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# Atropisomerism in palladacycles derived from the chloropalladation of heterosubstituted alkynes

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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<sub>6</sub>H<sub>4</sub>C=CCH<sub>2</sub>NMe<sub>2</sub> (**1a**, Y = H; **2a**, Y = CF<sub>3</sub>; **3a**, Y = OMe; **4a**, Y = SMe and **5a**, Y = NH<sub>2</sub>) affords palladacycles in different ratios of isomers (geometric and atropisomers). In solution, the parent alkyne (Y = H) and the CF<sub>3</sub> substituted derivative generate a mixture of *cisoid* and *transoid* chloro-bridged dimer palladacycles of the type {Pd[ $\kappa^1$ -C,  $\kappa^1$ -*N*-C=(Y-2-C<sub>6</sub>H<sub>4</sub>)C(Cl)CH<sub>2</sub>NMe<sub>2</sub>]( $\mu$ -Cl)}<sub>2</sub>. Moreover, in the case of Y = CF<sub>3</sub> 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<sub>3</sub>) 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[ $\kappa^1$ -C,  $\kappa^1$ -*N*,  $\kappa^1$ -*O*-C=(MeO-2-C<sub>6</sub>H<sub>4</sub>)C(Cl)CH<sub>2</sub>NMe<sub>2</sub>](Cl) assisted through the weak coordination of the OMe group. Pincer palladacycles Pd[ $\kappa^1$ -C,  $\kappa^1$ -*N*,  $\kappa^1$ -*O*-C=(Y-2-C<sub>6</sub>H<sub>4</sub>)C(Cl)CH<sub>2</sub>NMe<sub>2</sub>](Cl) (Y = SMe and NH<sub>2</sub>) 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<sup>-1</sup> 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<sub>2</sub>, PR<sub>2</sub>, 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

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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

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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<sub>3</sub>)<sub>4</sub>/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, <sup>1</sup>H and <sup>13</sup>C NMR (Section 3).

The reaction of alkynes 1a-5a with a methanolic solution of Li<sub>2</sub>PdCl<sub>4</sub> 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, <sup>1</sup>H and <sup>13</sup>C NMR.



#### 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<sub>2</sub>Cl<sub>2</sub> rings (the Pd<sub>2</sub>Cl<sub>2</sub>-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<sub>2</sub> 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<sub>2</sub> (Table 2) and this can be attributed to the higher *trans influence* of the C compared to the NMe<sub>2</sub>. This bond length difference is similar to those usually observed in analogous halidebridged 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

<sup>1</sup>H NMR spectra of **1b** in CDCl<sub>3</sub> 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 <sup>1</sup>H NMR spectrum) and the proportion of the *cisoid* and *transoid* isomers do not change with time or temperature, as checked by <sup>1</sup>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<sub>2</sub> group and four AB spin systems for the methylene hydrogens in its <sup>1</sup>H NMR spectrum. As for compound 1b, the proportion of these isomers does not change with time or temperature (checked by <sup>1</sup>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 <sup>1</sup>H NMR spectrum of a solution prepared at 0 °C in CDCl<sub>3</sub> 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 <sup>1</sup>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<sub>2</sub> 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-C11	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.

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 <sup>1</sup>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

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

1b	2b <sup>a</sup>	
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"	2d	
36 <sup>th</sup> C1-Pd1-N1 82.74(16)	2d C1-Pd1-N2 93.02(10)	
3b <sup>a</sup> C1-Pd1-N1 82.74(16) C1-Pd1-Cl1 95.60(12)	2d C1-Pd1-N2 93.02(10) C1-Pd1-N1 82.56 (10)	
3b <sup>a</sup> C1-Pd1-N1 82.74(16) C1-Pd1-Cl1 95.60(12) N1-Pd1-Cl1 178.24(12)	2d C1-Pd1-N2 93.02(10) C1-Pd1-N1 82.56 (10) N2-Pd1-N1 175.02 (10)	
3b <sup>a</sup> C1-Pd1-N1 82.74(16) C1-Pd1-Cl1 95.60(12) N1-Pd1-Cl1 178.24(12) C1-Pd1-Cl2 176.93(13)	2d C1-Pd1-N2 93.02(10) C1-Pd1-N1 82.56 (10) N2-Pd1-N1 175.02 (10) C1-Pd1-Cl1 177.84 (8)	
3b <sup></sup> C1-Pd1-N1 82.74(16) C1-Pd1-Cl1 95.60(12) N1-Pd1-Cl1 178.24(12) C1-Pd1-Cl2 176.93(13) N1-Pd1-Cl2 95.99(11)	2d C1-Pd1-N2 93.02(10) C1-Pd1-N1 82.56 (10) N2-Pd1-N1 175.02 (10) C1-Pd1-Cl1 177.84 (8) N2-Pd1-Cl1 88.98 (7)	
3b <sup>a</sup> C1-Pd1-N1 82.74(16) C1-Pd1-Cl1 95.60(12) N1-Pd1-Cl1 178.24(12) C1-Pd1-Cl2 176.93(13) N1-Pd1-Cl2 95.99(11) Cl1-Pd1-Cl2 85.63(4)	2d C1-Pd1-N2 93.02(10) C1-Pd1-N1 82.56 (10) N2-Pd1-N1 175.02 (10) C1-Pd1-Cl1 177.84 (8) N2-Pd1-Cl1 88.98 (7) N1-Pd1-Cl1 95.47 (7)	
3b <sup>a</sup> C1-Pd1-N1 82.74(16) C1-Pd1-Cl1 95.60(12) N1-Pd1-Cl1 178.24(12) C1-Pd1-Cl2 176.93(13) N1-Pd1-Cl2 95.99(11) Cl1-Pd1-Cl2 85.63(4) Cl1-Pd2-Cl2 85.73(4)	2d C1-Pd1-N2 93.02(10) C1-Pd1-N1 82.56 (10) N2-Pd1-N1 175.02 (10) C1-Pd1-Cl1 177.84 (8) N2-Pd1-Cl1 88.98 (7) N1-Pd1-Cl1 95.47 (7) C1-C2-Cl2 123.5 (2)	
3b <sup>a</sup> C1-Pd1-N1 82.74(16) C1-Pd1-Cl1 95.60(12) N1-Pd1-Cl1 178.24(12) C1-Pd1-Cl2 176.93(13) N1-Pd1-Cl2 95.99(11) Cl1-Pd1-Cl2 85.63(4) Cl1-Pd2-Cl2 85.73(4) Pd2-Cl1-Pd1 97.16(4)	2d C1-Pd1-N2 93.02(10) C1-Pd1-N1 82.56 (10) N2-Pd1-N1 175.02 (10) C1-Pd1-Cl1 177.84 (8) N2-Pd1-Cl1 88.98 (7) N1-Pd1-Cl1 95.47 (7) C1-C2-Cl2 123.5 (2) C3-C2-Cl2 114.3 (2)	

<sup>a</sup> Mean values of both parts of the dimers for **2b** and **3b**.

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 <sup>1</sup>H NMR spectrum of 1c-3c indicated that these compounds were isolated as single isomers. As expected the methylene hydrogens and NMe<sub>2</sub> in 1c are equivalent (they appear as singlets) whereas in 2c and 3c they are inequivalent (AB spin pattern for the CH<sub>2</sub> and two singlets for the NMe<sub>2</sub> 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 <sup>1</sup>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<sup>-1</sup> 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 <sub>24</sub> H <sub>30</sub> Cl <sub>4</sub> N <sub>2</sub> O <sub>2</sub> Pd <sub>2</sub>	$C_{18}H_{19}Cl_2F_3N_2Pd$
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	$Pna2_1$
Ζ	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)
$\beta$ (°)	108.702(1)	116.523(1)	113.980(1)	90
Volume (Å <sup>3</sup> )	1218.66(5)	5881.3(2)	5699.96(11)	1990.93(7)
$\rho_{\rm calc} ({\rm g}{\rm cm}^{-3})$	1.83	1.83	1.71	1.66
$\mu (mm^{-1})$	1.93	1.64	1.66	1.23
Crystal shape	Polyhedron	Polyhedron	Polyhedron	Polyhedron
Crystal dimensions (mm <sup>3</sup> )	$0.50\times0.30\times0.04$	$0.22\times0.18\times0.05$	$0.36 \times 0.20 \times 0.06$	$0.37 \times 0.33 \times 0.24$
$\theta$ range for data collected (°)	3.0-27.5	1.8-27.5	1.9-27.5	2.3-27.5
Index range	$-16 \leq h \leq 16$	$-29 \leq h \leq 29$	$-26 \leq h \leq 23$	$-23 \leq h \leq 23$
	$-10 \leqslant k \leqslant 10$	$-10 \leq k \leq 13$	$-16 \leq k \leq 16$	$-8 \leq k \leq 10$
	$-15 \leq l \leq 15$	$-33 \leq l \leq 29$	$-25 \leq l \leq 30$	$-14 \leq l \leq 17$
Reflections collected	12064	9172	20 226	5720
Independent reflections	2794 ( $R_{\rm int} = 0.0285$ )	5833 ( $R_{\rm int} = 0.0393$ )	6477 ( $R_{\rm int} = 0.0404$ )	$3617 (R_{int} = 0.0172)$
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



time or temperature (determined by <sup>1</sup>H NMR spectro-scopy).

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, C11, 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<sup>-1</sup> more stable than its *syn* analogue corroborating the experimental results, which indicated the pre-





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-1propynes 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<sub>2</sub>NCH(Me)C=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-







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 Ka radiation. For 1b and 3b, frames corresponding to a sphere of data were collected using the omega-scan technique, 20 s exposures of  $0.3^{\circ}$  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  $0.3^{\circ}$ 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 fullmatrix 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]<sup>•+</sup>; 115, [M-NMe<sub>2</sub>]<sup>+</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.46–7.38 (m, 2H, H arom); 7.33–7.23 (m, 3H, H arom); 3.45 (s, 2H, CH<sub>2</sub>N); 2.35 (s, 6H, NMe<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  132.1, 128.5, 128.1 (CH arom); 124.1 (C arom quat); 85.9, 85.1 (C=C); 49.8 (CH<sub>2</sub>N); 44.4 (NMe<sub>2</sub>).

# 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<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (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). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.52–7.37 (m, 4H, H arom); 3.45 (s, 2H, CH<sub>2</sub>N); 2.30 (s, 6H, NMe<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  133.9, 131.1, 127.4 (CH arom); 131.1 (q, 1C, <sup>2</sup>J<sub>FC</sub> = 30.6 Hz, C arom quat ipso CF<sub>3</sub>); 125.4 (q, 1C, <sup>3</sup>J<sub>FC</sub> = 5.1 Hz, CH arom); 123.4 (q, 1C, <sup>1</sup>J<sub>FC</sub> = 273 Hz, CF<sub>3</sub>); 121.6 (C arom quat); 90.7, 81.0 (C≡C); 48.1 (CH<sub>2</sub>N); 43.6 (NMe<sub>2</sub>).

# 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  $(2 \times 10 \text{ ml})$  and the combined organic extract was dried with MgSO<sub>4</sub>. 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<sup>-1</sup>): 2232 ( $v_{C=C}$ ). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.40 (d, 1H,  ${}^{3}J_{\rm HH} = 7.4$  Hz, H arom); 7.25 (t, 1H,  ${}^{3}J_{\text{HH}} = 7.4$  Hz, H arom); 6.90–6.84 (m, 2H, H arom); 3.86 (s, 3H, OMe); 3.52 (s, 2H, CH<sub>2</sub>N); 2.37 (s, 6H, NMe<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  159.8, 112.3 (C arom quat); 133.5, 129.3, 120.2, 110.4 (CH arom); 88.6, 81.3  $(C \equiv C)$ ; 55.6 (OMe); 48.7 (CH<sub>2</sub>N); 44.0 (NMe<sub>2</sub>).

# 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 ( $v_{C=C}$ ). GC-MS (m/z, rel int%, [peak]): 205, 2, [M]<sup>•+</sup>; 204, 10, [M-1]<sup>+</sup>; 190, 15, [M-15]<sup>+</sup>; 160, 100, [M- $Me_2NH$ ]<sup>•</sup><sup>+</sup>; 82, 12,  $[Me_2NCH_2C \equiv C]$ <sup>+</sup>; 58, 18,  $[Me_2N =$  $(CH_2)^+$ . <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.44–7.06 (m, 4H, H arom); 3.59 (s, 2H, CH<sub>2</sub>N); 2.43 (s, 3H, SMe); 2.18 (s, 6H, NMe<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): 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<sub>2</sub>N); 44.4 (NMe<sub>2</sub>); 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), 3dimethylamino-1-propyne (1.89 g, 22.5 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (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  $(2 \times 10 \text{ ml})$  and the combined organic extract was dried with MgSO<sub>4</sub>. 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 ( $v_{C=C}$ ). GC-MS (m/z, rel int%, [peak]): 174, 29, [M]<sup>•+</sup>; 159, 7, [M-CH<sub>3</sub>]<sup>+</sup>; 130, 100, [M-NMe<sub>2</sub>]<sup>+</sup>; 58, 23,  $[Me_2N=CH_2]^+$ . <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.31, 6.72 (d, 1H,  ${}^{3}J_{HH} = 7.5$  Hz, H arom); 7.14, 6.70 (d, 1H,  ${}^{3}J_{HH} =$ 7.5 Hz, H arom); (4.24 (br s, 2H, NH<sub>2</sub>); 3.57 (s, 2H, CH<sub>2</sub>N); 2.40 (s, 6H, NMe<sub>2</sub>).  ${}^{13}C{}^{1}H{}$  NMR (CDCl<sub>3</sub>):  $\delta$ 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<sub>2</sub>N); 44.1  $(NMe_2).$ 

#### 3.9. Synthesis of palladacycles 1b-3b: general procedure

A Li<sub>2</sub>PdCl<sub>4</sub> solution was prepared by dissolving PdCl<sub>2</sub> (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  $^{\circ}$ 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<sub>11</sub>H<sub>13</sub>Cl<sub>2</sub>NPd)<sub>2</sub> (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<sup>-1</sup>): 1600 ( $v_{C=C}$ ). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.35–6.90 (m, 10H, H arom); 3.61 (s, 2H, CH<sub>2</sub>N); 3.59 (s, 2H, CH<sub>2</sub>N); 2.88 (s, 6H, NMe<sub>2</sub>); 2.77 (s, 6H, NMe<sub>2</sub>). <sup>1</sup>H NMR (CDCl<sub>3</sub>+Py-d<sub>5</sub>):  $\delta$  6.92–6.75 (m, 5H, H arom); 3.67 (s, 2H, CH<sub>2</sub>N); 3.01 (s, 6H, NMe<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  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<sub>2</sub>N); 53.2, 52.9 (NMe<sub>2</sub>).

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

Accordingly to the described general procedure, a yellow solid was obtained (1.10 g, 65% yield). Anal. (C12H12Cl2F3NPd)2 (809.11) requires C, 35.63; H, 2.99; N, 3.46. Found: C, 35.81; H, 2.93; N, 3.45. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.60–6.80 (m, 16H, H arom); 3.92–3.85 (m, 2H, CH<sub>2</sub>N); 3.82-3.75 (m, 2H, CH<sub>2</sub>N); 3.38 (d, 2H, J =6.1 Hz, CH<sub>2</sub>N); 3.30 (d, 2H, J = 6.1 Hz, CH<sub>2</sub>N); 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). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  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,  ${}^{3}J_{FC} = 5.1$ Hz, CH arom); 124.5, 124.4, 124.3, 124.1 (q, 1C,  ${}^{1}J_{FC} =$ 271 Hz, CF<sub>3</sub>); (C arom quat ipso CF<sub>3</sub>: not observed); 118.2, 117.8, 117.7 (C=C); 76.6, 74.6, 74.5, 74.4 (CH<sub>2</sub>N); 53.4, 53.2, 53.0, 52.8, 52.7 (NMe). <sup>13</sup>C{<sup>1</sup>H} NMR  $(CDCl_3 + Py-d_5): \delta$  141.9, 141.5 (C arom quat and C= C); 130.9, 128.9, 125.3, (CH arom); 125.7 (q, 1C,  ${}^{3}J_{CF} =$ 5 Hz, CH arom); 124.2 (q, 1C,  ${}^{1}J_{CF} = 275$  Hz, CF<sub>3</sub>); (C arom quat ipso CF<sub>3</sub>: not observed); 119.4 (C=C); 75.1 (CH<sub>2</sub>N); 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<sup>-1</sup>): 1631 ( $v_{C=C}$ ).<sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.18 (t, 1H,  ${}^{3}J_{HH} = 6.9$  Hz, H arom); 6.93 (d, 1H,  ${}^{3}J_{HH} = 7.4$  Hz, H arom); 6.77 (t, 1H,  ${}^{3}J_{HH} = 7.4$  Hz, H arom); 6.65 (d, 1H,  ${}^{3}J_{HH} = 7.6$  Hz, H arom); 3.68 (s, 3H, OMe); 3.59 (s, 2H, CH<sub>2</sub>N); 2.83 (s, 6H, NMe<sub>2</sub>).  ${}^{13}C{}^{1}H{}$  NMR (CDCl<sub>3</sub>):  $\delta$  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<sub>2</sub>N); 55.8 (OMe); 52.7 (NMe<sub>2</sub>).

#### 3.13. Synthesis of palladacycle (4b)

A Li<sub>2</sub>PdCl<sub>4</sub> solution was prepared by dissolving, with gentle heating, PdCl<sub>2</sub> (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<sub>2</sub>Cl<sub>2</sub>. 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<sub>12</sub>H<sub>15</sub>Cl<sub>2</sub>NSPd (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<sup>-1</sup>): 1590 ( $\nu_{C=C}$ ). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  8.51 (d, 1H, J = 7.7 Hz, H arom); 7.43–7.28 (m, 3H, H arom); 3.95 (s, 2H, CH<sub>2</sub>N); 3.00 (s, 6H, NMe<sub>2</sub>); 2.87 (s, 3H, SMe).  $^{13}C{^{1}H}$  NMR (CDCl<sub>3</sub>):  $\delta$  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<sub>2</sub>N); 52.1 (NMe<sub>2</sub>); 26.7 (SMe).

#### 3.14. Synthesis of palladacycle (5b)

A Li<sub>2</sub>PdCl<sub>4</sub> solution was prepared by dissolving PdCl<sub>2</sub> (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<sub>2</sub>Cl<sub>2</sub>. 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<sub>11</sub>H<sub>14</sub>Cl<sub>2</sub>N<sub>2</sub>Pd (351.57) requires C, 37.58; H, 4.01; N, 7.97. Found: C, 37.88; H, 3.91; N, 7.81. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  8.29 (m, 1H, H arom); 7.23–7.13 (m, 3H, H arom); 5.62 (br s, 2H, NH<sub>2</sub>); 3.72 (s, 2H, CH<sub>2</sub>N); 2.71 (s, 6H, NMe<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  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<sub>2</sub>N); 52.1 (NMe<sub>2</sub>).

# 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<sub>16</sub>H<sub>18</sub>Cl<sub>2</sub>N<sub>2</sub>Pd (415.66) requires C, 46.23, H, 4.36, N, 6.74. Found: C, 46.61, H, 4.37, N, 6.54. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  8.30 (d, 2H, <sup>3</sup>J<sub>HH</sub> = 4.9 Hz, H py); 7.42 (t, 1H, <sup>3</sup>J<sub>HH</sub> = 6.1 Hz, H py); 6.95–6.82 (m, 7H, H arom and H py); 3.69 (s, 2H, CH<sub>2</sub>N); 3.03 (s, 6H, NMe<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>)  $\delta$  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<sub>2</sub>N); 53.0 (NMe<sub>2</sub>).

#### 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<sub>17</sub>H<sub>17</sub>Cl<sub>2</sub>F<sub>3</sub>N<sub>2</sub>Pd (483.66) requires C, 42.22; H, 3.54; N, 5.79. Found: C, 42.37; H, 2.67; N, 5.42. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  8.32 (d, 2H, <sup>3</sup>J<sub>HH</sub> = 4.9 Hz, H py); 7.42 (t, 2H, <sup>3</sup>J<sub>HH</sub> = 6.2 Hz, H py); 7.29–6.81 (m, 6H, H arom and H py); 3.92 (d, 1H, <sup>2</sup>J<sub>HH</sub> = 15.2 Hz, CH<sub>2</sub>N); 3.46 (d, 1H, <sup>2</sup>J<sub>HH</sub> = 15.2 Hz, CH<sub>2</sub>N); 3.10 (s, 3H, NMe); 2.95 (s, 3H, NMe). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>)  $\delta$  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, <sup>3</sup>J<sub>FC</sub> = 5.1 Hz, CH arom); 124.3 (q, 1C, <sup>1</sup>J<sub>FC</sub> = 274 Hz, CF<sub>3</sub>); (C arom quat ipso CF<sub>3</sub>: not observed); 119.5 (C=C); 75.2 (CH<sub>2</sub>N); 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<sub>17</sub>H<sub>20</sub>Cl<sub>2</sub>N<sub>2</sub>OPd (445.68) requires C, 45.81; H, 4.52; N, 6.29. Found: C, 45.60; H, 4.55; N, 6.19. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  8.29 (d, 2H, <sup>3</sup>J<sub>HH</sub> = 4.9 Hz, H py); 7.41 (t, 2H, <sup>3</sup>J<sub>HH</sub> = 6.2 Hz, H py); 6.98–6.85 (m, 3H, H arom and H py); 6.64 (t, 1H, <sup>3</sup>J<sub>HH</sub> = 7.4 Hz, H arom); 6.34 (d, 1H, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz, H arom); 3.75 (d, 1H, <sup>2</sup>J<sub>HH</sub> = 15.2 Hz, CH<sub>2</sub>N); 3.62 (d, 1H, <sup>2</sup>J<sub>HH</sub> = 15.2 Hz, CH<sub>2</sub>N); 3.68 (s, 3H, NMe); 3.00 (s, 3H, NMe). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>)  $\delta$  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<sub>2</sub>N); 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 2picoline (0.025 g, 81% yield). Anal. C<sub>18</sub>H<sub>19</sub>Cl<sub>2</sub>F<sub>3</sub>N<sub>2</sub>Pd (497.68) requires C, 43.44; H, 3.85; N, 5.63. Found: C, 43.31; H, 3.92; N, 5.57. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 8.31 (d, 1H,  ${}^{3}J_{HH} = 5.8$  Hz, H arom picoline); 8.27 (d, 1H,  ${}^{3}J_{\rm HH} = 5.8$  Hz, H arom picoline); 7.39–6.56 (m, 14H, H arom and H arom picoline); 4.02 (d, 1H,  ${}^{2}J_{HH} = 15.2$ Hz, CH<sub>2</sub>N) and 3.41 (d, 1H,  ${}^{2}J_{HH} = 15.2$  Hz, CH<sub>2</sub>N); 3.74 (d, 1H,  ${}^{2}J_{HH} = 15.2$  Hz, CH<sub>2</sub>N) and 3.64 (d, 1H,  $^{2}J_{\text{HH}} = 15.2 \text{ Hz}, \text{CH}_{2}\text{N}$ ; 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). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ 160.3, 158.7 141.7, 141.2 (C arom guat 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,  ${}^{3}J_{FC} = 5.4$  Hz, CH arom); 124.3 (q, 1C,  ${}^{1}J_{FC} = 275$  Hz, CF<sub>3</sub>); (C arom quat ipso CF<sub>3</sub>: not observed); 119.3, 119.2 (C = C); 75.4, 75.2 (CH<sub>2</sub>N); 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 Crystal-lographic 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).

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