Available online at www.sciencedirect.com
SCIENCE DIRECT®
PERGAMON
Polyhedron 22 (2003) 1665–1671
POLYHEDRON
www.elsevier.com/locate/poly

The retro-chloropalladation reaction of heterosubstituted alkynes

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

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

Received 30 October 2002; accepted 15 April 2003

Abstract

The bridge-splitting reaction of dimeric palladacycles of the type $\{Pd[\kappa^1\text{-}C, \kappa^1\text{-}N\text{-}C(R)=C(Cl)CH_2NMe_2](\mu\text{-}Cl)\}_2$ (R = Ph, Me, CH_2CH_2OH), derived from the chloropalladation of propargyl amines ($RC\equiv CCH_2NMe_2$), with pyridine (Py), triphenylphosphine (PPh_3) and *tert*-butylisonitrile (^{t}BuNC) affords the monomeric compounds $[PdC(R)=CCH_2NMe_2(Cl)L]$ (L = Py, PPh_3, ^{t}BuNC). These monomeric compounds are not stable in solution and undergo retro-chloropalladation reactions yielding the propargyl amines and $[PdCl(L)\text{-}\mu\text{-}Cl]_2$. This process is strongly dependent upon the nature of the incoming nucleophile (L), the R group on the metallated ligand and the temperature. The retro-halopalladation reaction is almost instantaneous in the case of the reaction of the bromo derivative $[PdC(Ph)=C(Br)CH_2NMe_2\text{-}\mu\text{-}Br]_2$ and pyridine at room temperature. These results can be rationalized in terms of the stability of the Pd–C bond of the intermediate monomeric compound $[PdC(R)=C(X)CH_2NMe_2(X)L]$, that is directly related to the nature of its substituents R (Ph, Me and CH_2CH_2OH), of ligands which are both *cis* and *trans* to it (Py, CN^tBu, PPh_3, Cl and Br) and the temperature.

Keywords: Retro-chloropalladation reaction; Monomeric compounds; Alkynes; Propargyl amines

1. Introduction

The halopalladation reaction of alkynes leads to series of very useful Pd-vinyl intermediate species for organic synthesis. The Pd–C bond of these intermediates can be selectively trapped with electrophilic reagents such as allyl halides and dienes to afford highly functionalized organic molecules [1]. The presence of potentially two electron donor groups in the alkyne fragment, such as in the case of propargyl amines and thioethers, allows the isolation of these compounds in the form of palladacycles [2]. Indeed, the halopalladation of heterosubstituted alkynes, is now emerging as a new alternative method for the preparation of various types of palladacycles [3]. It has been proposed that this halopalladation, in particular chloropalladation, occurs via an intermolecular nucleophilic addition of the chloride anion onto the activated triple CC bond (Scheme 1) and that the stereochemical outcome (size of the formed palladacycle) of this reaction is under thermodynamic control.

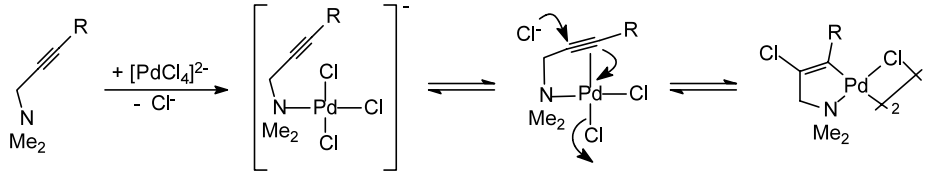
While investigating the bridge-splitting reaction of palladacycles derived from the chloropalladation of propargyl amines we have observed the retro-chloropalladation reaction. Herein we show for the first time the retro-chloropalladation of propargylamines and that this reaction is highly dependent on the alkyne and the other ligands around palladium.

2. Results and discussion

The reaction of **1a** with a methanolic solution of Li_2PdCl_4 at 5 °C affords almost instantaneously a yellow solid (palladacycle **2a**) that is isolated by filtration. It is interesting to note that prolonged reaction times significantly reduce the yield of **2a** that in solution slowly decomposes forming among various products $PdCl_2$ and **1a** (see below). Compound **2a** was isolated as

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

0277-5387/03/$ - see front matter
doi:10.1016/S0277-5387(03)00324-3



Scheme 1.

a yellow crystalline solid that is air and water stable, soluble in polar organic solvents such as dichloromethane and acetone and slightly soluble in hexanes. The ^{1}H and ^{13}C NMR spectra of **2a** in $CDCl_3$ show only one set of signals suggesting that it is present as a single isomer, that possesses the transoid-NMe_2 geometry through the chloro bridges (see later).

The molecular structure of **2a** has been ascertained by means of an X-ray diffraction analysis. Although the structure has a poor resolution ($R_1 = 0.152$) the obtained data can be used for the establishment of the nuclearity connectivity and the type of **2a** isomer formed. A ball and stick drawing is shown in Fig. 1 together with selected bond distances and angles. Crystallographic data and details of the structure determination are presented in Table 1. Tables of atomic coordinates, and thermal parameters are supplied as supporting information.

The crystal structure of **2a** contains discrete centrosymmetric dimeric palladacycles. The coordination sphere around each Pd center can be considered as essentially planar and this is also evident for the four-membered Pd_2Cl_2 rings.

The palladacycles **2b** and **2c** have been prepared from the chloropalladation of alkynes **1b** and **1c** as described earlier [3c]. The reaction of **2b** and **2c** with pyridine in dichloromethane at room temperature yields the corresponding monomeric palladacycles **3b** and **3c**, respectively, in almost quantitative yield (Scheme 2). Compounds **3b** and **3c** are stable in solution at room temperature. In contrast, the reaction of **2a** with pyridine, at room temperature, affords **1a** and $PdCl_2Py_2$ after 1 h, and the monomeric compound **3a** could not be isolated or detected in pure form. The formation of these products corresponds, formally, to the retro-chloropalladation reaction. The reaction of **2a** with an excess of pyridine was monitored by ^{1}H NMR spectroscopy at room temperature. Four compounds can be clearly identified in the ^{1}H NMR spectra immediately after addition of pyridine to a solution of **2a** in $CDCl_3$:

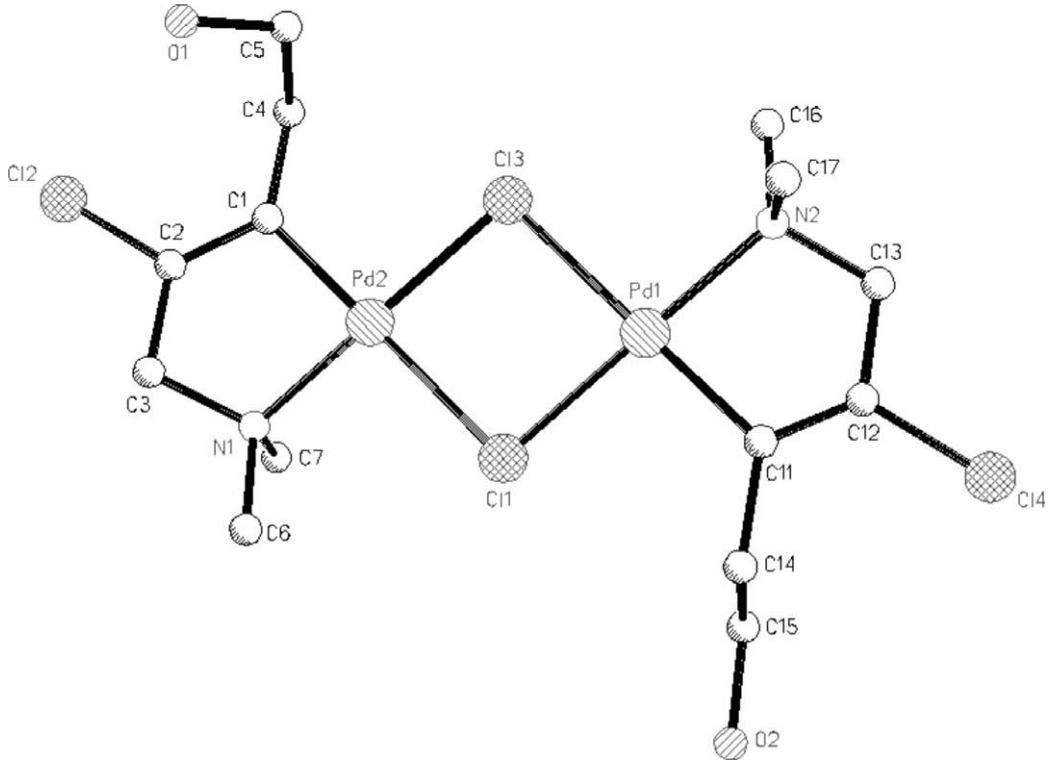
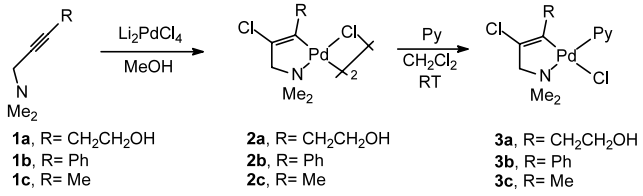


Fig. 1. Ball and stick drawing of **2a**. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Pd(1)–C(11): 1.96(2); Pd(1)–N(2): 2.05(2); Pd(1)–C(11): 2.347(7); Pd(1)–C(13): 2.463(7); C(11)–C(12): 1.32 (3); C(12)–C(l4): 1.76(3). C(11)–Pd(1)–C(l1): 95.9 (7); C(11)–Pd(1)–N(2): 82.8 (9); N(2)–Pd(1)–C(l3): 96.6 (6); C(l3)–Pd(1)–C(l1): 84.7 (2); C(l4)–C(12)–C(13): 114 (2).

Table 1
Crystal data and structure refinement for **2a**

Empirical formula	$C_{14}H_{26}Cl_4N_2O_2Pd_2$
Formula weight	608.97
Temperature (K)	200(2)
Wavelength (Å)	0.71073
Crystal system	monoclinic
Space group	$P2_1/c$
Unit cell dimensions	
a (Å)	5.7319(1)
b (Å)	13.0459(2)
c (Å)	22.6404(4)
α (°)	90
β (°)	96.317(1)
γ (°)	90
V (Å^3)	2067.12(6)
Z	4
D_{calc} (g cm^{-3})	1.96
Absorption coefficient (mm^{-1})	2.27
Crystal shape	polyhedron
Crystal size (mm)	0.28 × 0.18 × 0.05
θ Range for data collection (°)	0.9–24.7
Index ranges	$-6 \le h \le 6$, $-18 \le k \le 18$, $-26 \le l \le 26$
Reflections collected	17 422
Observed reflections [$I > 2\sigma(I)$]	3090
Independent reflections	3574 [$R_{int} = 0.1015$]
Absorption correction	none
Refinement method	full-matrix least-squares on F^2
Data/restraints/parameters	3574/0/98
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.152$, $wR_2 = 0.414$
Goodness-of-fit on F^2	3.37
Largest difference peak and hole (e Å^{-3})	7.03 and −2.99



Scheme 2.

alkyne **1a**, monomeric compound **3a**, $PdCl_2Py_2$ and ($PdCl_2$(**1a**)Py) **4a** (Scheme 3).

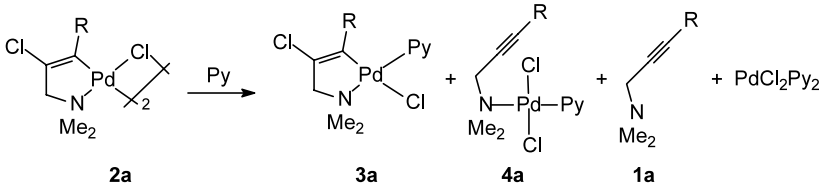
The evolution of this reaction with time is summarized in Fig. 3. The presence of alkyne **1a**, monomeric palladacycle **3a** and $PdCl_2Py_2$ in the reaction mixture was easily assigned in the ^{1}H NMR spectrum of the reaction mixture. The location of the pyridine ligand *trans* to the NMe_2 group in **3a** is based on the X-ray structure of analogous compounds [4] and on theoretical calculations (Gaussian) [5] which indicate that this isomer is 5.14 kcal mol^{-1} more stable than the *cis*-isomer (Fig. 2). Moreover, the *trans* isomer is always obtained in the bridge-splitting reaction of dimeric palladacycles upon reaction with L ligands such as pyridines, phosphines and isonitriles [6]. This selectivity can be explained by the antisymbiotic effect of the soft Pd(II) center that will place the incoming ligand *cis* to the Pd–C bond [7]. The structure of **4a** was based on the presence of a singlet at 2.73 ppm typical for a NMe_2 coordinated to Pd(II) and a triplet for the CH_2N at 3.60 ppm.

The monomeric compounds **5a**–**5c** and **6a**–**6b** could be observed in solution (^{1}H NMR spectroscopy) by the addition of ^{t}BuNC and PPh_3 to an NMR tube containing a $CDCl_3$ solution of the dimers **2a**–**2c** (Scheme 4). In the case of the reaction of **2c** with PPh_3 only free alkyne **1c** and the signals corresponding to PPh_3 were observed.

Compounds **5a**–**5c** and **6a**–**6b** are relatively stable at room temperature but eventually undergo retro-chloropalladation upon heating in $CDCl_3$ solution affording the free alkynes **1a**–**1c** and [Pd(L)Cl(μ-Cl)]$_2$. Note that isonitrile products resulting from the insertion of the isonitrile into the Pd–C bond have been observed [8]. It is also important to note that **2b** undergoes retro-chloropalladation even in the solid state at temperatures above 150 °C. Moreover, the retro-chloropalladation reaction also takes place almost instantaneously in the reaction of the bromo palladacycle **7b** (prepared by bromopalladation of alkyne **1b**) with pyridine at room temperature (Scheme 5).

It is also of note that attempts to prepare palladacycle **7b** by oxidative addition of (*E*)-1,2-dibromo-3-dimethylamino-1-phenyl-1-propene [9] with $Pd_2(dba)_3$ in $CHCl_3$ affords the alkyne **1b** and $PdBr_2$, among other unidentified products (Scheme 6). This result can be rationalized in terms of the formation of palladacycle **7b** followed by retro-bromopalladation to generate alkyne **1b** and $PdBr_2$. Indeed, heating a $CDCl_3$ solution of the palladacycle **7b** (prepared by reaction of **1b** with Li_2PdBr_4) generated the alkyne **1b** and $PdBr_2$. In contrast the chloro analogue **2b** does not undergo the retro-chloropalladation reaction under identical reaction conditions.

These results clearly indicate that the retro-halopalladation reaction is strongly dependent on the stability of



Scheme 3.

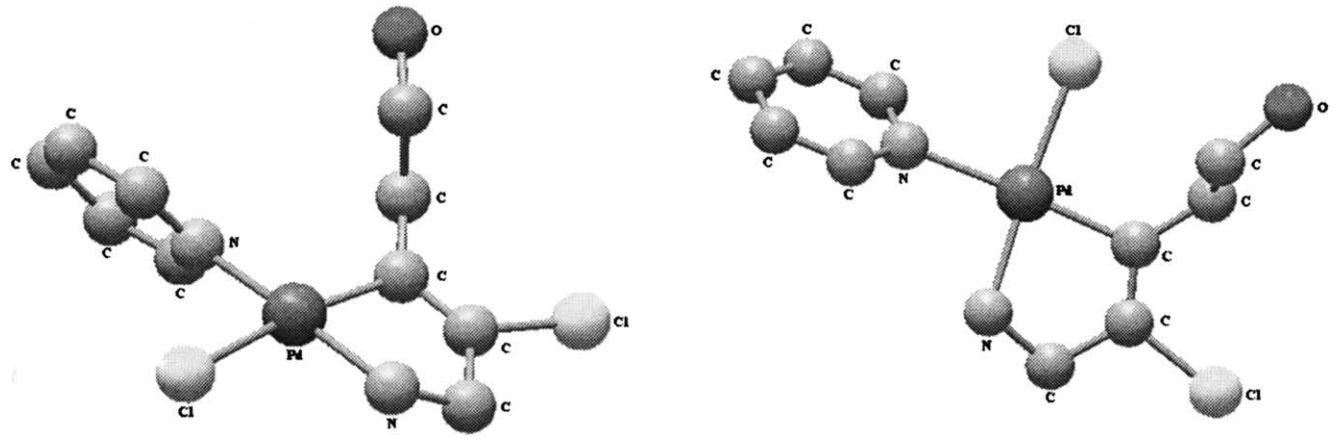
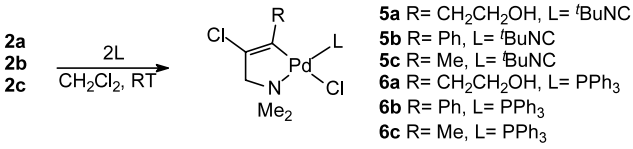
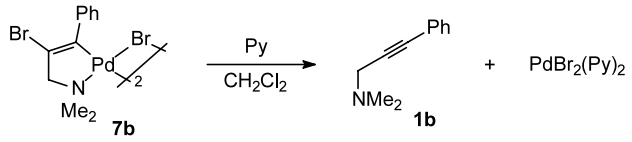


Fig. 2. Full optimized geometries of the *cis* and *trans* isomers of **3a** (H atoms have been omitted for clarity).



Scheme 4.



Scheme 5.

the Pd–C bond which is directly related to the nature of its substituents (Ph, Me and CH_2CH_2OH), to ligands which are in a relative *cis* or *trans* position (Py, CN^tBu, PPh_3, Cl and Br), and the temperature (Scheme 7).

The higher *trans*-influence of the bromo ligand than the chloro analogue can explain the difference of palladacycles **2b** and **7b** towards the retro-halopalladation reaction. The greater stabilization of the Pd–C bond in compounds **5a** and **6a** indirectly induced by the more effective back-donation properties of CNR and PPh_3 than Py in **3a** can account for the observed results. The influence of the R group linked to the Pd–C(vinyl) group (CH_2CH_2OH, Ph and Me) in **3a**–**3c** is not straightforward but it is reasonable to assume that the alcohol function in **3a** can provide anchimeric assistance during the C-halogen bond breaking step.

All these results strongly suggest that the retro-halopalladation reaction of alkynes occurs through a concerted mechanism identical to the one previously proposed for the halopalladation reaction. Moreover,

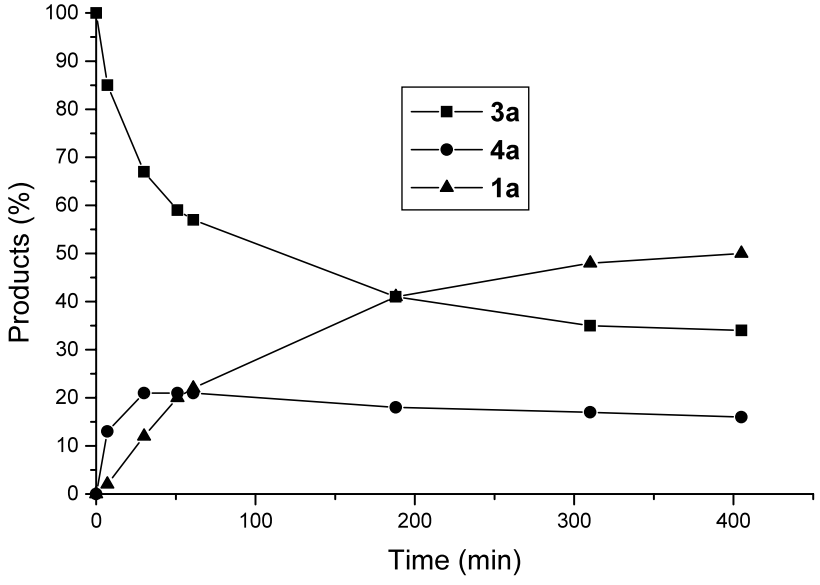
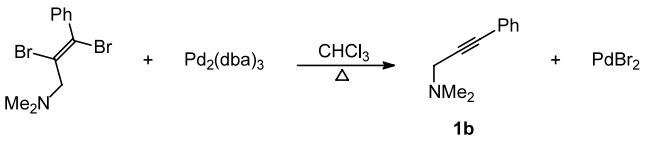


Fig. 3. The evolution of the reaction of **2a** with an excess of pyridine at room temperature in $CDCl_3$.



Scheme 6.

this process can explain why these palladacycles do not easily undergo insertion reactions with unsaturated substrates such as alkynes and isonitriles even at temperatures above 25 °C [10].

In summary the stability of palladacycles derived from the halopalladation of propargylamines in solution is strongly dependent upon the type of the alkyne substituents, halogen and temperature. Moreover, the retro-halopalladation is facilitated by the addition of nucleophiles such as pyridine, triphenylphosphine or *tert*-butylisonitrile.

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 alkynols were prepared according to known procedures [14]. Solvents were dried with adequate 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. The following compounds were prepared according to the published procedures: **1a** [3d]; **1b**, **1c**, **2b**, **2c** [3c]. 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

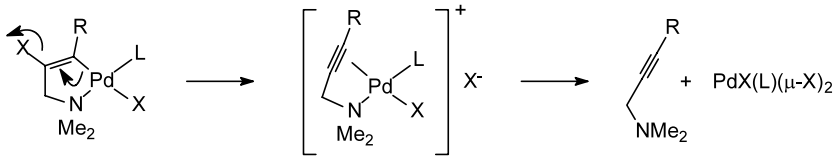
The energy of all calculated species was obtained by full geometry optimization without any constraint. The calculations were performed with the GAUSSIAN-98' [5] Program at a HF/B3LYP [11] level of theory, using a Dunning–Huzinaga D95 [12] basis set for the non-metal atoms and a DZ valence basis set plus an effective core potential for the palladium [13].

3.3. X-ray structure analysis of **2a**

Crystals were mounted on a glass fiber with perfluoropolyether. The measurements were carried out on a Bruker SMART-CCD diffractometer with graphite monochromated Mo Kα radiation. For **2a**, frames corresponding to a sphere of data were collected using the ω-scan technique, 20 s exposures of 0.3° in ω were taken. No absorption correction was applied, due to the bad quality of data. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods and expanded using Fourier techniques, all non-hydrogen atoms were refined with isotropic displacement parameters, hydrogen atoms were not considered. The full-matrix least-squares refinement against F^2 converged. All calculations were performed using the SHELXTL crystallographic software package of Bruker (G.M. Sheldrick, SHELXTL V5.10, Bruker REM AXS, Inc., Madison, WI, 1997).

3.4. Synthesis of palladacycle **2a**

A Li_2PdCl_4 solution was prepared by dissolving $PdCl_2$ (1.06 g, 6.00 mmol) and LiCl (0.63 g, 15.0 mmol) in hot methanol (20 ml), under vigorous stirring. After dissolution of the solids, this solution was cooled to 0 °C and a solution of 1-dimethylamino-2-pentyn-5-ol **1a** (0.76 g, 6.00 mmol) was added. The resulting yellow suspension was stirred at 0 °C for 15 min. Filtration and washing of the resulting solid with cold MeOH and drying under reduced pressure afforded the desired palladacycle (yellow solid, 1.18 g, 64% yield). M.p.: 105 °C (dec.). *Anal*.: $(C_7H_{13}Cl_2NOPd)_2$ (609.02) requires C, 27.61; H, 4.30; N, 4.60. Found: C, 27.41; H, 4.12; N, 4.54%. IR (KBr, cm^{-1}): 3304 (ν_{O-H}), 1617 ($\nu_{C=C}$). ^1H NMR ($CDCl_3$): δ 3.78 (t, 2H, $^3J_{HH} = 6.6$ Hz, CH_2O); 3.54 (s, 2H, CH_2N); 2.83 (s, 6H, NMe_2); 2.10 (t, 2H, $^3J_{HH} = 6.6$ Hz, $H_2C-C\equiv C$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 142.0, 117.4 (C≡C); 74.6 (CH_2N); 62.3 (CH_2O); 53.5 (NMe_2); 37.9 ($H_2C-C\equiv C$).



Scheme 7.

3.5. Synthesis of palladacycles **3a–c**, **5a–c** and **6a,b**

General procedure. The dimeric palladacycle (**2a**, **2b** or **2c**; 0.05 mmol) was dissolved in $CDCl_3$ (1.1 ml) and the required ligand (Py, ^{t}BuNC or Ph_3P; 0.05 mmol), dissolved in $CDCl_3$ (1 ml), was added and the ^{1}H NMR spectra recorded immediately.

3.6. Palladacycle **3a**

^{1}H NMR ($CDCl_3$): δ 8.77 (d, 2H, $^3J_{HH} = 5.4$ Hz, H py); 7.79 (1H, $^3J_{HH} = 7.6$ Hz, H py); 7.36 (m, 2H, H py); 3.60 (s, 2H, CH_2N); 3.38 (t, $^3J_{HH} = 6.6$ Hz, 2H, CH_2O); 2.91 (s, 6H, NMe_2); 1.77 (t, $^3J_{HH} = 6.6$ Hz, 2H, H_2C–C=C).

3.7. Palladacycle **3b**

This compound could be isolated from the NMR tube by addition of hexanes. *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%. ^{1}H 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).

3.8. Palladacycle **3c**

^{1}H NMR ($CDCl_3$): δ 8.77 (dd, $^3J_{HH} = 6.3$ Hz, $^4J_{HH} = 1.5$ Hz, 2H, H py); 7.79 (tt, 1H, $^3J_{HH} = 7.5$ Hz, $^4J_{HH} = 1.5$ Hz, H py); 7.36 (ddd, 2H, $^3J_{HH} = 6.3$ and 7.5 Hz, $^4J_{HH} = 1.5$ Hz, H py); 3.53 (q, 2H, $^5J_{HH} = 2.0$ Hz, CH_2N); 2.93 (s, 6H, NMe_2); 1.18 (t, 3H, $^5J_{HH} = 2.0$ Hz, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 152.8, 137.8, 125.3 (CH py); 141.8, 116.2 (C=C); 74.6 (CH_2N); 52.9 (NMe_2); 20.0 (CH_3).

3.9. Palladacycle **5a**

^{1}H NMR ($CDCl_3$): δ 3.75 (t, 2H, $^3J_{HH} = 6.9$ Hz, CH_2O); 3.56 (s, 2H, CH_2N); 2.83(s, 6H, NMe_2); 2.48 (t, 2H, $^3J_{HH} = 6.9$ Hz, H_2C–C=C); 1.54 (s, 9H, ^{t}Bu). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 143.9, 121.7 (C=C); 73.8 (CH_2N); 61.5 (CH_2O), 58.5 (C quat ^{t}Bu); 51.2 (NMe_2); 29.8 (Me_3C); isonitrile carbon: not observed.

3.10. Palladacycle **5b**

^{1}H NMR ($CDCl_3$): δ 7.45–7.10 (m, 5H, H arom); 3.70 (s, 2H, CH_2N); 2.92 (s, 6H, NMe_2); 1.07 (s, 9H, ^{t}Bu). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 146.5, 145.9, 120.2 (C arom quat and C=C); 127.9, 127.2, 125.7 (CH arom); 74.4 (CH_2N); 51.4 (NMe_2); 29.4 (Me_3C); C quat ^{t}Bu and isonitrile carbon: not observed.

3.11. Palladacycle **5c**

^{1}H NMR ($CDCl_3$): δ 3.55 (q, $^5J_{HH} = 2.0$ Hz, 2H, CH_2N); 2.83 (s, 6H, NMe_2); 1.96 (t, $^5J_{HH} = 2.0$ Hz, 3H, CH_3); 1.55 (s, 9H, ^{t}Bu). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 143.2, 119.1 (C=C); 74.0 (CH_2N); 58.5 (C quat ^{t}Bu); 51.5 (NMe_2); 30.3 (Me_3C); 26.0 (Me); isonitrile carbon: not observed.

3.12. Palladacycle **6a**

This reaction was performed in C_6D_6, although the signals were broad in the ^{1}H NMR spectrum. ^{1}H NMR (C_6D_6): δ 8.10–7.90 (m, 6H, H arom); 7.15–6.95 (m, 9H, H arom); 3.58 (br s, 2H, CH_2O); 3.44 (br s, 2H, CH_2N); 2.48 (br s, 6H, NMe_2); 2.33 (br s, 2H, H_2C–C=C).

3.13. Palladacycle **6b**

^{1}H NMR ($CDCl_3$) δ 7.80–7.20 (m, 15H, H arom); 6.80 (t, 1H, $^3J_{HH} = 7.5$ Hz, H arom); 6.61 (t, 2H, $^3J_{HH} = 7.5$ Hz, H arom); 6.48 (d, 2H, $^3J_{HH} = 7.5$ Hz, H arom); 3.87 (d, 2H, $^4J_{PH} = 1.8$ Hz, CH_2N); 2.97 (d, 6H, $^4J_{PH} = 2.7$ Hz, NMe_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 143.4 (d, $^3J_{PC} = 5.0$ Hz, C=C); 120.6 (d, $^2J_{PC} = 4.0$ Hz, C=C); 135.4, 135.3, 135.2, 135.1, 134.9, 134.5, 134.4, 132.1, 131.1, 130.8, 130.4, 130.3, 130.1, 128.7, 128.6, 128.4, 128.3, 128.2, 126.9, 124.9 (CH arom); 74.8 (d, $^3J_{PC} = 3.0$ Hz, CH_2N); 50.4 (d, $^3J_{PC} = 2.5$ Hz, NMe_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 35.1.

3.14. Synthesis of palladacycle **7b**

A Li_2PdBr_4 solution was prepared by dissolving $PdBr_2$ (1.59 g, 6.00 mmol) and LiBr (1.56 g, 18.0 mmol) in hot methanol (20 ml), under vigorous stirring. After dissolution of the solids, this solution was cooled to 5 °C and a solution of 1-phenyl-3-dimethylamino-1-propyne **1b** (1.00 g, 6.30 mmol) was added. The resulting brown suspension was stirred at 5 °C for 15 min. Filtration and washing of the resulting solid with cold MeOH and drying under reduced pressure afforded the desired palladacycle (brown solid, 1.70 g, 64% yield). *Anal*.: $(C_{11}H_{13}Br_2NPd)_2$ (850.92) requires C, 31.05; H, 3.08; N 3.29. Found: C, 29.87; H, 2.89; N, 3.11%. ^{1}H NMR ($CDCl_3$): δ 7.55–7.35 (m, 5H, Harom), 3.78 (s, 2H, CH_2N), 2.51 (s, 6H, NMe_2). ^{1}H NMR ($CDCl_3$ + Pyd5): δ 7.50–7.40 (m, 2H, H arom), 7.35–7.25 (m, 3H, H arom), 2.50 (s, 2H, CH_2N), 2.38 (s, 6H, NMe_2) (This spectrum is identical to the one recorded with an authentic sample of **1b**).

3.15. Attempted synthesis of palladacycle **6c**

The reaction of palladacycle **2c** with PPh_3, performed in $CDCl_3$ solution, affords almost instantaneously a yellow solid, identified as $PdCl_2(PPh_3)_2$. The presence of alkyne **1c** in the remaining solution was confirmed by CG–MS.

4. Supplementary material

Further details of the crystal structure investigation are available from CCDC quoting the deposition number 195545. These data can be obtained free of charge via www: http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgements

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

References

[1] See for example: (a) J.E. Backvall, Y.I.M. Nilsson, R.G.P. Gatti, Organometallics 14 (1995) 4242. (b) J.E. Backvall, Y.I.M. Nilsson, P.G. Andersson, R.G.P. Gatti, J.C. WU, Tetrahedron Lett. 35 (1994) 5713. (c) S.M. Ma, X.Y. Lu, J.Org. Chem. 58 (1993) 1245.

[2] For recent reviews of palladacycles see: (a) 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] (a) T. Yukawa, S. Tsutsumi, Inorg. Chem. 7 (1968) 1458;
(b) J. Dupont, N.R. Basso, M.R. Meneghetti, Polyhedron 15 (1996) 2299;
(c) J. Dupont, N.R. Basso, M.R. Meneghetti, R.A. Konrath, R. Burrow, M. Horner, Organometallics 16 (1997) 2386;
(d) G. Ebeling, M.R. Meneghetti, F. Rominger, J. Dupont, Organometallics 21 (2002) 3221.

[4] G.R. Newkome, W.E. Puckett, V.K. Gupta, G.E. Kiefer, Chem. Rev. 86 (1986) 451.

[5] 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.

[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 (and references therein).

[7] (a) R.G. Pearson, Inorg. Chem. 12 (1973) 712;
(b) C.K. Jorgensen, Inorg. Chem. 3 (1964) 1201.

[8] The action of isonitriles with palladacycles usually results in insertion of these unsaturated molecules into the Pd–C bond. See for example: (a) J. Dupont, M. Pfeffer, J.C. Daran, Y. Jeannin, Organometallics 6 (1987) 899. (b) J. Dupont, M. Pfeffer, J. Chem. Soc., Dalton Trans. (1990) 3193.

[9] E. Turgunov, M.K. Sadikov, T. Nurmakhmedova, T.S. Sirlibaev, Rus. J. Org. Chem. 35 (1999) 1131.

[10] The Pd–C of 'classical' palladacycles usually undergoes insertion reactions with these unsaturated reagents. See for example: (a) J. Dupont, M. Pfeffer, J.C. Daran, J. Gouteron, J. Chem. Soc., Dalton Trans. (1988) 2421. (b) M. Pfeffer, Rec. Trav. Chim. Pay.-Bas. 109 (1990) 567.

[11] (a) C. Lee, W. Yang, R.G. Parr, Phys. Rev. B. 37 (1988) 785;
(b) A.D. Becke, Phys. Rev. A. 38 (1988) 3098.

[12] T.H. Dunning, Jr., P.J. Hay, in: H.F. Schaefer (Ed.), Modern Theoretical Chemistry, vol. 3, 3rd ed., Plenum, New York, 1976.

[13] (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.

[14] P.A.A. Klusener, J.C. Hanekamp, L. Brandsma, P.V. Schleyer, J. Org. Chem. 55 (1990) 1311.