Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

CONFORMATIONAL STUDIES OF π-ALLYLIC PALLADIUM COMPLEXES OF 1,3-DIPHENYLTRIAZENE AND 1-METHYL-3-PHENYLTRIAZENE

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(Received September 8th, 1970)

SUMMARY

Solution isomers of dimeric allylic palladium 1,3-diphenyltriazene and 1-methyl-3-phenyltriazene complexes are identified by low temperature NMR spectroscopy. The data obtained indicate that the bridging triazenido ligands in these complexes are nonlabile and relatively inert to ligand substitution.

INTRODUCTION

Complexes of the anion derived from 1,3-diphenyltriazene (DptH), in which Dpt acts as a bridging ligand, are often related by the geometry of the anion to the complexes formed by carboxylates[1,2]. Recent variable temperature proton NMR studies on several π-allylic palladium carboxylate dimers have illustrated the presence of several conformational isomers in solution[3,4]. The temperature dependence of the NMR spectra of π-allylic palladium acetate dimers has been interpreted in terms of a rapid, non-dissociative, intramolecular acetate bridge inversion (*i.e.* an inversion of the boat conformation of the $Pd_2C_2O_4$ ring), together with a bimolecular exchange of π-allylic palladium units similar to that observed in π-(2-methylallyl)-palladium halide dimers[5]. In this paper, we describe the preparation of the structurally analogous π-allylic palladium Dpt and Mpt (1-methyl-3-phenyltriazenido) complexes and their proton NMR spectra.

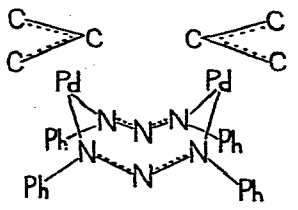
RESULTS AND DISCUSSION

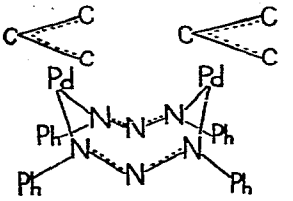
π-Allylic palladium triazene complexes were isolated, in high yield, as orange crystals by a displacement reaction of the appropriate triazene with the corresponding acetate complex:

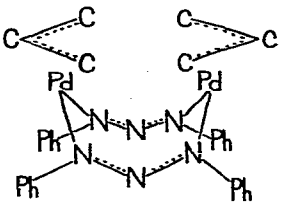
$$[\pi\text{-}C_3H_5PdOAc]_2 + 2\ DptH \rightarrow [\pi\text{-}C_3H_5Pd\ Dpt]_2 + 2\ HOAc$$

These triazenido complexes are more stable than their acetate analogs and have been shown to be dimeric by osmometric studies.

By analogy with previous structural studies on π-allylic palladium acetate dimers[3,4,6], three possible conformational isomers may be envisaged for π-allyl-palladium Dpt: (I_a), (I_b), (I_c). [(I_a) and (I_c) have a plane of symmetry bisecting the Pd–Pd axis, (I_b) does not.]


(Ia)


(Ib)

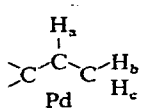

(Ic)

The proton NMR spectrum of π-allylpalladium Dpt at 30° in $CDCl_3$ consists of three overlapping π-allylic AM_2X_2 patterns of relative intensities, ca. 2/2/7 (Table 1 and Fig. 1, the separate resonance patterns are clearest in the region of the *anti*-proton resonances) together with low field aromatic proton resonances of the Dpt ligand (not tabulated). By analogy with the low temperature NMR spectrum of π-allylpalladium acetate[4], the two AM_2X_2 patterns of equal intensity are assigned to isomer (I_b) (contains two non-equivalent allyls) and, on the basis of steric arguments, and analogy with the 2-methylallyl complex (see below), the AM_2X_2 pattern of highest intensity is assigned to isomer (I_c). Unlike the analogous acetate complex, the NMR spectrum of π-allylpalladium Dpt dimer is temperature invariant from $-60°$ to $+30°$ (in $CDCl_3$) and from $+50°$ to $+110°$ (in $CHBr_3$).

The proton NMR spectrum in bromoform at $+35°$ of π-(2-methylallyl)palladium Dpt contains only one π-2-methylallyl resonance pattern which may be assigned

TABLE 1

NMR SPECTRAL DATA FOR ALLYLIC PROTONS



Compound	Isomer	Chemical shift, τ (ppm)				J(Hz)
		H_a	H_b	H_c	CH_3	
(π-Allylpalladium Dpt)$_2$[a]	(Ic)	c[b] 4.26	d 6.21	d 6.95		J_{ab} 7.1
	(Ib)	c 4.95	d 6.30	d 7.25		J_{ac} 12.6
			d 6.14	d 7.15		
[π-(2-Methylallyl)palladium Dpt]$_2$[c]	(Ic)		s 6.59	s 7.37	s 7.82	
[π-(1,1-Dimethylallyl)palladium Dpt]$_2$[a]	(Ib)	dd 4.93	dd 6.31[d]	dd 7.14	s 8.89	J_{ab} 7.7
		dd 4.81		dd 7.06	s 8.73	J_{bc} 2.2
						J_{ac} 12.5
	(Ia) or (Ic)	dd 5.26	dd 6.55	dd 7.21	s 9.06	
					s 8.80	

[a] In $CDCl_3$ at 30°, 100 MHz. [b] c: complex pattern; d: doublet; dd: doublet of doublets; s: singlet. [c] In $CHBr_3$ at 35°, 60 MHz. [d] The other (Ib) *syn* proton NMR resonance is masked by the more intense *syn* proton resonance of (Ia) or (Ic).

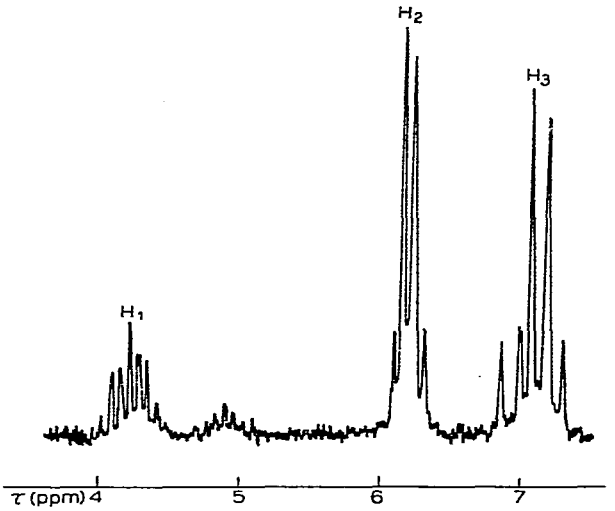


Fig. 1. Proton NMR spectrum of (π-allylpalladium Dpt)$_2$

to conformational isomer (I_c) in which the allylic units are related by symmetry. Steric interactions between the methyl groups in isomer (I_a) eliminate this conformation as a possibility.

The allylic NMR spectrum of π-(1,1-dimethylallyl)palladium Dpt dimer in $CDCl_3$ consists of three overlapping AMX patterns in the ratio ca. 1/1/20 together with at least four high field methyl singlet resonances. Owing to the asymmetry of the 1,1-dimethylallyl ligand, six possible conformational isomers can be envisaged for this complex. Steric arguments suggest that the 1,1-dimethylallyl will be arranged so that the methyl substituents are on opposite ends of their respective allylic units. By analogy with the π-allyl case, the two minor AMX patterns may be assigned to conformational isomer (I_b). The major solution species could have the π-1,1-dimethylallyl ligands in the arrangement (I_a) or (I_c), depending on the relative magnitude of the nonbonding steric interactions associated with *anti*-methyl substituents in (I_c) and those between the central hydrogen atoms of the two allylic ligands in (I_a). Analysis of the *anti*-proton region of the NMR spectra in $CDCl_3$ of π-(*syn*-1-methylallyl)palladium Dpt dimer and π-allylpalladium Dpt dimer and π-allylpalladium Mpt dimer shows the presence of at least five non-equivalent allylic patterns and six non-equivalent allylic patterns respectively. The spectrum of the latter complex is temperature invariant from $-50°$ to $+35°$.

In contrast to allylic palladium acetates[3,4], the temperature invariance of the π-allylpalladium Dpt and Mpt dimers precludes the operation of a non-dissociative, low energy ring flip or bridge inversion, or bimolecular exchange. Molecular models indicate that this inactivity is probably due to steric repulsions between phenyl substituents on the triazenido bridges during the inversion process and/or to an electronic effect in which loss of delocalization through the triazenido bridge[1,7] during the inversion process increases the energy barrier and prevents the process. Since the geometrically similar acetate systems do undergo bridge inversion the possibility of metal–metal bonding interactions would seem to be negligible in these systems.

Addition of pyridine or triphenylphosphine to allylic palladium Dpt complexes has no effect on their NMR spectra indicating that the Dpt bridge is not broken by these ligands. Addition of a stronger bridge splitting ligand, dimethylphenylphosphine, results in a complex reaction. Molecular weight studies of π-allylpalladium Dpt on addition of increasing amounts of PMe_2Ph are not consistent with phosphine co-ordination to the dimer nor with a simple bridge splitting reaction. The NMR spectra of π-allylpalladium Dpt and π-(2-methylallyl)palladium Dpt on addition of one PMe_2Ph per palladium atom still show the presence of ca. 30% and ca. 70% respectively dimeric reagent, which persists in the latter case even at a ratio of two PMe_2Ph per palladium atom. In all cases, the phosphorus methyl proton coupling constant is consistent with phosphorous co-ordination but the reaction products are not those expected of a simple bridge splitting mechanism.

The rigidity and resistance to bridge splitting reagents displayed by the triazenido-ligands in these complexes indicate that the bridges formed are relatively non-labile and of fixed configuration. The short metal–metal distances found in several dimeric complexes of these ligands, such as Ni_2Dpt_4 or Cu_2Dpt_2[7], may well be accounted for by the restrictive nature of these bridging ligands.

EXPERIMENTAL

Melting points were measured on a Kofler Hot Stage Apparatus and are corrected. Molecular weight determinations were carried out using a Mechrolab 301A Osmometer. NMR spectra were recorded on Varian HA-100 and A56/60D Spectrometers.

The allylic palladium acetate complexes were prepared by the method of Robinson and Shaw[8]. 1-Methyl-3-phenyltriazene was prepared by the method of White *et al.*[9]

Bis-μ-(1,3-diphenyltriazenido)diallyldipalladium(II)

A solution of diazoaminobenzene (1.08 g) in chloroform (10 ml) was added dropwise to a solution of di-μ-acetatodiallyldipalladium(II) (1.09 g) in chloroform (15 ml). The solution was evaporated to dryness under reduced pressure and the residue left under vacuum until no further trace of acetic acid could be detected. Recrystallization of the residue from chloroform, petroleum ether (b.p. 30–60°) yielded the required product as orange needles (1.35 g; 75%), decomposing without melting 165–180°. (Found: C, 52.46; H, 4.24; N, 12.27; mol.wt. osmometrically in 1.4% w/v chloroform solution, 659. $C_{30}H_{30}N_6Pd_2$ Calcd.: C, 52.43; H, 4.40; N, 12.23%; mol.wt., 665).

Also prepared in this manner were:

Bis-μ-(1,3-diphenyltriazenido)bis(2-methylallyl)dipalladium(II). Yield 92%. Orange prisms, m.p. 197–201° (decompn.). (Found: C, 53.51; H, 4.95; N, 11.74. $C_{32}H_{34}N_6Pd_2$ Calcd.: C, 53.67; H, 4.79; N, 11.74%.)

Bis-μ-(1,3-diphenyltriazenido)bis(1,1-dimethylallyl)dipalladium(II). Yield 76%. Orange-yellow needles, m.p. 188–192° (decompn.). (Found: C, 54.84; H, 5.21; N, 11.06. $C_{34}H_{38}N_6Pd_2$ calcd.: C, 54.88; H, 5.15; N, 11.29%.)

Bis-μ-(1,3-diphenyltriazenido)bis(1-methylallyl)dipalladium(II). Yield 81%. Orange prisms, m.p. 175–180° (decompn.). (Found: C, 47.30; H, 3.99. $C_{32}H_{34}N_6Pd_2$-$CHCl_3$ calcd.: C, 47.43; H, 4.22%.)

Bis-μ-(1-methyl-3-phenyltriazenido)diallyldipalladium(II)

1-Methyl-3-phenyltriazene (0.55 g) and di-μ-acetatodiallyldipalladium(II) (0.68 g) were dissolved in chloroform (15 ml). The solution was evaporated under reduced pressure to give a dark yellow oil which on recrystallization from chloroform, petroleum ether (b.p. 30–60°) gave the required product as gold prisms, (0.66 g; 71%), m.p. 165–167° (decompn.). (Found: C, 42.54; H, 4.78%; mol.wt. osmometrically in 2.7% w/v chloroform solution, 528. $C_{20}H_{26}N_6Pd_2$ calcd.: C, 42.66; H, 4.62%; mol.wt., 562.)

ACKNOWLEDGEMENT

We thank the National Research Council of Canada and the Province of Ontario for financial support of this investigation.

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