Journal of Organometallic Chemistry 696 (2011) 1834–1839

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Synthesis, structural elucidation and catalytic activity toward a model Mizoroki–Heck C–C coupling reaction of the pyrazolic Tröger's base $Pd_4Cl_8(PzTB)_2$ complex

Fernando Cuenú [a,b], Rodrigo Abonia [b,*], Alberto Bolaños [b], Armando Cabrera [c]

[a] Laboratorio de Química Inorgánica y Catálisis, Programa de Química, Universidad del Quindío, Avenida Bolívar Calle 12 Norte, Armenia, Colombia
[b] Departamento de Química, Universidad del Valle, A.A. 25360, Cali, Colombia
[c] Instituto de Química, Universidad Nacional Autónoma de México, 04510 México D.F., Mexico

ARTICLE INFO

Article history:
Received 11 February 2011
Accepted 14 February 2011

Keywords:
Palladium(II) complexes
Tröger's base
Pyrazole derivatives
Metallomacrocycles
Stilbenes
Mizoroki–Heck reaction

ABSTRACT

The synthesis of a novel palladium (II) complex $Pd_4Cl_8(PzTB)_2$, where PzTB is a pyrazole Tröger's base analogue ligand is reported. A complete structure elucidation of the complex was achieved by spectroscopic and crystallographic data, exhibiting a metallomacrocycle supramolecular structure and a planar-square geometry on each palladium atom. This complex exhibited also a high activity and selectivity toward a model Mizoroki–Heck C–C coupling reaction of styrene with some iodobenzene derivatives.

1. Introduction

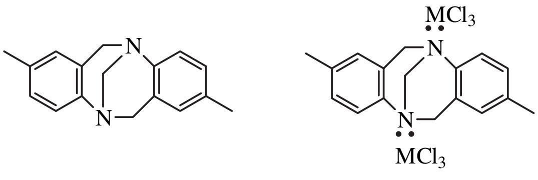
Tröger's base (Fig. 1), is a compound with a bridged and rigid V-shaped methanodiazocine skeleton and has been recognized as the first chiral tertiary amines which could be resolved [1,2]. Tröger's base has gained importance in the study of CH-π interactions [3], host molecules and molecular tweezers [4], and cyclophanes [5]. Also they have been considered as potential N-based ligand for the synthesis of transition metal complexes. In this sense, complexes type $TB \cdot 2MCl_3$ **2** with [(M = Rh(III) and Ir(III)], previously reported by Golberg and Alper [6], constituted the first example where a TB was used as a N-based ligand (Fig. 1). Some other examples like Rh (I) metallomacrocycles [7], Ru(II) complexes based on phenanthroline [8], and Pd(II) self-assembled complexes [9] have been reported.

Palladium-catalyzed Mizoroki–Heck type reaction is the most efficient route for the vinylation of aryl/vinyl halides or triflates involving the formation of a new C–C bond [10]. Among various commonly used reactions for C–C coupling (viz. Mizoroki–Heck, Suzuki, Stille and Sonogashira reactions), perhaps the Mizoroki–Heck is the most attractive organic reaction catalyzed by palladium complexes to produce chemicals for advanced synthesis of pharmaceuticals and natural products [11].

Continuing with our current studies on the synthesis and chemical properties of novel Tröger's bases [12], we were interested to evaluate the ability of complexation of a new pyrazolic Tröger's base (PzTB) toward the Pd(II) metal ion, on the structural elucidation of the novel palladium complex that was formed and in evaluating its catalytic potentiality through a model Mizoroki–Heck C–C coupling reaction.

2. Results and discussion

Based on the stoichiometry established for complex **2** [6], the treatment of $PdCl_2(CH_3CN)_2$ **3** [13] (2 eq) with the pyrazolic Tröger's



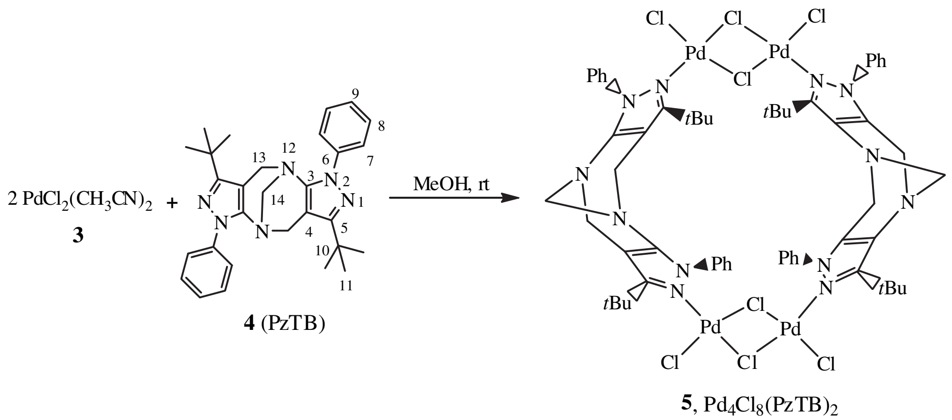
1 **2**

Fig. 1. Original Tröger's base **1** and the first transition metal complexes **2** bearing a Tröger's base as a N-based ligand.

---

* Corresponding author. Fax: +57 2 3393248.
E-mail address: rodrigo.abonia@correounivalle.edu.co (R. Abonia).

0022-328X/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2011.02.016



Scheme 1. Synthesis of the new Pd(II) complex **5** bearing the pyrazolic Tröger's base **4** as N-based ligand.

base, PzTB **4** [12], (1 eq), at ambient temperature and using MeOH as solvent afforded complex **5** as a red precipitate air stable, non-hygroscopic and soluble in $CHCl_3$, CH_2Cl_2 and DMSO (Scheme 1). The elemental analyses indicated that there are two palladium atoms for each molecule of the PzTB **4** in the structure of complex **5**, similarly as was found for complex **2** [6].

The IR spectrum of complex **5** showed new absorption bands and significant differences with respect to the IR of the free PzTB ligand **4**, indicating the formation of a new product. Table 1 summarizes the main absorption bands observed for both free and Pd-complexed PzTB ligand **4**.

According to the literature, halogens frequently tend to form bridges with two metal atoms and generally bridging M–X stretching frequencies [ν_b(M–X)] are lower than terminal M–X stretching frequencies [ν_t(M–X)] [14]. In addition, *trans*-planar $M_2X_4L_2$-type complexes with C_{2h} symmetry, exhibit three IR active ν(M–X) absorption bands [i.e. one ν_t(M–X) and two ν_b(M–X)] in the range of 360–294 cm^{-1} [15]. In the lower-frequencies region of the IR spectrum of complex **5** (Fig. 2), an absorption was observed at 369 cm^{-1} which could be assigned to the ν_t(M–X) mode, as well as, two absorption bands at 349 cm^{-1} and 308 cm^{-1}, respectively, which could be assigned to the two ν_b(M–X) modes. The second band (i.e. 349 cm^{-1}) is frequently related to a ν_b(M–X) *trans* to X mode whereas the last one (i.e. 308 cm^{-1}) is related to a ν_b(M–X) *trans* to (PzTB) mode since it is sensitive to the nature of the ligand [15]. These findings suggest initially a planar geometry around each Pd metal atom and their four ligands in complex **5**, as well as, the existence of a terminal Pd–Cl and two bridging Pd–Cl bonds in its structure, in agreement with the literature [15]. Finally, the absorption band at 258 cm^{-1} is assigned to a Pd–N stretching frequency.

Table 1
Main IR absorption bands for the free and Pd-complexed PzTB ligand **4**.

IR absorption bands (cm^{-1})[a]	
Free ligand	Pd–complexed ligand
3069 (s)	3052 (s)
3036 (s)	–
2964 (b)	2966 (b)
2869 (m)	2871 (m)
1667 (b)	1648 (b)
1597 (b)	1587 (m)
–	1517 (m)
1499 (b)	1491 (m)
1449 (m)	1456 (b)
1376 (b)	1387 (m)
1346 (b)	1356 (m)
1300 (m)	1287 (s)
–	1208 (m)
1144 (m)	1149 (b)
995 (m)	963 (s)
754 (b)	748 (b)
690 (m)	692 (m)

[a] (s), (m) and (b) refers to short, medium and broad size bands respectively.

As expected, the NMR spectra of complex **5** showed the same number of protons (with the same splitting pattern), and carbon atoms as the free ligand. Table 2 summarizes the comparison of the most relevant NMR signals observed for the both free and complexed PzTB ligand.

The ligand **4** possesses three types of nitrogen atoms (i.e. 1-N, 2-N and 12-N, see Scheme 1), from which 1-N and 12-N are suitable for coordination to the metal. In contrast to that observed for complex **2**, the proton and carbon atom NMR signals of the 13- and 14-methylene groups were not significantly shifted by complexation of the metal to the PzTB ligand **4**, as shown in Table 2. This finding may indicate a different coordination place of the Pd atoms to the PzTB ligand **4** with respect to complex **2**. To confirm without ambiguity the structure of complex **5**, single crystals suitable for X-ray diffraction were grown from a mixture of CH_2Cl_2/pentane. The X-ray diffractograms (see Fig. 3), showed that the metals are coordinated to the pyrazolic 1-N nitrogen atoms of **4** but not to the 12-N atoms in agreement with that observed by NMR.

Since the PzTB ligand **4** possesses two pyrazolic 1-N nitrogen atoms diametrically opposed and equivalent between them, PzTB **4** behaves as a bridged ligand, therefore, it coordinates two palladium ions, where each ion is dimerized obeying the 18 electron rule. Thus, generating a square-planar geometry around each palladium atom, with each one bonded to two bridged chloride ligands, to a terminal chloride and to a PzTB ligand **4**. The four bonding angles N1–Pd1–Cl2, N1–Pd1–Cl3, Cl1–Pd1–Cl3 and Cl2–Pd1–Cl1 with comparable values of 91.16 (9)°, 90.66 (9)°, 86.49 (4)° and 91.87 (4)° respectively, confirm the square-planar geometry of each Pd atom in the complex **5** (see Fig. 3 and Table 4). Interestingly, the supramolecular structure of complex **5** corresponded to a metallomacrocycle conformed by four palladium atoms, eight chlorines and two bridged PzTB ligands, as shown in (Fig. 3). According to our knowledge there are very few examples in the literature of metallomacrocycles bearing a Tröger's base as ligand [7,9,16].

2.1. Reactivity toward the C–C coupling reaction

In a preliminary study, complex **5** was probed as catalyst for a C–C coupling Mizoroki–Heck type reaction between styrene and

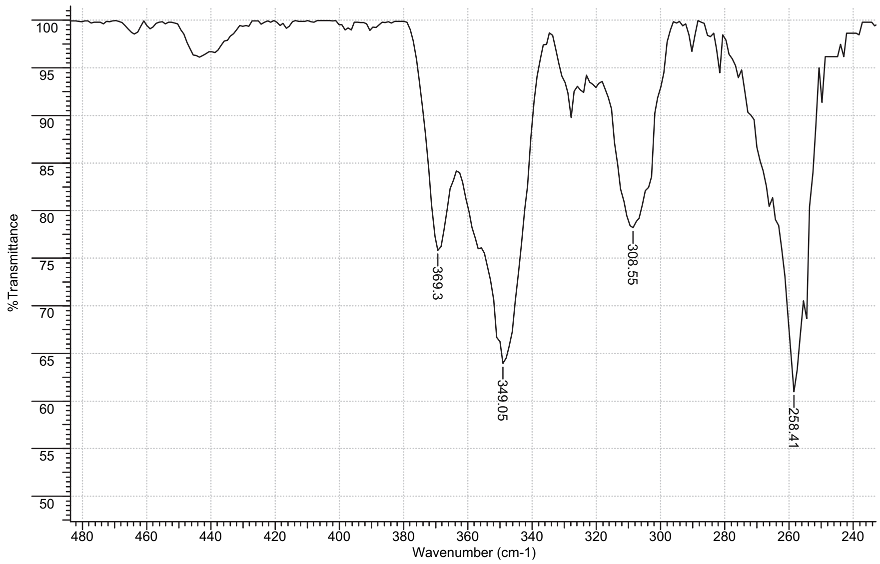


Fig. 2. Lower-frequencies region of the IR spectrum of compound **5**.

three different iodobenzene derivatives (i.e. iodobenzene, 4-iodoanisole and 4-iodonitrobenzene), as a model experiment to evaluate the catalytic ability of this complex (Scheme 2, see Table 3 and experimental).

Interestingly, compound **5** presented high catalytic activity and considerable selectivity towards the C–C coupling products, especially towards the formation of *trans*-stilbene derivatives, as shown in Table 3.

Table 2
Main ^{1}H and ^{13}C NMR signals for the free and complexed PzTB ligand **4**.

^{1}H and ^{13}C NMR signals (ppm) in DMSO-d_6		
Type of signal	Free ligand	Pd–complexed ligand
11-H	1.09	1.06
13-Ha	3.69	3.66
13-Hb	4.36	4.34
14-H	4.31	4.30
C-5	156.5	156.0
C-10	33.3	32.7
C-11	29.6	29.0
C-13	47.4	48.9
C-14	67.8	67.2

The Table 3 also shows that the electron-donating OMe group decreased the reactivity of the aryl substrate (ArI) giving only a 76% of conversion after 3.5 h of reaction with TOF = 21.8. When X = H it had a major conversion (89%, TOF = 25.5) for the same giving time, but the strong electron-withdrawing NO_2 group increased significantly its reactivity and consequently the conversion was 100% with a TOF = 28.6 after 3.5 h. These findings are in agreement with previous reports about the substrate dependence [17], and with the proposed mechanism for the Mizoroki–Heck reactions [17a,18].

2.2. *Effect of the complex:substrate ratio over the reactivity and selectivity of the complex **5***

The (Fig. 4) shows that complex **5** is highly active toward the C–C coupling reaction between iodobenzene and styrene, reaching the 100% of conversion of iodobenzene into products during the first 100 min with a TOF = 29.5, for a complex:substrate ratio 1:2950. During the course of the reaction the selectivity toward the *trans*-stilbene and 1,1-diphenylethene was 89% and 11%, respectively.

When the complex:substrate ratio was increased to 1:19600 (Table 4, entry 2), the activity of the complex **5** increased too, reaching the 100% of conversion of iodobenzene in 435 min, with

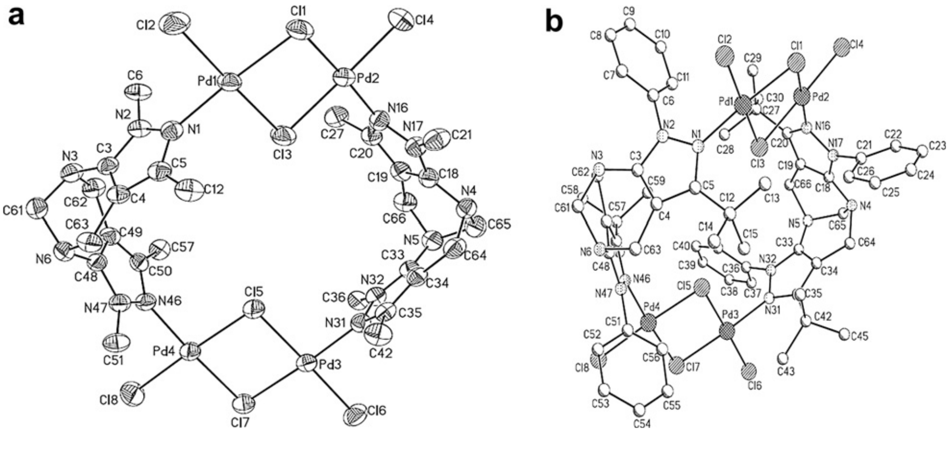
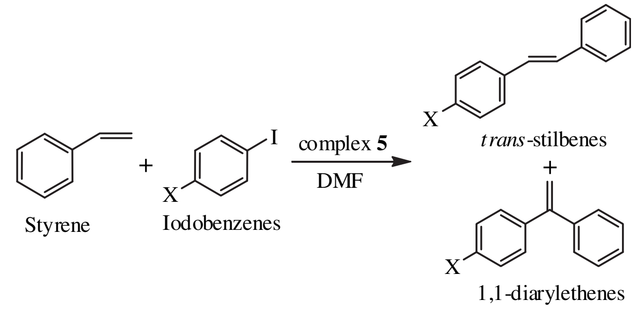


Fig. 3. ORTEP drawing of $Pd_4Cl_8(PzTB)_2$ complex **5** with 50% probability ellipsoids. a) Hydrogen atoms, phenyl rings and solvent molecules have been omitted for clarity. b) Phenyl and *tert*-butyl groups are shown.



Scheme 2. General procedure for a model Mizoroki–Heck C–C coupling reaction.

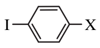
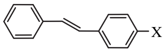
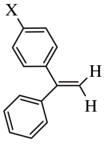
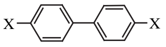
a TOF of 45.0. The selectivity toward the *trans*-stilbene and 1,1-diphenylethene remained almost the same with respect to the above experiment (i.e. 88% and 11% respectively).

To determine the homogeneity of the catalyst **5**, an Hg drop test was carried out [19]. As shown in (Fig. 5), the reaction performed in the presence of an excess of mercury had a very similar behavior than when reaction was carried out without mercury as depicted in (Fig. 4). This experiment indicated that amalgamation of Pd particles and for instance poisoning of complex **5** do not proceeded in the course of the reaction, confirming a homogeneous character of catalyst **5**.

2.3. Effect of the temperature over the reactivity and selectivity of the complex 5

From a comparative study to evaluate the effect of the variation of the temperature of reaction over the reactivity and selectivity of complex **5** maintaining the same catalyst:substrate ratio (i.e. 1:19600), we found that the increasing of the temperature from 90 °C, 120 °C–160 °C (Table 4, entries 1, 2 and 3) improved the reactivity of complex **5** showing TOF's of 12.1, 45.0 and 490.0 respectively. Interestingly the selectivity toward *trans*-stilbene kept almost the same in all three experiments (i.e. 92, 88 and 92% respectively), see Table 4.

Table 3
Mizoroki–Heck C–C coupling reaction of styrene with iodobenzene derivatives catalyzed by the $Pd_4Cl_8(PzTB)_2$ complex **5**.

Entry			
Substituent	X = NO_2	X = H	X = OMe
Total conversion (%)	100	89	76
Structure of products	Yield (%)	Yield (%)	Yield (%)
	93[a]	90[a]	89[a]
	7	10	9
	0	0	2
TON	6000	5346	4580
TOF	28.6	25.5	21.8

Reaction conditions: 1.794 mmol of (iodobenzene, 4-iodonitrobenzene or 4-iodoanisol), styrene (2.602 mmol), Et_3N (2.152 mmol), palladium complex **5** (0.299 μmol). Temperature 120 $\underline{o}$C, solvent DMF (10 mL), reaction time 3.5 h (210 min), catalyst:substrate ratio 1:6000.
[a] *trans*-stilbene isomer. TON = mol of product/mol Pd. TOF = TON/min.

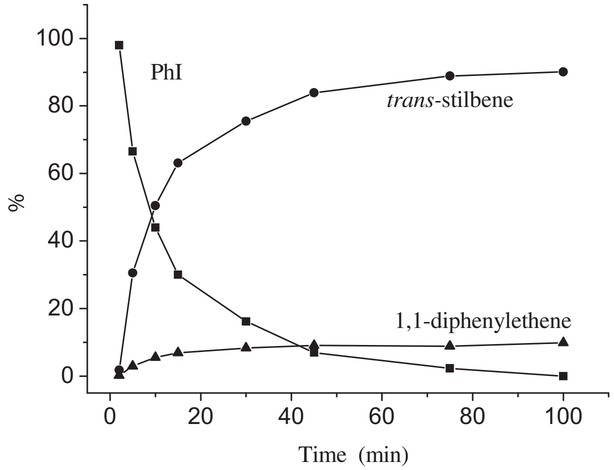


Fig. 4. Kinetic behavior for the Mizoroki–Heck C–C coupling reaction of iodobenzene and styrene catalyzed by complex **5**. Reaction conditions: iodobenzene (1.794 mmol), styrene (2.602 mmol), Et_3N (2.152 mmol), complex **5** (0.609 μmol), temperature 120 °C, solvent DMF (10 mL), catalyst:substrate ratio 1:2950, TOF = 29.5.

As shown in Table 4, complex **5** worked efficiently even at 160 °C. In contrast, it has been reported that the efficiency of monodentate PPh_3-based Pd complexes used as catalyst for Mizoroki–Heck C–C coupling reactions commonly decreases their activities when temperature exceeds 140 °C. This drawback is frequently associated with oxidation processes of the phosphorous in such ligands [20].

In a final experiment, we evaluated the activity of the phosphine-based ligand complex $PdCl_2(PPh_3)_2$ as catalyst for our model Mizoroki–Heck reaction, (Table 4, entry 4), in comparison with complex **5** (Table 4, entry 2). It is observed that the selectivities toward *trans*-stilbene and 1,1-diphenylethene were almost the same for both catalysts (i.e. 88:12 and 88:11 respectively). However, the reactivity of complex **5** was higher (100% conversion) than $PdCl_2(PPh_3)_2$ (86% of conversion) for the same giving reaction time, even with a higher catalyst:substrate ratio (i.e. 1:19600, TOF = 45.0 for complex **5** *vs* 1:1000, TOF = 2.9 for $PdCl_2(PPh_3)_2$).

3. Conclusions

We established that the reaction of the starting compound $PdCl_2(CH_3CN)_2$ with a pyrazolic Tröger's base (PzTB) readily afforded the new (2:1) $Pd_4Cl_8(PzTB)_2$ complex **5**. The supramolecular structure of this complex interestingly corresponded to a metallomacrocycle conformed by four palladium atoms, each of them possessing a planar-square geometry, and bonded to two bridged PzTB ligands. Complex **5** displayed high catalytic activity and considerable selectivity towards the formation of *trans*-stilbenes from a model Mizoroki–Heck C–C coupling reaction of styrene with iodobenzene derivatives. The mercury drop test confirmed that complex **5** behaved as a homogeneous catalyst during the course of the Mizoroki–Heck C–C coupling reactions performed. Further kinetic studies directed to establish the reaction mechanism are currently in progress.

4. Experimental section

4.1. Solvent and starting materials

All chemicals palladium chloride, iodobenzene, 4-iodoanisole, ; 4-iodo-nitrobenzene, styrene, triethylamine (Et_3N), N,N-dimethylformamide (DMF), phenylhydrazine, 4,4′-dimethyl-3-

Table 4
Effect of the temperature over the reactivity and selectivity of the complex **5**.

Entry	Temperature °C	Time min	Conversion of PhI (%)	TOF	Selectivity toward *trans*–stilbene (%)	Selectivity toward 1,1-diphenylethene (%)
1	90	1620	93	12.1	92	8
2	120	435	100	45.0	88	11
3	160	40	100	490.0	92	8
4[a]	120	300	86	2.9	88	12

Standard reaction conditions: iodobenzene (1.794 mmol), styrene (2.602 mmol), Et_3N (2.152 mmol), complex **5** (0.091 μmol), solvent DMF (10 mL), catalyst:substrate ratio 1:19600. Time in minutes.

[a] $PdCl_2(PPh_3)_2$:substrate ratio 1:1000.

oxopentanenitrile, paraformaldehyde, hydrochloric acid, ammonium hydroxide, acetonitrile (ACN) and dichloromethane (DCM) were purchased from Aldrich Chemical Co, Sigma and Fluka companies and were used as received. All solvents were distilled and dried by standard methods just before use. A sample of the $PdCl_2(ACN)_2$ salt **3** was prepared as described in the literature [13]. The pyrazolic Tröger's base PzTB **4**, was obtained when 5-amino-3-*tert*-butyl-1-phenylpyrazole was treated with paraformaldehyde in acetic acid, as described in the literature [12].

4.2. Analytical and physico–chemical measurements

Melting points were determined on a Büchi melting point apparatus and are uncorrected. IR spectra were recorded on a Perkin Elmer FT spectrophotometer series 2000 in KBr disks. ^1H and ^{13}C NMR spectra were recorded on a Varian-Inova 500 MHz spectrometer operating at 500 MHz and 125 MHz respectively, and on a Bruker Avance 400 spectrophotometer operating at 400 MHz and 100 MHz respectively, using DMSO-d_6 as solvent and tetramethylsilane as internal standard. Microanalyses were performed on an Agilent elemental analyzer and the values are within ±0.4% of the theoretical values. Silica gel aluminum plates (Merck 60 F254) were used for analytical TLC. Catalytic reactions were carried out in a 50 mL 2-necked round bottom flask fitted with a condenser immersed into an oil bath and maintained at the desired temperature. The stirring was carried out by means of a spinbarr. Analysis of the content of the reaction mixtures were made by using an Agilent 6890A Chromatograph, with an AT5 capillary column (5% phenylmethylsiloxane) 30 m × 0.25 mm × 0.1 μm and the GC–MS FID's were made by using a Jeol-GC-mate mass selective detector. Identification of the reaction products was carried out by GC–MS analysis (comparing with standard samples) and NMR techniques of the pure products after column chromatography on silica gel and DCM-AcOEt mixtures as eluent.

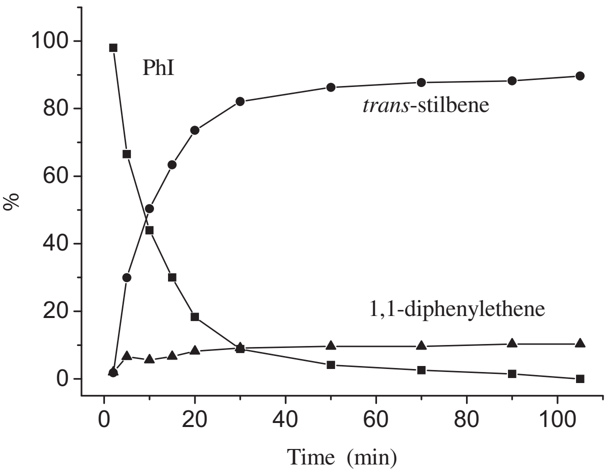


Fig. 5. Mercury drop test: Kinetic behavior for the Mizoroki–Heck C–C coupling reaction of iodobenzene and styrene catalyzed by complex **5** in the presence of an excess of mercury. Reaction conditions: iodobenzene (8.97 mmol), styrene (13.01 mmol), Et_3N (10.76 mmol), complex **5** (3.045 μmol), Hg(0) (125.7 μmol, 25.57 mg), temperature 120 °C, solvent DMF (50 mL), catalyst:substrate ratio 1:2950.

4.3. Synthesis of the $Pd_4Cl_8(PzTB)_2$ complex **5**

The reaction was performed under a nitrogen atmosphere using standard Schlenk techniques and vacuum line. A sample of $PdCl_2(CH_3CN)_2$ **3** (100 mg, 0.386 mmol) was added to a solution of PzTB **4** (90.4 mg, 0.194 mmol) dissolved in MeOH (3 mL). The reaction mixture was stirred for 1 h at ambient temperature. The red precipitated formed was filtered off, washed with MeOH and dried under reduced pressure yielding pure complex **5** 148 mg, 93% yield. Mp 266–267 °C ^1H NMR (500 MHz, $[D_6]$ DMSO): $\delta = 1.06$ (s, 18H, 11-H), 3.66 (d, *Jgem* = 16.0 Hz, 2H, 13-Ha), 4.30 (s, 2H, 14-H), 4.34 (d, *Jgem* = 15.5 Hz, 2H, 13-Hb), 7.30 (t, *J* = 7.5 Hz, 2H, 9-H), 7.49 (t, *J* = 8.0 Hz, 4H, 8-H), 7.86 (d, *J* = 8.5 Hz, 4H, 7-H) ppm. ^{13}C NMR (125 MHz, $[D_6]$ DMSO): $\delta = 29.0$ (C-11), 32.7 (C-10), 48.9 (C-13), 67.2 (C-14), 102.1 (C-4), 120.6 (C-7), 125.8 (C-9), 129.2 (C-8), 139.1 (C-6),

Table 5
Crystal and structure refinement parameters for complex **5**.

Parameter	Value
Empirical formula	$C_{60}H_{72}Cl_{12}N_{12}Pd_4$
Formula weight	1812.30
Temperature	298(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 13.6868(10) Å, $\alpha = 90°$ b = 20.5808(15) Å, $\beta = 101.3490(10)°$ c = 26.6607(19) Å, $\gamma = 90°$
Z	4
Volume	7363.1(9) $Å^3$
Density (calculated)	1.635 Mg/m^3
Absorption coefficient	1.442 mm^{-1}
F(000)	3616
Crystal size/shape/color	0.26 × 0.24 × 0.22 mm/Prism/Red
Theta range for data collection	1.81–25.36°
Diffractometer used/Scan Mode Bruker Smart omega scans	APEX AXS CCD area detector/
Index ranges	16< = h< = 16, −24< = k< = 24, −32< = l < = 32
Reflections collected	60385
Independent reflections	13468 [R(int) = 0.0645]
Completeness to theta = 25.36°	99.7%
Max. and min. transmission	0.7723 and 0.6686
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	13468/272/907
Goodness-of-fit on F^2	0.896
Final R indices[I > 2sigma(I)]	$R_1 = 0.0390$, $wR_2 = 0.0703$
R indices (all data)	$R_1 = 0.0652$, $wR_2 = 0.0764$
Largest diff. peak and hole	0.654 and −0.440 e.$Å^{-3}$

Table 6
Selected bonding lengths (A°) and angles (°) for complex **5**.

Bond lengths		
Pd1−N1; 2.013(3)	Pd1−Cl2; 2.2582(12)	Pd1−Cl3; 2.3462(11)
Pd1−Cl1; 2.312(11)	Pd2−Cl1; 2.3035(12)	Pd2−Cl4; 2.2660(12)
Pd2−N16; 2.026(3)	Pd2−Cl3; 2.3496(11)	C5−C12; 1.519(5)
N1−N2; 1.364(4)	C6−N2, 1.343(5)	N2−C5, 1.343(5)
C3−N2; 1.354(5)	N3−C3, 1.08(5)	C3−C4, 1.366(5)
Bonding angles		
N1−Pd1−Cl1; 176.13(10)	N1−Pd1−Cl2; 91.16(9)	N1−Pd1−Cl3; 90.66(9)
N16−Pd2−Cl1; 175.03(10)	N16−Pd2−Cl4; 92.00(10)	N16−Pd2−Cl3; 89.80(9)
Cl2−Pd1−Cl3; 175.60(5)	Cl1−Pd1−Cl3; 86.49(4)	Cl4−Pd2−Cl3; 178.19(5)
N1−N2−Pd1; 119.70(2)	Cl2−Pd1−Cl1; 91.87(4)	Cl4−Pd2−Cl1; 91.58(4)
N1−N2−C6; 125.21(3)	C3−N2−C6; 125.22(3)	C3−N2−N1; 109.30(3)

145.1 (C-3), 156.0 (C-5) ppm. $C_{58}H_{68}Cl_8N_{12}Pd_4$ (1646.52): calcd. C 41.05, H 4.01, N 16.73; found C 41.16, H 4.16, N 16.68.

*4.4. Crystal structure of complex **5***

Crystals suitable for single X-ray diffraction were grown by diffusing pentane into a DCM solution. Crystallographic data were collected at 298 K on a Bruker Smart APEX AXS CCD area diffractometer using Mo-Kα X-ray radiation ($\lambda = 0.71073$ Á) and deposit at Cambridge Crystallographic Data Center (CCDC reference: 775353). The main crystallographic data of complex **5** are listed in (Tables 5 and 6).

4.5. General procedure for the model C−C coupling Mizoroki−Heck reactions

In a typical experiment according to (Scheme 2), a mixture of iodobenzene (1.787 mmol), styrene (2.602 mmol), Et_3N (2.152 mmol), complex **5** (1.158 μmol) and DMF (8 mL) in a 50 mL 2-necked bottle was immersed in a pre-heated oil bath at 120 °C with magnetic stirring. Samples were removed from the reaction mixture at regular intervals and analyzed by GC−MS until complete consumption of iodobenzene. *trans*-Stilbene. mp 123−124 °C (Lit. mp 122−124 °C) [21]; *(E)*-4-nitrostilbene, mp 156−158 °C, (Lit. mp 157 °C) [22]. ^1H NMR (400 MHz, $[D_6]$ DMSO): $\delta = 7.34$ (t, $J = 7.2$ Hz, 1H, Ph-H), 7.41 (d, $J = 15.2$ Hz, 1H, H*trans*), 7.42 (t, $J = 7.4$ Hz, 2H, Ph-H), 7.53 (d, $J = 16.8$ Hz, 1H, H*trans*), 7.68 (d, $J = 7.2$ Hz, 2H, Ph-H), 7.87 (d, $J = 8.9$ Hz, 2H, Ar−H), 8.23 (d, $J = 8.8$ Hz, 2H, Ar−H) ppm. ^{13}C NMR (100 MHz, $[D_6]$ DMSO): $\delta = 124.5$, 126.8, 127.6, 127.8, 129.2, 129.3, 133.7, 136.7 (Cq), 144.5 (Cq), 146.7 (Cq) ppm. *(E)*-4-Methoxystilbene, mp 132−133 °C, (Lit. mp 131−132 °C) [23]. ^1H NMR (400 MHz, $[D_6]$ DMSO): $\delta = 3.78$ (s, 3H, OCH_3), 6.96 (d, $J = 8.8$ Hz, 2H, Ph-H), 7.09 (d, $J = 16.4$ Hz, 1H, H*trans*), 7.20 (d, $J = 16.4$ Hz, 1H, H*trans*), 7.24 (t, $J = 7.6$ Hz, 1H, Ph-H), 7.36 (t, $J = 7.6$ Hz, 2H, Ph-H), 7.56 (bt, 4H, Ar−H) ppm. ^{13}C NMR (100 MHz, $[D_6]$ DMSO): $\delta = 55.6$ (OCH_3), 114.6, 126.5, 126.6, 127.6, 128.3, 128.5, 129.1, 130.1 (Cq), 137.8 (Cq), 159.5 (Cq) ppm.

Acknowledgments

Authors wish to credit the Universidad del Quindío, Armenia-Colombia, the Universidad del Valle, Cali-Colombia, and the Instituto de Química de la Universidad Nacional Autónoma de México, Ciudad de México-Mexico for financial support.

Appendix A. Supplementary material

CCDC 775353 contains the supplementary crystallographic data for for complex **5**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

References

[1] (a) J. Tröger, J. Prakt. Chem. 63 (1887) 225–245;
(b) M.D. Cowart, I. Sucholeiki, R.R. Bukownik, C.S. Wilcox, J. Am. Chem. Soc. 110 (1988) 6204–6210.

[2] (a) M. Demeunynck, A. Tatibouët, in: G.W. Gribble, T.L. Gilchrist (Eds.), Prog. Heterocycl. Chem., 11, Pergamon, Oxford, 1999, pp. 1–20;
(b) B.G. Bag, Curr. Sci. 68 (1995) 279–288.

[3] (a) S. Paliwal, S. Geib, C.S. Wilcox, J. Am. Chem. Soc. 116 (1994) 4497–4498;
(b) E. Kim, S. Paliwal, C.S. Wilcox, J. Am. Chem. Soc. 120 (1998) 11192–11193;
(c) K. Nakamura, K.N. Houk, Org. Lett. 1 (1999) 2049–2051.

[4] (a) S. Goswami, K. Ghosh, Tetrahedron Lett. 38 (1997) 4503–4506;
(b) S. Goswami, K. Ghosh, S. Dasgupta, J. Org. Chem. 65 (2000) 1907–1914;
(c) A.P. Hansson, P.-O. Norrby, K. Wärnmark, Tetrahedron Lett. 39 (1998) 4565–4568.

[5] (a) M. Miyake, C.S. Wilcox, Heterocycles 57 (2002) 515–522;
(b) A.A. Ibrahim, M. Matsumoto, Y. Miyahara, K. Izumi, M. Suenaga, N. Shimizu, T. Inazu, J. Heterocycl. Chem. 35 (1998) 209–215;
(c) B.G. Bag, G. von Kiedrowski, Angew. Chem. Int. Ed. 38 (1999) 3713–3714.

[6] Y. Goldberg, H. Alper, Tetrahedron Lett. 36 (1995) 369–372.

[7] M.S. Khoshbin, M.V. Ovchinnikov, C.A. Mirkin, J.A. Golen, A.L. Rheingold, Inorg. Chem. 45 (2006) 2603–2609.

[8] (a) C. Bresson, M. Luhmer, M. Demeunynck, A. Kirsch-De Mesmaeker, F. Pierard, Tetrahedron Lett. 45 (2004) 2863–2866;
(b) O. Van Gijte, A. Tatibouët, M. Demeunynck, J. Lhomme, A. Kirsch-De Mesmaeker, Tetrahedron Lett. 38 (1997) 1567–1570.

[9] T. Weilandt, U. Kiehne, G. Schnakenburg, A. Lützen, Chem. Commun. (2009) 2320–2322.

[10] (a) R.F. Heck, Pure Appl. Chem. 50 (1978) 691–701;
(b) R.F. Heck, W.A. Herrmann, Angew. Chem. Int. Ed. 41 (2002) 1290–1309.

[11] S. Bräse, A. de Meijere, in: A. de Meijere, F. Diederich (Eds.), Metal-Catalyzed Cross-Coupling Reactions, second ed.. Wiley-VCH, Weinheim, Germany, 2004, pp. 218–225.

[12] For the synthesis of compound 4 see (a) R. Abonia, A. Albornoz, H. Larrahondo, J. Quiroga, B. Insuasty, H. Insuasty, A. Hormaza, A. Sánchez, M. Nogueras, J. Chem. Soc. Perkin Trans. 1 (2002) 1588–1591;
(b) R. Abonia, E. Rengifo, J. Quiroga, B. Insuasty, A. Sánchez, J. Cobo, J.N. Low, M. Nogueras, Tetrahedron Lett. 43 (2002) 5617–5620.

[13] Compound 3 was obtained following a similar procedure as described by A.G.M. Mostafa-Hossain, T. Nagaoka, K. Ogura, Electrochim. Acta 41 (1996) 2773–2780.

[14] K. Nakamoto, in: J. Wiley, Sons (Eds.), Infrared and Raman Spectra of Inorganic and Coordination Compounds, Part B, sixth ed.. Wiley-VCH, Weinheim, Germany, 2009, p. 193.

[15] R.J. Goodfellow, P.L. Goggin, L.M. Venanzi, J. Chem. Soc. A (1967) 1897–1900.

[16] (a) U. Kiehne, T. Weilandt, A. Lützen, Org. Lett. 9 (2007) 1283–1286;
(b) T. Weilandt, U. Kiehne, J. Bunzen, G. Schnakenburg, A. Lützen, Chem. Eur. J. 16 (2010) 2418–2426.

[17] (a) M. Oestreich, in: M. Oestreich (Ed.), The Mizoroki–Heck Reaction, John Wiley & Sons, Ltd., Chichester, United Kingdom, 2009, pp. 56–57;
(b) V.P. Böhm, W.A. Herrmann, Chem. Eur. J. 7 (2001) 4191–4197.

[18] C. Amatore, A. Jutand, Acc. Chem. Res. 33 (2000) 314–321.

[19] (a) D.R. Anton, R.H. Crabtree, Organometallics 2 (1983) 855–859;
(b) J.A. Widegren, R.G. Finke, J. Mol. Catal. A 198 (2003) 317–341.

[20] (a) W.A. Herrmann, C. Brossmer, K. Öfele, C.P. Reisinger, T. Priermeier, M. Beller, H. Fischer, Angew. Chem. Int. Ed. Engl. 34 (1995) 1844–1848;
(b) M. Larhed, A. Hallberg, J. Org. Chem. 61 (1996) 9582–9584;
(c) M.R. Buchmeiser, K. Wurst, J. Am. Chem. Soc. 121 (1999) 11101–11107.

[21] J.C. van Miltenburg, J.A. Bouwstra, J. Chem. Thermodyn. 16 (1984) 61–65.

[22] F. Bergmann, D. Schapiro, J. Org. Chem. 12 (1947) 57–66.

[23] L.-T. Chu, P.-C. Yu, B.-J. Wu, Y.-C. Liao, C.-H. Chow, Heterocycles 71 (2007) 165–173.