Atropisomerism in palladacycles derived from the chloropalladation of heterosubstituted alkynes

ARTICLE *in* INORGANICA CHIMICA ACTA · JULY 2003

Impact Factor: 2.05 · DOI: 10.1016/S0020-1693(03)00011-2

Available online at www.sciencedirect.com
SCIENCE DIRECT®
Inorganica Chimica Acta 350 (2003) 527–536
Inorganica Chimica Acta
www.elsevier.com/locate/ica

Atropisomerism in palladacycles derived from the chloropalladation of heterosubstituted alkynes

Mara L. Zanini [a], Mario R. Meneghetti [a], Günter Ebeling [a], Paolo R. Livotto [a], Frank Rominger [b], Jairton Dupont [a,*]

[a] Laboratory of Molecular Catalysis, Instituto de Quimica, UFRGS, Av. Bento Gonçalves 9500, Porto Alegre RS 91501-970, Brazil
[b] Organisch-Chemisches Institut der Ruprecht-Karls-Universität Heidelberg, Im Neuenheimer Feld 270, D-69120 Heidelberg, Germany

Received 5 August 2002; accepted 27 November 2002

Dedicated to Dr Pierre Braunstein for his out standing contribution in Organometallic Chemistry.

Abstract

The chloropalladation of 2-substituted phenyl *N*,*N*-propargylamines, Y-2-$C_6H_4C{\equiv}CCH_2NMe_2$ (**1a**, Y = H; **2a**, Y = CF_3; **3a**, Y = OMe; **4a**, Y = SMe and **5a**, Y = NH_2) affords palladacycles in different ratios of isomers (geometric and atropisomers). In solution, the parent alkyne (Y = H) and the CF_3 substituted derivative generate a mixture of *cisoid* and *transoid* chloro-bridged dimer palladacycles of the type $\{Pd[\kappa^1\text{-}C, \kappa^1\text{-}N\text{–}C{=}(Y\text{-}2\text{-}C_6H_4)C(Cl)CH_2NMe_2](\mu\text{-}Cl)\}_2$. Moreover, in the case of Y = CF_3 palladacyclic derivative each of the geometric isomers comprises a mixture of two diastereoisomers due to the restricted rotation of the C(vinyl)–C(aryl) sigma bond (atropisomers). Palladacycles **1a** (Y = H) and **2a** (Y = CF_3) crystallize as the single *transoid* and *cisoid-anti* isomer, respectively. The OMe substituted alkyne yields a similar dimeric compound that crystallizes as a single *cisoid-anti* isomer. In solution this dimeric compound is in fast equilibrium with a monomeric pincer compound of the type $Pd[\kappa^1\text{-}C, \kappa^1\text{-}N, \kappa^1\text{-}O\text{–}C{=}(MeO\text{-}2\text{-}C_6H_4)C(Cl)CH_2NMe_2](Cl)$ assisted through the weak coordination of the OMe group. Pincer palladacycles $Pd[\kappa^1\text{-}C, \kappa^1\text{-}N, \kappa^1\text{-}Y\text{–}C{=}(Y\text{-}2\text{-}C_6H_4)C(Cl)CH_2NMe_2](Cl)$ (Y = SMe and NH_2) were the sole products obtained in the chloropalladation of alkynes **4a** and **5a**. The bridge splitting reaction of the dimeric palladacycles **1b**–**3b** with pyridine is highly selective, affording exclusively the corresponding monomeric compounds **1c**–**3c**. The monomeric palladacycle **2d**, which comprises a mixture of two atropisomers (2:1 ratio of *anti*/*syn*) was obtained from the reaction of **2b** with 2-methylpyridine. Theoretical calculations indicated that the *anti* isomer of **2d** is 5.42 kJ mol^{-1} more stable than its *syn* isomer.

Keywords: Palladacycles; Chloropalladation; Atropisomerism; Antisymbiotic effect

1. Introduction

Palladacycles possessing a Pd–C bond stabilized intramolecularly by a Pd–Y bond (Y = two electron donor group, such as NR_2, PR_2, SR, etc.) have been known since the 1960s [1] and have a large variety of applications in areas ranging from new molecular materials (liquid crystals, non-linear optics, molecular electronics, etc.) to precursors for organometallic catalysis [2]. These compounds are easily accessible through various methods such as C–H bond activation, transmetallation using aryllithium or magnesium organometallic derivatives, oxidative addition of arylhalides, transcyclometallation or chloropalladation of heterosubstituted alkynes [2]. Structural geometric and stereoisomers are quite common in this class of organopalladium compounds and these isomers can have distinct physical–chemical properties and reactivities. The presence of stereoisomers (enantio- and diastereo-isomers) is usually related to the presence of a stereogenic center in the palladated organic ligand. *Cisoid* and *transoid* isomers are almost a general case in dimeric halides palladacycles (Chart 1) and the *transoid*-geometry is usually the major compound of the mixture

* Corresponding author. Tel.: +55-51-316 6321; fax: +55-51-3316 7304.
E-mail address: dupont@iq.ufrgs.br (J. Dupont).

0020-1693/03/$ - see front matter © 2003 Elsevier Science B.V. All rights reserved.
doi:10.1016/S0020-1693(03)00011-2

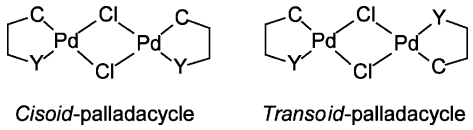


Chart 1.

and the one most commonly observed in the solid state [3].

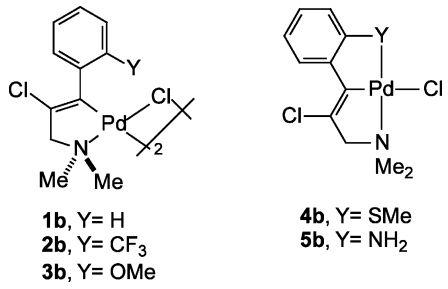
While investigating the chloropalladation reaction [4] of various 2-phenylsubstituted *N*,*N*-dimethylpropargylamines we have isolated *cisoid* isomers of chloro bridged dimeric palladacycles and we have established that these compounds can also generate atropisomers. It is interesting to note that atropisomers are classical in organic molecules but rare in organometallic compounds [5]. We wish to disclose herein some of our experimental and theoretical results on the formation and stabilization of atropisomers in *cisoid* palladacycles.

2. Results and discussion

2.1. Syntheses of the alkynes and palladacycles

The propargylalkynes **1a** and **4a** were prepared by Mannich reaction of, respectively, phenylacetylene and the easily available 2-methylthio-phenylacetylene with $HNMe_2/CH_2O$. The alkynes **2a**, **3a** and **5a** have been obtained by $Pd(PPh_3)_4$/CuI promoted Sonogashira couplings of the corresponding 2-aryl iodides or bromides with 3-dimethylamino-1-propyne in diethylamine (Scheme 1). These alkynes were characterized by means of mass spectroscopy, IR, ^1H and ^{13}C NMR (Section 3).

The reaction of alkynes **1a**–**5a** with a methanolic solution of Li_2PdCl_4 at 5 °C, using an identical procedure to the one described earlier [4d], affords in almost quantitative yields, the air and water stable palladacycles **1b**–**5b** as orange–yellow crystalline solids (Scheme 2). Palladacycles **1b**–**5b** have been fully characterized by means of CHN combustion analysis, IR, ^1H and ^{13}C NMR.



Scheme 2.

2.2. Solid-state structure of the palladacycles

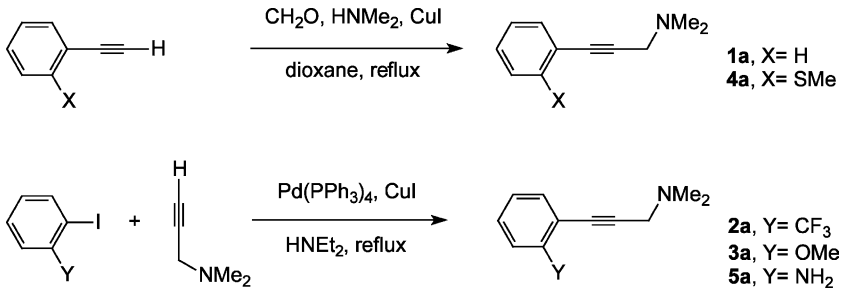
The molecular structure of compounds **1b**–**3b** has been also ascertained by means of X-ray diffraction analysis. ORTEP diagrams are presented in Figs. 1–3, respectively, and selected bond distances and angles are summarized in Tables 1 and 2, respectively. Crystallographic data and details of the structure determination are presented in Table 3. Tables of atomic coordinates and anisotropic thermal parameters are supplied as Supporting Information.

The coordination sphere around each Pd center can be considered as essentially planar and this is also evident for the centrosymmetric four-membered Pd_2Cl_2 rings (the Pd_2Cl_2-rings of **2b** and **3b** are bent (butterfly shape) by 10 and 9°, respectively). The conformation of the five-membered rings formed by the ligands and the Pd centers can be described as envelopes in which C(2) is 0.45 Å in **1b**, 0.43 Å in **2b** and 0.46 Å in **3b**, below the planes containing Pd, C(1), C(3) and N(1).

However, it is noteworthy that there is a *transoid* relationship through the chlorine bridges between the NMe_2 groups or the Pd–C bonds in **1b** whereas a *cisoid* geometry is observed in palladacycles **2b** and **3b**.

Of note are the Pd–Cl distances in compounds **1b**–**3b**; those located *trans* to the Pd–C moiety are significantly longer than those *trans* to NMe_2 (Table 2) and this can be attributed to the higher *trans influence* of the C compared to the NMe_2. This bond length difference is similar to those usually observed in analogous halide-bridged dimer palladacycles [3].

Unlike what was observed in compounds **1b**–**3b**, the palladacycles **4b** and **5b** are monomeric with the



Scheme 1.

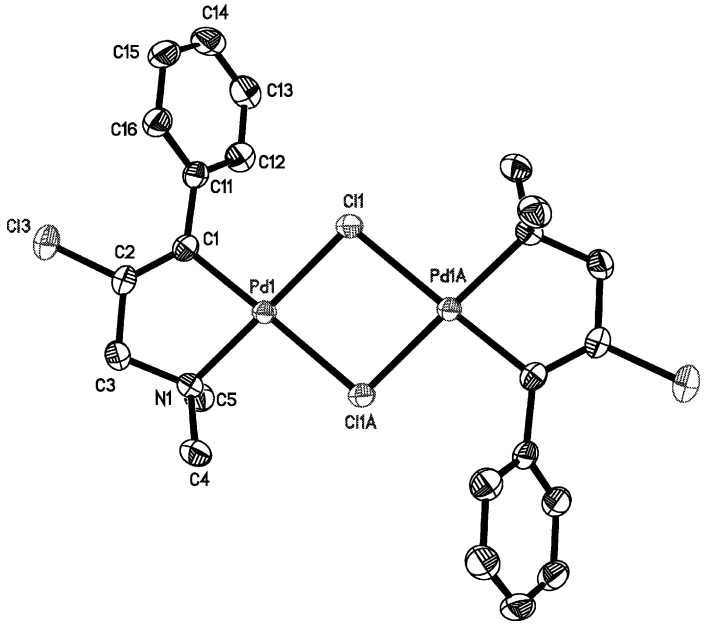


Fig. 1. ORTEP plot with atom-labeling scheme of the structure of **1b**. Displacement ellipsoids are at the 50% level; H atoms are omitted for clarity.

formation of a pincer arrangement through the coordination of the SMe or NH_2 groups. The structure **5b** was assigned by analogy with that of **4b** (its X-ray molecular structure has been recently reported [4e]) and on the basis of its spectroscopic and chemical properties (see below).

2.3. Solution structures of the palladacycles

^{1}H NMR spectra of **1b** in $CDCl_3$ at room temperature indicated the presence of two isomers in a 1:1 ratio, that can be attributable to the *cisoid* and *transoid* geometries (Scheme 3). We observed that for each isomer the methylene hydrogens and the dimethylamino groups are equivalent (they appear as singlets in the ^{1}H NMR spectrum) and the proportion of the *cisoid* and *transoid* isomers do not change with time or temperature, as checked by ^{1}H NMR spectroscopy at various temperatures (from −30 to 30 °C). Note that above 40 °C the dimer **1b** decomposes.

Compound **2b** in solution is composed of four isomers in a 1:1:1:1 proportion since eight singlets are observed for the NMe_2 group and four AB spin systems for the methylene hydrogens in its ^{1}H NMR spectrum. As for compound **1b**, the proportion of these isomers does not change with time or temperature (checked by ^{1}H NMR up to 40 °C). The most probable structure of these isomers are *anti* and *syn* atropisomers (*cisoid* and *transoid* chloro-bridged dimers) due to restricted rotation of the 2-trifluoromethanearyl group through the C(vinyl)–C(aryl) bond (Scheme 4) within the NMR time scale. It is of note that the ^{1}H NMR spectrum of a solution prepared at 0 °C in $CDCl_3$ of isolated crystals **2b** shows the presence of four isomers in a 1:1:1:1 ratio, indicating that at this temperature the isomerization process was already completed.

The ^{1}H NMR spectrum of **3b** shows the presence of a single compound in which the OMe group is *not* coordinated to the Pd center since its chemical shift (3.68 ppm) is close to that of the free ligand **3a**. Moreover, the methylene hydrogens and the dimethylamino groups are equivalent and they appear as singlets at 3.59 and 2.83 ppm, at temperatures ranging from −40 to 40 °C. This is a strong indication of a dynamic process that renders the methylene hydrogens and NMe_2 groups equivalent over this temperature range. However, also a fast rotation of the 2-methoxyaryl group through the C(vinyl)–C(aryl) single bond could explain

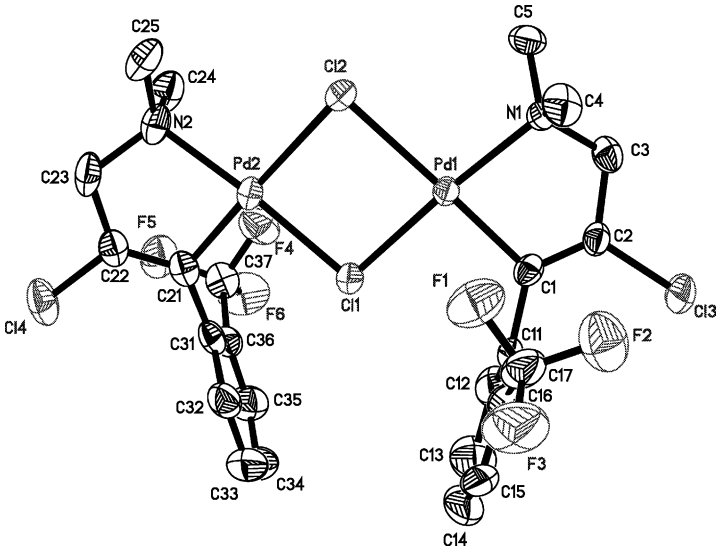


Fig. 2. ORTEP plot with atom-labeling scheme of the structure of **2b**. Displacement ellipsoids are at the 50% level; H atoms are omitted for clarity.

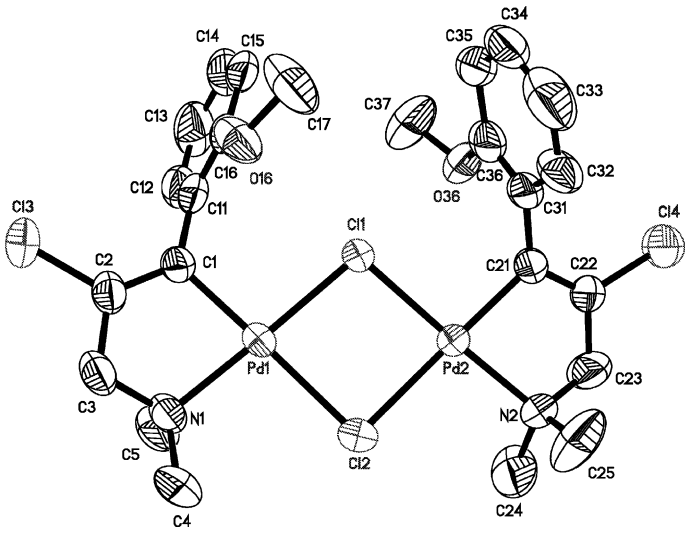


Fig. 3. ORTEP plot with atom-labeling scheme of the structure of **3b**. Displacement ellipsoids are at the 50% level; H atoms are omitted for clarity.

Table 1
Selected bond distances (Å) of palladacycles **1b**–**3b** and **2d**

1b	**2b**	**3b**	**2d**
Pd1–C1	Pd1–C1	Pd1–C1	Pd1–C1
1.9974(18)	1.983(4)	1.987(4)	2.002(3)
Pd1–N1	Pd1–N1	Pd1–N1	Pd1–N2
2.0641(16)	2.086(3)	2.077(4)	2.042(2)
Pd1–Cl1	Pd1–Cl1	Pd1–Cl1	Pd1–N1
2.3362(5)	2.312(11)	2.324(10)	2.079(2)
Pd1–Cl1A	Pd1–Cl2	Pd1–Cl2	Pd1–Cl1
2.4583(5)	2.453(11)	2.448(13)	2.3876(7)
C1–C2 1.328(3)	C1–C2	C1–C2	C1–C2
	1.309(5)	1.321(6)	1.320(4)
	C1–Cl1	C1–Cl1	C1–C11
	1.479(6)	1.469(6)	1.488(4)
	C16–C17	C16–O16	C16–C17
	1.477(8)	1.336(6)	1.499(4)
	C17–F1		C17–F1
	1.340(6)		1.331(4)

Mean values of both parts of the dimers for **2b** and **3b**.

Table 2
Selected bond angles (°) of palladacycles **1b**–**3b** and **2d**

1b	**2b**[a]
C1–Pd1–N1 82.75(7)	C1–Pd1–N1 82.59(15)
C1–Pd1–Cl1 96.43(6)	C1–Pd1–Cl1 93.45(12)
N1–Pd1–Cl1 179.07(5)	N1–Pd1–Cl1 175.23(10)
C1–Pd1–ClA 178.79(6)	C1–Pd1–Cl2 177.10(13)
N1–Pd1–ClA 96.05	N1–Pd1–Cl2 98.44(9)
Cl1–Pd1–ClA 85.77(17)	Cl1–Pd1–Cl2 85.64(4)
Pd1–Cl1–Pd1A 95.22(17)	Cl1–Pd2–Cl2 85.25(4)
	Pd1–Cl1–Pd2 97.91(4)
	Pd1–Cl2–Pd2 90.25(4)
3b[a]	**2d**
C1–Pd1–N1 82.74(16)	C1–Pd1–N2 93.02(10)
C1–Pd1–Cl1 95.60(12)	C1–Pd1–N1 82.56 (10)
N1–Pd1–Cl1 178.24(12)	N2–Pd1–N1 175.02 (10)
C1–Pd1–Cl2 176.93(13)	C1–Pd1–Cl1 177.84 (8)
N1–Pd1–Cl2 95.99(11)	N2–Pd1–Cl1 88.98 (7)
Cl1–Pd1–Cl2 85.63(4)	N1–Pd1–Cl1 95.47 (7)
Cl1–Pd2–Cl2 85.73(4)	C1–C2–Cl2 123.5 (2)
Pd2–Cl1–Pd1 97.16(4)	C3–C2–Cl2 114.3 (2)
Pd2–Cl2–Pd1 90.73(4)	N2–C26–C27 118.2 (3)

[a] Mean values of both parts of the dimers for **2b** and **3b**.

this behavior if we assume the presence of a single geometric isomer (*cisoid* or *transoid*) or their fast interconversion. It is, however, more reasonable to assume that this transformation occurs through the formation of a 'pincer' intermediate (Scheme 5) where the coordination of the OMe group assists the isomerization ('anchimerically-assisted isomerization process').

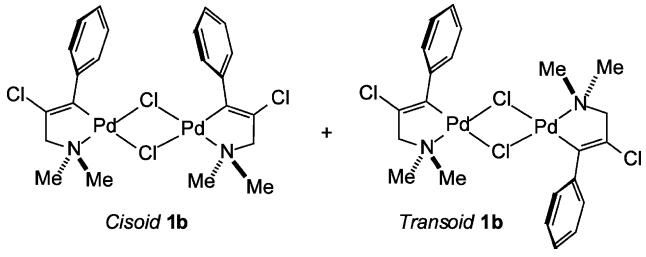
The ^{1}H NMR spectra of compounds **4b** and **5b** are clearly consistent with the formation of a highly stable 'pincer' type structure, which does not undergo reaction with donor ligands such as pyridine. In opposition, the chloro-bridged dimers **1b**–**3b** do react with pyridine in dichloromethane at room temperature to afford the adducts **1c**–**3c**, respectively, in very good yields (Scheme 6). These compounds were isolated as light-yellow air and stable solids, and are soluble in polar organic solvents such as dichloromethane and acetone.

The ^{1}H NMR spectrum of **1c**–**3c** indicated that these compounds were isolated as single isomers. As expected the methylene hydrogens and NMe_2 in **1c** are equivalent (they appear as singlets) whereas in **2c** and **3c** they are inequivalent (AB spin pattern for the CH_2 and two singlets for the NMe_2 group), indicating that there is restricted rotation around the C(vinyl)–C(aryl) bond in compounds **2c** and **3c**. The location of the pyridine ligand *cis* to the Pd–C bond in **1c**–**3c** is based on their ^{1}H NMR spectra, which shows the shielding of the phenyl hydrogens to a lower frequency (< 6.8 ppm) and by analogy of the X-ray structure of analogous compounds [6]. Theoretical calculations (Gaussian 98) [7] clearly indicated that the *cis* C–Pd–Py **1c** isomer is 6.1 kcal mol^{-1} more stable than its *trans* C–Pd–Py counterpart. Moreover, this selectivity can be explained by the *antisymbiotic* effect [8] of the soft Pd(II) center that will place the incoming ligand *cis* to the Pd–C bond. This is an indication that the *stereochemical out-come* of the bridge-splitting reaction is under *thermodynamic* control.

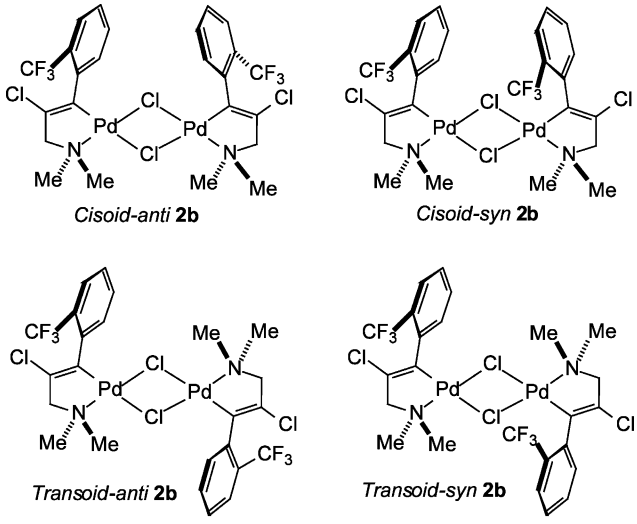
Interesting, atropo-diastereoisomers can be easily prepared by reaction of dimeric compounds **2b** and **3b** with substituted pyridines. Thus the reaction of **2b** with 2-methylpyridine affords in almost quantitative yield the monomeric palladacycle **2d** (Scheme 7) as a mixture of two atropisomers in 2:1 ratio, that do not change with

Table 3
Summary of the crystal data and structure refinement for **1b**–**3b** and **2d**

	1b	**2b**	**3b**	**2d**
Chemical formula	$C_{22}H_{26}Cl_4N_2Pd_2$	$C_{24}H_{24}Cl_4F_6N_2Pd_2$	$C_{24}H_{30}Cl_4N_2O_2Pd_2$	$C_{18}H_{19}Cl_2F_3N_2Pd$
Temperature (K)	200(2)	200(2)	200(2)	200(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_1/c$	$C2/c$	$C2/c$	$Pna2_1$
Z	2	8	8	4
a (Å)	13.0324(3)	23.0218(5)	20.2663(2)	18.0239(2)
b (Å)	8.2305(2)	11.1004(3)	13.0459(2)	8.1098(2)
c (Å)	11.9947(3)	25.7210(4)	23.5953(1)	13.6206(3)
β (°)	108.702(1)	116.523(1)	113.980(1)	90
Volume (Å^3)	1218.66(5)	5881.3(2)	5699.96(11)	1990.93(7)
ρ_{calc} (g cm^{-3})	1.83	1.83	1.71	1.66
μ (mm^{-1})	1.93	1.64	1.66	1.23
Crystal shape	Polyhedron	Polyhedron	Polyhedron	Polyhedron
Crystal dimensions (mm^3)	0.50 × 0.30 × 0.04	0.22 × 0.18 × 0.05	0.36 × 0.20 × 0.06	0.37 × 0.33 × 0.24
θ range for data collected (°)	3.0–27.5	1.8–27.5	1.9–27.5	2.3–27.5
Index range	$-16 \leqslant h \leqslant 16$	$-29 \leqslant h \leqslant 29$	$-26 \leqslant h \leqslant 23$	$-23 \leqslant h \leqslant 23$
	$-10 \leqslant k \leqslant 10$	$-10 \leqslant k \leqslant 13$	$-16 \leqslant k \leqslant 16$	$-8 \leqslant k \leqslant 10$
	$-15 \leqslant l \leqslant 15$	$-33 \leqslant l \leqslant 29$	$-25 \leqslant l \leqslant 30$	$-14 \leqslant l \leqslant 17$
Reflections collected	12 064	9172	20 226	5720
Independent reflections	2794 ($R_{int} = 0.0285$)	5833 ($R_{int} = 0.0393$)	6477 ($R_{int} = 0.0404$)	3617 ($R_{int} = 0.0172$)
Observed reflections	2506 ($I > 2\sigma(I)$)	3952 ($I > 2\sigma(I)$)	4558 ($I > 2\sigma(I)$)	3337 ($I > 2\sigma(I)$)
Max./min. transmission	0.94 and 0.73	0.93 and 0.68	0.92 and 0.69	0.84 and 0.71
Data/restraints/parameters	2794/0/138	5833/0/347	6477/0/313	3617/1/236
R indices ($I > 2\sigma(I)$)	$R_1 = 0.019$, $wR_2 = 0.048$	$R_1 = 0.036$, $wR_2 = 0.066$	$R_1 = 0.039$, $wR_2 = 0.088$	$R_1 = 0.019$, $wR_2 = 0.047$
Largest difference peak/hole (e Å^{-3})	0.47 and −0.34	0.49 and −0.78	0.89 and −0.73	0.50 and −0.32



Scheme 3.



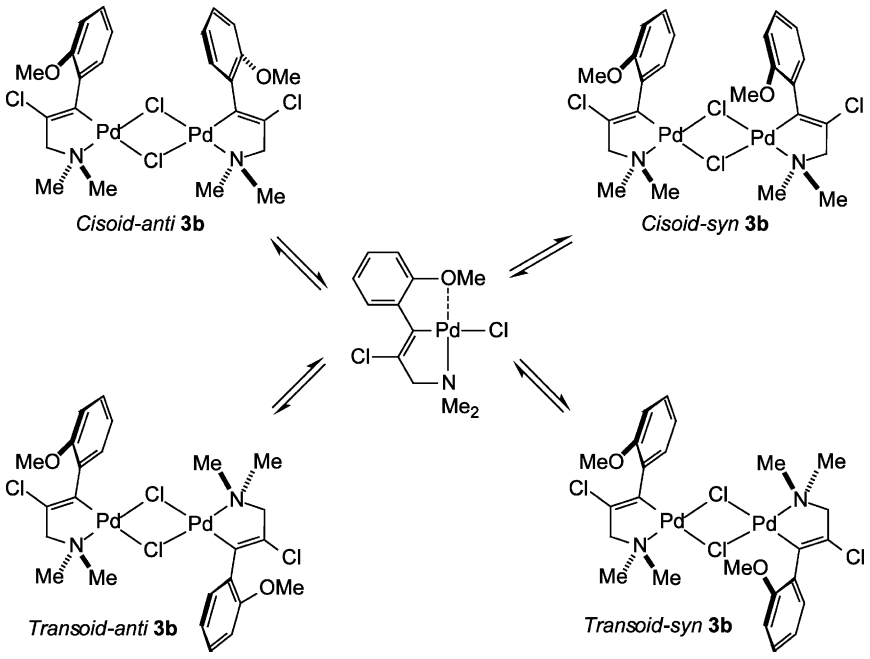
Scheme 4.

time or temperature (determined by ^{1}H NMR spectroscopy).

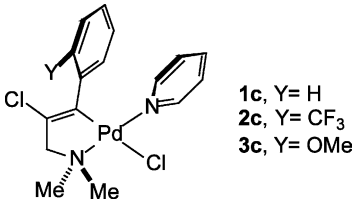
The structure of the major isomer of **2d** was determined by an X-ray diffraction study. An ORTEP drawing of **2d** is shown in Fig. 4 and selected bond angles and distances are summarized in Tables 1 and 2, respectively. Crystallographic data and details of the structure determination are presented in Table 3.

The coordination sphere of Pd including the C1, Cl1, N1 and N2 atoms can be considered as being essentially planar, with mean atomic deviation from the best plane of the five atoms of 0.024 Å. The *cis* stereochemistry between C1–Pd–N2 is evident with an angle of 93.02°. The two aryl rings are almost parallel with an angle between the two aryl ring planes of 45.7°. Of note is the *anti*-relationship between the two 2-substituted aryl rings, thus the major diastereoisomer has an *R*,*R* (*S*,*S*) relative stereochemistry.

As already pointed out this diastereoisomer presents restricted rotation around the C1–C11 and Pd–N2 single bonds. Theoretical calculations on the *syn* and *anti* isomers of **2d** show that the *anti* isomer is 5.42 kJ mol^{-1} more stable than its *syn* analogue corroborating the experimental results, which indicated the pre-



Scheme 5.



Scheme 6.

sence of both isomers at room temperature in a 2:1 ratio. The rotational barrier is expected to be very high due to the steric congestion between the Cl-vinyl moiety and the 2-aryl substituent. This suggests that the *anti–syn* isomerization can only occur through a dissociative mechanism.

The results show that the chloropalladation reaction of 1-[2-(substituted)-phenyl]-3-*N*,*N*-dimethylamino-1-propynes can lead to palladacycles constituted of stable atropisomers. The stereoselection on the bridge splitting reaction of these dimers with 2-methylpyridine is sufficient for the separation of the atropisomers. This opens the possibility for the preparation of optically active organometallic atropisomers, similar to biphenyl organic compounds [5], by the use of non-racemic propargylamines such as $Me_2NCH(Me)C{\equiv}CAr$.

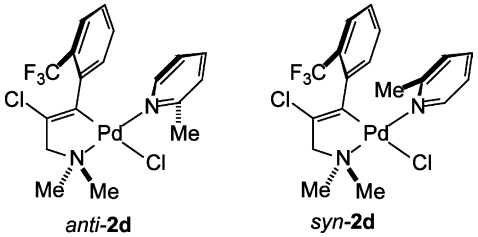
3. Experimental

3.1. General methods

All reactions involving organometallic compounds were carried out under argon or nitrogen atmosphere in oven dried Schlenk tubes. The alkynes were prepared according to known procedures. Solvents were dried with suitable drying agents and distilled under argon prior to use. All the other chemicals were purchased from commercial sources (Acros or Aldrich) 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.

3.2. Theoretical calculations

The energy of all calculated species was obtained by full geometry optimization without any constrain. The calculations were performed with the Gaussian 98' Program [7], at a HF/B3LYP [9] level of theory, using a Dunning-Huzinaga DZ95 [10] basis set for the non-



Scheme 7.

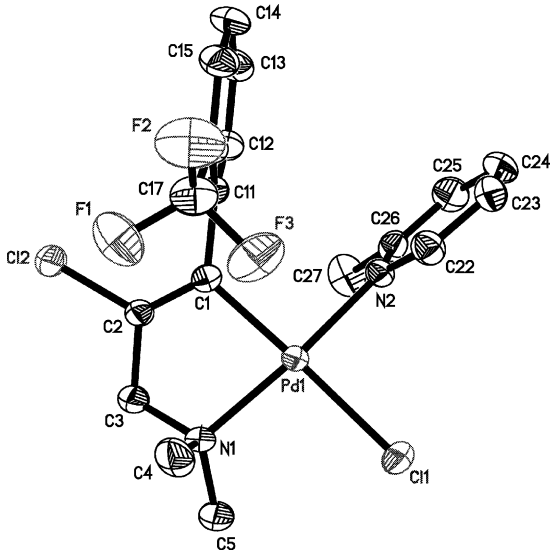


Fig. 4. ORTEP plot with atom-labeling scheme of the structure of **2d**. Displacement ellipsoids are at the 50% level; H atoms are omitted for clarity.

metal atoms and a DZ valence basis set plus an effective core potential [11] for the palladium.

3.3. X-ray structures analysis of *1b–3b* and *2d*

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 **1b** and **3b**, frames corresponding to a sphere of data were collected using the omega-scan technique, 20 s exposures of 0.3° in omega were taken. For **2b** and **2d**, frames corresponding to at least one complete set of independent reflections (one asymmetric unit of reciprocal space) were collected using the omega-scan technique, 10 s exposures of 0.3° in omega were taken. An absorption correction was applied, in each case, using SADABS based on the laue symmetry of the reciprocal space, 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 [12].

3.4. Synthesis of 1-phenyl-3-(dimethylamino)-1-propyne (*1a*)

Dimethylamine (40% aqueous solution, 91 ml, 0.72 mol) was added to a stirred mixture of phenylacetylene (49.0 g, 0.48 mol), paraformaldehyde (30.0 g; 0.53 mol) and cuprous iodide (0.45 g) in 250 ml dioxane. The reaction mixture was refluxed for 4 h and the solvent was removed under reduced pressure. Distillation of the residue afforded a colorless liquid of boiling point 114 °C/5 mmHg (71.8 g, 94% yield). GC–MS (*m*/*z*, [peak]): 159, $[M]^{\bullet +}$; 115, $[M\text{-}NMe_2]^+$. ^1H NMR ($CDCl_3$): δ 7.46–7.38 (m, 2H, H arom); 7.33–7.23 (m, 3H, H arom); 3.45 (s, 2H, CH_2N); 2.35 (s, 6H, NMe_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 132.1, 128.5, 128.1 (CH arom); 124.1 (C arom quat); 85.9, 85.1 (C≡C); 49.8 (CH_2N); 44.4 (NMe_2).

3.5. Synthesis of 1-[2-(trifluoromethyl)-phenyl]-3-(dimethylamino)-1-propyne (*2a*)

A mixture of 3-dimethylamino-1-propyne (2.0 g, 24.0 mmol), 2-trifluoromethyl-bromobenzene (5.42 g, 24.0 mmol), $PdCl_2(PPh_3)_2$ (0.20 g, 0.29 mmol), cuprous iodide (0.026 g, 0.14 mol) and diethylamine (30 ml) was maintained under gentle reflux for 24 h. Solvent evaporation under reduced pressure and bulb-to-bulb distillation furnished a colorless liquid of boiling point 90 °C/16 mmHg (0.88 g, 16% yield). ^1H NMR ($CDCl_3$): δ 7.52–7.37 (m, 4H, H arom); 3.45 (s, 2H, CH_2N); 2.30 (s, 6H, NMe_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 133.9, 131.1, 127.4 (CH arom); 131.1 (q, 1C, $^2J_{FC} = 30.6$ Hz, C arom quat ipso CF_3); 125.4 (q, 1C, $^3J_{FC} = 5.1$ Hz, CH arom); 123.4 (q, 1C, $^1J_{FC} = 273$ Hz, CF_3); 121.6 (C arom quat); 90.7, 81.0 (C≡C); 48.1 (CH_2N); 43.6 (NMe_2).

3.6. Synthesis of 1-[2-(methoxy)-phenyl]-3-(dimethylamino)-1-propyne (*3a*)

A mixture of 3-dimethylamino-1-propyne (1.00 g, 12.0 mmol), 2-iodo-anisole (2.30 g, 10.0 mmol), $Pd(PPh_3)_4$ (0.120 g, 0.100 mmol), cuprous iodide (0.040 g, 0.200 mmol), DMF (1.5 ml) and diethylamine (20 ml) was maintained under reflux for 24 h. The volatiles were removed under reduced pressure, ether (20 ml) and KOH solution (10% aqueous, 20 ml) were added and the mixture was stirred for 5 min. The organic layer was separated, the aqueous layer was extracted with ether (2×10 ml) and the combined organic extract was dried with $MgSO_4$. The solvent was evaporated and the crude reaction product was purified by column chromatography (silica-gel, hexanes/EtOAc: 90/10 v/v) giving a colorless liquid (1.72 g, 75% yield). IR (film, cm^{-1}): 2232 ($\nu_{C\equiv C}$). ^1H NMR ($CDCl_3$): δ 7.40 (d, 1H, $^3J_{HH} = 7.4$ Hz, H arom); 7.25 (t, 1H, $^3J_{HH} = 7.4$ Hz, H arom); 6.90–6.84 (m, 2H, H arom); 3.86 (s, 3H, OMe); 3.52 (s, 2H, CH_2N); 2.37 (s, 6H, NMe_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 159.8, 112.3 (C arom quat); 133.5, 129.3, 120.2, 110.4 (CH arom); 88.6, 81.3 (C≡C); 55.6 (OMe); 48.7 (CH_2N); 44.0 (NMe_2).

3.7. Synthesis of 1-[2-(methylthio)-phenyl]-3-(dimethylamino)-1-propyne (**4a**)

A mixture of 2-methylthio-phenylacetylene [13] (0.833 g, 5.60 mmol), paraformaldehyde (0.185 mg, 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 (0.970 g, 85% yield). IR (film, cm^{-1}): 2262 ($\nu_{C\equiv C}$). GC–MS (*m*/*z*, rel int%, [peak]): 205, 2, $[M]^{\bullet +}$; 204, 10, $[M\text{-}1]^+$; 190, 15, $[M\text{-}15]^+$; 160, 100, $[M\text{-}Me_2NH]^{\bullet +}$; 82, 12, $[Me_2NCH_2C\equiv C]^+$; 58, 18, $[Me_2N{=}CH_2]^+$. ^1H NMR ($CDCl_3$): δ 7.44–7.06 (m, 4H, H 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, 121.5 (C arom quat); 132.8, 128.8, 124.4, 124.1 (CH arom); 91.6, 83.0 (C≡C); 48.9 (CH_2N); 44.4 (NMe_2); 15.2 (SMe).

3.8. Synthesis of 1-[2-(amino)-phenyl]-3-(dimethylamino)-1-propyne (**5a**)

A mixture of 2-iodo-aniline (3.50 g, 15.0 mmol), 3-dimethylamino-1-propyne (1.89 g, 22.5 mmol), $Pd(PPh_3)_4$ (0.120 g, 0.100 mmol), cuprous iodide (0.040 g, 0.200 mmol) and DMF (1.5 ml) in diethylamine (20 ml) was stirred overnight. The solvent was evaporated, ether (20 ml) and aqueous 10% potassium hydroxide (20 ml) were added and the mixture was stirred for 5 min. The layers were separated, the aqueous layer was extracted with ether (2×10 ml) and the combined organic extract was dried with $MgSO_4$. The solvent was evaporated and the crude reaction product was chromatographed over basic alumina (hexanes/EtOAc: 90/10 v/v) giving a pale brown solid of melting point 40–42 °C (2.00 g, 77% yield). IR (Nujol, cm^{-1}): 2208 ($\nu_{C\equiv C}$). GC–MS (*m*/*z*, rel int%, [peak]): 174, 29, $[M]^{\bullet +}$; 159, 7, $[M\text{-}CH_3]^+$; 130, 100, $[M\text{-}NMe_2]^+$; 58, 23, $[Me_2N{=}CH_2]^+$. ^1H NMR ($CDCl_3$): δ 7.31, 6.72 (d, 1H, $^3J_{HH} = 7.5$ Hz, H arom); 7.14, 6.70 (d, 1H, $^3J_{HH} = 7.5$ Hz, H arom); (4.24 (br s, 2H, NH_2); 3.57 (s, 2H, CH_2N); 2.40 (s, 6H, NMe_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 147.8, 107.8 (C arom quat); 132.8, 129.3, 117.3, 114.1 (CH arom); 89.5, 81.8 (C≡C); 48.6 (CH_2N); 44.1 (NMe_2).

3.9. Synthesis of palladacycles **1b**–**3b**: general procedure

A Li_2PdCl_4 solution was prepared by dissolving $PdCl_2$ (0.745 g, 4.20 mmol) and LiCl (0.45 g, 10.5 mmol) in hot methanol (15 ml). After dissolution of the solids, this solution was cooled to 0 °C and the appropriate alkyne (**1a**, **2a** or **3a**, 5.00 mmol) was added. The resulting suspension was stirred for 1 h. Filtration and washing of the resulting solid with cold MeOH and drying under reduced pressure afforded the desired palladacycles.

3.10. Synthesis of palladacycle (**1b**) [4d]

Accordingly to the described general procedure, a yellow solid of melting point 172–175 °C (dec.) was obtained (1.24 g, 88% yield). *Anal.* $(C_{11}H_{13}Cl_2NPd)_2$ (673.11) requires C, 39.26; H, 3.89; N, 4.16. Found: C, 39.40; H, 3.99; N, 4.15. IR (KBr, cm^{-1}): 1600 ($\nu_{C=C}$). ^1H NMR ($CDCl_3$): δ 7.35–6.90 (m, 10H, H arom); 3.61 (s, 2H, CH_2N); 3.59 (s, 2H, CH_2N); 2.88 (s, 6H, NMe_2); 2.77 (s, 6H, NMe_2). ^1H NMR ($CDCl_3$ + Py-d_5): δ 6.92–6.75 (m, 5H, H arom); 3.67 (s, 2H, CH_2N); 3.01 (s, 6H, NMe_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 142.9, 142.7, 141.9, 141.7, 116.1, 115.7 (C arom quat and C=C); 128.1, 127.7, 127.5, 127.4, 125.9, 125.8 (CH arom); 74.6, 74.3 (CH_2N); 53.2, 52.9 (NMe_2).

3.11. Synthesis of palladacycle (**2b**)

Accordingly to the described general procedure, a yellow solid was obtained (1.10 g, 65% yield). *Anal.* $(C_{12}H_{12}Cl_2F_3NPd)_2$ (809.11) requires C, 35.63; H, 2.99; N, 3.46. Found: C, 35.81; H, 2.93; N, 3.45. ^1H NMR ($CDCl_3$): δ 7.60–6.80 (m, 16H, H arom); 3.92–3.85 (m, 2H, CH_2N); 3.82–3.75 (m, 2H, CH_2N); 3.38 (d, 2H, $J = 6.1$ Hz, CH_2N); 3.30 (d, 2H, $J = 6.1$ Hz, CH_2N); 2.98 (s, 6H, NMe); 2.92 (s, 3H, NMe); 2.88 (s, 3H, NMe); 2.75 (s, 3H, NMe); 2.73 (s, 3H, NMe); 2.60 (s, 3H, NMe); 2.57 (s, 3H, NMe). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 141.7, 141.4, 141.0 (C=C); 138.3, 138.0, 137.9 (C arom quat); 131.2, 131.1, 130.9, 130.7, 129.9, 129.8, 129.7, 129.3, 125.9, 125.7, 125.6 (CH arom); 125.4 (q, 1C, $^3J_{FC} = 5.1$ Hz, CH arom); 124.5, 124.4, 124.3, 124.1 (q, 1C, $^1J_{FC} = 271$ Hz, CF_3); (C arom quat ipso CF_3: not observed); 118.2, 117.8, 117.7 (C=C); 76.6, 74.6, 74.5, 74.4 (CH_2N); 53.4, 53.2, 53.0, 52.8, 52.7 (NMe). $^{13}C\{^1H\}$ NMR ($CDCl_3$ + Py-d_5): δ 141.9, 141.5 (C arom quat and C=C); 130.9, 128.9, 125.3, (CH arom); 125.7 (q, 1C, $^3J_{CF} = 5$ Hz, CH arom); 124.2 (q, 1C, $^1J_{CF} = 275$ Hz, CF_3); (C arom quat ipso CF_3: not observed); 119.4 (C=C); 75.1 (CH_2N); 53.1, 52.4 (NMe).

3.12. Synthesis of palladacycle (**3b**)

Accordingly to the described general procedure, a yellow solid was obtained (0.78 g, 51% yield). *Anal.* $(C_{12}H_{15}Cl_2NOPd)_2$ (733.17) requires C, 39.32; H, 4.12; N, 3.82. Found: C, 39.34; H, 3.92; N, 4.01. IR (KBr, cm^{-1}): 1631 ($\nu_{C=C}$).^1H NMR ($CDCl_3$): δ 7.18 (t, 1H, $^3J_{HH} = 6.9$ Hz, H arom); 6.93 (d, 1H, $^3J_{HH} = 7.4$ Hz, H arom); 6.77 (t, 1H, $^3J_{HH} = 7.4$ Hz, H arom); 6.65 (d, 1H, $^3J_{HH} = 7.6$ Hz, H arom); 3.68 (s, 3H, OMe); 3.59 (s, 2H, CH_2N); 2.83 (s, 6H, NMe_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 155.1, 139.5 131.2 (C arom quat and C=C); 128.7, 127.5,

120.0, 110.8 (CH arom); 116.0 (C=C); 74.2 (CH_2N); 55.8 (OMe); 52.7 (NMe_2).

3.13. Synthesis of palladacycle (*4b*)

A Li_2PdCl_4 solution was prepared by dissolving, with gentle heating, $PdCl_2$ (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 1-[2-(methylthio)-phenyl]-3-(dimethylamino)-1-propyne **(4a)** (0.385 g, 1.88 mmol), dissolved in methanol (5 ml). The resulting suspension was stirred for 30 min, 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 of melting point 148–150 °C (dec.) (0.480 g, 67% yield). *Anal.* $C_{12}H_{15}Cl_2NSPd$ (382.6) requires C, 37.67; H, 3.95; N, 3.66. Found: C, 37.97; H, 4.11; N, 3.67. IR (Nujol, cm^{-1}): 1590 ($\nu_{C=C}$). ^1H NMR ($CDCl_3$): δ 8.51 (d, 1H, $J = 7.7$ Hz, H arom); 7.43–7.28 (m, 3H, H 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 (C arom quat and C=C); 130.8, 129.4, 128.8, 127.0 (CH arom); 118.3, (C=C); 77.8 (CH_2N); 52.1 (NMe_2); 26.7 (SMe).

3.14. Synthesis of palladacycle (*5b*)

A Li_2PdCl_4 solution was prepared by dissolving $PdCl_2$ (0.178 g, 1.00 mmol) and LiCl (0.107 g, 2.50 mmol) in hot methanol (5 ml), under vigorous stirring. After dissolution of the solids, this solution was cooled to 0 °C and a solution of 1-[2-(amino)-phenyl]-3-(dimethylamino)-1-propyne **5a** (0.174 g, 1.00 mmol) in 2 ml of MeOH was added. The resulting yellow suspension was stirred at 0 °C for 3 h. The solvent was evaporated to dryness under reduced pressure and the residue was extracted with CH_2Cl_2. The organic solution was filtered through a plug of Celite and concentrated to 5 ml. Addition of hexanes, filtration, washing of the resulting solid with hexanes and drying under reduced pressure furnished a pale brown solid (0.250 g, 71% yield). *Anal.* $C_{11}H_{14}Cl_2N_2Pd$ (351.57) requires C, 37.58; H, 4.01; N, 7.97. Found: C, 37.88; H, 3.91; N, 7.81. ^1H NMR ($CDCl_3$): δ 8.29 (m, 1H, H arom); 7.23–7.13 (m, 3H, H arom); 5.62 (br s, 2H, NH_2); 3.72 (s, 2H, CH_2N); 2.71 (s, 6H, NMe_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 146.2, 145.8, 139.8 (C arom quat and C=C); 128.4, 127.0, 126.9, 125.3 (CH arom); 114.2 (C=C); 77.8 (CH_2N); 52.1 (NMe_2).

3.15. Synthesis of palladacycles *1c–3c, 2d*: general procedure

The dimeric palladacycle **1b**, **2b** or **3b** (0.08 mmol) was dissolved in CH_2Cl_2 (5 ml) and the appropriate pyridine (pyridine or 2-picoline, 0.22 mmol) was added. The solution was concentrated to 1 ml and hexanes (10 ml) were added. The resulting yellow solid was filtered, washed with hexanes and dried under reduced procedure.

3.16. Palladacycle *1c*

This compound was obtained accordingly to the general procedure using palladacycle **1b** and pyridine (0.030 g, 81% yield). *Anal.* $C_{16}H_{18}Cl_2N_2Pd$ (415.66) requires C, 46.23, H, 4.36, N, 6.74. Found: C, 46.61, H, 4.37, N, 6.54. ^1H NMR ($CDCl_3$): δ 8.30 (d, 2H, $^3J_{HH} =$ 4.9 Hz, H py); 7.42 (t, 1H, $^3J_{HH} = 6.1$ Hz, H py); 6.95–6.82 (m, 7H, H arom and H py); 3.69 (s, 2H, CH_2N); 3.03 (s, 6H, NMe_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 153.3, 138.4, 137.0, 131.7, 128.2, 127.6, 127.3, 125.2, 125.0, 124.3 (CH arom and CH py); 146.1, 142.3 (C arom quat and C=C); 117.4 (C=C); 75.2 (CH_2N); 53.0 (NMe_2).

3.17. Palladacycle *2c*

This compound was obtained accordingly to the general procedure using the palladacycle **2b** and pyridine (0.032 g, 89% yield). *Anal.* $C_{17}H_{17}Cl_2F_3N_2Pd$ (483.66) requires C, 42.22; H, 3.54; N, 5.79. Found: C, 42.37; H, 2.67; N, 5.42. ^1H NMR ($CDCl_3$): δ 8.32 (d, 2H, $^3J_{HH} =$ 4.9 Hz, H py); 7.42 (t, 2H, $^3J_{HH} = 6.2$ Hz, H py); 7.29–6.81 (m, 6H, H arom and H py); 3.92 (d, 1H, $^2J_{HH} =$ 15.2 Hz, CH_2N); 3.46 (d, 1H, $^2J_{HH} = 15.2$ Hz, CH_2N); 3.10 (s, 3H, NMe); 2.95 (s, 3H, NMe). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 152.4, 139.9, 124.3 (CH py); 142.1, 141.6 (C arom quat and C=C); 130.9, 128.9, 124.3 (CH arom); 125.8 (q, 1C, $^3J_{FC} = 5.1$ Hz, CH arom); 124.3 (q, 1C, $^1J_{FC} = 274$ Hz, CF_3); (C arom quat ipso CF_3: not observed); 119.5 (C=C); 75.2 (CH_2N); 53.2 (NMe); 52.5 (NMe).

3.18. Palladacycle *3c*

This compound was obtained accordingly to the general procedure using the palladacycle **3b** and pyridine (0.030 g, 83% yield). *Anal.* $C_{17}H_{20}Cl_2N_2OPd$ (445.68) requires C, 45.81; H, 4.52; N, 6.29. Found: C, 45.60; H, 4.55; N, 6.19. ^1H NMR ($CDCl_3$): δ 8.29 (d, 2H, $^3J_{HH} =$ 4.9 Hz, H py); 7.41 (t, 2H, $^3J_{HH} = 6.2$ Hz, H py); 6.98–6.85 (m, 3H, H arom and H py); 6.64 (t, 1H, $^3J_{HH} = 7.4$ Hz, H arom); 6.34 (d, 1H, $^3J_{HH} = 7.5$ Hz, H arom); 3.75 (d, 1H, $^2J_{HH} = 15.2$ Hz, CH_2N); 3.62 (d, 1H, $^2J_{HH} =$ 15.2 Hz, CH_2N); 3.58 (s, 3H, OMe); 3.08 (s, 3H, NMe); 3.00 (s, 3H, NMe). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 154.5, 142.6, 131.2 (C arom quat and C=C); 153.3, 152.5, 138.6, 136.7, 128.6, 127.2, 124.9, 123.6, 120.0 (CH arom and CH py); 117.4 (C=C); 75.0 (CH_2N); 55.1 (OMe); 53.0, 52.6 (NMe).

3.19. Palladacycle **2d**

This compound was obtained accordingly to the general procedure using the palladacycle **2b** and 2-picoline (0.025 g, 81% yield). *Anal.* $C_{18}H_{19}Cl_2F_3N_2Pd$ (497.68) requires C, 43.44; H, 3.85; N, 5.63. Found: C, 43.31; H, 3.92; N, 5.57. ^{1}H NMR ($CDCl_3$): δ 8.31 (d, 1H, $^3J_{HH} = 5.8$ Hz, H arom picoline); 8.27 (d, 1H, $^3J_{HH} = 5.8$ Hz, H arom picoline); 7.39–6.56 (m, 14H, H arom and H arom picoline); 4.02 (d, 1H, $^2J_{HH} = 15.2$ Hz, CH_2N) and 3.41 (d, 1H, $^2J_{HH} = 15.2$ Hz, CH_2N); 3.74 (d, 1H, $^2J_{HH} = 15.2$ Hz, CH_2N) and 3.64 (d, 1H, $^2J_{HH} = 15.2$ Hz, CH_2N); 3.17 (s, 3H, Me picoline); 3.09 (s, 3H, NMe); 3.06 (s, 3H, Me picoline); 3.00 (s, 3H, NMe), 2.98 (s, 3H, NMe), 2.95 (s, 3H, NMe). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 160.3, 158.7 141.7, 141.2 (C arom quat and C=C); 152.0, 151.8, 136.8, 136.7, 131.0, 130.7, 129.2, 127.4, 125.5, 125.2, 125.0, 124.9, 121.5 (CH arom and CH picoline); 126.3, 125.8 (q, 1C, $^3J_{FC} = 5.4$ Hz, CH arom); 124.3 (q, 1C, $^1J_{FC} = 275$ Hz, CF_3); (C arom quat ipso CF_3: not observed); 119.3, 119.2 (C = C); 75.4, 75.2 (CH_2N); 53.2, 52.9, 52.5, 52.3 (NMe); 27.5, 27.0 (Me picoline).

4. Supplementary material

Tables of full crystal data, atomic coordinates, calculated hydrogen coordinates, anisotropic thermal parameters, and a complete list of bond lengths and angles have been posited with the Cambridge Crystallographic Data Centre, CCDC Nos. 197910-197913. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 IE2, UK (fax +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www:http://www.ccdc.cam.ac.uk).

Acknowledgements

This work was supported by grants from FAPERGS and CNPq (Brazil). Dr. M.R.M. thanks the CNPq for a visiting scientific grant.

References

[1] A.C. Cope, E.C. Friedrich, J. Am. Chem. Soc. 90 (1968) 909.
[2] (a) See for recent reviews M. Albrecht, G. van Koten, Angew. Chem. Int. Ed. 40 (2001) 3750;
(b) J. Dupont, M. Pfeffer, J. Spencer, Eur. J. Inorg. Chem. (2001) 1917.
[3] G.R. Newkome, W.E. Puckett, V.R. Gupta, G.E. Kiefer, Chem. Rev. 86 (1986) 451.
[4] (a) See for the chloropalladation of heterosubstituted alkynes T. Yukawa, S. Tsutsumi, Inorg. Chem. 7 (1968) 1458;
(b) J.E. Bäckvall, Y.I.M. Nilsson, R.G.P. Gatti, Organometallics 14 (1995) 4242;
(c) J. Dupont, N.R. Basso, M.R. Meneghetti, Polyhedron 15 (1996) 2299;
(d) J. Dupont, N.R. Basso, M.R. Meneghetti, R.A. Konrath, R. Burrow, M. Horner, Organometallics 16 (1997) 2386;
(e) G. Ebeling, M.R. Meneghetti, F. Rominger, J. Dupont, Organometallics 21 (2002) 3221.
[5] E.L. Eliel, S.H. Wilen, Stereochemistry of Organic Compounds, Wiley, New York, 1993, pp. 1142–1155.
[6] A.D. Ryabov, L.G. Kuzmina, V.A. Polyakov, G.M. Kazankov, E.S. Ryabova, M. Pfeffer, R. Vaneldik, J. Chem. Soc. Dalton Trans. (1995) 999.
[7] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery Jr., R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, J.L. Andres, C. Gonzalez, M. Head-Gordon, E.S. Replogle, J.A. Pople, Gaussian 98, Revision A.5; Gaussian, Inc., Pittsburgh, PA, 1998.
[8] (a) R.G. Pearson, Inorg. Chem. 12 (1973) 712;
(b) See for recent example of antisymbiotic effect P. Braunstein, F. Naud, A. Dedieu, M.-M. Rohmer, A. DeCian, S.J. Rettig, Organometallics 20 (2001) 2966.
[9] (a) C. Lee, W. Yang, R.G. Parr, Phys. Rev. B 37 (1988) 785;
(b) A.D. Becke, Phys. Rev. A 38 (1988) 3098.
[10] T.H. Dunning, Jr., P.J. Hay, in: H.F. Schaefer, III (Ed.), Modern Theoretical Chemistry, vol. 3, Plenum, New York, 1976, p. 1.
[11] (a) P.J. Hay, W.R. Wadt, J. Chem. Phys. 82 (1985) 270;
(b) W.R. Wadt, P.J. Hay, J. Chem. Phys. 82 (1985) 284;
(c) P.J. Hay, W.R. Wadt, J. Chem. Phys. 82 (1985) 299.
[12] G.M. Sheldrick, SHELXTL, Bruker Analytical X-ray-Division, Madison, WI, 1997
[13] P.A.A. Klusener, J.C. Hanekamp, L. Brandsma, P.V. Schleyer, J. Org. Chem. 55 (1990) 1311.