The *trans*-Chloropalladation Reaction of Propargyl Amines and Thioethers. X-ray Crystal Structure of *trans*-[Pd-*trans*-C(Ph)=C(Cl)CH(Me)S(*i*-Pr)(Cl)(Py)]

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The reaction of the propargyl amines R^1—C≡CCH(R^2)NMe(R^3) and thioethers R^1—C≡CCH(R^2)SR^4 (R^1= Me, *n*-Bu, Ph; R^2 = H, Me; R^3 = Me, bn; and R^4 = Me, *i*-Pr, Ph) with Li_2PdCl_4 in methanol affords the air-stable five-membered palladocyclic compounds [Pd—C(R^1)=C(Cl)CH(R^2)NMe(R^3)(μ-Cl)]$_2$ and [Pd—C(R^1)=C(Cl)CH(R^2)SR^4(μ-Cl)]$_2$, respectively, resulting formally from the *trans* nucleophilic addition of the chlorine anion onto the C≡C bond. On the other hand, alkynes with more sterically demanding groups (R^1 = *t*-Bu or $SiMe_3$) only form adducts of the type $PdCl_2$(alkyne)$_2$. Under the same reaction conditions, the terminal alkynes (R^1 = H) afford analogous five-membered palladocyclic compounds in very low yields and an ill-defined mixture of organic/organometallic products. However, the treatment of these terminal alkynes with catalytic amounts of palladium(II) salts and copper dichloride in the presence of lithium chloride and water yields (2-chloroallyl)amines and thioethers in good yields.

Introduction

The carbopalladation reaction of alkynes is a well-investigated reaction and widely used in both organic and organometallic synthesis.[1−3] In marked contrast, only recently the chloropalladation reaction has received some attention[4] despite the fact that this reaction can lead to series of useful Pd−vinyl intermediate species for organic synthesis.[5−11] This is probably due to the highly reactive behavior of alkynes toward the Pd−Cl bond. Indeed, in most of the cases, the reaction of alkynes with palladium−chloride compounds results in polymerization of the alkynes, therefore, restricting the study of this reaction.[12−14] This limitation can be overcome by trapping the Pd−vinyl intermediates with electrophilic reagents, such as allyl halides and cyclohexadiene, and analyzing the nature of the organic or organometallic species formed.[4] It has been demonstrated that *trans*-chloropalladated species (with respect to the metal center and the chlorine atom) were preferentially formed in the presence of high Cl^- concentration, whereas the *cis*-product is formed predominantly in reactions with low Cl^- concentrations. However, the chloropalladation reaction product has been isolated in only one case.[15] In fact, in this case, the presence of a potentially coordinating dimethylamino group attached to the C≡C bond allows the direct isolation of the chlorovinylpalladium compound.[15]

In this respect, we have started investigating the chlorometalation reaction of alkynes bearing heteroatom units that might potentially coordinate to the metal center and thus stabilize the desired chlorovinylpalladium moiety. We have already shown that this reaction depends on the nature of the coordinating group.[16] In this work, we wish to report results concerning the steric and electronic influence of various groups linked to the C≡C bond on the chloropalladation reaction for a series of propargyl amines and thioethers (Chart 1). Moreover, we also present experimental evidence indicating that the chloropalladation reaction for this type of alkyne occurs via intermolecular nucleophilic addition of Cl^- onto the activated C≡C bond. Some aspects of the present work have been communicated previously.[17]

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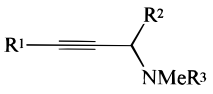
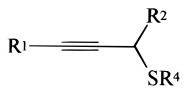
Chart 1

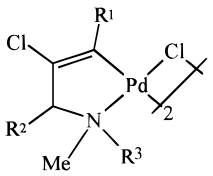


	R^1	R^2	R^3
1	Ph	H	Me
2	Ph	Me	Me
3	Ph	H	bn
4	Me	H	Me
5	*n*-Bu	Me	Me
6	*t*-Bu	Me	Me
7	H	H	Me

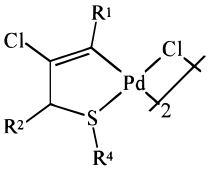


	R^1	R^2	R^4
8	Ph	H	Ph
9	Ph	Me	*i*-Pr
10	Ph	Me	Me
11	Ph	Me	Ph
12	Me	H	*i*-Pr
13	*n*-Bu	Me	*i*-Pr
14	*t*-Bu	Me	*i*-Pr
15	$SiMe_3$	H	*i*-Pr
16	H	H	Ph
17	H	Me	Ph

Chart 2



	R^1	R^2	R^3
18	Ph	H	Me
19	Ph	Me	Me
20	Ph	H	bn
21	Me	H	Me
22	*n*-Bu	Me	Me
23	H	H	Me

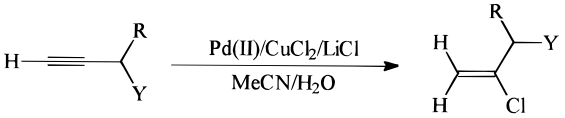


	R^1	R^2	R^4
24	Ph	H	Ph
25	Ph	Me	*i*-Pr
26	Ph	Me	Me
27	Ph	Me	Ph
28	Me	H	*i*-Pr
29	^{n}Bu	Me	*i*-Pr

Results and Discussion

Synthesis. The propargyl amines and thioethers chosen for this study are shown in Chart 1. The addition of equimolar amounts of the phenyl-substituted propargyl amines **1**−**3** to a methanolic solution of lithium tetrachloropalladate/lithium chloride at 5 °C produces almost instantaneously the air- and water-stable compounds **18**−**20**, respectively, as yellow solids in good yields (Chart 2). However, under the same reaction conditions, the phenylpropargyl thioethers **8**−**11** require 5−10 min to produce, in similar yields, the analogus five-membered cyclopalladated complexes **24**−**27**, respectively. Under the same reaction conditions, the alkyl-substituted alkynes **4**, **5**, **12**, and **13** afford dark-yellow solutions, from which the five-membered palladocyclic compounds **21**, **22**, **28**, and **29**, respectively, have been isolated in good yields. In these cases, the chloropalladation reaction is completed after 30−45 min for the propargyl amines and 1−2 h for the propargyl thioethers. The conversion of these reactions was monitored by the disappearance of the ν(C≡C) band in the IR spectra of the crude reaction mixture at different reaction times. It is important to note that, whereas the reaction is almost instantaneous in the case of the phenyl-substituted alkynes **1**−**3**, 30−45 min is needed in the case of the alkyl-substituted alkynes **4** and **5**. The same trend was observed in comparing the phenylpropargyl thioethers with the alkyl propargyl thioethers, *i.e.*, the chloropalladation reaction occurs relatively much faster with the former alkynes than with the latter ones. It is important to note that only five-membered cyclopalladated compounds **18**−**22** and **24**−**29** have been isolated from these chloropalladation reactions.

Scheme 1



Alkyne			Product
7	Y= NMe_2	R= H	**31**
16	Y= SPh	R= H	**32**
17	Y= SPh	R= Me	**33**

Compounds **18**−**20** and **24**−**27** are sparingly soluble in dichloromethane and chloroform, whereas the palladocycles **21**, **22**, **28**, and **29** are soluble in these chlorinated solvents. It is worthwhile to mention that these chloropalladation reaction rates depend on [Cl^-]. For example, the reaction of alkynes **1**−**3** occurs almost instantaneously with lithium tetrachloropalladate whereas the reaction with $PdCl_2(MeCN)_2$ or $PdCl_2(SEt_2)_2$ requires 4−6 h in methanol, dichloromethane, or benzene.

In the reaction of the alkynes containing more sterically demanding groups (**6**, **14**, and **15**) with lithium tetrachloropalladate, only adducts of the type $PdCl_2(i\text{-}PrSCH_2C{\equiv}CSiMe_3)_2$, **30**, have been detected, even at higher temperatures (refluxing in methanol), at different concentrations of lithium chloride, or in other solvents, such as dichloromethane or benzene.

The reaction of the terminal alkynes **7**, **16**, and **17** with palladium chloride salts, such as Li_2PdCl_4, $PdCl_2(RCN)_2$ (R = Ph, Me), or $PdCl_2(SEt_2)_2$, under various reaction conditions (different solvents, temperature, and lithium chloride concentrations) affords an ill-defined mixture of organic/organometallic products. However, in one case, the cyclopalladated compound **23** has been isolated in very low yield (<10%). This result suggests that these terminal alkynes follow, preferentially, the classical alkyne oligomerization reaction in contact with palladium chloride salts, *i.e.*, the chloropalladation reaction is succeeded by a series of alkyne insertion reactions into the Pd−C vinyl bond.[12−14,18] Moreover, it is well-established that the reaction between terminal alkynes and cyclopalladated compounds affords an ill-defined mixture of organic and organometallic products.[3]

However, these undesired insertion reactions could be suppressed by trapping the chlorination product with acid hydrolysis, and the 2-chlorovinyl compounds **31**−**33** have thus been isolated (Scheme 1). Moreover, this hydrochlorination reaction can be performed with catalytic amounts of palladium(II) salts. Thus, under optimized reaction conditions, the alkynes **7**, **16**, and **17** produce the 2-chlorovinyl compounds **31**−**33** in 80−95% yield, in the presence of catalytic amounts of

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palladium acetate, copper dichloride, and an excess of lithium chloride in acetonitrile/water (9:1). It is important to note that this hydrochlorination reaction only occurs in the presence of Pd(II) salts.

Characterization of the Compounds. The elemental analysis of compounds **18**−**29** indicate that one alkyne has been incorporated per $PdCl_2$ fragment. The infrared spectra of the cyclopalladated compounds exhibit the characteristic ν(C═C) bands between 1600 and 1650 cm^{-1}. The ^1H and ^{13}C NMR data of the dimeric cyclopalladated compounds show, in various cases, the presence of two sets of signals indicating the existence of two isomers. These isomers are probably the *cisoid* and *transoid* dimeric forms, as usually observed in this type of dimeric complexes.[19,20] However, the ^1H and ^{13}C NMR data of the monomeric compounds derived from **18**−**29** (prepared *in situ* by the addition of Py-d_5 to a solution of the dimeric compounds in the NMR tube) show, with the exception of **26**, the presence of a single isomer. The ^1H and ^{13}C NMR data of the nitrogen containing cyclopalladated compounds are consistent with the proposed structures shown in Chart 2. The chlorovinyl palladium group provides two distinct resonances for the carbon−carbon double bond, *i.e.*, a characteristic low-field signal (δ 140−150 ppm) of an sp^2 carbon bound to a chlorine atom and a high-field signal (δ 115−125 ppm) for the carbon atom bound to the palladium center. The $^3J_{C,H}$ of 6.5 Hz between the vinylic proton and the allylic carbon of compound **23** is a strong indication of the *trans* relationship between the carbon and the proton.[21]

In the ^1H NMR spectra of compounds **24** and **28** (R^2 = H), the methylene protons are diasterotopic (AB spin system, $^2J_{HH}$ = 16.5 and 14.7 Hz, respectively), imposed by the chirality of the sulfur atom. It is interesting to note that in compounds **25**−**27** (where R^2 = Me), different diastereoisomer populations have been observed depending on the nature of R^4. Thus, if R^4 is a bulky group (isopropyl), a single isomer has been observed. In contrast, with R^4 = Me (a less sterically demanding group), the appearance of two sets of signals in the ^1H NMR spectrum indicates the presence of two diastereoisomers in a 4:1 ratio. It is reasonable to assume for steric reasons an *anti* relationship between the C−Me and the SR^4 groups in compound **25** and in the major isomer of **26**. In order to determine the exact stereochemistry of compound **25**, an X-ray diffraction analysis has been undertaken on its monomeric derivative **34**. Compound **34** has been quantitatively prepared by the addition of equimolar amounts of pyridine to a dichloromethane solution of **25** (see Experimental Section). Crystallographic data and details of the structure determination of compound **34** are presented in Table 1. Selected bond lengths and angles of **34** are given in Table 2. An ORTEP[22] drawing of the structure of **34** is shown in Figure 1.

The coordination sphere of Pd including the C(3), Cl(1), N(1), and S atoms can be considered as essentially planar, with root mean square atomic displacements from the mean plane of the five atoms of 0.024 Å. The sum of the angles about the Pd atom is 360(2)°; the C(3) atom is moved about 4° from the ideal square planar position (as seen by the nearly 90° angles for the Cl(1)−Pd−S and Cl(1)−Pd−N(1) angles) to close up the cyclo ring; the S−Pd−C(3) angle is 85.7(3)° and increases the N(1)−Pd−C(3) angle to 93.9(3)°.

The *trans* stereochemistry at the C(2)−C(3) vinyl bond between Cl(2) and the metal center is noteworthy. For steric reasons, the methyl (C(41)) and the isopropyl (C(31)) groups display an *anti* relationship.

Interestingly, in the ^1H NMR spectrum at low temperatures (below 0 °C) of compound **27**, the CH group appears as a quartet centered at 4.05 ppm. The signal of this proton broadens at higher temperatures and coalesces at *ca.* 20 °C. This dynamic behavior in solution can be explained by the pyramidal inversion of the configuration of the sulfur atom in **27**, as already pointed out earlier for related sulfur containing cyclo-

Table 1. Crystal Data and Structure Refinement for 34, with Esd's in Parentheses

empirical formula	$C_{18}H_{21}Cl_2NPdS$
fw	460.72
temp (K)	293(2)
wavelength (Å)	0.710 73
cryst syst	monoclinic
space group	$P2_1/c$
unit-cell dimens	a = 18.4234(3) Å b = 8.4994(1) Å c = 13.1598(2) Å β = 102.98(2)°
volume (Å^3), Z	2008.03(5), 4
density (calcd) (Mg/m^3)	1.524
abs coeff (mm^{-1})	1.292
F(000)	928
cryst size (mm)/color	0.30 × 0.20 × 0.15/ light yellow
θ range for data collection (deg)	3.61−24.97
limiting indices	$-21 \le h \le 21$, $-10 \le k \le 10$, $0 \le l \le 15$
no. of reflns collected	7084
no. of independent reflns	3510 [R_{int} = 0.0954]
abs corr	ψ scans
max and min transmission	0.445 and 0.382
refinement method	full-matrix least-squares on F^2
no. of data/restraints/parameters	3460/0/215
goodness-of-fit on F^2	1.165
final R indices [$I > 2\sigma(I)$]	R1 = 0.0526, wR2 = 0.1315
max (Δ/σ)	0.000
ext coeff	0.0008(8)
largest diff peak and hole (e·Å^{-3})	1.082 and −0.718

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 1, with Esd's in Parentheses

Pd−C(3)	1.998(9)	C(2)−C(3)	1.349(13)
Pd−N(1)	2.066(8)	C(2)−Cl(2)	1.756(11)
Pd−S	2.250(3)	C(3)−C(21)	1.471(14)
Pd−Cl(1)	2.380(3)	N(1)−C(15)	1.328(12)
S−C(1)	1.819(11)	N(1)−C(11)	1.333(12)
S−C(31)	1.822(12)	C(31)−C(32)	1.52(2)
C(1)−C(2)	1.48(2)	C(31)−C(33)	1.54(2)
C(1)−C(41)	1.50(2)		
C(3)−Pd−N(1)	93.9(3)	C(3)−C(2)−C(1)	125.4(10)
C(3)−Pd−S	85.7(3)	C(3)−C(2)−Cl(2)	121.7(9)
N(1)−Pd−S	177.0(2)	C(1)−C(2)−Cl(2)	112.9(8)
C(3)−Pd−Cl(1)	175.6(3)	C(2)−C(3)−C(21)	120.3(9)
N(1)−Pd−Cl(1)	90.5(2)	C(2)−C(3)−Pd	117.9(8)
S−Pd−Cl(1)	89.95(10)	C(21)−C(3)−Pd	121.9(6)
C(1)−S−C(31)	104.2(6)	C(15)−N(1)−C(11)	118.2(9)
C(1)−S−Pd	103.0(4)	C(15)−N(1)−Pd	119.4(6)
C(31)−S−Pd	106.8(4)	C(11)−N(1)−Pd	122.4(7)
C(2)−C(1)−C(41)	115.6(11)	C(32)−C(31)−C(33)	114.5(11)
C(2)−C(1)−S	107.8(7)	C(32)−C(31)−S	113.4(9)
C(41)−C(1)−S	111.4(10)	C(33)−C(31)−S	107.4(9)

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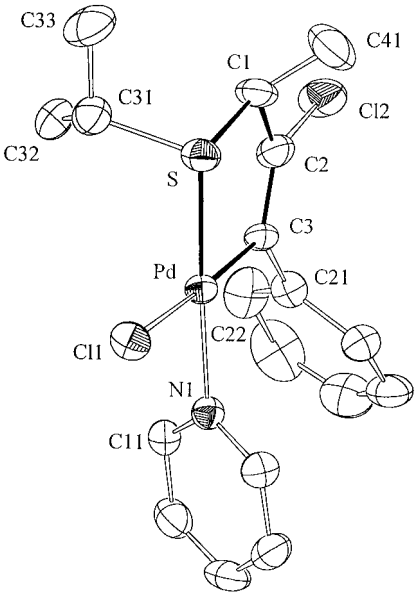


Figure 1. ORTEP[22] plot with atom-labeling scheme of the structure of **34**. Displacement ellipsoids are at the 30% level; H atoms are omitted for clarity.

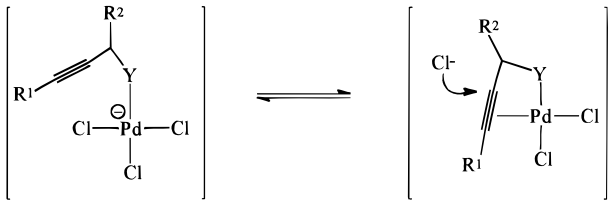
palladated compounds.[23] The relatively facile sulfur inversion in the case of compound **27** containing the SPh group compared with the analogous compounds **25** and **26** (SMe and S-*i*-Pr) is a classical trend in these types of compounds.[24−26] In fact, it is known that the pyramidal sulfur inversion occurs through a planar transition state, which is stabilized by (3p−2p)π conjugation between the sulfur lone pair and the phenyl aromatic ring in the case of compound **27**.

The Chloropalladation Reaction Path. Two types of mechanisms have been adopted for the stereochemical outcome in the chloropalladation reaction of substituted alkynes. The first involves the intramolecular insertion of the triple bond into the Pd−Cl bond to afford the *cis*-chloropalladation kinetic product, which in some cases can be further isomerized into the thermodynamically more stable *trans*-isomer. In the second mechanism, it is assumed that the reaction occurs via an external nucleophilic addition of the Cl^- onto the palladium-coordinated triple bond, yielding the *trans*-isomer. It was also proposed that depending on the nature of the alkyne substituents and the reaction conditions, both mechanisms can be operative.[4]

A mechanism involving an intermolecular nucleophilic addition of the chlorine anion onto the palladium-activated C≡C bond (Scheme 2) can account for the results observed in the case of propargyl amines and thioethers.

Therefore, in the first step, the alkyne is coordinated to the metal center only through its heteroatom (Scheme 2). Indeed, in the case of the analogous chloroplatination reaction, we have been able to isolate such species.[16] In addition, the propargyl amines appear to react somewhat faster than their thioether-substituted analogues, suggesting some indirect electronic control of the

Scheme 2



alkyne reactivity. This might be related to the relative decrease in the palladium electrophilicity by coordination of the thioether group compared with the amino units and, therefore, to a decreasing activation influence of the metal center toward the C≡C bond (see below). Coordination of the triple bond via a Cl^- displacement reaction will lead to alkyne-chelated complexes. An external nucleophilic addition of the chlorine anion will afford the most stable five-membered palladocyclic compound. Indeed, the reaction rate increases with [Cl^-] and only *trans*-chlorovinylpalladium compounds have been observed. In the central step, *i.e.*, the activation of the triple bond, the steric effects play an important role on the C≡C bond reactivity toward the chloropalladation reaction. Thus, the presence of bulky groups (*t*-Bu or $SiMe_3$) attached to the C≡C bond prevent, for steric reasons, the coordination of the unsaturated system to the metal center, therefore, inhibiting the chloropalladation reaction. Electronic effects also play an important role on the chloropalladation reaction rate. In this respect, increasing the electron density on the C≡C bond makes the chloropalladation reaction difficult (comparing the reactivity of the alkyl-substituted alkynes with the analogous phenyl ones).

Conclusions. The chloropalladium reaction of propargyl amines and thioethers occurs readily to give exclusively five-membered palladocyclic compounds in good yields. A wide range of both sulfur and nitrogen containing alkynes can be employed. However, the presence of bulkyl groups attached to the carbon−carbon triple bonds (alkynes **6**, **14**, and **15**) inhibited the chloropalladation reaction, while the presence of terminal alkynes (**7**, **16** and **17**) produces an ill-defined mixture of organic and organometallic products. Qualitatively, the relative rates of the chloropalladation reaction follow approximately the order **1** ≃ **2** ≃ **3** > **8** ≃ **9** ≃ **10** ≃ **11** ≫ **4** ≃ **5** > **12** ≃ **13**. The reaction occurs more readily with increasing [Cl^-]. All of these observations indicate that the chloropalladation occurs by an overall intermolecular nucleophilic addition of the chlorine anion onto the palladium-coordinated carbon−carbon triple bond. The high *trans* selectivity observed for the chloropalladation of the propargyl amines and thioethers is most likely a result of a thermodynamic control.

Experimental Section

General Considerations. All preparations were performed under dry, oxygen-free argon using standard techniques. All solvents were dried and distilled under argon prior to use. Infrared (KBr pellets) spectra were recorded in the region 4000−400 cm^{-1} using a Mattson 3020 FTIR spectrophotometer. The ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded at 200.13 and 50.32 MHz, respectively, using a Varian VXR-

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200 instrument. Proton and carbon chemical shifts (δ in ppm, J in Hertz) are positive downfield relative to external $SiMe_4$. Elemental analyses were carried out by the Central Analítica IQ/UFRGS (Porto Alegre, Brazil). Mass spectra were obtained with a GC-MS HP5988A (EI, 70 eV).

The propargyl amines and thioethers were easily prepared in 70−95% yields by substitution of the corresponding mesylated hydroxyl groups of the propargyl alcohols with dimethylamine and NaSR,[4] respectively.[27] The phenyl derivatives **1**, **2**, **3**, and **8**−**11** were prepared from the corresponding terminal alkynes with phenyl iodide in the presence of catalytic amounts of $PdCl_2(PPh_3)_2$/CuI.[28] Lithium tetrachloropalladate was prepared by the reaction of an excess amount (20 mol %) of lithium chloride with palladium chloride in methanol at reflux temperature. All other reagents were obtained from commercial sources and were used as received without further purification. Note that the ^{1}H and ^{13}C NMR of compounds **18**−**22**, **26**, **28**, and **29** were performed in $CDCl_3$ + ϵPy-d_5, therefore, these data are referred to their Py-d_5 monomeric derivatives.

Synthesis. [Pd-*trans*-C(Ph)=C(Cl)CH(Me)NMe$_2$(μ-Cl)]$_2$ (19). A solution of **2** (0.29 g, 1.7 mmol) in methanol (5 mL) was slowly added to a solution of lithium tetrachloropalladate (0.44 g, 1.7 mmol) in methanol (50 mL) at 5 °C to afford, almost instantaneously, a yellow solid. The reaction mixture was stirred for 0.5 h, and the yellow solid was recovered by filtration, washed with methanol (3 × 25 mL), and dried under reduced pressure (0.42 g, 71%). Anal. Calcd for $C_{12}H_{15}Cl_2NPd$: C, 41.11; H, 4.31; N, 4.00. Found: C, 41.13; H, 4.17; N, 3.88. IR (KBr): 1622 cm^{-1} (ν (C=C)). ^{1}H NMR ($CDCl_3$ + ϵPy-d_5): 7.03−6.79 (m, 5H, aromatics) 3.02 (q, 1H, ^3J = 6.5 Hz, CH) 2.88 and 2.58 (2s, 6H, NMe_2), 1.44 (d, 3H, Me). ^{13}C{^{1}H}NMR ($CDCl_3$ + ϵPy-d_5): 142.8 (CCl), 124.5 (C−Pd) 78.3 (CH), 48.6 and 48.5 (NMe_2), 19.6 (Me).

An identical procedure was used to prepare compounds **18**, **20**, and **24**−**27** using alkynes **1**, **3**, and **8**−**11**, respectively. The yields in these cases were 70−90%.

[Pd-*trans*-C(Ph)=C(Cl)CH$_2$NMe$_2$(μ-Cl)]$_2$ (18).[15] Anal. Calcd for $C_{11}H_{13}Cl_2NPd$: C, 39.26; H, 3.89; N, 4.16. Found: C, 39.40; H, 3.99; N, 4.15. IR (KBr): 1600 cm^{-1} (ν(C=C)). ^{1}H NMR ($CDCl_3$ + ϵPy-d_5): 6.95−6.85 (m, 5H, aromatics) 3.71 (s, 2H, CH_2), 3.05 (s, 6H, NMe_2).

[Pd-*trans*-C(Ph)=C(Cl)CH$_2$NMe(bn)(μ-Cl)]$_2$ (20). Anal. Calcd for $C_{17}H_{17}Cl_2NPd$: C, 49.48; H, 4.15; N, 3.39. Found: C, 49.60; H, 4.19; N, 3.45. IR (KBr pellets): 1612 cm^{-1} (ν(C=C)). ^{1}H NMR ($CDCl_3$ + ϵPy-d_5): 7.94, 7.44, 6.80, and 6.54 (4m, 10H, aromatic), 4.76 and 3.76 (2d, 2H, AB system, J_{AB} = 12.7 Hz, CH_2), 3.95 and 3.50 (2d, 2H, AB system, J_{AB} = 15.9 Hz, CH_2), 3.16 (s, 3H, Me). ^{13}C{^{1}H} NMR ($CDCl_3$ + ϵPy-d_5): 145.0 (CCl), 142.1 and 133.7 (C_{ipso}), 131.9, 131.5, 129.0, 128.2, 127.2 and 126.9 (aromatic CH), 117.2 (C−Pd), 70.4 and 67.0 (CH_2), 52.0 (Me).

[Pd-*trans*-C(Ph)=C(Cl)CH$_2$SPh(μ-Cl)]$_2$ (24). Anal. Calcd for $C_{15}H_{12}Cl_2PdS$: C, 44.86; H, 3.01. Found: C, 45.31; H, 3.16. IR (KBr pellets): 1607 cm^{-1} (ν(C=C)), 693 cm^{-1} (ν(C−S)). ^{1}H NMR ($CDCl_3$): 7.91, 7.52, 7.20, and 7.03 (4m, 10H, aromatic H), 4.27 and 3.70 (2d, 2H, AB system, J_{AB} = 16.5 Hz, CH_2). ^{13}C{^{1}H} NMR ($CDCl_3$): 148.0 (CCl), 143.8 and 132.0 (C_{ipso}), 131.9, 130.9, 130.2, 128.1, 127.9, and 126.6 (aromatic CH), 120.4 (C−Pd), 50.7 (CH_2).

[Pd-*trans*-C(Ph)=C(Cl)CH(Me)S(*i*-Pr)(μ-Cl)]$_2$ (25). Anal. Calcd for $C_{13}H_{16}Cl_2PdS$: C, 40.91; H, 4.23. Found: C, 41.22; H, 4.30. IR (KBr pellets): 1606 cm^{-1} (ν(C=C)), 695 cm^{-1} (ν(C−S)). ^{1}H NMR ($CDCl_2$): 7.17−6.94 (m, 5H, aromatic H), 3.54 (q, 1H, $^3J_{HH}$ = 6.8 Hz, CH), 3.34 (m, 1H, CH), 1.67 (d, 6H, $^3J_{HH}$ = 6.8 Hz, Me), (1.55, d, 3H, Me). ^{13}C{^{1}H} NMR ($CDCl_3$): 145.6 (CCl), 143.0 (C_{ipso}), 128.1, 128.0, and 126.5 (aromatic CH), 127.0 (C−Pd), 52.9 and 45.4 (CH), 24.7, 23.4 and 21.3 (Me).

[Pd-*trans*-C(Ph)=C(Cl)CH(Me)SMe(μ-Cl)]$_2$ (26). Anal. Calcd for $C_{11}H_{12}Cl_2PdS$: C, 37.36; H, 3.42. Found: C, 37.19; H, 3.41. IR (KBr pellets): 1602 cm^{-1} (ν(C=C)), 697 cm^{-1} (ν(C−S)). ^{1}H NMR ($CDCl_3$ + ϵPy-d_5): major isomer 7.02−6.83 (m, 5H, aromatic H), 3.80 (q, 1H, $^3J_{HH}$ = 6.9 Hz, CH), 2.87 (s, 3H, SMe), 1.72 (d, 3H, Me); minor isomer 7.02−6.83 (m, 5H, aromatic H), 4.13 (br s, 1H, CH), 2.65 (s, 3H, SMe), 1.70 (d, 3H, $^3J_{HH}$ = 7.2 Hz, Me). ^{13}C{^{1}H} NMR ($CDCl_3$ + ϵPy-d_5): major isomer 148.3, 144.4 and 126.8 (C=C and C_{ipso}), 128.5, 127.8, and 125.1 (aromatic CH), 57.8 (SMe), 23.6 (CH), 21.1 (Me); minor isomer 52.9 (SMe), 20.1 (CH), 18.2 (Me).

[Pd-*trans*-C(Ph)=C(Cl)CH(Me)SPh(μ-Cl)]$_2$ (27). Anal. Calcd for $C_{16}H_{14}Cl_2PdS$: C, 46.23; H, 3.39. Found: C, 46.39; H, 3.45. IR (KBr pellets): 1608 cm^{-1} (ν(C=C), 690 cm^{-1} (ν(C−S)). ^{1}H NMR ($CDCl_3$): 7.94−6.86 (m, 10H, aromatic H), 3.87 (br s, 1H, CH), 1.75 (br s, 3H, Me). ^{1}H NMR ($CDCl_3$, −20 °C): 8.32, 8.05, 7.50, and 6.80 (4m, 10H, aromatic H), 4.05 (q, 1H, $^3J_{HH}$ = 7.7 Hz, CH), 1.82 (d, 3H, Me). ^{13}C{^{1}H} NMR ($CDCl_3$): 146.0, 143.5, 131.8, and 128.8 (C=C and C_{ipso}), 132.2, 130.9, 128.8, 128.1, 127.9, and 126.4 (aromatic CH), 61.2 (CH), 20.5 (Me).

[Pd-*trans*-C(Me)=C(Cl)CH$_2$S(*i*-Pr)(μ-Cl)]$_2$ (28). A solution of alkyne **12** (0.21 g, 1.7 mmol) in methanol (5 mL) was slowly added to a solution of lithium tetrachloropalladate (0.44 g, 1.7 mmol) in methanol (25 mL) at 5 °C. The solution became, first dark-red then turns to orange. After 2 h of stirring at the same temperature, the volatiles were removed under reduced pressure. The dark-orange oil thus formed was dissolved in dichloromethane (25 mL) and filtered through a plug of Celite. The orange filtrate was concentrated to ca. 2 mL. Addition of hexanes affords an orange solid, which was recovered by filtration and dried under reduced pressure. The remaining solution kept at −20 °C affords more orange solid (0.21 g, combined yield 41%). Anal. Calcd for $C_7H_{12}Cl_2PdS$: C, 27.52; H, 3.96. Found: C, 27.64; H, 3.81. IR (KBr): 1604 cm^{-1} (ν(C=C)). ^{1}H NMR ($CDCl_3$ + ϵPy-d_5): 3.67 and 3.28 (2d, AB spin system, 2H, ^2J = 14.7 Hz, CH_2), 3.26 (m, 1H, CH), 1.64 (s, 3H, Me), 1.56 and 1.51 (2d, 6H, ^3J = Hz, CMe_2). ^{13}C{^{1}H}NMR ($CDCl_3$ + ϵPy-d_5): 145.5 (CCl), 118.7 (C−Pd), 44.3 (CH), 41.5 (CH_2), 24.6 (Me), 23.5 and 22.8 (CMe_2).

An identical procedure was used to prepare compounds **21**, **22**, **23**, and **29** using alkynes **4**, **5**, **7**, and **13**, respectively. The yields in these cases were 40−70%.

[Pd-*trans*-C(Me)=C(Cl)CH$_2$NMe$_2$(μ-Cl)]$_2$ (21). Anal. Calcd for $C_6H_{11}Cl_2NPd$: C, 26.25; H, 4.04; N, 5.10. Found: C, 26.13; H, 4.08; N, 4.76. IR (KBr): 1622 cm^{-1} (ν(C=C). ^{1}H NMR ($CDCl_3$ + ϵPy-d_5): 3.50 (d, 2H, CH_2), 2.90 (br s, 6H, NMe_2), 1.13 (t, 3H, ^3J = 1.8 Hz, Me). ^{13}C{^{1}H}NMR ($CDCl_3$ + ϵPy-d_5): 142.5 (CCl), 116.9 (C−Pd), 75.2 (CH_2), 53.5 (NMe_2), 20.7 (Me).

[Pd-*trans*-C(*n*-Bu)=C(Cl)CH(Me)NMe$_2$(μ-Cl)]$_2$ (22). Anal. Calcd for $C_{10}H_{19}Cl_2NPd$: C, 36.33; H, 5.79; N, 4.24. Found: C, 36.53; H, 6.02; N, 4.09. IR (KBr): 1600 cm^{-1} (ν(C=C)). ^{1}H NMR ($CDCl_3$ + ϵPy-d_5): 3.17 (q, 1H, ^3J = 6.4 Hz, CH), 3.01 and 2.68 (2s, 6H, NMe_2), 2.41 (m, 2H, CH_2), 1.62 (d, 3H, Me), 1.20 (m, 4H, CH_2), 0.68 (t, 3H, ^3J = 7.2 Hz). ^{13}C{^{1}H}NMR ($CDCl_3$ + ϵPy-d_5): 148.2 (CCl), 123.4 (C−Pd), 78.2 (CH), 53.6 and 48.8 (NMe_2), 33.8, 31.7, and 23.1 (CH_2), 20.4 (**Me**CH), 14.4 (**Me**CH_2).

[Pd-*trans*-C(H)=C(Cl)CH$_2$NMe$_2$(μ-Cl)]$_2$ (23). This compound has been obtained in 9% yield using a similar procedure to that described above. Compound **22** was further purified by recrystallization in dichloromethane. Anal. Calcd for $C_5H_9C_{12}NPd$: C, 23.06; H, 3.48; N, 5.38. Found: C, 23.31; H, 3.26; N, 5.19. IR (KBr pellets): 1609 cm^{-1} (ν(C=C)). ^{1}H NMR

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($CDCl_3$ + ϵPy-d_5 7.23 (m, 5H, aromatic), 5.72 (s, 1H, =CH), 3.52 (s, 2H, CH_2), 2.93 (s, 6H, Me).

[Pd-*trans*-C(*n*-Bu)=C(Cl)CH(Me)S(*i*-Pr)(μ-Cl)]$_2$ (29). Anal. Calcd for $C_{11}H_{20}Cl_2PdS$: C, 36.53; H, 5.57. Found: C, 36.31; H, 5.29. IR (KBr): 1602 cm^{-1} (ν(C=C)). ^1H NMR ($CDCl_3$ + ϵPy-d_5): 3.42 (q, 1H, ^3J = 7.1 Hz, CH), 3.25 (m, 1H, CH), 2.20 (m, 2H, CH_2), 1.61 (d, 3H, ^3J = 6.8, Me), 1.51 (2dd, 6H, CMe_2), 1.28 (m, 4H, CH_2), 0.95 (m, 3H, Me). $^{13}C\{^1H\}$NMR ($CDCl_3$ + ϵPy-d_5): 150.0 (CCl), 124.0 (C−Pd), 52.2 and 44.5 (CH), 36.5, 24.0, and 22.5 (CH_2), 31.5 and 31.0 (CMe_2), 22.5 and 14.0 (Me).

Reaction of Alkynes 6, 14, and 15 with Li_2PdCl_4. Synthesis of Compound 30. A solution of **15** (0.77 g, 4.2 mmol) in methanol (10 mL) was slowly added to a solution of lithium tetrachloropalladate (1.10 g, 4.2 mmol) in methanol (70 mL) at 5 °C. The light yellow solution that formed after 2 h of stirring was concentrated to ca. 5 mL to afford a light yellow solid, which was recovered by filtration, washed with hexanes (3 × 15 mL), and dried under reduced pressure (0.44g, 38% based on **15**). Anal. Calcd for $C_{18}H_{36}Cl_2PdSi_2S_2$: C, 39.3; H, 6.60. Found: C, 38.9; H, 6.49. IR (KBr): 2174 cm^{-1} (ν(C≡C)). ^1H NMR ($CDCl_3$): 3.73 (s, 2H, CH_2), 3.65 (m, 1H, CH), 1.61 (d, 6H, ^3J = 6.8 Hz, CMe_2), 0.18 (s, 9H, $SiMe_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 98.5 and 92.6 (C≡C), 42.7 (CH), 25.1 (CH_2), 22.9 (CMe_2), 0.3 ($SiMe_3$).

The reaction of alkynes **6** and **14** with lithium tetrachloropalladate under the same reaction conditions described above produce similar compounds, which upon treatment with pyridine yield $PdCl_2(Py)_2$ and the palladium-free alkynes **5** and **14**.

Catalytic Hydrochlorination Reaction. *N*,*N*-Dimethylpropargylamine **7** (0.25 g, 3 mmol) was added dropwise to a solution of palladium acetate (36 mg, 0.16 mmol), $CuCl_2$ (0.1 g, 0.78 mmol), and lithium chloride (0.42g, 10 mmol) in MeCN:H_2O (9:1, 8.6 mL), and the reaction mixture was stirred at room temperature for 24 h. After the addition of water (15 mL), the organic phase was extracted with diethyl ether (3 × 10 mL) and dried over magnesium sulfate and the solvents were removed under reduced pressure, affording *N*,*N*-dimethyl-(2-chloroallyl)amine **31** (0.25 g, 69%). Compound **31**: IR (film) 1620 cm^{-1} (ν(C=C). ^1H NMR ($CDCl_3$): 4.77(s, br, 2H, $=CH_2$), 3.34 (s, 2H, CH_2), 2.02 (s, 6H, NMe_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 138.5 (CCl), 117.0 ($=CH_2$), 48.5 (CH_2), 44.2 (NMe_2). Compound **32**: IR (film) 1618 cm^{-1} (ν(C=C)). ^1H NMR ($CDCl_3$): 8.05−7.21 (m, 5H, Ph), 5.25 (d, 2H, $^2J_{HH}$ = 8.6 Hz, $=CH_2$), 3.69 (s, 2H, CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 139.5 (CCl), 116.9 ($=CH_2$), 129.2, 131.1, 132.9, and 136.8 (Ph), 44.8 (CH_2). Compound **33**: IR (film): 1623 cm^{-1} (ν(C=C)). ^1H NMR ($CDCl_3$): 7.58−7.21 (m, 5H, Ph), 5.07 (d, 2H, $^2J_{HH}$ = 9.8 Hz, $=CH_2$), 3.88 (q, 1H, $^3J_{HH}$ = 7.0 Hz, CH), 1.58 (d, 3H, Me). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 143.5 (CCl), 113.7 ($=CH_2$), 127.8, 129.2, 133.5, and 137.4 (Ph), 51.5 (CH), 19.8 (Me).

Preparation of *trans*-[Pd-*trans*-C(Ph)=C(Cl)CH(Me)S-(*i*-Pr)(Cl)(Py)] 34. Pyridine (40 mg, 0.5 mmol) was added to an orange solution of **25** (206 mg, 0.5 mmol) in dichloromethane (15 mL) at room temperature, and the reaction mixture was stirred for 15 min. The light yellow solution thus obtained was concentrated under reduced pressure to ca. 3 mL. The addition of hexanes (50 mL) affords a light yellow solid that was recovered by filtration, washed with hexanes (3 × 20 mL), and dried under reduced pressure (215 mg, 94%). Crystals suitable for X-ray analysis have been obtained by slow diffusion of diethyl ether to a solution of **34** in acetone. Anal. Calcd for $C_{18}H_{21}Cl_2NPdS$: C, 46.92; H, 4.59; N, 3.04. Found: C, 46.75; H, 4.71; N, 2.87. IR (KBr pellets): 8.91 (d, 2H, $^3J_{HH}$ = 5.2 Hz, H_oPy), 7.66 (t, 1H, H_pPy), 7.29 (m, 2H, H_mPy), 6.94 and 6.71 (2m, 5H, aromatic H), 3.60 (m, 2H, 2CH), 1.65 (m, 9H, Me). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 151.4 (CCl), 144.0 (C_{ipso}), 151.0, 136.7, 130.0, 128.1, 128.0, and 126.5 (aromatic CH), 51.4 and 43.8 (CH), 23.4 and 21.3 (Me).

X-ray Structure Determination. A fragment of **34** with approximate dimensions of 0.30 × 0.20 × 0.15 mm was cut from a transparent light yellow crystal and used for intensity data collection at 293(2) K. The unit-cell dimensions and the orientation matrix for the data collection resulted from a least-squares fit of 25 reflections in the range 17.45 < θ < 20.78°. The automatic intensity search and indexing method indicated a cell possessing a monoclinic crystal system with a *P* lattice. Diffractometric intensity data were collected on an automatic four-circle diffractometer (Enraf-Nonius CAD4),[29] using graphite-monochromated Mo Kα radiation and ω−2θ scans with a scan speed of 45 s/reflection. Every 60 min the intensity and orientation of three standard reflections were measured; the observed intensity decay was less than 1.4% over the data collection. A total of 7084 reflections were collected involving the half Ewald sphere, with the limiting indices −21 ≤ *h* ≤ 21, −10 ≤ *k* ≤ 10, 0 ≤ 1 ≤ 15 and the θ range of 3.61−24.97°. On the basis of the Bravais lattice and observed reflection conditions, the space group was chosen to be $P2_1/c$. Lorentz and polarization corrections were made on the intensity data. After the equivalent reflections (R_{int} = 9.54%) were merged, 3510 reflections were unique. Due to the observed linear absorption coefficient (1.292 mm^{-1}), an empirical absorption correction based on ψ scans was performed with T_{min} = 0.382 and T_{max} = 0.445.

The structure was solved using direct methods employing the SHELXS-86[30] program, and all non-hydrogen atoms were located by subsequent Fourier difference synthesis. For structure refinement, the SHELXL-93[31] program was employed and the full-matrix least-squares method minimized on $\sum w(F_o^2 - F_c^2)^2$, where *w* is a weighting scheme detailed below. All non-hydrogen atoms were refined using anisotropic thermal parameters. The positions of the hydrogen atoms were calculated based on the geometry of the molecule, and the thermal displacement parameters were refined isotropically on a group basis. For the final refinement of the structure, an isotropic extinction correction was included. Scattering factors for all atoms were as in the SHELXL-93[31] program. The final refinement including 215 parameters gave R1 = 5.26% and wR2 = 13.15%, with the weighting scheme $w = 1/[s^2(F_o^2) + (0.0654P)^2 + 7.63P]$ and $P = (F_o^2 + 2F_c^2)/3$ with a maximum shift/esd = 0.000. Table 1 summarizes the crystal data and structure refinement parameters for **34**.

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Supporting Information Available: Tables of non-hydrogen and hydrogen positional and isotropic displacement parameters, anisotropic parameters, interatomic distances and angles, least-squares planes, and short intermolecular contacts and unit cell and packing diagram for **34** (7 pages). Ordering information is given on any current masthead page.

OM970064R

(29) CAD4, Automatic Four-Circle Diffractometer ENRAF-NONIUS, Delft, Holland.

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(31) Sheldrick, G. M. *SHELXL-93, Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1993.