy_3	15
4	PBu_3	2
5	DPPB	2
6	DPPE	0
7	$P(OPh)_3$	4
8	$P(OBu)_3$	99
9	$P(O\textit{i}Pr)_3$	99

[a] The reactions were carried out in toluene at 80 °C for 15 h with 1.5 mol % of Pd_2dba_3 and 30 mol % of the ligand. [b] Determined by NMR.

some cases caused significant difficulties during the product separation and purification stage.

In the present article we report a new catalytic system for the S−S and Se−Se bond addition to alkynes catalyzed by palladium complexes with phosphite ligands. Both problems of the studied addition reaction—catalyst polymerization and product purification—have been solved using phosphite ligands. The methodology has several advantages, since phosphite ligands are readily available and cheaper than corresponding phosphines.

2. Results and Discussion

Using the model reaction of Ph_2S_2 addition to 3-butyn-1-ol ($R = CH_2CH_2OH$; Scheme 1) we have investigated the catalytic activity of the palladium complexes with various mono- and bidentante phosphine and phosphite ligands (Table 1). The catalytic reaction with PPh_3 studied earlier[3,5] was used for comparison (entry 1; Table 1). Introducing fluorine in *trans*-position of the phenyl ring slightly decreases the yield of the addition reaction (entry 2; Table 1). The electron-donating trialkylphosphines performed rather poorly (entries 3, 4; Table 1). The reaction did not take place with bidentante ligands DPPB and DPPE (entries 5, 6; Table 1). Only a small amount of product was observed with $P(OPh)_3$ (entry 8; Table 1). Surprisingly, excellent results were achieved with trialkyl phosphite ligands (entries 9, 10; Table 1).

Using $P(OAlk)_3$ instead of PPh_3 slightly increased the NMR yield of the addition reaction and greatly increased the isolated yields. In addition, the product separation procedure was significantly simplified (Table 2). This is especially important in the case of the Ph_2E_2 addition to nonpolar alkynes (without heteroatoms), because it is rather difficult to separate these products from the PPh_3 ligand using chromatography on silica. High NMR yields of the Ph_2S_2 and Ph_2Se_2 addition to hexyne-1 were found for both ligands; however isolated yields of 60−62% and 91−92% were found for PPh_3 and $P(O\textit{i}Pr)_3$, respectively (Table 2). For the phosphite ligand simple flash chromatography performed very well and allowed the product of >98% purity to be isolated (determined by ^1H and ^{13}C NMR). The kinetic measurements have indicated that catalytic S−S bond addition to hexyne-1 using PPh_3 and $P(O\textit{i}Pr)_3$ ligands requires approximately the same time.[8]

Both factors—nature and amount of the ligand—need to be optimized to achieve high yield in the catalytic reaction (entries 1−3; Table 3). We found that the $[Pd]/P(O\textit{i}Pr)_3$ ratio should be at least 1/6 to perform the catalytic process under homogeneous conditions. With the lower amount of the ligand, an insoluble brown precipitate of the polymeric palladium complex $[Pd(PhS)_2]_n$ is formed (see related discussion for the phosphine ligands[3b,5]). The $[Pd]/P(O\textit{i}Pr)_3$ ratio of 1/10 was sufficient for the reactions of the S−S and Se−Se addition with high yields. Further increase of the ligand amount does not influence the product yield. The observed ligand dependence is in contrast with the common framework of the catalytic E−E bond addition reactions (E = B, Si, Sn, etc.).[1] Excess of the ligand retards alkyne coordination to the metal complex, thus blocking the catalytic reaction. In our case even with a large excess of the ligand an excellent product yield was obtained (entry 5; Table 3).

Readily available $Pd(OAc)_2$ may also be utilized in the catalytic reaction; however it requires a larger excess of the ligand, which in part acts as a reducing agent converting Pd(II) precursor to the catalytically active Pd(0) complex (entries 6, 7; Table 3). In this case the formation of the oxide, $O{=}P(OR)_3$, has been detected by ^{31}P NMR.

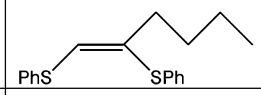
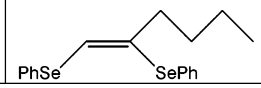
We have found that toluene and THF are the best solvents for this reaction, giving 85−89% yield after 3 h (entries 1, 2; Table 4). Surprisingly, even hexane (or petroleum ether) may be used as a solvent, leading to 61% product yield after 3 h (entry 3, Table 4). Increasing the reaction time to 15 h resulted in quantitative yields (95−98%) in toluene, THF, and hexane. Among the studied solvents toluene is a better choice to perform the reactions at higher temperature. In $CHCl_3$ and CH_3CN an insoluble brown precipitate was formed, in contrast to homogeneous solutions observed in the other studied cases (Table 4). Due to catalyst precipitation, rather poor product yields were obtained in $CHCl_3$ and CH_3CN solutions (entries 4, 5; Table 4).

In the optimized conditions—3 mol % of the Pd catalyst, 30 mol % of the $P(O\textit{i}Pr)_3$ ligand in toluene solution at 100 °C—the catalytic reaction was carried out with very good yields for several alkynes and dichalcogenides (Table 5). Quantitative NMR yields and high isolated yields were achieved in the S−S and Se−Se bond addition to hexyne-1 and heptyne-1 (entries 1−5; Table 5). A simplified purification procedure with flash chromatography performed very well for all of these products. In the same conditions the addition of Ph_2S_2 to heptadiyne-1,6 involves both triple bonds (entry 6; Table 5). The catalytic system based on the phosphite ligand is tolerant of the functional groups in the alkyne molecule (R = OH, OMe, NMe_2), which have no influence on the product yield (entries 7−9; Table 5). In all of the cases above high stereoselectivity of the addition reaction was observed, as confirmed by 2D NOESY experiments (entries 1−9; Table 5).

Arylacetylenes are rather difficult substrates to achieve high stereoselectivity in the S−S and Se−Se bond addition. In this case the noncatalytic side-reaction leading to the *E*-isomer takes place and decreases the

(8) Catalytic reaction with PPh_3 ligand is faster than catalytic reaction with $P(O\textit{i}Pr)_3$ ligand. Particularly, after 60 min of the reaction 89% and 72% product yields were detected for $L = PPh_3$ and $P(O\textit{i}Pr)_3$, respectively. Quantitative yields were observed in both cases after 100 min of reaction. See supporting Figure S1 for details.

Table 2. Isolated and NMR Yields of the Products of the Ph_2S_2 and Ph_2Se_2 Addition to Hexyne-1 in the Palladium-Catalyzed Reaction with Different Ligands (L)[a]

Entry	Product	NMR yield, %		Isolated yield,[b] %	
		L = PPh_3	L = $P(OiPr)_3$	L = PPh_3	L = $P(OiPr)_3$
1		96	97	62	92
2		94	97	60	91

[a] The reaction was carried out in toluene at 80 °C for 15 h with 1.5 mol % of Pd_2dba_3 and 30 mol % of the ligand. [b] Using flash chromatography, see Experimental Part for details.

Table 3. Yields of the Ph_2S_2 Addition to Hexyne-1 Depending on the Nature of the Palladium Complex and Amount of Ligand[a]

entry	[Pd]	$P(OiPr)_3$/[Pd] ratio	yield,[b] %
1	$Pd_2(dba)_3$	2	31
2	$Pd_2(dba)_3$	4	82
3	$Pd_2(dba)_3$	6	97
4	$Pd_2(dba)_3$	10	99
5	$Pd_2(dba)_3$	30	99
6	$Pd(OAc)_2$	6	28
7	$Pd(OAc)_2$	15	99

[a] The reaction was carried out in toluene at 100 °C for 3 h with 1.5 mol % of Pd_2dba_3 or 3 mol % of $Pd(OAc)_2$. [b] Determined by NMR.

Table 4. Effect of Solvent in the Palladium-Catalyzed Ph_2S_2 Addition to Hexyne-1[a]

entry	solvent	yield,[b] %
1	toluene	85
2	THF	89
3	hexane	61
4	$CHCl_3$	14
5	CH_3CN	5

[a] The reaction was carried out in a sealed tube at 80 °C for 3 h with 3 mol % of $Pd(OAc)_2$ and 45 mol % of P(O-*i*Pr)$_3$. [b] Determined by NMR.

overall selectivity of the addition reaction.[1,3,5] Particularly, in Pd-catalyzed Ph_2Se_2 addition to phenylacetylene with PPh_3 ligand a noncatalytic pathway makes a major contribution to the reaction ($Z/E = 1/4$).[9] However, in the palladium-catalyzed reaction with the $P(OiPr)_3$ ligand the stereoselectivity was greatly improved by dramatically decreasing the contribution of the noncatalytic pathway: $Z/E > 10/1$ (entries 10−12; Table 5). Therefore, not only the isolated yield but also the stereoselectivity of the reaction can be improved using the catalytic system developed in the present study.

The mechanistic study of the catalytic system has been started with reaction of Ph_2S_2 and palladium complex in the presence of the excess of ligand. Heating $Pd(OAc)_2$, Ph_2S_2, and $P(OiPr)_3$ (1/2/12 ratio) in benzene at 70 °C for 2 h resulted in a dark brown homogeneous solution without insoluble species. Two new resonances were detected in the $^{31}P\{^1H\}$ NMR spectrum, $\delta = 102.7$ and 110.5 ppm, indicating that two different transition metal complexes were formed. Two sets of signals were also found in the ^1H NMR spectrum. The integration of the proton signals showed that for each complex the ratio SPh/$P(OiPr)_3 = 1$ is maintained, thus suggesting that mononuclear *trans*-$[Pd(SPh)_2(P(OiPr)_3)_2]$ and *cis*-$[Pd(SPh)_2(P(OiPr)_3)_2]$ complexes were obtained (Scheme 2; E = S, Ar = Ph, R = *i*Pr). Regular workup of the reaction mixture (see Experimental Part for details) followed by crystallization from hexane gave pure crystals of *trans*-$[Pd(EAr)_2(P(OiPr)_3)_2]$ in 85% isolated yield. The structure of the complex has been determined by X-ray analysis (Figure 2). Exactly the same complexes were synthesized using $Pd_2(dba)_3$ precursor instead of $Pd(OAc)_2$, as confirmed by $^{31}P\{^1H\}$ and ^1H NMR.

Most likely *cis*-$[Pd(SPh)_2(P(OiPr)_3)_2]$, **3**, is formed first after the oxidative addition reaction, followed by isomerization to thermodynamically more stable *trans*-$[Pd(SPh)_2(P(OiPr)_3)_2]$, **4** (Scheme 2).

Dissolving pure crystals of *trans*-$[Pd(EAr)_2(P(OiPr)_3)_2]$, **4**, in benzene and recording the $^{31}P\{^1H\}$ NMR spectrum showed five resonances: $\delta = 98.8$, 101.2, 102.7, 110.5, 138.7 ppm. The low-field resonance at 138.7 ppm corresponds to the free ligand $P(OiPr)_3$. The resonances at $\delta = 102.7$ and 110.5 ppm correspond to **3** and **4** (see above). The remaining signals correspond to two new palladium complexes that were formed upon dissociation of the $P(OiPr)_3$. This suggests the formation of dinuclear complexes **5** and **6** ($\delta = 98.8$, 101.2 ppm) as the products of the ligand dissociation reaction. The following ratio was determined by $^{31}P\{^1H\}$ NMR upon dissolving **4** in benzene: (**3**+**4**)/(**5**+**6**)/P(O-*i*Pr)$_3$ = 1/1/1. Adding an excess of $P(OiPr)_3$ to this solution resulted in the disappearance of the signals at $\delta = 98.8$, 101.2 ppm (**5** and **6**) and increasing intensity of the signals at $\delta = 102.7$, 110.5 ppm (**3** and **4**).

The pure dinuclear complex *trans*-$[Pd_2(EAr)_4(P(OiPr)_3)_2]$, **5**, was obtained after removing excess $P(OiPr)_3$ from complex **4** by flash chromatography. The structure of the complex has been unambiguously determined by X-ray analysis (Figure 1). A solution of the pure dinuclear complexes in C_6D_6 exhibits two singlets in the $^{31}P\{^1H\}$ NMR spectrum at $\delta = 98.8$ and 101.2 ppm in 8/1 ratio (**5** and **6**). In the ^1H NMR spectrum two sets of resonances were also observed with the same 8/1 ratio. As identified by the integration of the ^1H NMR spectrum, each complex (**5** and **6**) contains four SPh and two $P(OiPr)_3$ groups, which clearly correspond to the dinuclear structure. Adding P(O-*i*Pr)$_3$ to the solution of **5** resulted in the appearance of the signals corresponding to **3** and **4** ($\delta(^{31}P) = 102.7$, 110.5 ppm). The concentration of the mononuclear complexes increased upon increasing the excess of the ligand. When the ratio between the complex and the free ligand was >30, only the mononuclear complexes were detected by $^{31}P\{^1H\}$ NMR.

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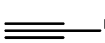
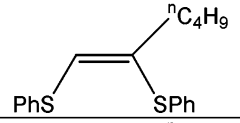
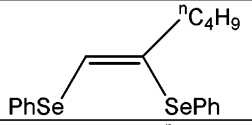
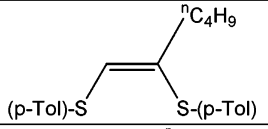
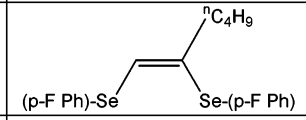
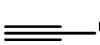
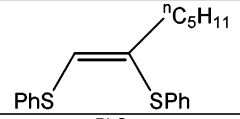
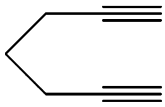
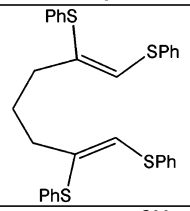
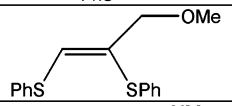
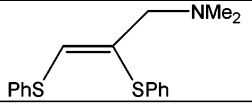
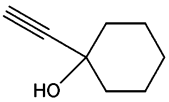
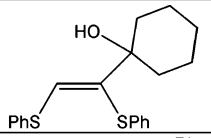
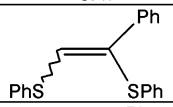
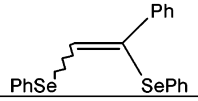
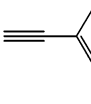
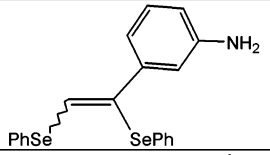
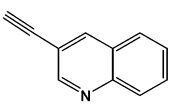
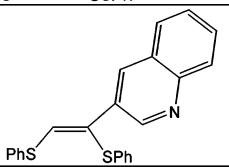
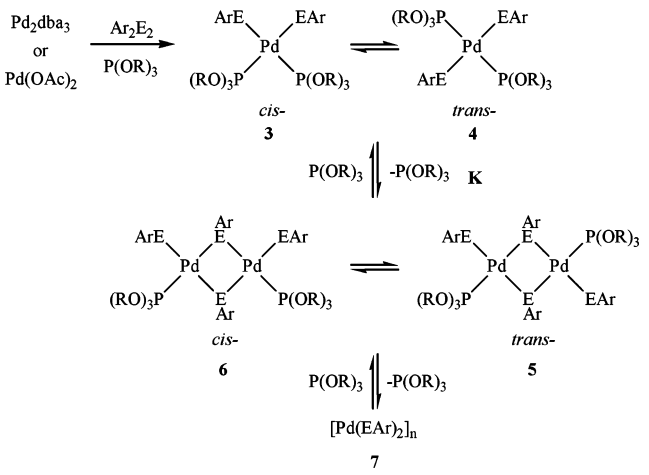
Table 5. Scope of the S–S and Se–Se Bond Addition to Alkynes Catalyzed by Palladium Complexes with Phosphite Ligand[a]

Entry	Alkyne	Ar_2E_2	Product		Z/E	Yield,[b] %
1		Ph_2S_2		**2a**	>97/3	99(91)
2		Ph_2Se_2		**2b**	>97/3	99(91)
3		$(p\text{-}MePh)_2S_2$		**2c**	>97/3	99(92)
4		$(p\text{-}FPh)_2Se_2$		**2d**	>97/3	99(90)
5		Ph_2S_2		**2e**	>97/3	99(90)
6[c]		Ph_2S_2		**2f**	>97/3	95(88)
7		Ph_2S_2		**2g**	>97/3	99(87)
8		Ph_2S_2		**2h**	>97/3	99(90)
9		Ph_2S_2		**2i**	>97/3	99(85)
10		Ph_2S_2		**2j**	>10/1	99(91)
11		Ph_2Se_2		**2k**	>10/1	99(96)
12		Ph_2Se_2		**2l**	>10/1	99(85)
13		Ph_2S_2		**2m**	>10/1	98(85)

[a] See the Experimental Part for detailed description of the synthetic procedure. [b] NMR and isolated yields (in parentheses). [c] The ratio alkyne/Ph_2S_2 = 1.0/2.5 was used.

The experiments with **4** and **5** clearly confirm that in solution the mono- and dinuclear complexes are in equilibrium and the observed ratio of the complexes depends on the amount of the free ligand. Using NMR

Scheme 2



spectroscopy the equilibrium constant of dinuclear complex dissociation to mononuclear form has been measured, $K = (0.066 \pm 0.007)$ M at 30 °C.

It should be emphasized that the nature of the Pd complexes with trialkyl phosphite ligands (mono- or dinuclear) can be easily determined by the analysis of the ^{1}H spectra, since the resonances of the aromatic (SPh) and aliphatic (*i*Pr) protons are clearly resolved. This was not possible for the catalytic system with triphenylphosphine studied earlier, since the SPh signals strongly overlap with the ligand signals (PPh_3).

The dinuclear complexes **5** and **6** slowly decompose in benzene at room temperature; the corresponding signals in $^{31}P\{^1H\}$ and ^{1}H NMR spectra disappeared in 3−5 days. The mononuclear complexes **3** and **4** are more stable at room temperature than dinuclear ones; however they quickly decompose upon heating at 70−80 °C (1−2 h). Decomposition of both mono- and dinuclear complexes is accompanied with insoluble dark brown precipitate formation, corresponding to the polymer $[Pd(EAr)_2]_n$ (**7**). If an excess of the $P(OiPr)_3$ ligand was added to the solutions, the complexes did not decompose in a noticeable manner neither at room temperature nor upon heating (80 °C, 10 h). Therefore, ligand excess suppresses polymerization and stabilizes the complexes in solution.

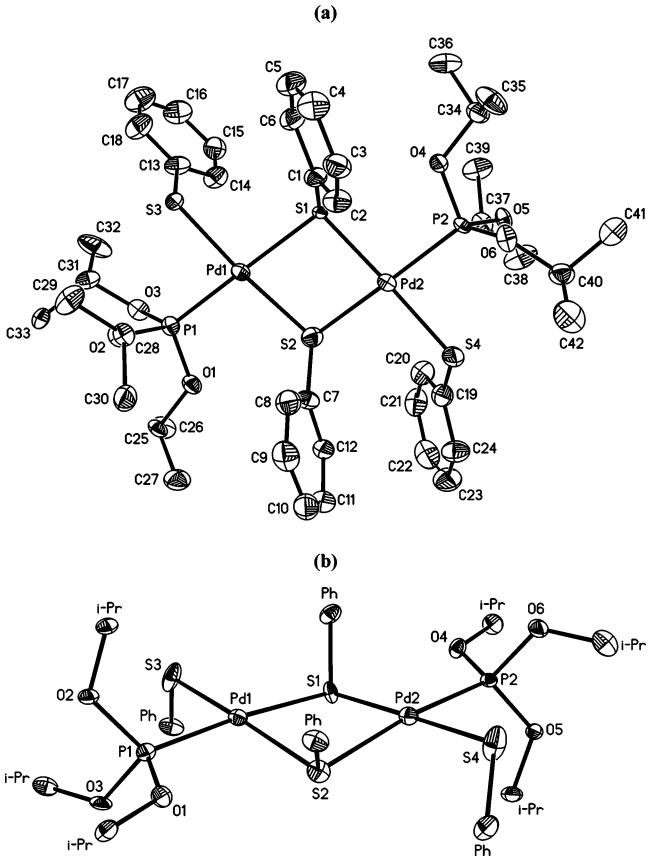


Figure 1. Molecular structure of dinuclear complex *trans*-$[Pd_2(SPh)_4(P(O\text{-}iPr)_3)_2]$, **5**.

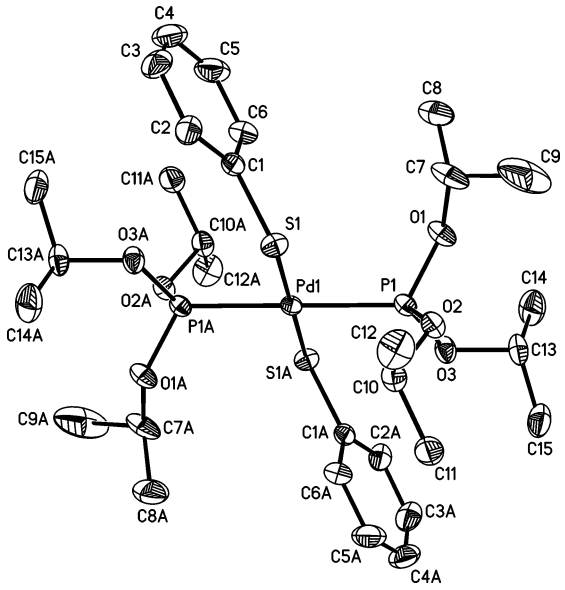


Figure 2. Molecular structure of mononuclear complex *trans*-$[Pd(SPh)_2(P(O\text{-}iPr)_3)_2]$, **4**.

According to the literature data, the structure of palladium complexes with EAr ligands ($Pd_nL_x(EAr)_y$, E = S, Se; $n = 1, 2$) strongly depends on the nature of L. With trialkylphosphines (L = PBu_3) the mononuclear complex *trans*-$[Pd(SePh)_2(PBu_3)_2]$ was isolated.[10] Triphenylphosphine (L = PPh_3) facilitates dinuclear complex formation, as was found for *trans*-$[Pd_2(SePh)_4(PPh_3)_2]$[6b] and *trans*-$[Pd_2(SPh)_4(PPh_3)_2]$.[6d] It is the unique feature of $P(OR)_3$ ligands that allows both complexes to be isolated. To the best of our knowledge, this study is the first example where both mono- and dinuclear complexes have been isolated and the equilibrium between these complexes in solution was established.

The molecular structures and the numbering of the atoms of **5** and **4** are shown in Figure 1 and Figure 2. Selected bond distances and angles are listed in Tables 6 and 7.

The Pd atoms in the dinuclear complex **5** show expectedly a slightly distorted square-planar coordination geometry. The sums of the four bond angles around the metal atoms are 359.5° and 360.1°, in agreement with the virtually planar coordination.

The two square-planar coordination spheres in dinuclear Pd(II) complexes can adopt either a coplanar or hinged arrangement (Scheme 3).

Complex **5** exhibits the hinged arrangement (see Figure 1b), which seems to be a less common feature in

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Table 6. Selected Bond Lengths [Å] and Angles [deg] for 5

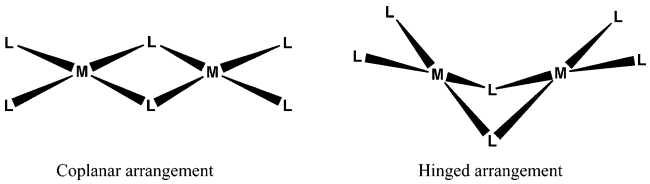
Pd(1)−S(1)	2.380(2)	P(1)−O(1)	1.581(7)
Pd(1)−S(2)	2.396(2)	P(1)−O(2)	1.602(6)
Pd(1)−S(3)	2.305(3)	P(1)−O(3)	1.592(6)
Pd(1)−P(1)	2.208(3)	P(2)−O(4)	1.573(7)
Pd(2)−S(1)	2.298(2)	P(2)−O(5)	1.583(5)
Pd(2)−S(2)	2.384(2)	P(2)−O(6)	1.561(6)
Pd(2)−S(4)	2.354(3)	O(1)−C(25)	1.456(9)
Pd(2)−P(2)	2.254(2)	O(2)−C(28)	1.440(8)
S(1)−C(1)	1.729(7)	O(3)−C(31)	1.469(10)
S(2)−C(7)	1.775(7)	O(4)−C(34)	1.467(10)
S(3)−C(13)	1.678(7)	O(5)−C(37)	1.473(9)
S(4)−C(19)	1.714(8)	O(6)−C(40)	1.489(11)
S(1)−Pd(1)−S(2)	81.57(7)	O(1)−P(1)−O(2)	106.4(3)
S(1)−Pd(1)−S(3)	94.88(8)	O(1)−P(1)−O(3)	100.2(3)
S(2)−Pd(1)−S(3)	173.47(11)	O(2)−P(1)−O(3)	99.8(4)
P(1)−Pd(1)−S(1)	174.85(7)	O(4)−P(2)−Pd(2)	108.0(3)
P(1)−Pd(1)−S(2)	96.60(9)	O(5)−P(2)−Pd(2)	115.9(2)
P(1)−Pd(1)−S(3)	86.48(10)	O(6)−P(2)−Pd(2)	119.6(3)
S(1)−Pd(2)−S(2)	83.54(7)	O(4)−P(2)−O(5)	107.5(3)
S(1)−Pd(2)−S(4)	178.09(8)	O(4)−P(2)−O(6)	103.1(3)
S(2)−Pd(2)−S(4)	94.70(9)	O(5)−P(2)−O(6)	101.5(4)
P(2)−Pd(2)−S(1)	95.92(8)	C(25)−O(1)−P(1)	125.5(5)
P(2)−Pd(2)−S(2)	172.03(8)	C(28)−O(2)−P(1)	121.3(5)
P(2)−Pd(2)−S(4)	85.93(10)	C(31)−O(3)−P(1)	126.4(5)
Pd(1)−S(1)−Pd(2)	96.96(6)	C(34)−O(4)−P(2)	122.3(5)
Pd(1)−S(2)−Pd(2)	94.24(8)	C(37)−O(5)−P(2)	121.0(5)
C(1)−S(1)−Pd(1)	108.4(3)	C(40)−O(6)−P(2)	123.8(5)
C(1)−S(1)−Pd(2)	109.9(3)	C(2)−C(1)−S(1)	123.1(5)
C(7)−S(2)−Pd(1)	110.8(3)	C(6)−C(1)−S(1)	118.3(6)
C(7)−S(2)−Pd(2)	106.5(2)	C(8)−C(7)−S(2)	123.1(6)
C(13)−S(3)−Pd(1)	107.9(3)	C(12)−C(7)−S(2)	117.4(6)
C(19)−S(4)−Pd(2)	112.3(3)	C(14)−C(13)−S(3)	122.2(6)
O(1)−P(1)−Pd(1)	111.1(3)	C(18)−C(13)−S(3)	118.5(6)
O(2)−P(1)−Pd(1)	118.4(2)	C(20)−C(19)−S(4)	122.5(6)
O(3)−P(1)−Pd(1)	118.8(2)	C(24)−C(19)−S(4)	119.6(7)

Table 7. Selected Bond Lengths [Å] and Angles [deg] for 4

Pd(1)−S(1)	2.3526(8)	P(1)−O(3)	1.579(2)
Pd(1)−P(1)	2.3050(9)	O(1)−C(7)	1.451(4)
S(1)−C(1)	1.771(3)	O(2)−C(10)	1.473(4)
P(1)−O(1)	1.595(2)	O(3)−C(13)	1.469(4)
P(1)−O(2)	1.602(2)		
P(1)−Pd(1)−S(1)	85.61(3)	O(3)−P(1)−Pd(1)	112.64(8)
C(1)−S(1)−Pd(1)	108.76(11)	C(7)−O(1)−P(1)	127.1(2)
O(1)−P(1)−O(2)	101.00(12)	C(10)−O(2)−P(1)	121.7(2)
O(1)−P(1)−O(3)	100.54(12)	C(13)−O(3)−P(1)	124.2(2)
O(2)−P(1)−O(3)	106.73(12)	C(2)−C(1)−S(1)	117.7(3)
O(1)−P(1)−Pd(1)	114.97(10)	C(6)−C(1)−S(1)	123.7(3)
O(2)−P(1)−Pd(1)	118.82(8)		

dinuclear palladium centers involving bridging chalcogen donors than the coplanar arrangement.[6,11] Moreover, until now the hinged arrangement was observed only in complexes in which the bridging ligands were coordinated to Pd atoms in a chelate fashion.[12] The hinged arrangement in these compounds is determined

Scheme 3



by the geometrical requirements of the ligands. Complex **5** is the first dinuclear Pd(II) compound with the hinged arrangement of nonchelating ligands. The fold angle between the two neighboring PdL_4 coordination planes is 166.0°.

The bridging phenylthiolato ligands in **5** are not equidistant from the two palladium atoms. The Pd−S bond lengths are noticeably different (2.298(2)−2.396(2) Å, Table 6) and practically cover the range of values known for analogous compounds (2.283(6)−2.3887(7) Å).[6,11,13] The differences in the Pd−S bond lengths can be attributed to the relative effects of the *trans* influence as well as to the steric effects.

The Pd−P distances in **5** (2.208(3) and 2.254(2) Å, Table 6) are within the range 2.1837(8)−2.281(5) Å of Pd−P distances observed in previously investigated Pd(II) complexes with $P(OR)_3$ ligands.[14] The differences in the bond lengths can again be explained by the effects of relative *trans* influence.

The phenyl groups bound to terminal and bridging sulfur atoms have the s*yn* conformation relative to the Pd_2S_2 ring, respectively. The Pd···Pd length of 3.503(1) Å seems too long to be assigned as any direct metal−metal interaction.

The Pd atom in mononuclear complex **4** lies in an inversion center, and the coordination geometry is thus required to be *trans* and strictly planar. The planar coordination is not exactly square, as the crystallographically unique P(1)−Pd(1)−S(1) angle is 85.61(3)°. The deviations from the square-planar geometry are imposed by the steric hindrances of the ligands. The Pd−S distance of 2.3526(8) Å (Table 6) is similar to those observed in other mononuclear Pd(II)-phenylthi-

(11) (a) Fenn, R. H.; Segrott, G. R. *J. Chem. Soc. A* **1970**, 3197. (b) Fenn, R. H.; Segrott, G. R. *J. Chem. Soc., Dalton Trans.* **1972**, 330. (c) Padilla, E. M.; Golen, J. A.; Richmann, P. N.; Jensen, C. M. *Polyhedron* **1991**, *10*, 1343. (d) Guangming, L.; Sihai, L.; Tan, A. L.; Yip, W.-H.; Mak, C. W.; Hor, T. S. A. *J. Chem. Soc., Dalton Trans.* **1996**, 4315. (e) Cao, R.; Hong, M.; Jiang, F.; Kang, B.; Xie, X.; Liu, H. *Polyhedron* **1996**, *15*, 2661.

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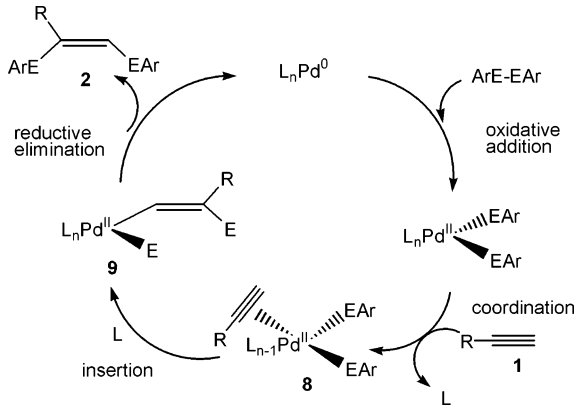
Scheme 4



olato complexes such as $Pd(SPh)_2(dppe)$ (2.3486(7) Å),[13a] $Pd(SPh)_2(PHCy_2)_2$ (2.336(2) and 2.338(2) Å),[13b] $Pd(SC_6F_5)_2(dppe)_2$ (2.354(1) and 2.361(1) Å),[13c] $Pd(SPy\text{-}2)_2(dppe)_2$ (2.333(2) and 2.382(2) Å),[13d] or $Pd(SPh)_2(dippf)$ (2.3703(7) and 2.3887(7) Å),[13e] and the Pd(1)−S(1)−C(1) angle shows the almost ideal tetrahedral value of 108.76(11)°. The Pd(1)−P(1) distance of 2.3050(9) Å is considerably longer than those in previously investigated Pd(II)-tertiary tri(alkyl)phosphito complexes.[14] The tri(isopropyl)phosphito groups are staggered with respect to each other.

The reaction of the isolated mononuclear complex **4** with alkynes (R = *n*Bu, CH_2OMe, CH_2NMe_2) resulted in the quantitative formation of the corresponding products **2** (>90% yield after 3 h at 80 °C in toluene). In the same conditions the reaction of the dinuclear complex **5** with alkynes gave only 30−40% of **2** and insoluble polymeric species. The quantitative yield of **2** was obtained only if two or more equivalents of $P(OiPr)_3$ were added to the solution. Therefore, the role of the ligand excess is to prevent palladium complex polymerization. It should be noted that in all cases the reactions of the isolated palladium complexes with alkynes lead to the same product as the corresponding catalytic reaction does (**2**).

After studying the stoichiometric reactions and establishing the structure of the palladium complexes we have investigated the catalytic reaction. Using ^{31}P and ^1H NMR monitoring of the catalytic reaction complexes **3**−**6** were detected in solution with the ratio (**3**+**4**)/(**5**+**6**) = 10/1, therefore confirming intermediate formation of these complexes under the catalytic conditions. Finally, to prove this assumption, we have performed the catalytic reactions using the isolated mono- and dinuclear complexes (**4** and **5**) as the catalysts. Exactly the same yields and stereoselectivity were obtained in these catalytic reactions as compared to the $Pd(OAc)_2/P(OiPr)_3$ and $Pd_2(dba)_3/P(OiPr)_3$ catalytic systems.

The mechanism of *E*−*E* bond addition to alkynes involves the following stages: (1) oxidative addition, (2) ligand dissociation and alkyne coordination to form the π-complex (**8**), (3) alkyne insertion into the M−E bond (**9**), and (4) C−E reductive elimination releasing the final product **2** (Scheme 4). In many cases it was reported that an excess of the ligand retards alkyne coordination and blocks the catalytic cycle.[1] In the studied case excellent yields were obtained only with an excess of the ligand, which is rather unusual behavior.

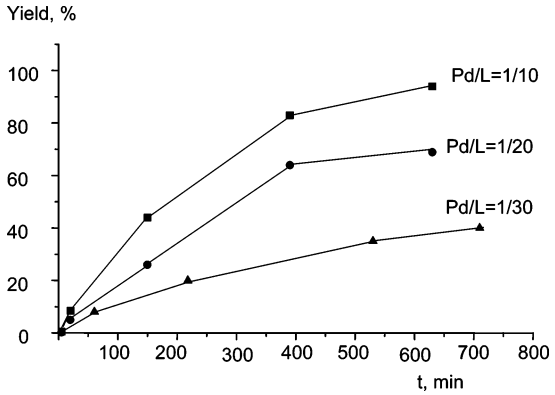


Figure 3. Yield of **2** vs time in the reaction of hexyne-1 with complex **4** at different [Pd]/$P(O\text{-}iPr)_3$ ratios (see Experimental Part for details).

To reveal the mechanism of the reaction, we have studied the reactions of isolated palladium chalcogenide complexes with hexyne-1 at different $P(O\text{-}iPr)_3$ ligand concentrations (Figure 3). It was found that the excess of the ligand in solution decreases the rate of the product **2** formation in the reaction of the palladium complex with alkyne (Pd/L ratios of 1/10, 1/20, and 1/30 were used; see Figure 3). This finding is in agreement with the catalytic reaction mechanism (Scheme 4). Increasing ligand concentration decreases the observed rate of the product **2** formation, since coordination vacancy is needed to bind alkyne and facilitate insertion to the M−E bond.

According to the performed study, an excess of phosphite ligands retards alkyne coordination to the metal complex (**8**) and decreases the rate of the product formation (Figure 3). However, an excess of the ligand is of vital importance to prevent catalyst deactivation via the insoluble polymer (**7**) formation. The ratio [Pd]/[L] = 1/10 seems to be a good compromise to achieve high yields in reasonable reaction time (Table 5).

According to the ^{31}P NMR, both types of complexes (mononuclear and dinuclear) are present under catalytic conditions. Neither complex **8** nor **9** was detected in the NMR monitoring of the stoichiometric or catalytic reactions. Therefore, for the moment it is difficult to find out whether dinuclear (**5**+**6**) or mononuclear (**3**+**4**) complexes make major contributions to the product formation under catalytic conditions. For simplicity only the mononuclear complexes are shown in Scheme 4, assuming that dinuclear complexes may react in the same way. A detailed investigation of this problem will be undertaken in our future studies.

3. Conclusions

It was shown that Pd complexes with trialkyl phosphite ligands are very efficient catalysts for the addition reactions of Ar_2E_2 (E = S, Se) to terminal alkynes. The reaction catalyzed by $Pd(0)-P(OR)_3$ has many advantages in comparison with $Pd(0)-PR_3$, since phosphite ligands are readily available and can be easily removed from the reaction mixture upon completing the catalytic process.

Both mononuclear and dinuclear complexes were detected in solution after oxidative addition of the E−E bond to palladium. The relative concentration of the complexes depends on the amount of the ligand in

solution. The complexes were isolated and fully characterized by NMR and X-ray diffraction studies, and it was shown that in solution the complexes are in equilibrium with each other.

The stoichiometric reactions of the isolated palladium complexes with alkynes lead to the same product as the catalytic reaction. It was found that increasing the concentration of the phosphite ligand in solution decreases the rate of the product formation, but increases the product yield by suppressing catalyst polymerization.

Exploring the potential of phosphite ligands in the catalytic carbon−element bond formation reactions and further mechanistic details are the subjects of ongoing studies.

4. Experimental Part

4.1. General Comments. The synthetic work was carried out under argon atmosphere. Solvents were purged with argon before use. 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 ^{1}H, ^{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 an active shielded Z-gradient coil. ^{1}H 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) was used for ^{31}P, and $Ph_2Se_2/CDCl_3$ ($\delta = 463.0$ ppm) was used for ^{77}Se. See the previous study for a detailed description of the 2D experiments.[5]

4.2. General Synthetic Procedure. (i) Pd_2dba_3 as Catalyst Precursor. Under argon Ar_2E_2 (4.0×10^{-4} mol), Pd_2dba_3 (5.6 mg, 6.1×10^{-6} mol), P(O*i*Pr)$_3$ (25 mg, 1.2×10^{-4} mol), and the alkyne (6.1×10^{-4} mol) were dissolved in 0.6 mL of degassed toluene. The reaction was performed in a sealed tube for 3 h at 100 °C. The mixture remained homogeneous during the reaction without noticeable catalyst polymerization.

(ii) $Pd(OAc)_2$ as Catalyst Precursor. Under argon Ar_2E_2 (4.0×10^{-4} mol), $Pd(OAc)_2$ (2.7 mg, 1.2×10^{-5} mol), P(O*i*Pr)$_3$ (30 mg, 2.4×10^{-4} mol), and the alkyne (6.1×10^{-4} mol) were dissolved in 0.6 mL of degassed toluene. The reaction was performed in a sealed tube for 3 h at 100 °C. The mixture remained homogeneous during the reaction without noticeable catalyst polymerization.

(iii) Product Separation and Purification. After completing the reaction the solvent was evaporated on a rotary evaporator and the product was purified by flash chromatography on silica L5/40 with hexane/ethyl acetate gradient elution. After drying in a vacuum the pure products were obtained as a light oil. The yields are given in Table 5. The products **2a**, **2b, 2f, 2h, 2i, 2j,** and **2k** were identified according to the published data.[3,5,9] The data for the other compounds are given below. In all cases the structure of the products was confirmed with ^{1}H, ^{13}C, and ^{77}Se NMR. The stereochemistry was determined using 2D NOESY and COSY-LR experiments.

***Z*-HC(S-C$_6$H$_4$CH$_3$)=C(S-C$_6$H$_4$CH$_3$)-$^{\alpha}$CH$_2$$^{\beta}CH_2$$^{\gamma}CH_2CH_3$ (2c):** yellow oil; ^{1}H NMR (500 MHz; $CDCl_3$; δ, ppm) 0.83 (tr, 3H, CH_3), 1.22 (m, 2H, γ-CH_2), 1.48 (qw, 2H, β-CH_2), 2.22 (tr, 2H, α-CH_2), 2.33 (s, 3H, CH_3−Ar), 2.34 (s, 3H, CH_3−Ar), 6.48 (s, 1H, HC=), 7.12 (m, 4H, Ar), 7.32 (m, 4H, Ar); ^{13}C{^{1}H} NMR (126 MHz; $CDCl_3$; δ, ppm) 13.7, 20.9, 21.0, 21.8, 30.6, 36.5, 128.6, 129.6, 129.7 130.0, 130.1, 131.0, 132.4, 134.2, 136.8, 136.8; mass spectrum (EI) *m/z* 328 (M^+, 80). Anal. Calcd for $C_{20}H_{24}S_2$: C, 73.12; H, 7.36. Found: C, 73.14; H, 7.56.

***Z*-HC(Se-C$_6$H$_4$-F)=C(Se-C$_6$H$_4$-F)-$^{\alpha}$CH$_2$$^{\beta}CH_2$$^{\gamma}CH_2CH_3$ (2d):** yellow oil; ^{1}H NMR (500 MHz; $CDCl_3$; δ, ppm) 0.82 (tr, 3H, CH_3), 1.22 (m, 2H, γ-CH_2), 1.46 (qw, 2H, β-CH_2), 2.22 (tr, 2H, α-CH_2), 6.82 (s, 1H, HC=), 7.02 (m, 4H, Ar), 7.54 (m, 4H, Ar); ^{13}C{^{1}H} NMR (126 MHz; $CDCl_3$; δ, ppm) 13.7, 21.8, 31.0, 39.4, 116.3 (Ar, ^{3}J(C−F) = 11 Hz), 116.5 ^{3}J(C−F) = 11 Hz, 123.8, 125.6, 127.3, 135.1 ^{2}J(C−F) = 60 Hz, 135.2 ^{2}J(C−F) = 60 Hz, 136.8, 162.5 ^{1}J(C−F) = 248 Hz, 162.6 ^{1}J(C−F) = 248 Hz; mass spectrum (EI) *m/z* 432 (M^+, 70) Anal. Calcd for $C_{18}H_{18}F_2Se_2$: C, 50.25; H, 4.22. Found: C, 50.46; H, 4.32.

***Z*-HC(S-Ph)=C(S-Ph)-$^{\alpha}$CH$_2$$^{\beta}CH_2$$^{\gamma}CH_2$$^{\delta}CH_2CH_3$ (2e):** yellow oil; ^{1}H NMR (500 MHz; $CDCl_3$; δ, ppm) 0.83 (tr, 3H, CH_3), 1.21 (m, 4H, γ-CH_2, δ-CH_2), 1.50 (qw, 2H, β-CH_2), 2.24 (tr, 2H, α-CH_2), 6.57 (s, 1H, HC=), 7.20−7.33 (m, 6H, Ar), 7.37 (d, 2H, Ar), 7.42 (d, 2H, Ar); ^{13}C{^{1}H} NMR (126 MHz; $CDCl_3$; δ, ppm) 13.9, 22.3, 28.1, 30.9, 37.0, 126.6, 126.7, 128.8, 128.9, 129.0, 129.6 130.4, 133.8, 134.3, 135.8; mass spectrum (EI) *m/z* 314 (M^+, 70). Anal. Calcd for $C_{19}H_{22}S_2$: C, 72.56; H, 7.05. Found: C, 72.58; H, 7.50.

***Z*-HC(S-Ph)=C(S-Ph)CH$_2$OCH$_3$ (2g):** yellow oil; ^{1}H NMR (500 MHz; $CDCl_3$; δ, ppm) 3.28 (s, 3H, CH_3), 3.95 (s, 2H, CH_2), 6.98 (s, 1H, HC=), 7.20−7.35 (m, 6H, Ar), 7.40 (d, 2H, Ar), 7.43 (d, 2H, Ar); ^{13}C{^{1}H} NMR (126 MHz; $CDCl_3$; δ, ppm) 57.9, 74.4, 126.8, 127.1, 127.2, 129.0, 129.1, 130.0 130.2, 133.3, 134.4, 134.9; mass spectrum (EI) *m/z* 288 (M^+, 70). Anal. Calcd for $C_{16}H_{16}OS_2$: C, 66.63; H, 5.59. Found: C, 66.48; H, 5.99

***Z*-HC(Se-Ph)=C(Se-Ph)C$_6$H$_4$NH$_2$ (2l):** yellow oil; ^{1}H NMR (500 MHz; $CDCl_3$; δ, ppm) 3.60 (br s, 2H, NH_2), 6.49 (ddd, 1H), 6.82 (tr, 1H), 6.90 (ddd, 1H), 6.98 (tr, 1H), 7.10−7.18 (m, 3H), 7.29 (m, 3H), 7.36 (dd, 2H), 7.56 (s, 1H, HC=), 7.59 (m, 2H); ^{13}C{^{1}H} NMR (126 MHz; $CDCl_3$; δ, ppm) 114.1, 114.6, 118.0, 126.5, 127.8, 129.1, 129.2, 129.4, 130.6, 130.7, 131.1, 131.4, 133.2, 136.2, 141.7, 146.0; mass spectrum (EI) *m/z* 431 (M^+, 20). Anal. Calcd for $C_{20}H_{17}NSe_2$: C, 55.96; H, 3.99; N, 3.26. Found: C, 55.96; H, 3.99; N, 3.05.

***Z*-HC(S-Ph)=C(SPh)(3-C$_9$H$_6$N) (2m):** yellow oil; ^{1}H NMR (500 MHz; $CDCl_3$; δ, ppm) 7.00 (tr, 1H), 7.10 (tr, 2H), 7.24 (d, 2H), 7.26 (d, 1H), 7.32 (tr, 2H), 7.39 (s, 1H, HC=), 7.39 (tr, 1H), 7.47 (d, 2H), 7.55 (tr, 1H), 7.65 (d, 1H), 7.95 (d, 1H), 8.17 (d, 1H), 9.07 (d, 1H); ^{13}C{^{1}H} NMR (126 MHz; $CDCl_3$; δ, ppm) 126.2, 126.3, 126.8, 127.5, 127.8, 127.9, 128.6, 129.0, 129.0, 129.2, 129.3, 130.6, 131.5, 132.8, 133.7, 134.6, 138.8, 147.1, 148.9; mass spectrum (EI) *m/z* 371 (M^+, 70). Anal. Calcd for $C_{23}H_{17}NS_2$: C, 74.36; H, 4,61; N, 3.77. Found: C, 74.09, H, 4.80; N, 3,43.

4.3. Synthesis of the Mononuclear Complex *trans*-[Pd(SPh)$_2$(P(O*i*Pr)$_3$)$_2$] (4). $Pd(OAc)_2$ (0.200 g, 0.89 mmol), Ph_2S_2 (0.389 g, 1.78 mmol), P(O*i*Pr)$_3$ (2.23 g, 10.7 mmol), and 10 mL of benzene were placed into a 50 mL round-bottom flask. The mixture was stirred at room temperature for 20 min until a homogeneous reddish-brown solution was formed. The solution was stirred for 2 h at 70 °C. The solvent was removed on a rotary evaporator, giving the crude product as a dark brown oil. The oil was dissolved in a minimum amount of hexane and kept at −20 °C overnight. Brown crystals were washed with 2 mL of cold hexane and dried under vacuum. Yield: 0.561 g (85%). Anal. Calcd for $C_{30}H_{52}O_6P_2PdS_2$: C, 48.61; H, 7.07; S, 8.65; Pd, 14.36; P, 8.36. Found: C, 48.81; H, 7.22; S, 8.71; Pd, 14.40; P, 8.38. ^{31}P{^{1}H} NMR (202 MHz; C_6D_6; δ, ppm) 102.7; ^{1}H NMR (500 MHz; C_6D_6; δ, ppm; *J*, Hz) 7.82 (m, 4H, Ph), 7.03 (m, 4H, Ph), 6.88 (m, 2H, Ph), 4.95 (m, 6H, CH), 1.10 (d, $J = 6.0$, 36H, CH_3).

4.4. Synthesis of the Dinuclear Complex *trans*-[Pd$_2$(SPh)$_4$(P(O*i*Pr)$_3$)$_2$] (5). $Pd(OAc)_2$ (0.200 g, 0.89 mmol), Ph_2S_2 (0.389 g, 1.78 mmol), P(O*i*Pr)$_3$ (2.23 g, 10.7 mmol), and 10 mL of benzene were placed into a 50 mL round-bottom flask. The mixture was stirred at room temperature for 20 min until a homogeneous reddish-brown solution was formed. The solution was stirred for 2 h at 70 °C. The solvent was removed on a rotary evaporator, giving the crude product as a dark brown oil. The oil was preadsorbed on 3 g of silica L40/100 stirring with 10 mL of $CHCl_3$. The solvent was evaporated followed by the flash chromatography on silica L5/40 with

hexane/ethyl acetate gradient elution. X-ray quality dark brown crystals were obtained after crystallization from hexane (20 h, −20 °C). Yield: 0.327 g (69%). Anal. Calcd for $C_{42}H_{62}O_6P_2Pd_2S_4$: C, 47.32; H, 5.86; P, 5.81; Pd, 19.97; S, 12.03. Found: C, 48.07; H, 5.89; P, 5.80; Pd, 19.92; S, 12.17. ^{1}H NMR (500 MHz; C_6D_6; δ, ppm; J, Hz) 8.13 (m, 4H, Ph), 7.98 (m, 4H, Ph), 7.09 (m, 4H, Ph), 6.96 (m, 8H, Ph), 4.95 (m, 6H, CH), 1.04 (d, J = 6.1, 36H, CH_3); ^{31}P{^{1}H} NMR (202 MHz; C_6D_6; δ, ppm) 98.8.

4.5. Kinetic Measurements of the Alkyne Reaction with Complex 4 at Different Ligand Concentrations. Complex **4** (4.44×10^{-2} mmol, 0.033 g), 0.010 mL of hexyne-1 (8.88×10^{-2} mmol), and 0.3 mL of C_6D_6 were placed into each of the three NMR tubes and purged with argon. $P(OiPr)_3$—0.101 mL (0.44 mmol), 0.201 mL (0.89 mmol), and 0.302 mL (1.33 mmol)—was added to the NMR tubes, maintaining [Pd]/$P(OiPr)_3$ ratios of 1/10, 1/20, and 1/30, respectively. The necessary amount of C_6D_6 was added to each of the NMR tubes to increase the total solution volume to 0.7 mL. The NMR tubes were purged with argon and sealed. The reactions were carried out at 70 °C and monitored with ^{1}H NMR. The dependence of the product **2a** yield versus time is shown in Figure 3.

4.6. Reactions of Palladium Complexes with Alkynes. The same as above; see the text for the [Pd]/$P(OiPr)_3$ ratio and other details.

4.7. X-ray Structure Determinations. Data were collected on a Bruker three-circle diffractometer equipped with a SMART 1000 CCD detector (for **5**) and Syntex $P2_1$ automated four-circle diffractometer (for **4**); in the case of **5** data were corrected for absorption.[15] For details see Table 8. The structures were solved by direct methods and refined for all data by full-matrix least-squares methods on F^2 with anisotropic thermal parameters for non-hydrogen atoms. The refinement of the Flack parameter for compound **5**, which was equal to 0.32(4), indicates that the absolute structure in this case cannot be determined unambiguously due to the specific centrosymmetric arrangement of heavy atoms Pd and P. The hydrogen atoms were placed in calculated positions and refined in the riding model with fixed thermal parameters. All calculations were carried out by use of the SHELXTL PLUS (PC Version 5.10) program.[16]

Crystallographic data for **5** and **4** have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 253771 and No. 253772, respectively, and 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.ccdc.cam.ac.uk).

Table 8. Crystallographic Data for 5 and 4

	5	**4**
empirical formula	$C_{42}H_{62}O_6P_2S_4Pd_2$	$C_{30}H_{52}O_6P_2S_2Pd$
fw	1065.90	741.18
temp (K)	120(2)	173(2)
cryst size (mm)	0.30 × 0.28 × 0.21	0.50 × 0.40 × 0.30
cryst syst	monoclinic	monoclinic
space group	*Pc*	$P2_1/c$
a (Å)	14.6763(19)	12.274(3)
b (Å)	14.9844(19)	12.865(3)
c (Å)	11.8916(15)	13.011(3)
β (deg)	113.396(2)	112.62(3)
V (Å^3)	2400.1(5)	1896.5(7)
Z	2	2
d_c (g cm^{-3})	1.475	1.298
F(000)	1096	776
μ (mm^{-1})	1.032	0.719
θ range (deg)	1.51 to 27.00	2.40 to 26.05
index range	$-18 \le h \le 18$ $-19 \le k \le 19$ $-15 \le l \le 15$	$-9 \le h \le 15$ $-15 \le k \le 15$ $-16 \le l \le 14$
no. of rflns collected	22 257	6821
no. of unique rflns	10 394	3725
no. of rflns with $I > 2\sigma(I)$	9028	3091
R1; wR2 ($I > 2\sigma(I)$)	0.0611; 0.1442	0.0416; 0.1013
R1; wR2 (all data)	0.0698; 0.1526	0.0532; 0.1093
no. of data/restraints/params	10394/2/506	3725/0/187
GOF on F^2	0.999	1.069
max. shift/error	0.001	0.001
absolute struct param	0.32(4)	
largest diff peak/hole (e Å^{-3})	1.880/−1.538	1.233/−0.710
abs corr T_{max}; T_{min}	0.812; 0.747	none

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Supporting Information Available: Kinetic measurements of the catalytic reaction with PPh_3 and $P(OiPr)_3$ ligands. Tables of atom coordinates, bond lengths and angles, torsion angles, and anisotropic displacement parameters for **5** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM049082G

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