Asymmetrical Dimeric - Allyl - Palladium Complexes
1. Data from ^{1}H-NMR Spectra

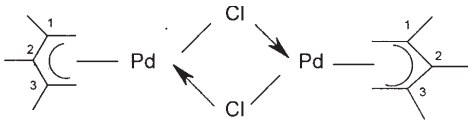
MARIA MAGANU*, FILIP CHIRALEU, MĂDĂLINA HRUBARU, GHEORGHE MIHAI
Center of Organic Chemistry, "Costin D. Nenitzescu" Spl. Independentei 202B, 050461, Bucharest, Romania

π-Allyl palladium complexes are known as being either symmetrical dimeric complexes with Pd-Cl bridges or asymmetric monomeric complexes with chlorine and other organic ligands. The question is if the two forms are clearly delimited or if even in the symmetrical complexes there is a certain asymmetry of the π-allyl–palladium bond. In order to answer this question two series of π-allyl palladium complexes (tri- and tetrasubstituted) were studied by ^{1}H-NMR. The results showed that even for dimeric complexes, for a certain substitution pattern, an asymmetry of the Pd-π-allyl group may exist.

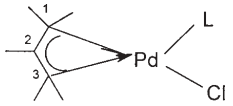
Keywords: π-allyl palladium complexes, ^{1}H-NMR spectroscopy

The structure of π–allyl palladium complexes was the subject of several NMR spectral studies [1] as well as X ray structure determinations [2].

For the parent compound, the allyl palladium chloride itself, a symmetrical dimeric structure (1) was ascribed. The same structure was established for several mono- and disubstituted π–allyl–$PdCl_2$ complexes [3]. The NMR spectral studies of a large number of π–allyl–$PdCl_2L$ complexes (L= PPh_3, DMSO) with monomeric structure, demonstrated an asymmetrical Pd-C bonding (2) between the allyl group and the metal atom [4-7].



1



2

^{1}H-NMR studies were performed in order to decide if the symmetric or asymmetric character of the complexes is perfectly delimited or even if in the dimeric complexes considered symmetric there is a certain asymmetry of the π-allyl–palladium bond.

Experimental part

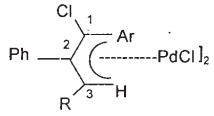
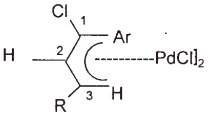
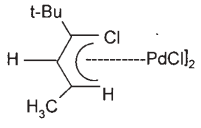
The ^{1}H-NMR spectra were recorded on a 300 MHz Varian Gemini spectrometer using a broadband probe. A solution of BNP (1.0 mmol) in benzene or chloroform (15 mL) was treated with alkene (1- 10 mmol) at room temperature, and acetylene (1. 0 mmol) dissolved in the same solvent (2- 3 mL), was then added. The mixture was kept for 1- 24 h at room temperature and then worked up[9].

Results and discussions

In this work we present spectral evidence concerning the asymmetrical bonding between the metal [8] and the allylic ligand in the dimeric tri- and tetrasubstituted π–allyl-palladium chloride complexes with general formulas A, B and dimeric complexes 11 and 12 (table 1).

The complexes from table 1 were obtained, by the general method previously reported [9], from the

Table 1
DIMERIC COMPLEXES SERIES A (3-8) AND SERIES B (9-12)

Comp.	 A		Comp.	 B	
	Ar	R		Ar	R
3	C_6H_5	CH_2–$C(CH_3)_3$	**9**	C_6H_5	CH_3
4	C_6H_5	CH_3	**10**	2,4,6-$(CH_3)_3C_6H_2$	CH_3
5	2,4,6-$(CH_3)_3C_6H_2$	CH_2-$C(CH_3)_3$	**11**		CH_3
6	2,4,6-$(CH_3)_3C_6H_2$	CH_3	**12**	-	C_6H_5
7	2,5 -$(CH_3)_2C_6H_3$	CH_2-$C(CH_3)_3$		-	
8	2,5 -$(CH_3)_2C_6H_3$	CH_3		-	

* *email: mmaganu@yahoo.com*

Table 2

^{1}H-NMR SPECTRAL DATA (δ ppm, J Hz) OF THE C-2 SUBSTITUTED π-ALLYLIC-COMPLEXES.

δ(ppm) J (Hz)

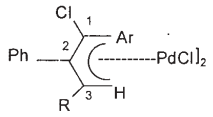
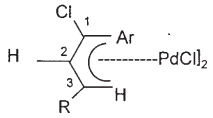
Comp.						
	t-Bu	CH_3 *(J)*	CH_2 *(J)*	H-3 allylic *(J)*	H aromatics	CH_3 mesitylic
3	0.80 s	-	1.63d (7.0)	4.35 t (7.0)	7.1 – 7.80m (10H)	
4	-	1.18 d (6.0)		4.38 t (6.0)	7.20 - 7.85m (10H)	
5	-		1.46d (6.0)	3.58 t (6.0)	6.76 s; 6.92s (2H) 7.51 (3H); 8.11 (2H)	2.28s; 2.50s (2 Me) 3.23s; 3.27s (1Me)
6	-	1.10 d (6.0)	-	3.55 t (6.0)	6.75 s; 6.88s (2H) 7.30 - 7.60m (3H) 7.80 - 8.20m (2H)	2.24s; 2.35s (2Me) 3.10s; 3.24s (1Me)
7	0.78 s	-	-	4.02 t (7.0)	6.85 - 8m (8H)	2.10 - 2.40m (2Me)
8	-	1.11d (6.0)	-	3.93 t (6.0)	6.83 - 8.08m (8H)	2.33s (2Me)
12	1.25 s	0.97d -		5.38	7.22 - 7.45m (2Me)	

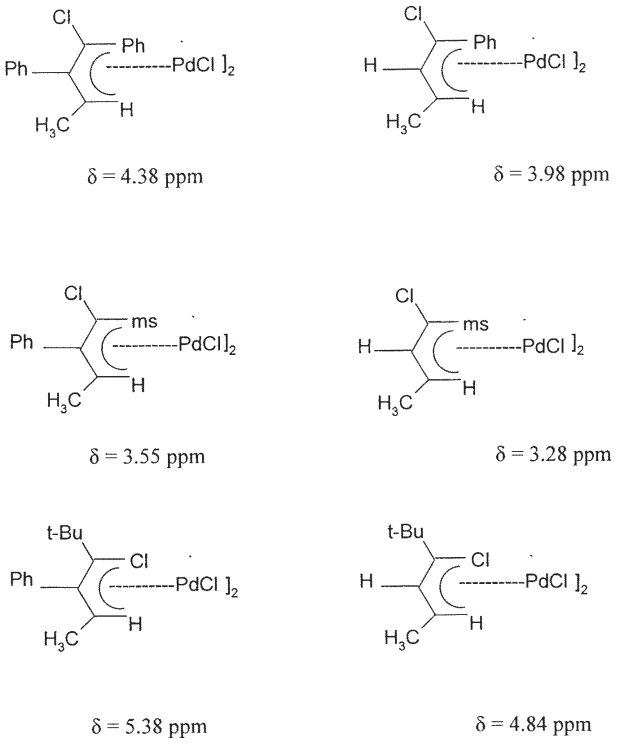
Table 3

NMR SPECTRAL DATA (δ ppm, J Hz) of the C-2 UNSUBSTITUTED π-ALLYLIC COMPLEXES

Comp.						
	t-Bu	CH_3 *(J)*	H-2 *(J)*	H-3	H aromatic	CH_3 Mesitylic
9	-	1.36 d (6.5)	5.55 d (13.0)	3.98 m	7 - 7.50 m	-
10	-	1.30 d (6.5)	6.13d (11.5)	3.28 m	6.73; 6.86 (2s)	2.23; 2.28 (2Me) 3.00 (Me)
11	1.35 s	1.43 d (7.0)	5.20d (11.0)	4.84 m	-	-

corresponding diaryl and monoaryl acetylenes with alkenes and BNP(Benzonytrilepalladium) in benzene or dichloromethane solution. In this manner two series of complexes were obtained. The first compounds (3-8) from series A are substituted at the C-2 carbon, while in the second series of complexes (B. 9 - 11) they are unsubstituted C-2

Tables 2 and 3 show the proton chemical shifts for both series of complexes. It may be observed that the H-3 chemical shifts varies as Ar change in both series of complexes. The chemical shifts of the CH_3 group is



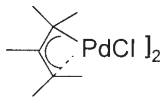
Scheme 1. Chemical shift values for allylic protons H-3

practically unchanged. It is also observed that one methyl group of mesitylene is strongly deshielded in complex 10 and also splited in complexes 5 and 6.

The chemical shift of the H- 3 proton in each series of complexes elucidated the configuration of the π–allylic group. Comparing of chemical shifts the H-3 proton between the two complexes series one remarks a maximum deshielding of 0.54 ppm for the C-2 substituted complexes. This difference gives useful information about the nature of π–allyl–Pd bonding.

Considering the available literature data [1, 3, 10]. it was expected that in the presence of the phenyl group at the C-2 of the allylic system, the signal of the H-3 proton should remain unchanged or shifts a little coresponding to a shielding effect.

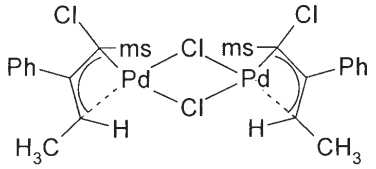
The observed deshielding can be connected with the increase of the double bond character of the linkage between C-2 and C-3 and consequently the increase of the single bond character between the C-1 and C-2 carbons. Due to the fact that the C-1 carbon atom becomes more pronounced sp^3 in character than the C-3 carbon, the complexes having aryl or alkyl groups in z configuration at C-2 and C-3, have the C_2- C_3 bonds shortened than the C_1-C_2 bonds. The Pd-C_1 bond has a more pronounced character than the Pd-C_3 bond. This fact has steric consequences. The distance between Pd and C-1 is shortened, while the distance Pd-C_3 is lengthened (13). It is possible also that the bonding of the metal at C-1 with σ character is favored by nature of the substituents at this carbon atom.



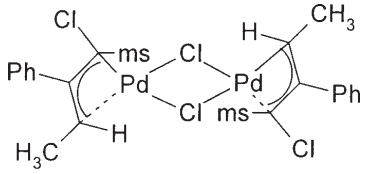
13

The asymmetry of the bonding between the organic ligand and palladium in the dimeric complexes 5 and 6 is similar to the bonding asymmetry in monomeric complexes (formula 13). Favouring the asymmetric π–allyl–palladium bonding in the studied complexes we present some spectroscopic evidences

For the complexes with mesityl at C-1 carbon we observed the deshielding of one mesitylic methyl and even the signal splitting in complexes 5 and 6. These effects can be explained by the proposed asymmetry of the π–allyl–Pd bonding. It is shown that the mesityl group is perpendicular to the allyl system bringing a methyl group near to a chlorine atom of the Pd-Cl bridge leading to its deshielding. The effect is greater for complexes 5 and 6 with substituted C-2 and determines a steric hindrance of the allyl group rotation around the bonding to the palladium atom. In this way the *sin – anti* isomers of organic ligands 6A and 6B are evidenced and the signal splitting of the deshielded methyl is explained.



6 A



6B

ms = mesityl

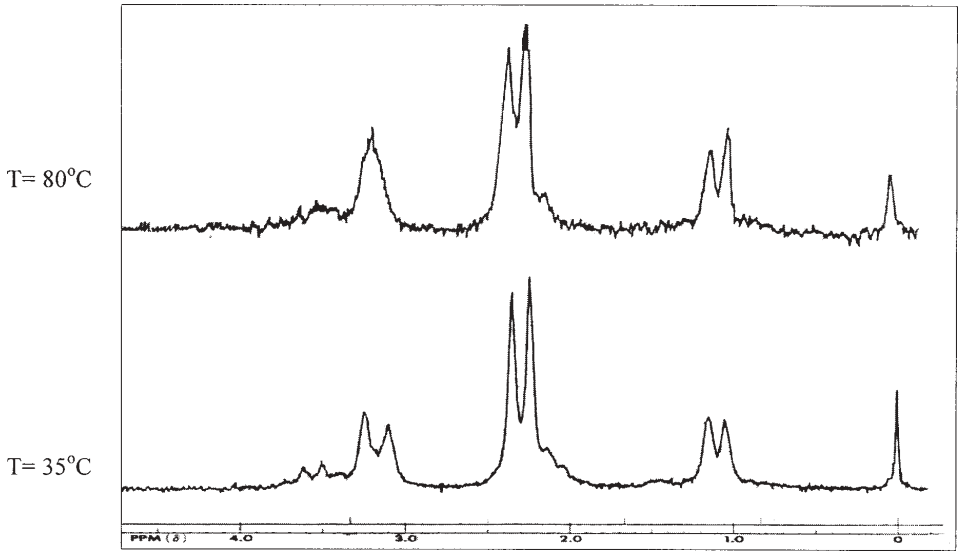


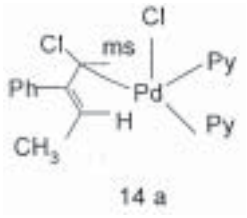
Fig. 1. NMR spectrum ($CDCl_3$) of allylic complexes 6

As the temperature is raised the rotation energy is increased and may exceed steric hindrance, so that the two singlets at 3.10 and 3.24 ppm coalescence into a singlet at 3.16 ppm. In the complex unsubstituted at C-2 the π–allyl–Pd bonding asymmetry and steric hindrance are smaller and the π- allyl group can rotate freely at room temperature. The ^{1}H- NMR spectrum of these complexes shows only a singlet at 3.00 ppm for the deshielded methyl.

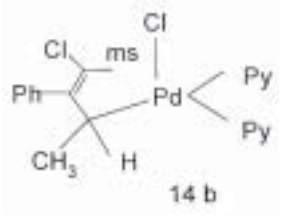
It is known that in the presence of other donors (DMSO, pyridine, PPh_3) the dimeric Pd-Cl bonding complexes yield σ-allylic monomeric complexes [11-13].

For instance in the ^{1} H- NMR spectrum of complexes 6 in the presence of pyridine small but significant changes appear. Thus the mesitylic methyls show signals at smaller values: 2.20 ppm (1Me) and 2.51 ppm (2Me); the two aromatic singlets (6.76 and 6.88 ppm) become a singlet at 6.76 ppm; other spectral singlets are practically unchanged. After removing of pyridine the spectrum returns to the initial form. This fact shows that in the presence of pyridine the π–allyl complex changes to σ–allylic complex as a short–lived intermediate.

The complexes 5 and 6 give to rise two short lived intermediates, the complex 14 a (bonded to the carbon C-1) and the complex 14 b (bonded to the carbon C-3).



14 a



14 b

ms = mesityl

It is known that protons attached to a carbon atom σ bonded to palladium are more shielded [14-16]. in fact, the spectrum with pyridine shows a deshielding of the H-3 proton (from 3.55 to 3.63 ppm) and as a consequence we consider that the short–lived intermediate has the structure 14a. This intermediate is in very good agreement with the asymmetry of the π-allyl–palladium bonding proposed before.

Conclusion

In conclusions we can say that for some π–allyl–Pd dimeric complexes there is some asymmetrical character of the π–allyl–palladium bond, which has effects into spectral and chemical data [17, 18].

Bibliography

1.DEHM, H. C., CHIEN, J. C., J. Am. Chem. Soc., **82**, 1960, p. 4429, ROBINSON, S. D., SHAW, B. L., J. Chem. Soc., 1963, p. 4806

2.ROWE, J. M., Proc. Chem. Soc., 1962, p. 66; OBERHANSLY, W. E., DAHL, L. F., J. Organometalics. Chem., **3**, 1965, p. 43

3.VOLGER, H. C., Rec. Trav. Chim., **88,** 1969; HUTTEL H., CHRIST HERZOG, R K., Chem. Ber., **97**, 1964, p. 2710.

4.POWELL, J., ROBINSON, S. D., SHAW, B. L., Chem. Commun., 1965, p. 78

5.SATTON, G. L., RAMEY, K., C J. Am. Chem. Soc., **88,** 1966, p. 1327, DOUGLAS, R. CHRISOPE., BEAK, P., SAUNDRES, W. H., J. Am. Chem. Soc., **110,** 1988, p. 230

6.MASON, R., RUSSELL, D. R., Chem. Commun., 1966, p. 26

7.POWELL, J., SHAW, B. L., J. Chem. Soc., A, 1987, p. 1839; ALBERTI, D., GODDARD, R., RUFINSKA, A., PORSCHKE, K. R., Organometallics., **22**, 2003, p. 4025

8.HOSOKAVA, T., MORITANI, I., NISCHIOV, S., Tetrahedron Lett., 1969, p. 3833.; BAECKVALL, JAN E., G. ADOLF, G., Tetrahedron Lett., **29,** Nr. 18 **,** 2002, p. 2243-6

9.STAICU, S., DINULESCU, I.G., CHIRALEU, F., AVRAM, M., J. Organomet. Chem., **113**, 1976, p. 69

10.OGSSAWARA, M., TAKIAZAWA, K. I., HAYASHI, T., Organometallics., 21, 2005, p. 4853-4861

11.VRIEZE, K., MACLEAN, C., COSSEE, P., HILBERS, C.W., Rec. Trav. Chim., **85,** 1966, p. 1077

12.VRIEZE, K., PRAAT, A. P., COSSEE, P., J. Organomet. Chem., 1968, p. 533.; CANTAT, T., GENIN, E., GIROUND, C., MEYER, G., JUTAND, A., J. Organomet. Chem., 687, 2003, p. 365

13.RAMEY, K. C., STATTON, G. L., J. Am. Chem. Soc., **88**, 1966, p. 4387.; CHRISOPE DOUGLAS, R., BEAK, P., J. Am. Chem. Soc., **108,** 1996, p. 334

14.CALVO, C., HOSOKAVA, T., REINHEIMER, H., MAITLIS, P. M., J. Am. Chem. Soc., **94,** 1972, p 3257; AUBRUN, P .M., MACKENZIE, P .B., BOSNISH, B., J. Am. Chem. Soc., **107,** 2005, p. 2003

15.AVRAM, M., AVRAM, E., CHIRALEU, F., SLIAM, E., NENITESCU, C. D., Chem. Ber., **108,** 1975, p 1830

16.CALABRO, G., DROMMI, D., BRUNO,G., FARONE., F., J. Chem. Soc. Dalton Trans, 2004, p. 81

17.GREENFIELD, S. J., GARKOV, A., GILBERTON. S. R., Organic Lett., **5** (17) Nr 17, 2003, p. 3069

18.KAWATSURA, M., UOZUMI, Y., OGASAWARA, M., HAYASHI, T., Tetrahedron., **59**, 2004, p. 2247

Manuscript received: 24.04.2007