

A. SUÁREZ  
J.M. VILA  
E. GAYOSO  
M. GAYOSO \*

Departamento de Química Inorgánica  
Facultad de Química  
Centro Coordinado del C.S.I.C.  
Universidade de Santiago de Compostela  
España



## CYCLOMETALLATION REACTIONS OF Pd(II) WITH N-( $\alpha$ -NAPHTHYLIDENE)- o-TOLUIDINE \*\*

*Reaction of N-( $\alpha$ -naphthylidene)-o-toluidine with palladium(II) acetate yields a bridged acetato complex, [(nf-N,C)PdAc]<sub>2</sub>. Metathetical reactions with sodium chloride or bromide give bridged chlorine or bromine complexes, [(nf-N,C)PdX]<sub>2</sub> (X = Cl, Br). Halogen bridge splitting reactions have been carried out with triphenylphosphine in 1:2 and 1:4 molar ratio to obtain the corresponding cyclometallated and non-cyclometallated monomers. The elemental analyses, IR and NMR spectra are in accordance with the structures given for the present compounds, and they allow us to distinguish the bridged complexes from the monomers, and among the latter between the cyclometallated [(nf-N,C)PdLX] and non-cyclometallated ones [(nf-C)PdL<sub>2</sub>X], in which the five membered ring disappears due to the presence of two triphenylphosphine ligands bonded to the central atom.*

\* Author to whom correspondence should be submitted.

\*\* Part of this work was presented at the 4.º Encontro Anual da Sociedade Portuguesa de Química; Lisbon, April, 1981.

## INTRODUCTION

Cyclometallation reactions have been widely studied [1,2] most of all with aromatic N-donor ligands, although other ligands with group VB and VIB donor atoms have been used [2]. In the course of our investigations regarding the formation of orthometallated complexes we have already studied the reactions of a typical N-donor ligand [3] and we now report the synthesis and characterization of the complexes derived from N-( $\alpha$ -naphthylidene)-o-toluidine. The acetato, chloro and bromo bridged complexes have been prepared first. Halogen bridge splitting reactions with triphenylphosphine yielded the cyclometallated and non-cyclometallated monomers when a 1:2 and 1:4 molar ratio was used, respectively. Our aims were to study the different types of complexes formed on the basis of the spectroscopical data, specially in the cases of the non-cyclometallated compounds in which the  $\nu(\text{C}=\text{N})$  stretching frequency appears unusually low for this type of compounds.

## EXPERIMENTAL

### MATERIALS

o-toluidine and  $\alpha$ -naphthaldehyde were distilled before use. Palladium(II) acetate (Fluka) and triphenylphosphine (Merck) were not further purified. N-( $\alpha$ -naphthylidene)-o-toluidine was synthesized by refluxing equimolar amounts of o-toluidine and  $\alpha$ -naphthaldehyde in chloroform solution during 1 hour. The solvent was distilled "in vacuo" after which a yellow solid was obtained. Solvents were purified by the standard methods. The reaction between palladium acetate and the Schiff base was carried out in a N<sub>2</sub> atmosphere.

### ANALYSES

C, H, N, analyses were carried out in a Perkin-Elmer model 240-B elemental analyzer. IR spectra were recorded on a Perkin-Elmer model 180 spectrophotometer as nujol mulls or polyethylene pellets. The NMR spectra were recorded with a Varian CFT-20 in deuterochloroform using tetramethylsilane as an internal standard. Pd was determined polarographically. The analytical results are reported in Table 1.

Table 1  
Analyses and colour of the complexes

Complex	Colour	% C*	% H*	% N*	% Pd*
$[(nf-N,C)PdAc]_2$	Light Orange	58,8(58,6)	4,7(4,2)	3,1(3,4)	25,65(25,97)
$[(nf-N,C)PdCl]_2$	Yellow	56,1(56,0)	3,8(3,7)	3,5(3,6)	27,35(25,55)
$[(nf-N,C)PdBr]_2$	Yellow	48,9(50,2)	3,3(3,3)	2,9(3,2)	24,25(24,70)
$[(nf-N,C)PdLCl]$	Pale Yellow	66,9(66,7)	4,6(4,5)	1,7(2,2)	16,36(16,41)
$[(nf-N,C)PdLBr]$	Pale Yellow	61,6(63,4)	4,4(4,2)	1,7(2,0)	14,81(15,35)
$[(nf-C)PdL_2Cl]$	Pale Yellow	69,8(71,2)	4,9(4,9)	1,4(1,5)	12,13(11,68)
$[(nf-C)PdL_2Br]$	Pale Yellow	67,5(67,9)	4,7(4,7)	1,3(1,5)	11,50(11,14)

\* The calculated analyses are in parentheses.

nf-N,C and nf-C = N-( $\alpha$ -naphthylidene)-*o*-toluidine bi- and monodentate, respectively.

L =  $P(C_6H_5)_3$

### $[(nf-N,C)PdAc]_2$

In a 100 ml round-bottomed flask 0.3 g (1.36 mmol) of palladium acetate and 0.34 g (1.4 mmol) of N-( $\alpha$ -naphthylidene)-*o*-toluidine were dissolved in 25 ml of acetic acid. The dark-red solution turns orange-red upon heating. After refluxing for 1 hour the solution is cooled, diluted with water and extracted with dichloromethane. The extract was concentrated and chromatographed on silica gel. With benzene a yellow green band was eluted, which once analyzed showed to be the initial Schiff base. With dichloromethane containing 1 % ethanol a yellow-red band was eluted. After being concentrated it was again chromatographed on silica gel. A green band eluted with dichloromethane produced an oil that was not further investigated. The title complex was eluted with dichloromethane containing 1 % ethanol and recrystallized from chloroform/*n*-hexane to give a light orange solid.

### $[(nf-N,C)PdX]_2$

To a solution of 0.1 g (0.12 mmol) of  $[(nf-N,C)PdAc]_2$  in acetone an aqueous solution of sodium chloride (X=Cl) or sodium bromide (X=Br) was added, and a yellow precipitate was obtained in each case. The solids were filtered off, washed with water and dried.

### $[(nf-N,C)PdLX]$

To a suspension of 0.050 g (0.065 mmol) of  $[(nf-N,C)PdX]_2$  (X=Cl) and to another one of 0.05 g (0.058 mmol) (X=Br), both in acetone (5 ml), 0.034 g (0.13 mmol) and 0.030 g (0.116 mmol) of triphenylphosphine were added, respec-

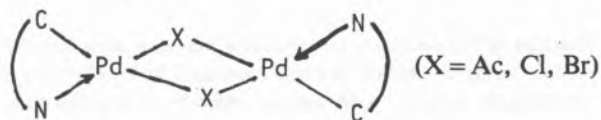
tively. In both cases a yellow solution forms. Addition of *n*-hexane to the solution gave a precipitate that was filtered off, washed with *n*-hexane and dried in vacuum.

### $[(nf-C)PdL_2X]$

To a suspension of 0.050 g (0.065 mmol) of  $[(nf-N,C)PdX]_2$  (X=Cl) and to another one of 0.050 g (0.058 mmol) (X=Br), both in acetone (5 ml), 0.068 g (0.26 mmol) and 0.061 g (0.23 mmol) of triphenylphosphine were added, respectively. In both cases a yellow solution forms. Addition of *n*-hexane to the solution gave a precipitate that was filtered off, washed with *n*-hexane and dried in vacuum.

## RESULTS AND DISCUSSION

The bridged complexes are of the type



the organic ligand being bonded to the metal atom by a  $\sigma$  carbon bond and a coordinated nitrogen bond. In the cyclometallated monomers the five-membered ring remains, with the halogen atom "trans" to the carbon atom. In the non-cyclometallated monomers the organic moiety is linked to the metal atom only through the carbon atom. All this is confirmed by the IR data, which are reported in Table 2.

The acetato bridged complexes exhibit two IR bands at 1565 and 1410  $cm^{-1}$  that correspond to  $\nu_{as}(CH_3COO)$  and  $\nu_s(CH_3COO)$ , respectively.

Table 2

Complex	$\nu(\text{C}=\text{N})$	$\nu_{\text{op}}(\text{Pd}-\text{C})$	$\nu_{\text{ip}}(\text{Pd}-\text{C})$	$\nu(\text{Pd}-\text{C})$	$\nu_{\text{op}}(\text{Pd}-\text{N})$	$\nu_{\text{ip}}(\text{Pd}-\text{N})$	$\nu(\text{Pd}-\text{N})$	$\nu(\text{Pd}-\text{P})$	$\nu_{\text{as}}(\text{Pd}-\text{X}_b)$	$\nu_s(\text{Pd}-\text{X}_b)$	$\nu(\text{Pd}-\text{X}_t)$
Ligand	1628m										
$[(\text{nf}-\text{N}, \text{C}(\text{PdAc}))_2]$	1615m	580m	562w		418m	370vw					
$[(\text{nf}-\text{N}, \text{C}(\text{PdCl}))_2]$	1615s	580m	563w		415m	360vw			308m	248m	
$[(\text{nf}-\text{N}, \text{C}(\text{PdBr}))_2]$	1617s	580m	564w		417m	360vw			192m	160w	
$[(\text{nf}-\text{N}, \text{C}(\text{PdLCl}))]$	1612m			582vw				350w	180w		295m
$[(\text{nf}-\text{N}, \text{C}(\text{PdLBr}))]$	1614s			582m				365w	176w		202w
$[(\text{nf}-\text{C})\text{PdL}_2\text{Cl}]$	1611m			582vw					184w		290m
$[(\text{nf}-\text{C})\text{PdL}_2\text{Br}]$	1609m			578m					166w		196m

L =  $\text{P}(\text{C}_6\text{H}_5)_3$ 

They also show absorptions between 460 and 540  $\text{cm}^{-1}$ , which can be assigned to Pd-O vibrations.

The bridged halogen complexes exhibit two  $\nu(\text{Pd}-\text{X})$  frequencies due to  $\nu_{\text{as}}(\text{Pd}-\text{X}_b)$  (308  $\text{cm}^{-1}$ , X = Cl; 192  $\text{cm}^{-1}$ , X = Br) and  $\nu_s(\text{Pd}-\text{X}_b)$  (248  $\text{cm}^{-1}$ , X = Cl; 160  $\text{cm}^{-1}$ , X = Br). By their position the higher ones belong to the  $\nu(\text{Pd}-\text{X})$  "trans" to the nitrogen atom and the lower ones to the  $\nu(\text{Pd}-\text{X})$  "trans" to the carbon atom, as is expected by the lower "trans" influence of the nitrogen atom [11], and as CROCIANI *et al.* have observed with similar types of complexes [12]. In the monomers there is only one band assignable to  $\nu(\text{Pd}-\text{X}_t)$ , as is expected. Thus, the second monomers (Table 2) are non ionic, which is in accordance with the fact that they are only slightly soluble in water and with the absence of precipitation by treatment with silver nitrate. Also by their position [7,12] we may conclude that the halogens are "trans" to atoms of high "trans" influence, *i.e.*, "trans" to the carbon atom or to one of the phosphine ligands in the second two monomers. The "cis" or "trans" positions of the two phosphine ligands can be ascertained, according to MASTIN [14], by the intensity of a band near 550  $\text{cm}^{-1}$ ; the weak intensity of this band in the spectra of the second two monomers leads to a "trans" disposition of the phosphine ligands in these compounds, so that the halogen atom must be "trans" to the carbon atom.

The spectra of all these compounds show weak to medium intensity bands between 580 and 560  $\text{cm}^{-1}$ , which are characteristic of Pd-C vibrations [7], indicating the presence of Pd-C bonding. So, in the bridged complexes there are two Pd-C bands at 580 and *ca.* 560  $\text{cm}^{-1}$  due to the out-of-phase and in-phase vibrations, respectively, whereas in the four monomers there is only one *ca.* 580  $\text{cm}^{-1}$ .

For the Pd-N vibrations we find in the spectra of the dimers bands at *ca.* 415 and *ca.* 360  $\text{cm}^{-1}$ , corresponding to the out-of-phase and in-phase motions. Between 450 and 350  $\text{cm}^{-1}$  only the spectra of the first two monomers show a band, which can be attributed to a  $\nu(\text{Pd}-\text{N})$  mode with the nitrogen atom "trans" to a high "trans" influence ligand, that is, a phosphine ligand; so, these complexes are cyclometallated. The absence of such a band in the spectra of the second two monomers indicates that these cannot be cyclometallated.

The shift towards lower wavenumbers of the band assigned to the  $\nu(\text{C}=\text{N})$  frequency in the complexes in comparison with the original Schiff base has been claimed to be a sign of coordination through the nitrogen atom [4,5]. A lower frequency shift can be expected in the formation of an ordinary coordination complex, where the Schiff base is bonded to the central atom by the nitrogen atom only. But in our case we must not forget a possible conjugation of the  $\text{C}=\text{N}$  double bond not only with the phenyl ring bonded to the carbon atom, but also with the one linked to the nitrogen atom. In the  $-\text{C}=\text{C}-\text{C}=\text{N}-$  system there are two conjugated double bonds and it is possible that there may be strong coupling between  $\nu(\text{C}=\text{N})$ ,  $\nu(\text{C}=\text{C})$ ,  $\nu(\text{N}-\text{C})$ , and  $\delta(\text{C}-\text{H})$ , so it is quite difficult to foresee the modification that will take place when a simultaneous coordination by the carbon and nitrogen atoms is produced in the formation of a chelate ring. Furthermore, the electron pair of the M-C bond is bonding as it was in the Schiff base, while the electron pair of the M-N bond, initially non bonding, is now slightly bonding. On the other hand, the possible presence of metal-to-ligand back bonding should cause a partial occupation of the  $>\text{C}=\text{N}-\pi^*$  orbitals. In our complexes the  $\nu(\text{C}=\text{N})$  frequency shifts are all

towards lower wavenumbers,  $-12\text{ cm}^{-1}$  in the bridged complexes,  $-15\text{ cm}^{-1}$  in the cyclometallated monomers and  $-18\text{ cm}^{-1}$  in the non-cyclometallated ones. With these results we can only conclude that the formation of a complex, whether cyclometallated or not, results in lower wavenumbers of the  $\nu(\text{C}=\text{N})$  frequency.

The assignment of metal-phosphine vibrations has been a subject of controversy [6-10], but the criterion most widely accepted nowadays is that they lie below  $200\text{ cm}^{-1}$ . In the spectra of our complexes we find bands for  $\nu(\text{Pd-P})$ , whose wavenumbers can be seen in Table 2.

The  $^1\text{H}$  NMR spectrum of the Schiff base shows a singlet at 8.98 ppm (azomethine proton). The high field chemical shift of an azomethine proton indicates that the coordination of the palladium atom is through the nitrogen atom and not through the  $\text{C}=\text{N}$  double bond [13], and that the Pd-N bond is effectively established. In the bridged complexes there are singlets at 8.21 ppm ( $\text{X}=\text{CH}_3\text{COO}$ ), 8.60 ppm ( $\text{X}=\text{Cl}$ ), and 8.64 ppm ( $\text{X}=\text{Br}$ ), all of them shifted to higher field.

Received 24.Mars.1983 (1st version)

28. December.1983 (revised version)

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## RESUMO

Reacções de Ciclometalación de Pd(II) con N-( $\alpha$ -naftiliden)-o-toluidina.

A reacção de N-( $\alpha$ -naftiliden)-o-toluidina com acetato de paládio(II) produce um complexo cas pontes acetato  $[(\text{nf-N,C})\text{PdAc}]_2$ . As reacções de matáteses com cloruro e bromuro de sódio dan complexos com pontes cloro e bromo,  $[(\text{nf-N,C})\text{PdX}]_2$  ( $\text{X}=\text{Cl, Br}$ ). A reacção dos dímeros com pontes halógeno com trifenílfsfina, en relación molar 1:2 e 1:4, conduce aos monómeros ciclometalados e non ciclometalados, respectivamente. As análises elementais e os espectros de IR e RMN concordam cas estruturas que se propoñen e permiten distinguir entre os complexos dímeros e os monómeros, e nos derradeiros, entre os monómeros ciclometalados  $[(\text{nf-N,C})\text{PdLX}]$  e os non ciclometalados  $[(\text{nf-C})\text{PdL}_2\text{X}]$ , nos que o anel de cinco membros desaparece por mor da unión de dous ligandos trifenílfsfina ao metal central.