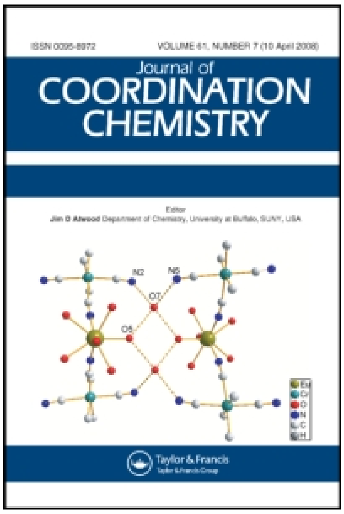
This article was downloaded by:
On: *23 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

SYNTHESIS, CHARACTERIZATION AND REACTIVITY OF NOVEL COORDINATION COMPOUNDS OF Pd(II) AND Pt(II) WITH PHENYL-2-PYRIDINYL ACETYLENE X-RAY STRUCTURE OF *trans*-$\{Pt[(O\text{-}NC_5H_4)CC(Ph)]Cl_2(SEt_2)\}$

Adriana C. Aiub[a]; Nara R. Basso[a]; Osvaldo L. Casagrande Jr[a]; Jairton Dupont[a]; Manfredo Hörner[b]; Adaílton J. Bortoluzzi[b]; Cacilia Maichle-Mössmer[c]
[a] Grupo de Catálise, Instituto de Química, UFRGS, Porto Alegre, RS, Brazil [b] Departamento de Química, UFSM, Santa Maria, RS, Brazil [c] Institut für Anorganische Chemie, Universität Tübingen, Tübingen, Germany

To cite this Article Aiub, Adriana C. , Basso, Nara R. , Casagrande Jr, Osvaldo L. , Dupont, Jairton , Hörner, Manfredo , Bortoluzzi, Adaílton J. and Maichle-Mössmer, Cacilia(1996) 'SYNTHESIS, CHARACTERIZATION AND REACTIVITY OF NOVEL COORDINATION COMPOUNDS OF Pd(II) AND Pt(II) WITH PHENYL-2-PYRIDINYL ACETYLENE X-RAY STRUCTURE OF *trans*-$\{Pt[(O\text{-}NC_5H_4)CC(Ph)]Cl_2(SEt_2)\}$', Journal of Coordination Chemistry, 40: 1, 35 — 44
To link to this Article: DOI: 10.1080/00958979608022844
URL: http://dx.doi.org/10.1080/00958979608022844

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

J. Coord. Chem., 1996, Vol. 40, pp. 35–44
Reprints available directly from the publisher
Photocopying permitted by license only

© 1996 OPA (Overseas Publishers Association)
Amsterdam B.V. Published in The Netherlands
under license by Gordon and Breach Science Publishers
Printed in Malaysia

SYNTHESIS, CHARACTERIZATION AND REACTIVITY OF NOVEL COORDINATION COMPOUNDS OF Pd(II) AND Pt(II) WITH PHENYL-2-PYRIDINYL ACETYLENE X-RAY STRUCTURE OF *trans*-$\{Pt[(o\text{-}NC_5H_4)C{\equiv}C(Ph)]Cl_2(SEt_2)\}$

ADRIANA C. AIUB,[a] NARA R. BASSO,[a]
OSVALDO L. CASAGRANDE JR,[a,*] JAIRTON DUPONT,[a,*]
MANFREDO HÖRNER,[b] ADAÍLTON J. BORTOLUZZI[b] and
CACILIA MAICHLE-MÖSSMER[c]

[a]*Grupo de Catálise, Instituto de Química, UFRGS, Av. Bento Gonçalves, 9500 91501-970 Porto Alegre, RS, Brazil;* [b]*Departamento de Química, UFSM, 97111-900 Santa Maria, RS, Brazil;* [c]*Institut für Anorganische Chemie, Universität Tübingen, D-72076 Tübingen, Germany*

Downloaded At: 15:54 23 January 2011

(Received 13 November 1995; Revised 22 February 1996; In final form 13 March 1996)

The reaction of phenyl-2-pyridinyl acetylene (1) with $[MCl_2(SEt_2)]$ (M=Pd, Pt) affords $\{M[(o\text{-}NC_5H_4)C{=}C(Ph)](SEt_2)Cl_2\}$ (M=Pd, Pt)(**2a-b**) in almost quantitative yield. The reaction of **2b** with nucleophiles such as water and diethylamine lead to nucleophilic addition of these molecules to the activated C=C bond to produce $\{Pt(\mathit{cis}\text{-}(o\text{-}NC_5H_4)CH_2C(O)(Ph)]Cl_2(SEt_2)\}$ (3) and $\{Pt[(\mathit{cis}\text{-}(o\text{-}NC_5H_4)CH{=}C(Ph)(NEt_2)]Cl_2(HNEt_2)\}$ (**4**), respectively. The reaction of **1** with equimolar amounts of Na_2PdCl_4 yields the cyclopalladated complex $\{Pd[(o\text{-}NC_5H_4)(Cl)C{=}C(Ph)](\mu\text{-}Cl)\}_2$ (**5**). On the other hand, only products resulting from the hydrolysis of the C=C bond are found in the reaction of **1** with K_2PtCl_4. The X-ray structure determination of **2b** shows a monoclinic system, space group $P2_1/n$, with a = 9.083 (2), b = 11.238 (2), c = 17.913 (3) Å, b = 93.00 (2)°, V = 1826 Å^3, Z = 4, D_x = 1.947 g.cm^3, R = 0.062 and Rw = 0.075 for the unique reflections and parameters.

Keywords: platinum; palladium; heterosubstituted alkyne; nucleophilic addition; crystal structure

INTRODUCTION

Transition-metal complexes enable nucleophilic addition reactions to C=C and C=C bonds as one of the most broadly applicable methodologies for the preparation

---

* Authors for correspondence; e-mail: osvaldo@if.ufrgs.br.

of new organometallic complexes and their application in synthetic organic chemistry.[1] It is assumed that these reactions proceed *via* coordination of the unsaturation to the electrophilic transition metal center followed by addition of the nucleophile to the coordinated multiple bond. We have previously demonstrated that reactions of heterosubstituted alkynes and olefins with nucleophiles, in the presence of Pt(II) and Pd(II) compounds, are strongly dependent on the nature of the heteroatoms attached to the unsaturated C-C bond.[2–3] In this manuscript we present full details of the reaction of phenyl-2-pyridinyl acetylene coordinated to Pd(II) and Pt(II) with nucleophiles.

EXPERIMENTAL

General

All reactions were performed in Schlenk-type flasks under oxygen- and water-free argon. Solvents were dried and distilled under argon, tetrahydrofuran and n-hexane over sodium benzophenone ketyl, dichloromethane and chloroform over P_2O_5, and methanol over CaO. ^1H NMR spectra were recorded at 200.13 MHz, ^{13}C NMR spectra at 50.32 MHz on a Varian Gemini - VXR - 200 MHz instrument, externally referenced to TMS. IR spectra were recorded on a Mattson 3020 FTIR spectrophotometer. Elemental analyses were performed by the 'Central Analítica do IQ-UFRGS (Brazil)'.

Downloaded At: 15:54 23 January 2011

Starting materials

Na_2PdCl_4 was purchased from Aldrich and the *trans*-$[MCl_2(SEt_2)_2]$ complexes (M=Pd, Pt) were synthesized as described in the literature.[4] Phenyl-2-pyridinyl acetylene (**1**) was synthesized in 85–90% yield by the reaction of 2- bromopyridine with phenyl acetylene in the presence of catalytic amounts of $[PdCl_2(PPh_3)_2]$ and CuI.[5] All other reagents were obtained from commercial sources (Aldrich or Merck) and were used as received.

Synthesis of $\{Pd[(o\text{-}NC_5H_4)C{\equiv}C(Ph)](SEt_2)Cl_2\}$ (2a)

Phenyl-2-pyridinyl acetylene (0.11 g, 0.61 mmol) was added to a solution of $[PdCl_2(SEt_2)_2]$ (0.20 g, 0.56 mmol) in THF (20 mL). The reaction mixture was stirred under reflux for 16 h. The solvent was concentrated to *ca.* 3 mL and then hexane (40 mL) was added, yielding an orange-yellow solid, that was recovered by filtration, washed with hexane (3 × 30 mL) and then dried *in vacuo*. Yield, 0.215 g (86%). *Anal.* Calcd. for $C_{17}Cl_2H_{19}NPdS$(%): C, 45.85; H, 4.30; N, 3.15; Pd 23.80. Found: C, 45.60; H, 4.22; N, 3.10; Pd 23.50. IR (KBr pellets): 2223 cm^{-1} (ν C≡C); ^{1}H NMR ($CDCl_3$): 8.74 (d, 1H, $^3J_{HH}$ = 5.6 Hz, *o*-Py); 7.70, 7.60, 7.40 and 7.20 (4m, 8H, CH aromatic); 2.81 (m, 4H, CH_2); 1.47 (t, 6H,$^3J_{HH}$ = 7.3 Hz, CH_3).^{13}C NMR ($CDCl_3$): 152.2 (CH-1-Py); 144.7 (Cipso-Py); 137.9 (CH-3-Py); 131.9 (CH-*o*-Ph); 129.6 (CH-*p*-Ph); 128.2 (CH-*m*-Ph); 127.1 (CH-4-Py); 124.0 (CH-2-Py); 121.3 (Cipso-Ph); 93.7 and 86.7 (C≡C); 76.1 and 75.4 (CH_2); 13.0 and 12.8 (CH_3).

Synthesis of {Pt[o-NC_5H_4)C≡C(Ph)](SEt_2)Cl_2} (2b)

Complex **2b** was obtained using a similar procedure to that described for **2a**. Yield, 0.221 g (92%). *Anal* Calcd. for $C_{17}Cl_2H_{19}NPtS$(%): 38.20; H, 3.59; N, 2.62; Pt 36.51. Found: C, 38.17; H, 3.56; N, 2.58; Pt 36,40. IR (KBr pellets) 2221 cm^{-1} (ν C≡C); ^{1}H NMR ($CDCl_3$): 8.71 (m, 1H,o-Py), 7.73-7.21 (m, 7H, aromatic), 2.96 and 2.56 (2m, 4H, SCH_2), 1.37 (t, 6H, $^3J_{HH}$ = 7.4 Hz, CH_3); ^{13}C NMR ($CDCl_3$): 153.1 (CH-1-Py); 145.4 (Cipso-Py); 138.2 (CH-3-Py); 132.4 (CH-*o*-Ph); 130.3 (CH-*p*-Ph); 130.0 (CH-*m*-Ph); 128.7 (CH-4-Py); 124.8 (CH-2-Py); 122.0 (Cipso-Ph); 98.5 and 87.2 (C≡C); 30.8 (SCH_2); 12.8 (CH_3).

Synthesis of {Pt[cis-(o-NC_5H_4)CH_2C(O)(Ph)]Cl_2(SEt_2)} (3)

Water (4.0 mL, 222.0 mmol) was added to a solution of **2b** (0.10 g, 0.10 mmol) in chloroform (15 mL) and the reaction mixture was stirred under reflux for 3 days. The resulting yellow solution was concentrated to *ca.* 4 mL and hexane (20 mL) was added yielding **3** as a dark yellow solid, that was recovered by filtration and dried *in vacuo*. Yield, 0.085 g (81%). Anal. Calcd. for $C_{17}Cl_2H_{21}NOPtS$(%): C, 36.90; H, 3.82; N 2.53; Pt, 35.32 Found: C, 36.75; H, 3.80; N, 2.51; Pt 35.20. IR (KBr pellets): 1756 cm^{-1} (ν C=O); ^{13}C NMR ($CDCl_3$): 195.1 (C=O); 157.6 (Cipso-Py); 152.3 (CH-1-Py); 138.2 (CH-3-Py); 136.0 (Cipso-Ph); 133.1 (CH-*o*-Ph); 129.1 (CH-*p*-Ph); 128.7 (CH-*m*-Ph); 127.9 (CH-4Py); 123.7 (CH-2-Py); 48.5 (CH_2); 31.8 and 30.1 (CH_2S); 12.7 and 12.2 (CH_3).

Synthesis of {Pt[(cis-(o-NC_5H_4)CH=C(Ph)(NEt_2)]Cl_2($HNEt_2$)} (4)

Complex **4** was obtained using a similar procedure to that described for **3**, the volume of diethylamine used was 10.0 mL (100.0 mmol). Yield, 0.103 g (91%). *Anal.* Calcd. for $C_{21}Cl_2H_{31}N_3Pt$(%); C, 42.64; H, 5.28; N 7.10; Pt, 32.98. Found: C, 42.59; H, 5.22; N, 7.08; Pt 32.70. IR (KBr pellets): 3196 cm^{-1} (νN-H); ^{1}H NMR ($CDCl_3$: 8.50 (m, 1H, o-Py), 7.68–7.18 (m, 5H, Ph), 6.97 (s, 1H,

Downloaded At: 15:54 23 January 2011

C≡CH), 6.80 (t, 1H, $^3J_{HH}$ = 6.5 Hz, aromatic), 6.02 (d, 1H, $^3J_{HH}$ = 7.9 Hz, aromatic), 3.65, 3.18, 2.87 and 2.58 (4m, 8H, CH_2), 1.63-1.08 (m, 12H, CH_3).

Synthesis of {Pd[(C(Ph)=C(Cl)(o-NC_5H_4)](μ-Cl)}$_2$ (5)

To a solution of Na_1PdCl_4 (0.50 g, 1.70 mmol) in methanol (50 mL), phenyl-2-pyridnyl acetylene (0.30 g, 1.70 mmol) in 10 mL of methanol was added. The reaction mixture was stirred under methanol reflux for 22 h. The formed orange precipitate was recovered by filtration and chromatographed in silica gel using CH_2Cl_2 as eluent. The resulting orange solution was concentrated under reduced pressure to *ca.* 3.0 mL. Addition of hexane (50 mL) afforded an orange solid which was recovered by filtration, washed with hexane (3 × 25 mL) and dried *in vacuo.* Yield, 0.424 g (70%). *Anal* Calcd. for $C_{26}H_{18}N_2Cl_4Pd_2$(%); C, 43.79; H, 2.54; N, 3.93; Pd, 29.85. Found: C, 43.40; H, 2.80; N, 3.70; Pd, 29.73. IR (KBr pellets): 1612 cm^{-1} (νC=C).

Crystal structure determination [6–12]

Dissolving *trans*-{Pt[(o-NC_5H_4)C≡C(Ph)]Cl_2(SEt_2)} in a minimum of acetone and allowing slow diffusion of pentane into the yellow solution, at room temperature, produced yellow crystals of the complex. A suitable crystal (0.10 × 0.10 × 0.2 mm) was mounted on an Enraf-Nonius CAD4 diffractometer using graphite monochromated MoKα radiation. The structure was solved by direct methods (SHELX86; Sheldrick, 1986) and refined with anisotropic displacement parameters (VAXSDP, version 3.0, 1986). The H atoms were calculated at ideal positions and used for calculation of the structure factors only. The DIFABS absorption correction was applied after isotropic refinement with T_{max} = 1.1013, T_{min} = 0.7753 and T_{aver} = 0.9884. The crystallographic parameters were obtained by automatic centering of 25 reflections. The ω/2θ scan technique was employed to measure the intensities for 6902 reflections. Unit cell dimensions were determined by least-squares refinement of the setting angles of 25 reflections with values for 2θ between 3 and 31°. Table I contains all the relevant crystallographic parameters for the structure of **2b**.

TABLE I X-ray crystallographic parameters of *trans*-{ Pt[(o-NC_5H_4)C≡C(Ph)]Cl_2(SEt_2)}

	Crystal parameters
Molecular formula	$C_{17}H_{19}Cl_2NPtS$
Formula mass	535.41
Crystal system	Monoclinic
Space group	$P2_1/n$

Downloaded At: 15:54 23 January 2011

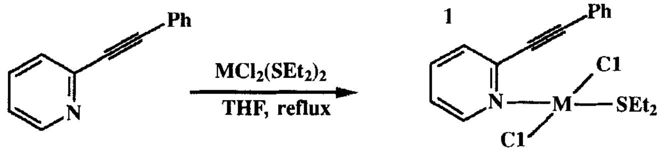
TABLE I *(Continued)*

	Crystal parameters
a(Å)	9.083(2),
b(Å)	11.238(2),
c(Å)	17.913(3)Å
β(°)	93.0112
V(Å^3)	1826.0
Z	4
D_x (g.cm^3)	1.947
F(000)	1024
	Data collection parameters
MoK$_\alpha$ (Å)	λ = 0.70930
T (K)	223
Reflections collected	6902
Independent reflections	3570 [R_{int} = 0.023]
Reflections observed	3570 ($I>3\sigma_{(I)}$)
μ (cm^{-1})	81.655
	Refinement parameters
Parameters	200
Extinction coefficient	1.5732.10^{-9}
R	0.062
Rw	0.075
Δ/σ	0.001

Downloaded At: 15:54 23 January 2011

RESULTS AND DISCUSSION

Reaction of the alkyne **1** with $MCl_2(SEt)_2$ (M=Pd or Pt) in THF, under reflux, produces the air stable complexes **2a** and **2b** in almost quantitative yield (Scheme 1). The structure of these compounds has been assigned on the basis of their IR, NMR (^{1}H and ^{13}C) spectra and elemental analysis (see experimental section). In the IR spectra of these compounds the band corresponding to the ν(C≡C) stretching frequency is relatively close to that of **1** (2225 cm^{-1}), indicating that the C-C triple bond is not η^2-coordinated to the metal center. The structure of **2b** has been determined by X-ray diffraction analysis and the results are presented below.



1

2a, M = Pd
2b, M = Pt

SCHEME 1

Downloaded At: 15:54 23 January 2011

Crystal structure studies of 2b

Atomic coordinates and thermal parameters of the non-hydrogen atoms are given in Table II. Selected bond lengths and angles are listed in Table III.

TABLE II Atomic positional fractional parameters ($\times 10^4$) and equivalent isotropic temperature factors ($Å^2 \times 10^3$)

	x/a	*y/b*	*z/c*	B_{eq}‡
Pt	0.25647(6)	0.21395(5)	0.10315(3)	2.166(8)
Cl(1)	0.4821(4)	0.1656(4)	0.0589(2)	3.00(7)
Cl(2)	0.0322(4)	0.2670(4)	0.1452(3)	3.78(8)
S	0.2397(5)	0.0424(4)	0.1685(2)	3.17(8)
N(11)	0.263(1)	0.373(1)	0.0474(6)	2.4(2)
C(1)	0.440(2)	0.445(1)	0.1355(9)	2.9(3)
C(2)	0.531(2)	0.426(1)	0.1890(8)	2.6(3)
C(3)	0.398(2)	0.046(2)	0.235(1)	4.8(4)
C(4)	0.378(3)	0.142(2)	0.292(1)	5.4(5)
C(5)	0.287(2)	−0.082(1)	0.108(1)	3.8(4)
C(6)	0.157(3)	−0.105(2)	0.054(1)	6.8(6)
C(12)	0.173(2)	0.390(1)	−0.0144(8)	2.9(3)
C(13)	0.168(2)	0.494(1)	−0.0544(8)	2.9(3)
C(14)	0.259(2)	0.586(1)	−0.0292(8)	2.7(3)
C(15)	0.349(2)	0.572(1)	0.0348(9)	3.1(3)
C(16)	0.350(2)	0.464(1)	0.0709(8)	2.7(3)
C(21)	0.628(2)	0.394(1)	0.2487(8)	2.7(3)
C(22)	0.655(2)	0.468(2)	0.3097(9)	3.4(3)
C(23)	0.759(2)	0.432(2)	0.3667(9)	4.2(4)
C(24)	0.822(2)	0.323(2)	0.3653(9)	3.9(4)
C(25)	0.800(2)	0.251(2)	0.305(1)	3.5(3)
C(26)	0.702(2)	0.285(2)	0.247(1)	3.9(3)

‡ B_{eq} is defined as $4/3[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + \ldots]$

TABLE III Selected interatomic distances (Å) and bond angles (°) for **2b**

Distances(Å)			
Pt-Cl(1)	2.301(4)	C(2)-C(21)	1.412(3)
Pt-Cl(2)	2.287(4)	C(21)-C(22)	1.38(2)
Pt-S	2.264(4)	C(22)-C(23)	1.41(2)
Pt-N(11)	2.060(1)	C(23)-C(24)	1.35(3)
C(16)-C(1)	1.400(2)	C(24)-C(25)	1.36(2)
C(1)-C(2)	1.250(3)	C(25)-C(26)	1.38(2)
N(11)-C(16)	1.34(2)	C(14)-C(13)	1.38(2)
C(16)-C(15)	1.37(2)	C(13)-C(12)	1.37(2)
C(15)-C(14)	1.39(2)	C(12)-N(11)	1.36(2)
Angles(°)			
N(11)-Pt-S	177.0(3)	C(2)-C(1)-C(16)	174.0(2)
N(11)-Pt-Cl(1)	89.3(3)	Cl(1)-Pt-S	93.6(1)
N(11)-Pt-Cl(2)	89.0(3)	Cl(1)-Pt-Cl(2)	178.3(1)
Pt-N(11)-C(1)	90.6(6)	Cl(2)-Pt-S	88.1
C(12)-N(11)-C(16)	118.0(1)	N(11)-C(16)-C(1)	117(1)
C(2)-C(21)-C(22)	122(1)	C(3)-S-C(5)	101.6(9)
C(1)-C(2)-C(21)	175.0(2)		

The platinum atom is almost square-planar with N(1) and S in a *trans* arrangement (Figure 1). The two chloride atoms are also *trans*. The substituted-pyridinyl-ligand is perpendicular to the plane of the '$PtCl_2S$' fragment.

The C(1) · · ·Pt and C(2) · · ·Pt distances are 3.123 and 3.722 Å, respectively, indicating a weak interaction of the platinum atom with the unsaturated carbon C(1).[13] It is important to note that platinum-η^2-alkynes complexes[14,15] usually have C-Pt bond lengths between 2.230–2.330 Å. It is significant that the C(1)-C(2) distance is 0.042 Å longer than the triple bond distance (1.208 Å) found in phenylacetylene.[16] These facts indicate strong conjugation involving the C(1)-C(2) bond, the pyridine and phenyl rings.

Reactions of water, diethylamine and chloride with 1 bound to Pt(II) and Pd(II)

The reaction of a large excess of water with complex **2b** gives compound **3** in a good yield (81%). The disappearance of the ν(C≡C) bond and the appearance of the characteristic stretching vibration of the C=O group (ν_{CO} = 1756 cm^{-1}) in the IR spectrum of **3** is a strong indication that the C≡C bond has been oxidized by H_2O. Compound **2b** also reacts with other nucleophiles such as diethylamine[2] to yield complex **4**. The structural assignment of **4** was based on its spectro-

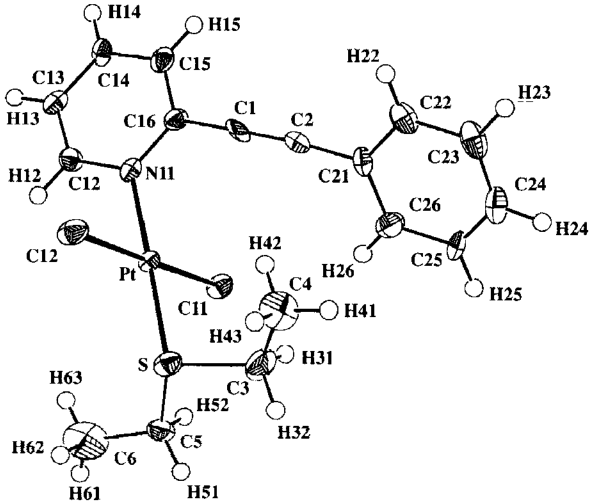


FIGURE 1 A perspective view of the compound **2b** with the atomic numbering scheme. Displacement ellipsoids are shown at the 50% probability level for non-H atoms.

Downloaded At: 15:54 23 January 2011

scopic data and has been confirmed by an X-ray diffraction analysis.[2] The observed *trans*-stereochemistry of the exocyclic C=C bond (with respect to the NEt_2 group and the proton) suggest that this reaction proceeds *via* an overall concerted $HNEt_2$ addition to the C≡C bond. This reaction can be understood in terms of oxidative addition of $HNEt_2$ to **2b** leading to Pt^{IV} complex. Insertion of the C≡C bond into the Pt-NEt_2 bond would give four-membered platinacycle that, followed by reductive elimination, affords compound **4** (Scheme 2).

In contrast to **2b**, compound **2a** is very stable and does not react with water or diethylamine under various reaction conditions. However, addition of equimolar amounts of **1** to a methanolic solution of Na_2PdCl_4, under reflux, yields compound **5** as a yellow insoluble microcrystalline solid (Scheme 3). The structure of compound **5** has been deduced from its CHN analysis and IR spectrum. Moreover the ^1H NMR spectrum of the monomeric derivative of **5** (prepared *in situ* by the addition of Py-d5 to the $CDCl_3$ suspension of **5** in an NMR tube) indicated the presence of phenyl and pyridinyl aromatic protons. It is important to note that the regio- and stereochemistry at the exocyclic C=C bond is as usually obtained from chloropalladation of propargyl amines,[17] thioetheres[18] and simple alkynes.[19] Indeed, these reactions are assumed to proceed *via* external Cl^- attack on the C≡C bond to form the most stable five-membered cyclopalladated complex. It is significant that the similar Pt(II) compound has not been detected from the reaction of **1** with K_2PtCl_4; only a complex mixture of organometallic products[†] were observed, probably arising from hydrolysis of the C≡C bond (see above).

It is important to note that alkyne 1 does not react with nucleophiles in the absence of Pt(II) and Pd(II) compounds, clearly indicating that the C≡C bond is activated by the metal center. The nature of the transition metal also plays an important role on the selectivity of the reaction of 1 with Na_2PdCl_4 and K_2PtCl_4. Thus, chloropalladation of the alkyne occurs easily, whereas chloroplatination has not been observed with alkyne **1**. This different behaviour can be attributed to the more easily access to Pt^{IV} compounds *via* oxidative addition of the nucleophilic than for Pd.[20]

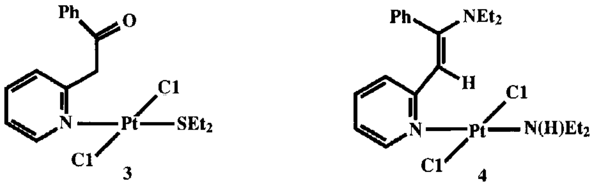
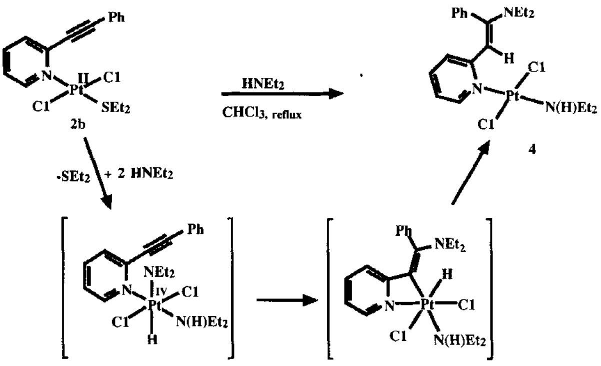


CHART 1

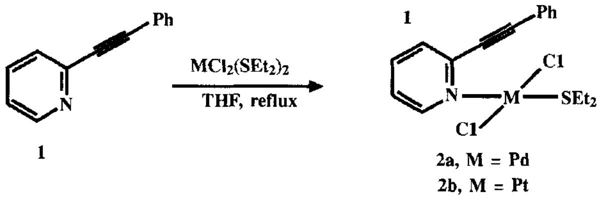
[†] The IR spectrum of this mixture of products shows $\nu_{C=O}$ at 1720 cm^{-1} 8 and ν_{C-H} at 2875, 2910 and 2940 cm^{-1}.

Downloaded At: 15:54 23 January 2011

Downloaded At: 15:54 23 January 2011



SCHEME 2



SCHEME 3

Acknowledgments

We acknowledge partial financial support from CNPq, CAPES, DAAD, FAPERGS and VW-Stiftung (Germany).

References

[1] J.P. Collman, L.S. Hegedus, J.R. Norton and G.F. Finke, *Principles and Applications of Organotransition Metal Chemistry.* (Mill Valley, University Science Books, 1987) pp 409–415 and 859–879.

[2] J. Dupont, O.L. Casagrande Jr., A.C. Aiub, M. Hörner and J. Beck, *Polyhedron*, **13**, 2583 (1994).

[3] J. Dupont, R.A.P. Halfen, F.K. Zinn and M. Pfeffer, *J. Organomet. Chem.*, **484**, **C8**, (1994).

[4] G.K. Anderson and M. Lin, *Inorg. Synth.*, **28**, 61 (1990).

[5] K. Sonogasshira, Y. Tohda and N. Hagihara, *Tetrahedron Lett.*, **50**, 4467 (1975).

[6] G.M. Sheldrick, SHELXS 86, Program for Crystal Structure Solution, University of Göttingen, Germany (1986).

[7] C.K. Johnson, ORTEP - A Thermal Ellipsoid Plot Programm, Oak Ridge National Laboratory, Tennessee (1965).

[8] CAD4, Automatic Four Circle Diffractometer ENRAF-NONIUS, Delft, Holland.

[9] B.A. Frenz, The Enraf-Nonius CAD4 SDP - A Real-Time for Concurrent X-Ray Data Collection and Crystal Structure Solution. Computing in Crystallography, edited by R. Schenk, H. Olthof-Hazekamp, van Koningsveld and G.C. Bassi, pp. 64–71, Delft Univ. Press (1978).
[10] B.A. Frenz and Associates Inc., College Station, Texas 77840, USA and ENRAF-NONIUS, Delft, Holland, Structure Determination Package VAXSDP, Version 3.0 (1986).
[11] N. Walker and D. Stuart, *Acta Cryst.*, **A39**, 158 (1983).
[12] W.H. Zachariansen, *Acta Cryst.*, **16**, 1139 (1963).
[13] J. Forniés, E. Lalinde, F. Martínez, M.T. Moreno and A.J. Welch, *J. Organomet. Chem.*, 271 (1993); O.M. Abu-Salah and C.B. Knobler, *J. Organomet. Chem.*, C10 (1986).
[14] J.R. Berenguer, J. Forniés, E. Lalinde, F. Martinez, E. Urriolabeitia and A.J. Welch, *J. Chem. Soc. Dalton Trans.*, **1291** (1994).
[15] M. Forniés, E. Lalinde, A. Martín and M.T. Moreno, *J. Chem.Soc. Dalton Trans.*, 135 (1994).
[16] A.P. Cox, I.C. Ewart and W.M. Stigliani, *J. Chem. Soc. F. Trans. II*, 504 (1975).
[17] T. Yukawa, S. Tsutsumi, *Inorg. Chem.*, 1968, 7, 1458.
[18] J. Dupont, N.R. Basso and M.R. Meneghetti, *Polyhedron*, **15**, 2299 (1996).
[19] J.E. Bäckvall, Y.I.M. Nilsson and R.G.P. Gatti, *Organometallics*, 4242 (1995).
[20] F.R. Hartley, The Chemistry of Palladium and Platinum, Applied Science, London, (1973).

Downloaded At: 15:54 23 January 2011