

Allylic Palladium(II) Triazenido Complexes: Synthesis and Spectroscopic Studies

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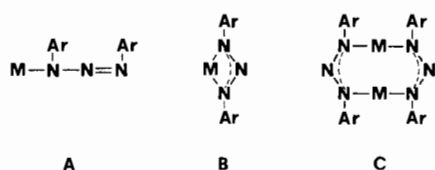
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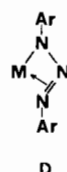
Reaction of $[Pd(1-3-\eta\text{-allyl})Cl]_2$ with lithium triazenide (triazenide = $p\text{-XC}_6\text{H}_4\text{N}=\text{N}-\text{NC}_6\text{H}_4\text{X-p}$; $X = \text{Cl}, \text{H}, \text{CH}_3$) affords dimeric complexes of the type $[Pd(1-3-\eta\text{-allyl})(\text{triazenide})]_2$. In the solid state the triazenido ligands are bridging two palladium atoms with their terminal nitrogen atoms, as shown by a preliminary X-ray determination of the complex with $X = \text{CH}_3$. The allyl groups are stereochemically equivalent. ^1H NMR spectra demonstrate the presence of two conformers in solution. The major component has the same configuration found in the solid. The other conformer has stereochemically non equivalent allyl groups. The concentration ratio of the two conformers is independent of the temperature, suggesting the absence of intramolecular processes and of palladium-triazenido bond breaking. This point is discussed also by comparing the (1-3- η -allyl)(triazenide)palladium (II) dimers with the closely related (1-3- η -allyl)(acetate)palladium(II) complexes.

Introduction

1-3-Diaryltriazenido anions (Ar_2N_3^-) are known to give a variety of metal complexes which may involve monodentate (**A**)¹, chelate (**B**)² and bridging (**C**)^{3,4} triazenido groups, as does the isoelectronic acetate ligand⁵:

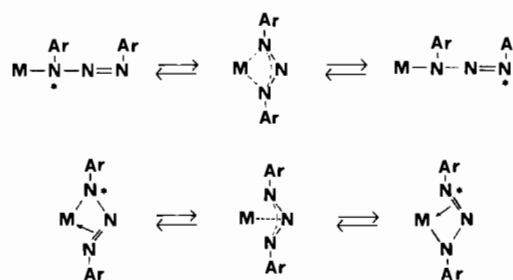


Structure **A** has been proposed, mainly on the basis of IR and NMR data, in complexes of platinum metals^{1,6}. An alternative formulation to this type of monomeric complexes has been given⁷ (**D**):



which involves bidentate triazenido groups. Both structures **A** and **D** are reasonable and we think that the choice between them can be made on the basis of the electronic requirements of the central metal atoms. Structure **B** has been found in $\text{Co}(\text{Ph}_2\text{N}_3)_3$ in which both terminal N atoms are coordinated to the same metal to form a 4-membered chelate ring, with delocalization of the π electrons. The bridging structure **C**, where the two Nitrogen terminal atoms are bonded to two different metals, occurs in $[\text{M}(\text{Ph}_2\text{N}_3)_x]_2$ ($\text{M} = \text{Cu}^3, x = 1; \text{M} = \text{Ni}^4, x = 2$).

Variable temperature ^1H or ^{19}F NMR spectra show that the equivalence of the groups CH_3 or F in some monomeric $p\text{-CH}_3$ or $p\text{-F}$ substituted aryl triazenido complexes is lost at lower temperatures. This fluxional behavior has been interpreted on the basis of the following mechanisms which account the above mentioned electronic requirement of the central metal atoms:^{1,6,7}



The second mechanism is similar to that found for the extensively studied complexes of the isoelectronic allyl groups⁸.

Here we report a series of dimeric palladium(II) complexes containing both triazenido and allyl groups,

extending the previous study by Jack and Powell⁹ with a preliminary X-ray determination and other spectroscopic data.

Experimental

Solvents were dried and saturated with nitrogen before use. IR spectra were recorded on Perkin-Elmer Model 457 spectrometer. ¹H NMR spectra were measured on Varian NV14 or Jeol C-60 HL spectrometers using TMS as internal references. Molecular weights were determined on Mechrolab osmometer at 36°C. Melting points were taken in air on a Kofler Hot Stage. Diaryltriazenes were prepared following literature methods¹⁰. Allylpalladiumchloride dimer was synthesized from Na₂PdCl₄ and allyl alcohol by the method of Moiseev, *et al.*¹¹

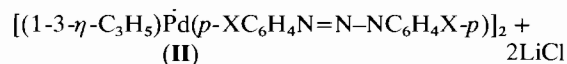
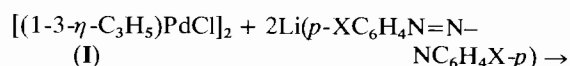
Di-μ-(1,3-di-p-tolyltriazenido)di-(1-3-η-allyl) dipalladium(II)

A solution of *n*-butyllithium in hexane (2.4 ml, 2.5 M, 6 mmol) was added to a THF solution of 1,3-di-*p*-tolyltriazene (25 ml, 1.35 g, 6 mmol) at room temperature. After two minutes allylpalladiumchloride dimer (0.915 g, 2.5 mmol) was added as a solid. The resulting solution was stirred at boiling point for 15 minutes, while the volume was reduced to ≈ 5 ml by flowing nitrogen through the reaction vessel. Addition of ethanol afforded the complex as a yellow crystalline material, which was recrystallized from benzene/ethanol. M.p. 177°C (dec). Y ≈ 80%.

The analogous phenyl- and *p*-chloro-aryl-triazenido complexes were similarly prepared. M.P. 179°C (Y ≈ 75%) and 178°C (dec)(Y = 95%) respectively. Analytical and infrared data are listed in Table I.

Results and Discussion

The reaction of triazenido ligands with allylpalladiumchloride dimer gives substitution of the chloride:



X = CH₃, H, Cl

The yield of the products (II) is high and practically independent of the nature of the *p*-substituent. One of this complexes (X = H) has been previously obtained by replacement of the acetate groups with triazene in the allylpalladium acetate dimer⁹.

The I.R. spectra of II (Table I) show bands at 1580–1600, 1275–1290, 1200–1210 and 1155–1165 cm⁻¹ which can be attributed to coordinate triazenido ligands^{1,7}.

There is some debate about the interpretation of the structures of triazenido complexes on the basis of I.R. data^{1,7}. Triazenido complexes have been divided in two classes: class A having absorptions at 1580–1600 and 1260–1300 cm⁻¹ (bidentate¹), class B with absorptions at 1580–1600, 1260–1300, 1190–1210 and ≈ 1150 cm⁻¹ (monodentate¹). Knoth⁷ has questioned these criteria and assigned the chelate structure D (see introduction) to some rhodium(I) complexes of class B. Moreover the I.R. spectrum of a known bridging bidentate triazenido complex [Ni(N₃Ph₂)₂]₂⁴ has I.R. bands characteristic of class B⁷. Therefore the I.R. spectra appear at least inconclusive in the assignment of the structure of these complexes. Our products have the characteristic absorptions of those designated as class B; however the presence of allyl bands in the range 1200–1300 cm⁻¹ makes more suspicious in our case the attribution of the structure from I.R. data.

The dimeric structures of II follow unambiguously from molecular weight determinations (Table I).

Allylpalladiumchloride dimer is known to have the centrosymmetrical structure¹² shown in Figure 1:

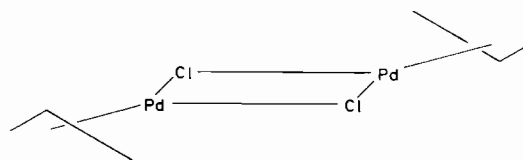


Figure 1. Schematic structure of (1-3-η-allyl)palladiumchloride dimer.

TABLE I. Analytical and IR Data of [(1-3-η-C₃H₅)Pd(p-XC₆H₄N=N-NC₆H₄X-p)]₂.

X	M.P. (°C)	Analytical Data ^a			M.W ^a	IR ^b (cm ⁻¹)
		C	H	N		
CH ₃	177°	55.44	4.82	11.32	762	1604, 1290,
	(dec)	(54.92)	(5.15)	(11.30)	(743.52)	1280, 1208, 1165
H	179°	52.60	4.28	12.06	691	1593, 1281,
	(dec)	(52.42)	(4.40)	(12.23)	(687.42)	1210, 1162
Cl	178°	43.44	3.01	10.23	835	1582, 1287,
	(dec)	(43.67)	(3.18)	(10.18)	(825.12)	1277, 1201, 1159

^a Calculated figures in parentheses. ^b Only bands associated with triazenes.

TABLE II. ^1H NMR Spectra of $[(1-3-\eta\text{-C}_3\text{H}_5)\text{Pd}(p\text{-XC}_6\text{H}_4\text{N}=\text{N}-\text{NC}_6\text{H}_4\text{X}-p)]_2$.

X	Conformer	Ratio IIa/IIb	Allyl*			Triazenido		
			τ_1	τ_2 <i>sin</i>	τ_3 <i>anti</i>	$\tau_{\text{C}_6\text{H}_4}$	$\tau_{\text{C}_6\text{H}_5}$	τ_{CH_3}
CH ₃	IIa	≈2.6	4.31m	6.26d	7.18d	2.78m	—	7.68s
	IIb		n.o. 4.96m	6.18d 6.36d	7.02d 7.30d	2.78m	—	7.68s
H	IIa	≈2.2	4.30m	6.25d	7.18d	—	2.70m	—
	IIb		n.o. 4.97m	6.20d 6.33d	6.97d 7.27d	—	2.70m	—
Cl	IIa	≈2.0	4.32m	6.25d	7.20d	2.72m	—	—
	IIb		n.o. 4.98m	6.17d 6.32d	7.01d 7.30d	2.72m	—	—

* $\text{H}_2\text{H}_3\text{C}-\text{CH}_1-\text{CH}_3\text{H}_2$; coupling constants (in Hz) are the same for all allyl groups: $J_{1,2} = 7$, $J_{1,3} = 12$, $J_{2,3} < 1$; s = singlet, d = doublet, m = multiplet; n.o. = not observed (overlapping τ_1 signal of conformer IIa).

The planes of the allyl units are approximately perpendicular to the plane of the $(\text{PdCl})_2$ bridge system. A preliminary X-ray study proves that our complex II (X = CH₃) has the structure IIa of Figure 2

place of triazenide) with two stereochemically non equivalent allyl units.

The ^1H NMR spectra of our allyl-triazenido complexes are temperature independent (see below) and

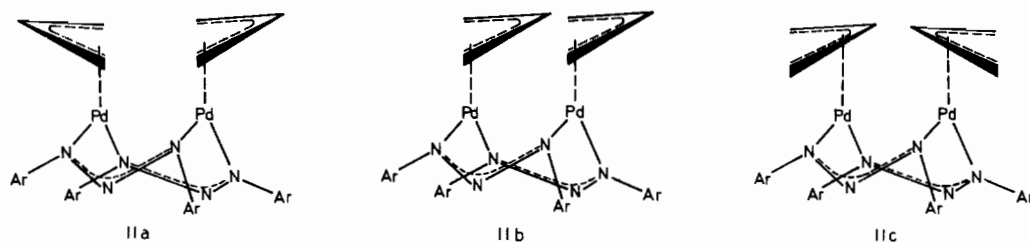


Figure 2. Possible conformational isomers (schematic) of (1-3- η -allyl)palladiumtriazenido dimer. See discussion.

in which the geometry of the bridging triazenido groups forces the allyl units to be in a close position*: The palladium atoms are bridged by two 1-3-ditolyltriazenido ligands bonded through the terminal nitrogen atoms. The allyl groups are stereochemically equivalent so that a plane of symmetry bisects the Pd-Pd axis. This structure resembles that found in the related (1-3- η -allyl)palladium acetate dimer¹³, the main difference being on the relative orientation of the allyl groups. The acetate complex has structure IIb (acetate in the

show three overlapping AA'BB'X patterns suggesting the presence of two conformers, the major one having electronically equivalent allyl groups. Both conformers IIa and IIc (Figure 2) satisfy this requirement but steric hindrance should disfavour the close head-to-head configuration IIc on respect to IIa, which has been found in the solid. Chemical shift and coupling constants (Table II) are well in agreement with other (1-3- η -allyl)palladium(II) complexes¹⁴.

The presence of the minor conformer is more evident in the region of the *anti*-proton resonances (Figure 3):

* Refinement of the structure is in progress and the results will be published later on.

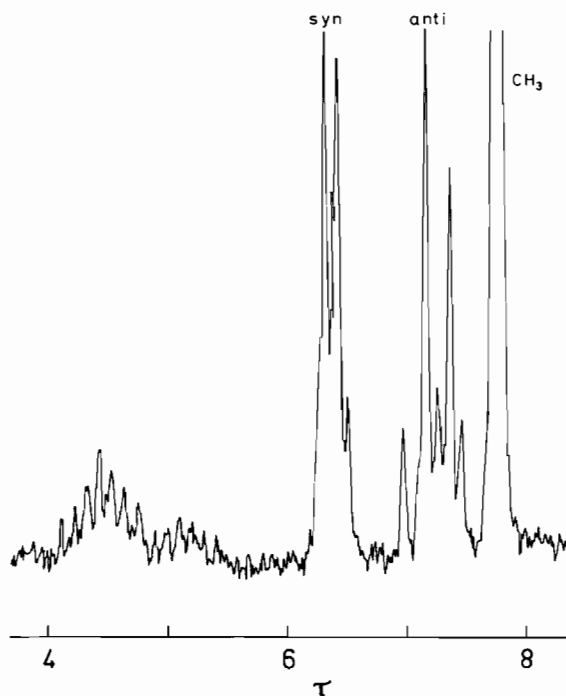


Figure 3. The 60 MHz ^1H NMR spectrum of **II** ($\text{X} = \text{CH}_3$). The phenyl region portion is not shown.

The methyl protons in the triazenido complex **II** ($\text{X} = \text{CH}_3$) appear as a singlet ($\tau = 7.68$) suggesting that the different disposition of the allyl groups in **IIa** and **IIb** does not affect the geometry of the triazenido moiety. Complexes **II** ($\text{X} = \text{CH}_3, \text{H}, \text{Cl}$) have very similar ^1H NMR spectra in the region of allyl resonances and comparable relative concentrations of the two conformers (Table II).

The diphenyl triazenido and the *p*-substituted triazenido complexes do not show any change in the ^1H NMR spectrum, within experimental errors, from -50 up to 50°C in CDCl_3 and up to $+90^\circ\text{C}$ in $\text{C}_6\text{H}_5\text{Cl}$ (above this temperature extensive decomposition occurs). Our results parallel those by Jack and Powell⁹ for the diphenyl triazenido complex. The *para* substitution in the phenyl group with groups having opposite electronic effect (CH_3 and Cl) has no significant influence on the variable temperature NMR behavior of the conformers.

The closely related allylpalladium acetate dimer¹⁵ (**IIa** and **IIb** with acetate in place of triazenido) shows NMR equivalence in the allyl groups of the **IIb** conformer at -20°C . This fact has been interpreted in terms of a bridge inversion of the acetate group. The π -conjugation extended to the aromatic rings possibly does not allow the bridge inversion in the triazenido complexes⁹. Alternatively a solvolytic cleavage of only one Pd–O bond in **IIb**, rearrangement and recomposi-

tion of the dimer accounts for the above NMR equivalence. In the triazenido complexes this cleavage could be prevented because of the stronger Pd–N bond. This is demonstrated by the displacement of the acetate ligand by triazene in the allylpalladium acetate dimer⁹.

The interconversion **IIa–IIb** at higher temperature in the acetate case is interpreted as a bimolecular exchange¹⁵; in addition the process is accelerated on adding weak bridging ligands (AcH or DMSO). Our di-*p*-tolyltriazenido complex does not show any interconversion **IIa–IIb** even in the presence of di-*p*-tolyltriazene or DMSO. This can be rationalized again by accounting the general trend of stronger bonding ability of nitrogen ligands compared to that of oxygen ones. Further support to this explanation follows from the absence of interchange in the ^1H NMR spectra of mixed chloride–triazenido palladium allyl dimers, which occurs on the contrary in mixed chloride–acetate¹⁵ or mixed halide systems¹⁶.

These results indicate that the two conformers **IIa** and **IIb** are formed when the reactants are mixed and, once obtained they do not interconvert. Although the crystal chosen for the X-ray determination has structure **IIa**, it is likely that crystals of conformer **IIb** are also present in the solid.

Further studies on closely related formamidinide complexes are in progress, in order to get more insight into these problems.

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