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The *trans*-Chlorometalation of Hetero-Substituted Alkynes: A Facile Entry to Unsymmetrical Palladium YCY′ (Y, Y′ = NR_2, PPh_2, $OPPh_2$, and SR) "Pincer" Complexes

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A simple and efficient method for the preparation of unsymmetrical palladium YCY′PdCl (Y, Y′ = NR_2, Py, PPh_2, $OPPh_2$, and SR) "pincer" complexes has been disclosed from the chloropalladation of hetero-substituted alkynes. This method tolerates a variety of alkyne functional groups (amines, pyridine, thioethers, phosphines, and phosphinites) and allows the preparation of palladacycles containing different metalated ring sizes. Thus the reaction of Li_2PdCl_4 with hetero-substituted alkynes $Me_2NCH_2C{\equiv}CCH_2CH_2Y$ (Y = S-*t*-Bu, NMe_2, PPh_2, and $OPPh_2$) **1**−**4** affords the "pincer" palladacycles ($Me_2NCH_2(Cl)C{=}CCH_2CH_2Y$-$\kappa N,\kappa C,\kappa Y$)PdCl **7**−**10**, in high yields. Under the same reaction conditions the chloropalladation of *o*-$MeSC_6H_4C{\equiv}CCH_2NMe_2$, **5**, and *o*-$NC_5H_4C{\equiv}CCH_2CH_2S$-*t*-Bu, **6**, yields ($C_6H_4$(*o*-MeS)C=C(Cl)$CH_2NMe_2$-$\kappa S,\kappa C,\kappa N$)PdCl, **11**, and (*t*-$BuSCH_2CH_2C{=}C(Cl)$(*o*-$NC_5H_4$)-$\kappa S,\kappa C,\kappa N$)PdCl, **12**, respectively. The molecular structures of compounds **7** and **11** have been ascertained by means of X-ray diffraction analyses. IR and NMR spectroscopic investigation of the species involved in these reactions suggests that the chloropalladation reaction proceeds through the coordination of only one donor group followed by coordination of the C≡C bond to the metal center. Selective intermolecular chloride nucleophilic addition on this activated unsaturated bond affords the more thermodynamically stable palladacyclic ring. Finally, coordination of the second donor group to the Pd center yields the "pincer" palladacycles.

Introduction

Palladium complexes containing NCN, PCP, and SCS "pincer" (tridentate and anionic six-electron donor) ligands are a popular and widely investigated class of palladacycles (Chart 1).[1]

These compounds exhibit a wide range of reactivity and applications encompassing precursors for organometallic catalysis, organometallic dendrimers, new materials, intermediates for organic synthesis, etc.[2] With rare exceptions[3,4] these palladium YCY′ "pincer" complexes are symmetrical (Y = Y′) and their synthesis is usually performed by direct palladation of the aryl ring (C−H bond activation), transmetalation reactions (mainly from aryllithium derivatives), by oxidative addition of the hetero-substituted aryl halide onto Pd(0) precursors (Scheme 1) or more recently by transcyclometalation.[1,2]

It can be anticipated that the availability of unsymmetrical palladium YCY′ (Y ≠ Y′) "pincer" complexes will facilitate the investigation of their steric and electronic properties by placing, for example, soft and hard donating groups on the same metalated ligand. We wish to disclose herein some of our results in the establishment of a general method for the synthesis of such palladacycles. The method is based on the chloropalladation reaction of propargylamines and -thioethers, which has been successfully used for the preparation

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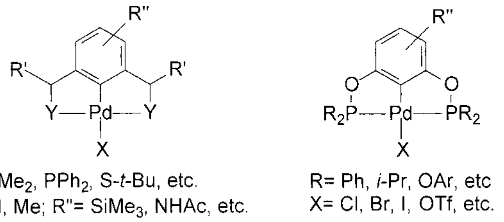
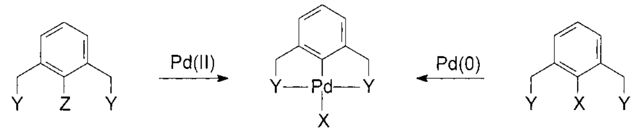
Chart 1. Examples of Symmetrical "Pincer Palladacyles"

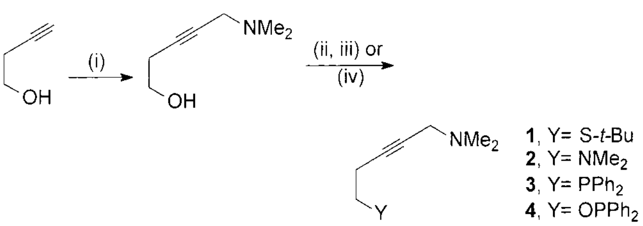


Scheme 1[a]



[a] Z = H, Li, MgCl, etc.; X = Br, I, etc.

Scheme 2[a]



[a] (i) HCHO/HNMe$_2$, CuI, dioxane, reflux; (ii) TsCl, CH_2Cl_2, NEt_3, 0 °C; (iii) *t*-BuSNa, EtOH, RT or $HNMe_2$, CH_2Cl_2, RT or $NaPPh_2$, THF, 0 °C; (iv) $ClPPh_2$, NEt_3, CH_2Cl_2, 0 °C.

of various "classical" five-membered nitrogen- and sulfur-containing palladacycles.[5]

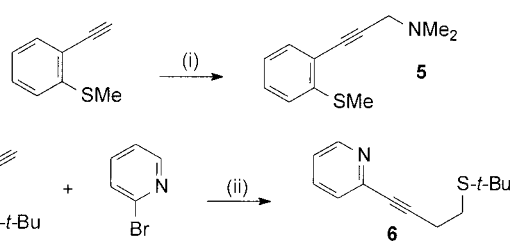
Results and Discussion

Synthesis of the Ligands. The hetero-substituted alkynes **1**−**4** were prepared by Mannich reactions[6] with the homopropargyl alcohol followed by functionalization with sodium thiolate, dimethylamine, lithiumdiphenylphosphide, or chlorodiphenyl phosphine (Scheme 2).

Alternatively, the alkyne containing amino and thioether groups **5** can be prepared directly from the easily available 1-methylthio-2-ethynylbenzene[7] (Scheme 3). The alkyne **6** was prepared using a Sonogashira[8] coupling as described in Scheme 3. All the alkynes were characterized by GC−MS, IR, and ^{1}H and ^{13}C{^{1}H} NMR spectroscopy (see Experimental Section).

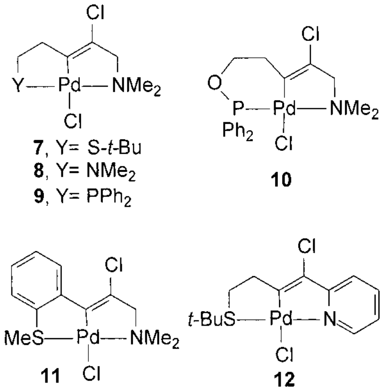
Syntheses and Characterization of the "Pincer" Palladacyles. The palladium YCY′ "pincer" complexes **7**−**12** (Chart 2) were obtained in high yields (70−95%) from the reaction of alkynes **1**−**6** with Li_2PdCl_4. Thus, the addition of equimolar amounts of alkynes **1** or **2** to a dark red methanolic solution of Li_2PdCl_4 at 5 °C affords almost instantaneously a dark yellow solution. Palladacycles **7** and **8** where isolated in good yields from these solutions by extraction with dichloromethane and precipitation with hexanes. On the other hand, the addition of an alkynes **3**−**6** to a methanolic solution of Li_2PdCl_4 at 5 °C leads almost instantaneously to the precipitation of a light yellow solid, which gradually dissolves to afford a dark yellow solution after stirring at room temperature for ca. 1−3 h. Evaporation of the volatiles under reduced pressure, extraction with dichloromethane, and filtration over a plug of Celite affords a yellow solution. Concentration of these reaction solutions under reduced pressure and addition of hexanes affords the palladacycles **9**−**12** as yellow solids.

Scheme 3[a]



[a] (i) HCHO/HNMe$_2$, CuI, dioxane, reflux; (ii) Pd(PPh$_3$)$_4$, CuI, NEt$_3$, DMF, RT.

Chart 2. "Pincer" Palladacycles Complexes Obtained via Chloropalladation Reaction of the Hetero-Substituted Alkynes



Palladacycles **7**−**12** are light yellow air- and moisture-stable crystalline solids, which are highly soluble in most polar organic solvents such as dichloromethane and acetone and slightly soluble in hexanes and diethyl ether. Compounds **7**−**12** have relatively high thermal stabilities. They start to decompose only above 140 °C.

The palladacycles **7**−**12** were characterized by means of CHN combustion analysis, IR, and ^{1}H and ^{13}C{^{1}H} NMR spectroscopy. The CHN analyses indicated that one $PdCl_2$ fragment has been incorporated per alkyne unit. The IR spectra of these compounds exhibit a band between 1580 and 1650 cm^{-1}, which is characteristic for a ν(C=C) vibration. Two distinct resonances for the nonaromatic C=C bond were observed in the ^{13}C NMR spectra of **7**−**12** in $CDCl_3$: one at low field (140−150 ppm) and another at high field (110−125 ppm) characteristic for sp^2 carbons bonded to a chlorine atom and a Pd(II) center, respectively. The ^{1}H NMR signals related to the NMe$_2$, S-*t*-Bu, and SMe groups of palladacycles **7**−**12** appear at ca. 0.6−1.0 ppm downfield shifted

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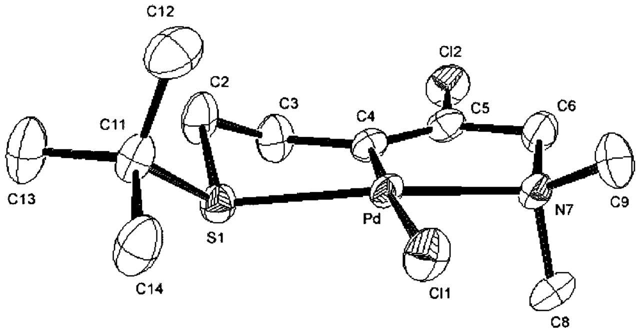


Figure 1. Molecular structure of the complex (t-BuSCH$_2$-CH$_2$C=C(Cl)CH$_2$NMe$_2$-$\kappa S,\kappa C,\kappa N$)PdCl (**7**). Hydrogen atoms were omitted for clarity.

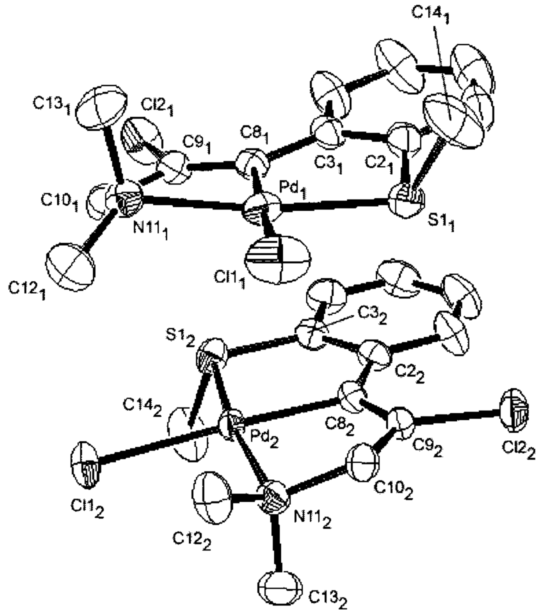


Figure 2. Molecular structures of the complex (C$_6$H$_4$-(o-SMe)C=C(Cl)CH$_2$NMe$_2$-$\kappa S,\kappa C,\kappa N$)PdCl (**11**). Hydrogen atoms were omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 7 and 11

	7		**11$_1$**	**11$_2$**
		Bond Lengths		
Pd−C4	1.980(2)	Pd−C8	1.986(3)	1.983(3)
Pd−N7	2.126(2)	Pd−N11	2.091(3)	2.091(3)
Pd−S	2.276(1)	Pd−S1	2.240(1)	2.242(1)
Pd−Cl1	2.393(1)	Pd−Cl1	2.388(1)	2.394(1)
Cl2−C5	1.772(3)	Cl2−C9	1.765(3)	1.761(3)
S1−C2	1.823(3)	S1−C2	1.783(4)	1.784(4)
S1−C11	1.854(3)	S1−C14	1.810(4)	1.810(4)
C2−C3	1.515(4)	C2−C3	1.405(5)	1.395(5)
C3−C4	1.507(4)	C3−C8	1.481(5)	1.486(5)
C4−C5	1.317(4)	C8−C9	1.323(4)	1.333(4)
C5−C6	1.493(4)	C9−C10	1.492(5)	1.481(5)
C6−N7	1.488(3)	C10−N11	1.495(4)	1.492(5)
		Bond Angles		
C4−Pd−N7	82.1(1)	C8−Pd−N11	84.59(12)	84.0(1)
C4−Pd−S1	83.5(1)	C8−Pd−S1	86.99(10)	85.9(1)
N7−Pd−S1	163.4(1)	N11−Pd−S1	170.65(8)	169.1(1)
C4−Pd−Cl1	175.5(1)	C8−Pd−Cl1	176.13(9)	176.7(1)
C2−S1−C11	104.7(1)	C2−S1−C14	102.42(17)	103.3(2)
C2−S1−Pd	99.2(1)	C21−S1−Pd	100.23(12)	100.0(1)
C11−S1−Pd	118.2(1)	C14−S1−Pd	103.17(15)	106.3(2)
C2−C3−C4	109.7(2)	C2−C3−C8	117.4(3)	116.4(3)
C5−C4−Pd	113.0(2)	C9−C8−Pd	111.3(3)	110.9(3)
C3−C4−Pd	120.4(2)	C3−C8−Pd	117.9(2)	118.6(2)
C4−C5−C6	122.7(2)	C8−C9−C10	122.0(3)	121.9(3)
C4−C5−Cl2	123.0(2)	C8−C9−Cl2	127.2(3)	126.4(3)
N7−C6−C5	108.7(2)	C9−C10−N11	109.1(3)	108.9(3)
C3−C2−S1	105.7(2)	C12−N11−C13	109.0(3)	108.6(3)
C6−N7−Pd	108.2(2)	C10−N11−Pd	106.6(2)	106.1(2)
C9−N7−Pd	116.7(2)	C13−N11−Pd	105.7(2)	105.9(2)
C11−S1−Pd−Cl1	45.0	C14−S1−Pd−Cl1	66.4	58.0
C9−N7−Pd−Cl1	37.7	C13−N11−Pd−Cl1	78.9	84.3
C11−S1−N7−C9	7.2	C14−S1−N11−C13	26.3	12.8

Table 2. Summary of the Crystal Data and Structure Refinement for 7 and 11

	7	**11**
chem formula	C$_{11}$H$_{21}$Cl$_2$NPdS	C$_{12}$H$_{15}$Cl$_2$NPdS
temperature (K)	200(2)	200(2)
wavelength (Å)	0.71073	0.71073
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$
Z	4	8
a (Å)	6.0892(1)	17.7871(1)
b (Å)	28.9582(3)	11.5507(1)
c (Å)	8.4416(1)	15.2392(1)
β (deg)	92.258(1)	109.951(1)
volume (Å^3)	1487.37(3)	2943.04(4)
ρ_{calc} (g/cm^3)	1.68	1.73
μ (mm^{-1})	1.72	1.744
max./min. transm	0.86 and 0.73	0.95 and 0.71
cryst shape	polyhedron	polyhedron
cryst dimens (mm^3)	0.44 × 0.14 × 0.11	0.28 × 0.18 × 0.12
θ range data collect. (deg)	1.4 to 27.5	2.14 to 27.49
index range	$-7 \le h \le 7$, $-37 \le k \le 37$, $-10 \le l \le 10$	$-23 \le h \le 18$, $-14 \le k \le 8$, $12 \le l \le 19$
no. of collect. reflns	12 555	11 109
no. of ind reflns	3389 ($R_{int} = 0.0360$)	6340 ($R_{int} = 0.0312$)
no. of obsd reflns ($I > 2\sigma(I)$)	3051	4807
no. of data/restr/params	3389/0/150	6340/0/314
R-indices ($I > 2\sigma(I)$)	$R(F) = 0.027$, $wR_2(F^2) = 0.056$	$R(F) = 0.034$, $wR_2(F_2) = 0.075$
largest peak/hole (e Å^{-3})	0.38 and −0.62	0.90 and −0.88

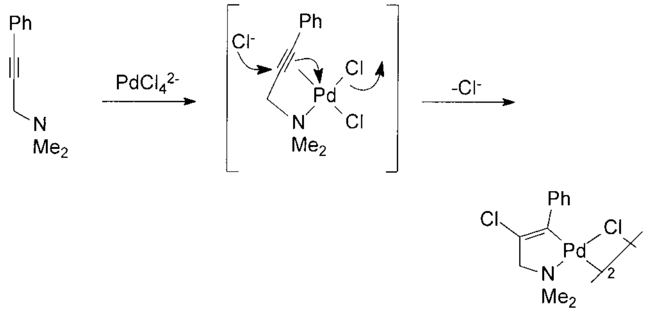
compared to the resonances of the free ligands (**1**−**6**). The typical spin-coupling values of $^4J_{PH} = 2.5-2.9$ Hz and $^3J_{PC} = 3.0$ Hz between the P atom and the hydrogens and carbons of the NMe$_2$ group, respectively, are strong indications of the *trans* relationship between the NMe$_2$ and PPh$_2$ groups for compounds **9** and **10**.

X-ray Structure of Palladacycles 7 and 11. The structures of compounds **7** and **11** were ascertained by means of X-ray diffraction analysis. ORTEP drawings of the structures of **7** and **11** are shown in Figures 1 and 2, respectively.

Selected bond distances and angles are presented in Table 1. Crystallographic data and details of the structure determination are presented in Table 2. Tables of atomic coordinates, hydrogen coordinates, and anisotropic thermal parameters are supplied as Supporting Information.

In compound **7** the Pd(II) center is coordinated in a distorted square-planar fashion by the N and the S donor groups, a C(sp^2) vinyl atom of the anionic terdentate ligand system, and a Cl atom. The C(vinyl)−Pd−Cl bond angle is 175.5° and the S and N donor groups are also in mutual *trans* positions with a bond angle of 163.4°, showing an angular deviation of 16.6° from exact *trans* coordination. This distortion from the ideal square-planar arrangement is the result of the small N−Pd−C(vinyl) and S−Pd−C(vinyl) bite angles in the two five-membered rings of 83.0° and 83.5°, respectively. The σ Pd−C(vinyl) single bond in **7** (1.980

Scheme 4

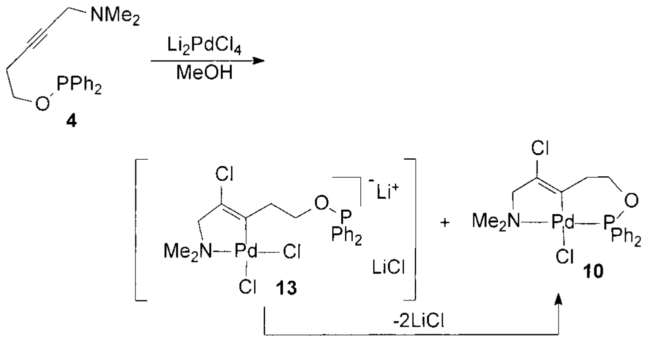


Å) is slightly shorter than observed in similar compounds, where the distances fall in the range between 1.991 and 2.011 Å.[9] The two five-membered rings have a distinct puckering; see Figure 1. This is due to the presence or not of a double bond in each ring. The bulky *tert*-butyl group, bounded to the S atom, is in an equatorial position as expected.

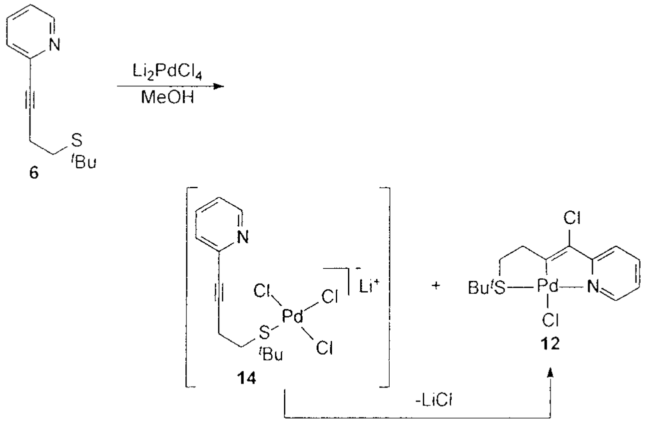
The crystal structure of **11** consists of two independent molecules found in the asymmetric unit, with a close nonbonding contact between the two Pd centers (3.77 Å). These two structures are quite similar to each other and show a coordination environment around each Pd(II) center similar to the one encountered in the "pincer" palladacycle **7**. In both molecules of **11** the distances between the Pd(II) center and the coordinated atoms are rather similar to that observed in the analogous compound **7** (see Table 1). Both molecules of **11** exhibit a Pd(II) center coordinated in a distorted square-planar fashion by the N and the S donor groups, a C(sp^2) vinyl atom of the anionic terdentate ligand system, and a Cl atom as in **7**. The average C(vinyl)−Pd−Cl bond angle of the two structures is 176.4°, and the S and N donor groups are in mutual *trans* positions with an average bond angle of 169.9°. As observed in compound **7**, the distortion from the ideal square-planar arrangement for both crystallographic structures of **11** results from the small N−Pd−C(vinyl) and S−Pd−C(vinyl) bite angles in the two five-membered rings of 84.3° and 86.4°, respectively.

Chloropalladation Reaction Path. It has been proposed earlier that the chloropalladation of hetero-substituted alkynes such as $PhC{\equiv}CCH_2NMe_2$ proceeds through the coordination of the N atom followed by interaction of the triple bond to the metal center. Intermolecular selective nucleophilic attack of the chloride anion to the activated triple bond yields the thermodynamically favored five-membered palladacycle (Scheme 4).[5]

Scheme 5



Scheme 6



We have observed that in the earlier stages of the reaction of **4** with Li_2PdCl_4 the precipitation of an intermediate compound that is gradually and quantitatively transformed into the "pincer" palladacycle **10** (Scheme 5). Although it was impossible to isolate this intermediate in pure form, spectroscopic data allow us to propose a structure **13**, as depicted in Scheme 5. The presence of a singlet at 2.81 ppm for the NMe_2 moiety in the ^{1}H NMR spectra is a strong indication that **4** is coordinated to the Pd center through its N atom only. IR and the ^{13}C{^{1}H} NMR spectrum clearly show the absence of the C≡C bond and the presence of a C=C bond.

Further evidence for the chloropalladation reaction path was obtained from the spectroscopic data of the yellow precipitate **14** formed immediately after the addition of **6** to a methanolic solution of Li_2PdCl_4 at room temperature. This compound slowly (2−3 h) rearranges in solution and/or in suspension (methanol or dichloromethane) to afford quantitatively the "pincer" palladacycle **12** (Scheme 6). The ^{1}H NMR spectrum of the **14**, immediately after dissolution in $CDCl_3$, shows the resonances of the ortho H of the substituted pyridine moiety and *t*-Bu hydrogens at 8.66 and 1.71 ppm, respectively. This is a strong indication that in **14** ligand **6** is coordinated to the Pd center through its sulfur group only (compare the selected spectroscopic data of ligand **6** and compounds **12** and **14** in Table 3). The presence of characteristic resonances of a C≡C bond at 80.5 and 96.3 ppm in the ^{13}C NMR spectra and $\nu_{C\equiv C}$ at 2230 cm^{-1} in the IR spectra of **14** indicates that the chloropalladation had not yet taken place.

These results indicate that it is most likely that the chloropalladation reaction of these hetero-substituted alkynes occurs through the coordination of only one donor group to afford compounds such as **14**. This is probably followed by coordination of the C≡C bond to the metal center to generate intermediates of the type **15** and **16** (Chart 3). The intermolecular Cl^- nucleophilic addition occurs on the carbon that will generate the thermodynamically more stable palladacyclic ring, i.e., five-membered ring rather than four-membered in the case of **15** or six-membered in the case of **16**. Finally, coordination of the pendant donor group through displacement of the chloro ligand yields the "pincer"

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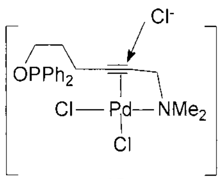
[9] Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Robin Taylor, R. *J. Chem. Soc., Dalton Trans* **1989**, S1−S83.

Table 3. Selected Spectroscopic Data of Observed Compounds in the Chloropalladation of 4 and 6

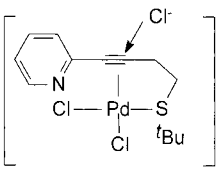
compd	IR (cm^{-1})	^1H NMR (δ, ppm)	^{13}C NMR (δ, ppm)
4	C≡C n.o.[a]	2.27 (NMe_2)	76.9 and 81.7 (C≡C)
10	1601 ($\nu_{C=C}$)	2.87 (NMe_2)	121.1 and 142.9 (C=C)
13	1616 ($\nu_{C=C}$)	2.81 (NMe_2)	119.0 and 138.8(C=C)
6	2226 ($\nu_{C\equiv C}$)	1.36 (*t*-BuS); 8.57 (H_0−Py)	81.2 and 89.2 (C≡C)
12	1594 ($\nu_{C=C}$)	1.68 (*t*-BuS); 9.17 (H_0−Py)	119.4 and 163.8(C=C)
14	2230 ($\nu_{C\equiv C}$)	1.71 (*t*-BuS); 8.66 (H_0−Py)	80.5 and 96.3 (C≡C)

[a] n.o.= not observed.

Chart 3. Postulated Intermediates in the Chloropalladation Reaction

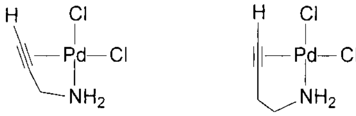


15



16

Chart 4. Model Systems for the Coordination of the CC Triple Bond



(A) (B)

palladacycles. Moreover, preliminarily theoretical calculations of full optimized geometries on the model systems A and B (Chart 4) using the Gaussian 98 package (DFT-B3LYP/3-21G*) indicated that both intermediates are prone to the formation of five-membered palladacycles rather than a four-membered ring in the case of A or a six-membered ring in the case of B.[10]

Conclusions. These results clearly show that the chloropalladation of hetero-substituted alkynes is a simple and efficient method for the preparation of a large variety of unsymmetrical palladium YCY′ "pincer" complexes. Various functional donor groups can be introduced in the metalated fragment such as amines, pyridine, thioethers, phosphines, and phosphinites. Moreover, metallacycles of different ring sizes, i.e., five- and six-membered rings, can be generated and this selectivity is under thermodynamic control. The extension of this method for the preparation of other transition metal "pincer" complexes and the investigation of their catalytic properties in C−C coupling processes such as Heck and Suzuki reactions are currently under investigation in our laboratory.

Experimental Section

General Methods. All reactions involving organometallic compounds were carried out under an argon or nitrogen atmosphere in oven-dried Schlenk tubes. The alkynols were prepared according to a known procedure.[11] Solvents were dried with adequate drying agents and distilled under argon prior to use. All the other chemicals were purchased from commercial sources and used without further purification. Elemental analyses were performed by the Analytical Central Service of IQ-USP (Brazil). NMR spectra were recorded on a Varian Inova 300 spectrometer. Infrared spectra were performed on a Bomem B-102 spectrometer. Mass spectra were obtained using a GC/MS Shimadzu QP-5050 (EI, 70 eV). Gas chromatography analyses were performed with a Hewlett-Packard-5890 gas chromatograph with a FID and 30 m capillary column with a dimethylpolysiloxane stationary phase.

X-ray Structures Analysis of 7 and 11. Crystals were mounted on a glass fiber with perfluoropolyether. The measurements were made on a Bruker SMART-CCD diffractometer with graphite-monochromated Mo Kα radiation. For **7**, frames corresponding to a sphere of data were collected using the ω-scan technique, and 20 s exposures of 0.3 deg in ω were taken. For **11**, frames corresponding to at least one complete set of independent reflections (one asymmetric unit of reciprocal space) were collected using the ω-scan technique, and 10 s exposures of 0.3 deg in ω were taken. An absorption correction was applied, in each case, using SADABS[12] based on the laue symmetry of the reciprocal space, and the data were corrected for Lorentz and polarization effects. The structures were solved by direct methods and expanded using Fourier techniques. All non-hydrogen atoms were refined with anisotropic displacement parameters; hydrogen atoms could be located in the Fourier map, but then were considered at calculated positions. The full-matrix least-squares refinement against F^2 converged. All calculations were performed using the SHELXTL crystallographic software package of Bruker.[13]

Synthesis of 5-Dimethylamino-3-pentyn-1-ol. A mixture of 3-butyn-1-ol (4.2 g, 60 mmol), paraformaldehyde (2.2 g, 72 mmol), dimethylamine (50% aqueous solution, 11 mL), dioxane (35 mL), and cuprous iodide (0.150 g) was refluxed for 3 h. Filtration of the reaction mixture through a plug of Celite, evaporation of the solvent under reduced pressure, and bulb-to-bulb distillation of the residue (bp 130 °C/5 mm Hg) afforded the desired amino alcohol as pale yellow oil. Yield: 6.1 g, 80%. IR (film, cm^{-1}): 2266 ($\nu_{C\equiv C}$). GC−MS (*m*/*z*, rel int, [peak]): 127, 60, $[M]^{\bullet +}$; 126, 74, $[M - 1]^+$; 109, 2.5, $[Me_2NCH_2C{=}CCHCH_2]^{\bullet +}$; 108, 26, $[Me_2NCH{=}C{=}C{=}CHCH_2]^+$; 96, 36, $[Me_2NCH_2C{=}CCH_2]^+$; 94, 41, $[MeN{=}CHC{=}CCH_2CH_2]^+$; 58, 46, $[Me_2N{=}CH_2]^+$; 53, 78, $[H_2C{=}C{=}CHCH_2]^+$. ^1H NMR ($CDCl_3$): δ 4.00 (br s, 1H, OH); 3.63 (t, 2H, CH_2O, $^3J_{HH} = 6.6$ Hz); 3.10 (br s, 2H, CH_2N); 2.39 (m, 2H, $CH_2C{=}C$); 2.22 (s, 6H, NMe_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 82.2 and 76.4 (C=C); 60.9 (CH_2O); 48.1 (CH_2N); 44.1 (NMe_2); 23.0 ($CH_2C{=}C$).

Synthesis of 5-Dimethylamino-3-pentynyl-*p*-toluenesulfonate. Triethylamine (2 mL) was slowly added to a vigorously stirred solution of 5-(dimethylamino)-3-pentyn-1-ol (0.640 g, 5.00 mmol) and *p*-toluenesulfonyl chloride (0.850

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[10] Calculations for the model systems A and B were performed with the Gaussian 98 program package: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A. Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.;. Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, Revision A.5; Gaussian, Inc.: Pittsburgh, PA, 1998.

[11] Brandsma, L.; Verkruijsse, H. D. *Synthesis of Acetylenes, Allenes and Cumulenes*; Elsevier: Amsterdam, 1981.

[12] Sheldrick, G. M. *SADABS*; Bruker AXS, Inc.: Madison, WI, 1996.

[13] Sheldrick, G. M. *SHELXTL* V5.10; Bruker AXS, Inc.: Madison, WI, 1997.

g, 5.00 mmol) in dichloromethane (10 mL) at 0 °C. The resulting suspension was stirred at this temperature for 1 h. Aqueous 10% Na_2CO_3 solution (20 mL) was then added and stirred for an additional 30 min at room temperature. The layers were separated, the aqueous phase was extracted with dichloromethane, and the combined organic extracts were dried with $MgSO_4$. Evaporation of the solvent afforded the desired compound as a clear yellow oil, sufficiently pure for further work. Yield: 0.785 g, 56%. IR (film, cm^{-1}): 2271 ($\nu_{C\equiv C}$). GC−MS (*m*/*z*, rel int, [peak]): 237, 72, [*p*-$MeC_4H_6SO_3$-$(CH_2)_2C{=}CCH_2]^+$; 236, 95, $[M - Me_2NH]^{\bullet +}$; 109, 33, $[Me_2NCH_2C{=}CCHCH_2]^{\bullet +}$; 108, 48, $[Me_2NCH{=}C{=}C{=}CHCH_2]^+$; 94, 100, $[MeN{=}CHC{=}CCH_2CH_2]^+$; 82, 93, $[Me_2NCH_2C{=}C]^+$; 66, 72, $[MeN{=}CHC{=}C]^+$; 65, 63, $[CH_2{=}CHC{=}CCH_2]^+$; 58, 75, $[Me_2N{=}CH_2]^+$. ^{1}H NMR ($CDCl_3$): δ 7.80 (d, 2H, CH arom, $^3J_{HH}$ = 8.6 Hz); 7.35 (d, 2H, CH arom, $^3J_{HH}$ = 8.5 Hz); 4.09 (t, 2H, CH_2O, $^3J_{HH}$ = 7.1 Hz); 3.14 (t, 2H, CH_2N, $^5J_{HH}$ = 2.2 Hz); 2.59 (tt, 2H, $CH_2C{=}C$, $^3J_{HH}$ = 7.1 Hz and $^5J_{HH}$ = 2.2 Hz); 2.46 (s, 3H, CH_3); 2.24 (s, 6H, NMe_2). $^{13}C\{^1H\}$NMR ($CDCl_3$): δ 281.36; 145.2 and 133.1 (C arom quat); 130.1 and 128.2 (CH arom); 79.3 and 77.9 ($C\equiv C$); 69.2 (CH_2O); 48.2 (CH_2N); 44.4 (NMe_2); 21.9 (CH_3); 19.9 ($CH_2C{=}C$).

Synthesis of 5-*tert*-Butylthio-1-(dimethylamino)-2-pentyne (1). Into a solution of sodium thio-*tert*-butoxide, prepared from a suspension of sodium ethoxide (0.408 g, 6.0 mmol) and 2-methyl-2-propanethiol (0.451 g, 5.0 mmol) in ethanol (50 mL), was added a solution of 5-(dimethylamino)-3-pentynyl-*p*-toluenesulfonate (1.40 g, 5.0 mmol) in ethanol (5 mL). After 6 h, the suspension was concentrated in vacuo, and brine (50 mL) and diethyl ether (50 mL) were added. The organic phase was washed with brine (3 × 20 mL) and dried in $MgSO_4$. Evaporation of the solvent afforded the desired compound as a clear yellow oil. Yield: 0.797 g, 80%. GC−MS ($C_{11}H_{21}NS$, 199.35); (*m*/*z*, rel int, [peak]): not detected, $[M]^{\bullet +}$; 142, 70, $[M - 57]^+$; 117, 10, $[M - 82]$; 82, 10, $[M - 117]$; 57, 100, $[M - 142]^+$. ^{1}H NMR ($CDCl_3$): δ 3.14 (t, 2H, CH_2N, $^5J_{HH}$ = 2.20 Hz), 2.64 (t, 2H, CH_2S, $^3J_{HH}$ = 7.00), 2.40 (tt, 2H, CH_2CH_2S, $^3J_{HH}$ = 7.00 Hz, $^5J_{HH}$ = 2.20 Hz), 2.22 (s, 6H, NMe_2), 1.27 (s, 9H, *t*-BuS). $^{13}C\{^1H\}$NMR ($CDCl_3$): δ 83.56, 76.57 ($C\equiv C$), 48.11 (CH_2N), 44.16 (NMe_2), 42.35 ($C(CH_3)_3$), 30.95 ($C(CH_3)_3$), 27.86, 20.38 (CH_2CH_2).

Synthesis of 1,5-Bis(dimethylamino)-2-pentyne (2). Into a Schlenk containing 5-(dimethylamino)-3-pentynyl-*p*-toluenesulfonate (2.81 g, 10 mmol) dimethylamine (30 mL) was condensed. After 16 h of reaction at room temperature brine (50 mL) and dichloromethane (50 mL) were added. The layers were separated, and the aqueous layer was extracted with dichloromethane (3 × 20 mL). The combined organic extract was dried with $MgSO_4$, and evaporation of the solvent afforded the desired compound as a clear yellow oil. Yield: 1.43 g, 72%. Anal. Calcd for $C_9H_{18}N_2$ (154.26): C, 70.08; H, 11.76; N, 18.16. Found: C, 69.88; H, 11.69; N, 17.89. IR (film, cm^{-1}): 2257 ($\nu_{C\equiv C}$). GC−MS ($C_9H_{18}N_2$, 154.26); (*m*/*z*, rel int, [peak]): not detected, $[M]^{\bullet +}$; 109, 10, $[M - 57]^+$; 58, 100, $[M - 96]^+$. ^{1}H NMR ($CDCl_3$): δ 3,26 (t, 2H, CH_2CH_2N, $^3J_{HH}$ = 6,92 Hz); 3.11(t, 2H, CH_2N, $^5J_{HH}$ = 1.71 Hz), 2.40 and 2.39 (2 s, 12H, 2 NMe_2), 2.25 (tt, 2H, CH_2CH_2N, $^3J_{HH}$ = 6.29 Hz, $^5J_{HH}$ = 1.71 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 83.44, 76.07 ($C\equiv C$), 58.88 (CH_2CH_2N), 48.49 (CH_2N), 45.45 and 44.46 (2 NMe_2), 17.91 (CH_2CH_2N).

Synthesis of 5-Dimethylamino-3-pentynyldiphenylphosphine (3). A lithium diphenylphosphide solution was prepared under argon by stirring, for 3 h, a mixture of chlorodiphenylphosphine (95% pure, 0.660 g, 2.80 mmol) and lithium pieces (0.100 g, excess) in dry THF (15 mL) containing dry TMEDA (2 mL). The lithium diphenyl phosphide solution, separated from the residual lithium pieces, was added slowly, under argon, to a vigorously stirred suspension of 5-(dimethylamino)-3-pentynyl-*p*-toluenesulfonate (0.785 g, 2.80 mmol) in dry THF (5 mL). After addition, stirring was continued for 10 min, the solvent was evaporated under reduced pressure, water (10 mL) and CH_2Cl_2 (20 mL) were added, and stirring continued for 5 min. The layers were separated, the organic phase was washed with water and dried with $MgSO_4$, and the solvent was evaporated. The crude product was purified by column chromatography under argon (basic alumina, activity grade II, hexanes then hexanes/EtOAc, 50:50), giving a pale yellow oil, easily oxidizable by atmospheric oxygen. Yield: 0.470 g, 57%. IR (film, cm^{-1}): 2269 ($\nu_{C\equiv C}$). ^{1}H NMR ($CDCl_3$): δ 7.55−7.20 (m, 10H, CH arom); 3.20 (br s, 2H, CH_2N); 2.40−2.25 (m, 4H, $PCH_2CH_2C{=}C$); 2.30 (s, 6H, NMe_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 138.2 (d, C arom quat, $^1J_{PC}$ = 12.5 Hz); 132.9 (d, CH arom, $^2J_{PC}$ = 18.5 Hz); 129.0, 128.8, 128.7, (CH arom); 85.1 (d, $C{=}C$, $^3J_{PC}$ = 16.0 Hz); 76.2 ($C{=}C$); 48.4 (CH_2N); 44.5 (NMe_2); 28.1 (d, $CH_2C{=}C$, $^2J_{PC}$ = 13.0 Hz); 16.0 (d, CH_2P, $^1J_{PC}$ = 21.5 Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −16.2.

Synthesis of 5-Dimethylamino-3-pentynyldiphenylphosphinite (4). Chlorodiphenylphosphine (95% pure, 1.80 g, 8.00 mmol) dissolved in CH_2Cl_2 (5 mL) was added slowly, under argon, to a stirred solution of 5-(dimethylamino)-3-pentyn-1-ol (1.02 g, 8.00 mmol) and triethylamine (3 mL) in CH_2Cl_2 (10 mL). After addition, stirring was continued for an additional 30 min. The organic solution was washed with aqueous 10% Na_2CO_3 solution and water then dried with $MgSO_4$, and the solvent was evaporated, affording a pale yellow oil. Yield: 2.13 g, 85%. IR (film, cm^{-1}): 2267 ($\nu_{C\equiv C}$). GC−MS ($C_{19}H_{22}NOP$, 311.36); (*m*/*z*, rel int, [peak]): not detected, $[M]^{\bullet +}$; 201, 3, $[Ph_2P{=}O]^+$; 58, 100, $[Me_2N{=}CH_2]^+$. ^{1}H NMR ($CDCl_3$): δ 7.45−7.55 (m, 4H, CH arom); 7.32−7.41 (m, 6H, CH arom); 3.99 (dt, 2H, CH_2OP, $^3J_{PH}$ = 9.6 Hz and $^3J_{HH}$ = 7.0 Hz); 3.19 (t, 2H, CH_2N, $^5J_{HH}$ = 1.9 Hz); 2.62 (tt, 2H, $CH_2C{=}C$, $^3J_{HH}$ = 7.0 Hz and $^5J_{HH}$ = 1.9 Hz); 2.27 (s, 6H, NMe_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 141.0 (d, C arom quat, $^1J_{PC}$ = 17.5 Hz); 130.6 (d, CH arom, $^2J_{PC}$ = 21.5 Hz); 129.6 (CH arom); 128.6 (d, CH arom, $^3J_{PC}$ = 6.5 Hz); 81.7 and 76.9 ($C{=}C$); 68.8 (d, CH_2OP, $^2J_{PC}$ = 20.0 Hz); 48.3 (CH_2N); 44.3 (NMe_2); 22.1 (d, $CH_2C{=}C$, $^3J_{PC}$ = 8.0 Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 113.7.

Synthesis of 1-(2-Methylthiophenyl)-3-(dimethylamino)-1-propyne (5). A mixture of 2-methylthiophenylacetylene[7] (0.833 g, 5.60 mmol), paraformaldehyde (0.185 g, 6.20 mmol), dimethylamine (50% aqueous solution, 0.8 mL), dioxane (5 mL), and cuprous iodide (0.014 g) was refluxed for 9 h. The solvent was evaporated and the residue was purified by column chromatography (basic alumina, activity grade II, hexanes/EtOAc, 50:50 v/v), furnishing a pale yellow oil. Yield: 0.970 g, 85%. IR (film, cm^{-1}): 2262 ($\nu_{C\equiv C}$). GC−MS (*m*/*z*, rel int, [peak]): 205, 2, $[M]^{\bullet +}$; 204, 10, $[M - 1]^+$; 190, 15, $[M - 15]^+$; 160, 100, $[M - Me_2NH]^{\bullet +}$; 82, 12, $[Me_2NCH_2C{=}C]^+$; 58, 18, $[Me_2N{=}CH_2]^+$. ^{1}H NMR ($CDCl_3$): δ 7.44−7.06 (m, 4H, CH arom); 3.59 (s, 2H, CH_2N); 2.43 (s, 3H, SMe); 2.18 (s, 6H, NMe_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 147.1 and 121.5 (C arom quat); 132.8, 128.8, 124.4, 124.1 (CH arom); 91.6 and 83.0 ($C\equiv C$); 48.9 (CH_2N); 44.4 (NMe_2); 15.2 (SMe).

Synthesis of 4-(*tert*-Butylthio)-1-(2-pyridinyl)-1-butyne (6). A mixture of diethylamine (20 mL), DMF (1.0 mL), 1-*tert*-butylthio-3-butyne (1.00 g, 7.04 mmol), 2-bromopyridine (0.948 g, 5.92 mmol), $PdCl_2(PPh_3)_2$ (0.070 g, 0.10 mol), and CuI (0.038 g, 0.20 mmol) was stirred under argon for 16 h at room temperature. The reaction mixture was concentrated; brine (50 mL) and dichloromethane (50 mL) were added. The layers were separated, and the aqueous layer was extracted with dichloromethane (3 × 20 mL). The combined organic extract was washed with brine (1 × 20 mL) and dried with $MgSO_4$. The volatiles were removed in vacuo, affording the desired compound as dark yellow oil. Yield: 0.777 g, 60%. IR (film, cm^{-1}): 2226 ($\nu_{C\equiv C}$). GC−MS ($C_{13}H_{17}NS$, 219.34); (*m*/*z*, rel int, [peak]): 219,5, $[M]^{\bullet +}$; 162, 95, $[M - 57]^+$; 130, 50, $[M - 89]$; 57, 100, $[M - 162]^+$. ^{1}H NMR ($CDCl_3$): δ 8.57 (d, 1H, py, $^3J_{HH}$ = 7.41 Hz), 7.64 (t, 1H, py, $^3J_{HH}$ = 7.69 Hz), 7.39 (d, 1H, py, $^3J_{HH}$ = 7.96 Hz), 7.21 (dd, 1H, py, $^3J_{HH}$ = 7.69 Hz, $^3J_{HH}$ = 7.41 Hz), 2.85 and 2.71 (2t, 4H, $^3J_{HH}$ = 7.69 Hz), 1.36 (s, 9H, CH_3). $^{13}C\{^1H\}$NMR ($CDCl_3$): δ 150.12, 143.81, 136.32, 127.12, 122.75

(py), 89.19, 81.24 (C≡C), 42.87 ($C(CH_3)_3$), 31.25 (CH_3), 27.55, 21.34 (CH_2CH_2).

Synthesis of Palladacycle (7). A Li_2PdCl_4 solution was prepared by dissolving $PdCl_2$ (0.285 g, 1.60 mmol) and LiCl (0.170 g, 4.00 mmol) in methanol (10 mL) with gentle heating. A solution of **1** (0.318 g, 1.60 mmol) in methanol (10 mL) was then added to the former at 5 °C. The resulting dark yellow solution was then stirred for 1 h. The mixture was concentrated in vacuo, leading to a dark solid. Dichloromethane (3 mL) was added, and the afforded solution was filtered through a plug of Celite. A yellow precipitate was obtained by addition of hexane to the formed solution. The solid was recuperated by filtration, washed with hexane, and dried in vacuo, affording a yellow solid. Yield: 0.361 g, 60%. Anal. Calcd for $C_{11}H_{21}Cl_2NPdS$ (376.68): C, 35.08; H, 5.62; N, 3.72. Found: C, 35.33; H, 5.59; N, 3.76. Mp = 142 °C. IR (Nujol, cm^{-1}): 1632 ($\nu_{C=C}$). ^1H NMR ($CDCl_3$): δ 3.68 (br s, 2H, CH_2N), 2.90 (s, 6H, NMe_2), 2.77 (br t, 2H, CH_2S, $^3J_{HH}$ = 7.50 Hz), 2.40 (br s, 2H, CH_2CH_2S), 1.59 (s, 9H, $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 157.45 (Cl−C=), 115.83 (Pd−C=), 75.91 (CH_2N), 52.36 (NMe_2), 50.80 and 36.22 (CH_2CH_2), 37.38 ($C(CH_3)_3$), 30.61 ($C(CH_3)_3$).

Synthesis of Palladacycle (8). Compound **8** was prepared using the same procedure and workup described in the synthesis of **7**. The methanolic solution of Li_2PdCl_4, prepared from $PdCl_2$ (0.285 g, 1.60 mmol) and LiCl (0.170 g, 4.00 mmol) in methanol (10 mL), reacted with a solution of **2** (0.247 g, 1.60 mmol) in methanol (10 mL), affording the desired complex as a yellow solid. Yield: 0.382 g, 72%. Anal. Calcd for $C_9H_{18}Cl_2N_2Pd$ (331.58): C, 32.60; H, 5.47; N, 8.45. Found: C, 31.75; H, 5.47; N, 7.36. Dp = 135−138 °C. IR (Nujol, cm^{-1}): 1639 ($\nu_{C=C}$). ^1H NMR ($CDCl_3$): δ 3.56 (t, 2H, CH_2N, $^5J_{HH}$ = 2.02 Hz), 2.88 and 2.78 (2 s, 12H, 2 NMe_2) 2.74 (t, 2H, CH_2CH_2N, $^3J_{HH}$ = 6.58 Hz), 2.30 (tt, 2H, CH_2CH_2N, $^3J_{HH}$ = 6.58 Hz, $^5J_{HH}$ = 2.02 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 153.95 (Cl−C=), 112.74 (Pd−C=), 76.6 1 (=C−CH_2N), 68.62 (CH_2CH_2N), 53.32 and 51.53 (2 NMe_2), 33.06 (CH_2CH_2N).

Synthesis of Palladacycle (9). The methanolic solution of Li_2PdCl_4 was prepared using the same procedure in the synthesis of **7**, $PdCl_2$ (0.285 g, 1.60 mmol), and LiCl (0.170 g, 4.00 mmol) in methanol (10 mL). The former solution was allowed to react with a solution of **3** (0.470 g, 1.60 mmol) in methanol (10 mL) at 5 °C. The resulting suspension was stirred for 1 h and filtered, and the precipitate was washed with cold methanol and dried under reduced pressure. Solubilization in dichloromethane, filtration through a plug of Celite, and precipitation with hexanes afforded the desired compound as a yellow solid, which was recuperated by filtration and dried in vacuo. Yield: 0.500 g, 66%. Anal. Calcd for $C_{19}H_{22}Cl_2NPPd$ (472.7): C, 48.28; H, 4.69; N, 2.96. Found: C, 47.91; H, 4.32; N, 2.74. Dp = 153−155 °C. IR (Nujol, cm^{-1}): 1616 ($\nu_{C=C}$). ^1H NMR ($CDCl_3$): δ 8.05−7.75 (m, 4H, CH arom); 7.60−7.40 (m, 6H, CH arom); 3.68 (br s, 2H, CH_2N); 2.91 (d, 6H, NMe_2, $^4J_{PH}$ = 2.5 Hz); 2.55−2.30 (m, 4H, $PCH_2CH_2C{=}C$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 159.4 (C=C); 133.2 (d, CH arom, $^2J_{PC}$ = 11.6 Hz); 131.3 (d, CH arom, $^4J_{PC}$ = 2.6 Hz); 130.7 (C arom quat); 129.0 (d, CH arom, $^3J_{PC}$ = 10.6 Hz); 117.6 (d, C=C, $^3J_{PC}$ = 4.7 Hz); 74.4 (d, CH_2N, $^3J_{PC}$ = 2.5 Hz); 50.8 (d, NMe_2, $^3J_{PC}$ = 3.0 Hz); 34.1 (d, CH_2P, $^1J_{PC}$ = 34.5 Hz); 33.2 (d, $CH_2C{=}C$, $^2J_{PC}$ = 10.6 Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 57.2

Synthesis of Cyclopalladate (10). The methanolic solution of Li_2PdCl_4 was prepared using the same procedure in the synthesis of **7**, with $PdCl_2$ (0.355 g, 2.00 mmol) and LiCl (0.213 g, 5.00 mmol) in methanol (10 mL). The former solution was allowed to react with a solution of **4** (0.622 g, 2.00 mmol) dissolved in methanol (5 mL) at 5 °C. The resulting suspension was stirred overnight at room temperature, and the solvent was evaporated under reduced pressure. The residue was taken up in dichloromethane (10 mL) and set aside overnight. Addition of hexanes (10 mL), filtration, and evaporation of the solvent afforded a pale yellow solid. Yield: 0.586 g, 60%. Anal. Calcd for $C_{19}H_{22}Cl_2NOPPd$ (488.7): C, 46.70; H, 4.54; N, 2.87. Found: C, 46.83; H, 4.77; N, 2.77. dp: 163−164 °C. IR (Nujol, cm^{-1}): 1601 ($\nu_{C=C}$). ^1H NMR ($CDCl_3$): δ 8.05−7.90 (m, 4H, CH arom); 7.55−7.40 (m, 6H, CH arom); 3.97 (dt, 2H, CH_2OP, $^3J_{PH}$ = 18.0 Hz and $^3J_{HH}$ = 5.3 Hz); 3.55 (q, 2H, CH_2N, J = 2.1 Hz); 2.87 (d, 6H, NMe_2, $^4J_{PH}$ = 2.9 Hz); 2.43 (m, 2H, $CH_2C{=}C$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 142.9 (C=C); 134.0 (d, C arom quat, $^1J_{PC}$ = 61 Hz); 133.4 (d, CH arom, $^2J_{PC}$ = 19.6 Hz); 131.8 (d, CH arom, $^4J_{PC}$ = 2.5 Hz); 128.5 (d, CH arom, $^3J_{PC}$ = 11.6 Hz); 121.2 (d, C=C, $^2J_{PC}$ = 5.6 Hz); 72.3 (d, CH_2N, $^3J_{PC}$ = 3.0 Hz); 69.3 (d, CH_2OP, $^2J_{PC}$ = 4.5 Hz); 50.5 (d, NMe_2, $^3J_{PC}$ = 3.0 Hz); 32.1 (d, $CH_2C{=}C$, $^3J_{PC}$ = 8.1 Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 114.6.

Synthesis of Cyclopalladate (11). The methanolic solution of Li_2PdCl_4 was prepared using the same procedure in the synthesis of **7**, with $PdCl_2$ (0.337 g, 1.88 mmol) and LiCl (0.200 g, 4.70 mmol) in methanol (10 mL). The former solution was allowed to react with a solution of **5** (0.385 g, 1.88 mmol), dissolved in methanol (5 mL). The resulting suspension was stirred for 1 h. The volatiles were removed under reduced pressure, and the residue was taken up in a minimum amount of CH_2Cl_2. Subsequent chromatographic purification (column, silica gel, EtOAc) afforded a yellow solid. Yield: 0.480 g, 67%. Anal. Calcd for $C_{12}H_{15}Cl_2NSPd$ (382.6): C, 37.67; H, 3.95; N, 3.66. Found: C, 37.97; H, 4.11; N, 3.67. Dp = 148−150 °C. IR (Nujol, cm^{-1}): 1590 ($\nu_{C=C}$). ^1H NMR ($CDCl_3$): δ 8.51 (d, 1H, CH arom, $^3J_{HH}$ = 7.7 Hz); 7.43−7.28 (m, 3H, CH arom); 3.95 (s, 2H, CH_2N); 3.00 (s, 6H, NMe_2); 2.87 (s, 3H, SMe). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 147.8, 145.1, 138.6, 118.3 (C quat); 130.8, 129.4, 128.8, 127.0 (CH arom); 77.8 (CH_2N); 52.1 (NMe_2); 26.7 (SMe).

Synthesis of Palladacycle (12). The methanolic solution of Li_2PdCl_4 was prepared using the same procedure in the synthesis of **7**, with $PdCl_2$ (0.337 g, 1.88 mmol) and LiCl (0.200 g, 4.70 mmol) in methanol (10 mL). The former solution was allowed to react with a solution of **6** (0.412 g, 1.88 mmol), dissolved in methanol (5 mL). Immediately after the addition of the alkyne a yellow solid is formed. After 15 mim the former suspension became a dark yellow solution. After 3 h the mixture was concentrated and the residue dissolved in a minimum amount of CH_2Cl_2. The resulting solution was filtered through a plug of Celite, and a yellow solid was obtained by addition of hexane. The solid was recuperated by filtration and dried in vacuo. Yield: 0.671 g, 90%. Anal. Calcd for $C_{13}H_{17}Cl_2NPdS$ (396.67): C, 39.36; H, 4.32; N, 3.53. Found: C, 39.06; H, 4.54; N, 3.33. Dp = 157 °C. IR (Nujol) (cm^{-1}): 1594 ($\nu_{C=C}$). ^1H NMR ($CDCl_3$): δ 9.16 (d, 1H, py, $^3J_{HH}$ = 5.70 Hz), 7.85 (t, 1H, py, $^3J_{HH}$ = 8.10 Hz), 7.35 (d, 1H, py, $^3J_{HH}$ = 8.10 Hz), 7.21 (t, 1H, py, $^3J_{HH}$ = 6.60 Hz), 3.03 (t, 2H, CH_2S, $^3J_{HH}$ = 6.59 Hz), 2.87 (br s, 2H, CH_2), 1.69 (s, 9H, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 179.44, 119.38 (C=C), 163.77, 149.43, 139.77, 121.94, 119.48 (py), 51.48 ($C(CH_3)_3$), 37.73, 36.72 (CH_2CH_2), 30.61 (CH_3).

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Supporting Information Available: Tables of full crystal data, atomic coordinates, calculated hydrogen coordinates, anisotropic thermal parameters, and a complete list of bond lengths and angles are available as Supporting Information. This material is available free of charge via the Internet at http://pubs.acs.org.

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