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XIV. STERIC FACTORS IN 1,2-DISUBSTITUTED-π-ALLYLPALLADIUM CHLORIDE COMPLEXES*

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SUMMARY

Increasing the bulkiness of the substituent on carbon 2 of some 1,2-disubstituted-1,2,3-h^3-allylpalladium complexes increases the fraction of *anti* isomer in a series of similar complexes. Even with bulky substituents in the 2-position, *syn* isomers may still predominate and the presence of the keto group is an essential feature in the greater stability of the *anti* isomer of the 1-acetyl and 1-benzoyl derivatives. The possibility of preparing solutions which contain only a specified allyl configuration by capitalizing on solid state isolation and relatively slow interconversions in solution is discussed.

INTRODUCTION

Recent investigations of certain bis[1,2,3-h^3-(1,2-disubstituted-allyl)chloropalladium] complexes have shown that the predominant isomeric configuration of the allyl moiety, *i.e.*, *syn* or *anti*, is dependent in solution on the steric interactions of the two substituent groups[2-4]. Placement of a "bulky" substituent at the central carbon often causes the predominance of an *anti* geometrical configuration at the terminal carbon for the other substituent, whereas for a "nonbulky" group the allyl moiety is found almost totally in a *syn* configuration. This generalization can be illustrated by contrasting the 1,2,3-h^3-(1-acetyl-2-methallyl)(pyridine)chloropalladium complex, ~75% of which is found in solution as the *anti*-acetyl isomer, with the 1,2,3-h^3-(1-acetylallyl)(pyridine)chloropalladium complex which has less than 5% in an *anti* configuration[2].

Our investigation of certain previously unreported 1,2-disubstituted-π-allylpalladium chloride complexes with a phenyl group in the 2-position substantiates the above generalization but also shows that the type of substituent attached to carbon 1 may also contribute to the stability of the various isomers in solution. Pertinent points may be demonstrated by consideration of the following allyl com-

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plexes: bis[1,2,3-h^3-(1-benzoyl-2-phenylallyl)chloropalladium], bis[1,2,3-h^3-(1-acetyl-2-phenylallyl)chloropalladium], bis[1,2,3-h^3-(1-benzoyl-2-methallyl)chloropalladium], and bis[1,2,3-h^3-(1,2-diphenylallyl)chloropalladium].

RESULTS AND DISCUSSION

NMR spectra of the bis[1,2,3-h^3-(1-benzoyl-2-phenylallyl)chloropalladium] and bis[1,2,3-h^3-(1-acetyl-2-phenylallyl)chloropalladium] complexes are shown in Fig. 1. In addition to the phenyl resonances at low field and in the case of the 1-acetyl-2-phenylallyl complex a methyl resonance, only three allylic proton resonances were observed for each complex. This indicated that both complexes must exist almost totally in either an *anti* configuration or a *syn* configuration in solution. The complexes were assigned an *anti* configuration on the basis of the following. Coupling of 1–2 Hz was observed between the first and second allylic resonances indicating the presence of two *syn* protons and therefore an *anti* configuration*. The chemical shifts of the

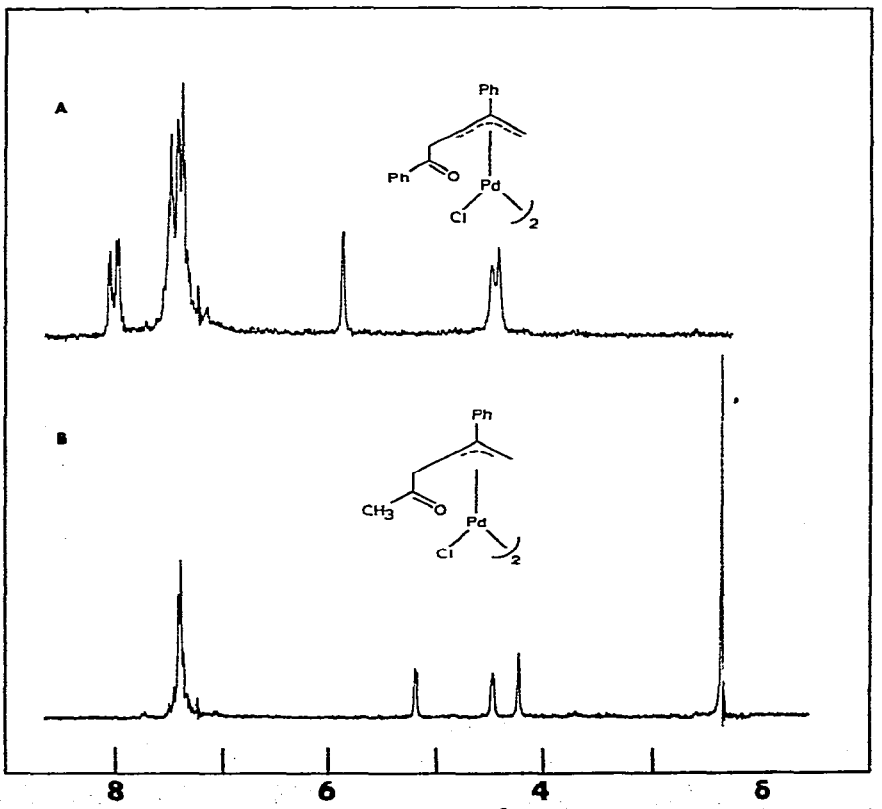


Fig. 1. A. NMR spectrum (100 MHz) of bis[1,2,3-h^3-(1-benzoyl-2-phenylallyl)chloropalladium] in deuterochloroform at 27°. B. NMR spectrum (100 MHz) of bis[1,2,3-h^3-(1-acetyl-2-phenylallyl)chloropalladium] in deuterochloroform at 27°.

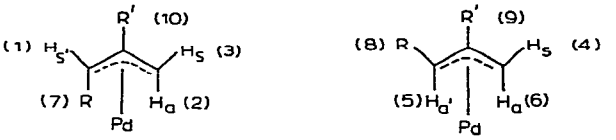
* It has been found for a variety of 1,2,3-h^3-allyl(amine)palladium halide complexes that the coupling between two *syn* protons is substantially greater than that between two *anti* protons or a *syn* and an *anti* proton[2].

allylic resonances were found in the same region as those of other *anti* complexes*. Preparation of the pyridine derivatives of both dimers showed that these pyridine complexes also existed totally as the *anti* isomer in solution. NMR parameters for the complexes are given in Table 1.

The NMR spectrum of the 1,2,3-h^3-(1-benzoyl-2-methallyl)(pyridine)chloropalladium complex had six resonances observable in the allylic region and two resonances in the methyl region (see Fig. 2). This complex must therefore exist as both *syn* and *anti* benzoyl isomers in solution. From the spectrum it was determined

TABLE 1

NMR PARAMETERS OF 1,2-DISUBSTITUTED-π-ALLYL PALLADIUM COMPLEXES[a]



Ligand	*R*	*R'*	*Anti isomer*					*Syn isomer*				
			(1) H_s·	(2) H_a	(3) H_s	(7) H_R	(10) H_R·	(4) H_s	(5) H_a·	(6) H_a	(8) H_R	(9) H_R·
Dimer[b]	COC_6H_5	C_6H_5	5.90	4.45	4.51	7.4 8.03	7.26					
Py[c]	COC_6H_5	C_6H_5	5.95	4.87	4.51	7.4[d]	7.4[d]					
Dimer[c]	$COCH_3$	C_6H_5	5.11	4.22	4.41	2.26	7.3[d]					
Py[c]	$COCH_3$	C_6H_5	5.21	4.65	4.41	2.48	7.3[d]					
Py[e]	COC_6H_5	CH_3	5.39	4.46	3.94	7.4[d]	2.06	3.83	4.28	3.06	7.4[d]	2.52
Py[f]	C_6H_5	C_6H_5	6.12	3.78	4.18	7.2[d]	7.2[d]	(3.90)	4.47	(3.40)	7.2[d]	7.2[d]

[a] In ppm with respect to TMS.
[b] Spectrum taken in deuterochloroform at 29°.
[c] Spectrum taken in a 3/1 deuterochloroform/benzene solution at 29°.
[d] Resonance masked by presence of solvent-benzene. Approximate value is given.
[e] Spectrum taken in a 2/1 deuterochloroform/benzene solution at 30°.
[f] Spectrum taken in a 3/1 deuterochloroform/benzene solution at 30°.

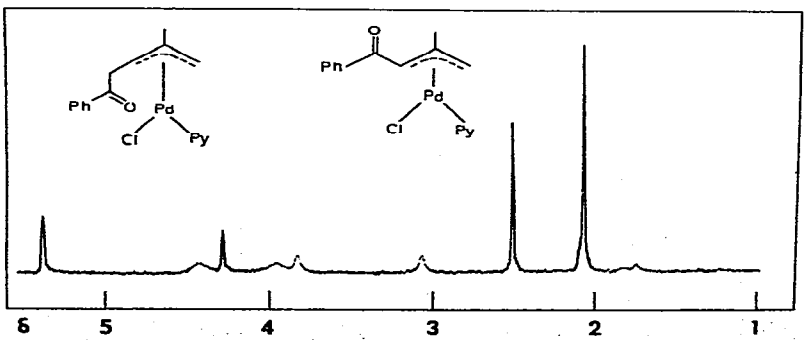


Fig. 2. NMR spectrum (100 MHz) of 1,2,3-h^3-(1-benzoyl-2-methallyl)(pyridine)chloropalladium in a 3/1 deuterochloroform/benzene solution at 27°. (Py = pyridine).

* The resonances of allylic protons on an *anti* isomer are usually found at lower field (δ 3.5–6 ppm) than the comparable resonances of a *syn* isomer (δ 2.5–4 ppm).

that the more abundant isomer was the *anti* isomer (60%). NMR parameters for this complex are reported in Table 1.

It can readily be seen that the greater the steric requirements of the substituent attached to the central carbon of the allyl moiety, the greater the tendency for a terminal keto substituent to occupy an *anti* position. Thus for the 1-acetyl-2-phenylallyl complex the percentage of *anti* isomer is 100%, for the 1-acetyl-2-methallyl it is ~75%, and for the 1-acetylallyl complex it is < 5%. The same trend was observed for the 1-benzoyl complexes. For the 1-benzoyl-2-phenylallyl complex the percentage of *anti* isomer was 100% whereas for the 1-benzoyl-2-methallyl complex it is 60%.

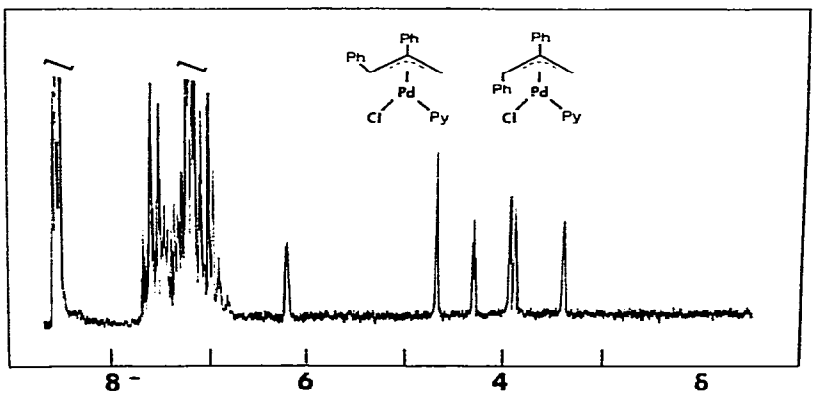


Fig. 3. NMR spectrum (100 MHz) of 1,2,3-h^3-(1,2-diphenylallyl)(pyridine)chloropalladium in a 3/1 deuterochloroform/benzene solution at 30°.

Investigation of the pyridine derivative of the bis[1,2,3-h^3-(1,2-diphenylallyl)chloropalladium] complex showed that this complex existed as both *syn* and *anti* isomers in solution (see Fig. 3). The percentage of *anti* isomer for this complex is only 48%. NMR parameters for the complex are given in Table 1. That this complex was not found exclusively as the *anti* isomer as were the 1-benzoyl-2-phenylallyl complex and the 1-acetyl-2-phenylallyl complex points perhaps to a special role for a terminal keto group. Interaction of the carbonyl group with the palladium atom might be the cause of the added stabilization of the *anti* geometrical isomer. Thus one generally finds that increasing the bulkiness of the substituent on carbon 2 increases the fraction of *anti* isomer. Nevertheless, it is now clear that even with a bulky substituent in the 2-position, *syn* isomers may predominate and the presence of the keto group is an essential feature in the greater stability of the *anti* isomer of the 1-acetyl and 1-benzoyl derivatives.

The NMR spectra of the 1,2,3-h^3-(1,2-disubstituted-π-allyl)(amine)chloropalladium complexes are temperature dependent. For each allylic moiety broadening of the *syn* proton (H_s) and *anti* proton (H_a) on both the *anti* and *syn* geometrical isomers was observed when the temperature was raised. Indeed the *syn* and *anti* protons for the 1,2,3-h^3-(1-benzoyl-2-methallyl)(pyridine)chloropalladium complex are already broad at 27° (see Fig. 2). It has been established that the mechanism by which the complexes interchange their *syn* and *anti* protons is by formation of a 3-*h*

TABLE 2

KINETIC PARAMETERS FOR FORMATION OF A 3-*h* σ-BONDED INTERMEDIATE

Allylic moiety in 1,2,3-h^3-*(allyl)Pd(Py)Cl*	*k* (sec^{-1})	ΔF^* (*kcal/mole*)	*Temp.* (°C)
anti-1-Benzoyl-2-phenylallyl	3.14	16.5	21
anti-1-Acetyl-2-phenylallyl	3.89	17.7	43
anti-1-Benzoyl-2-methallyl	7.25	16.4	28
syn-1-Benzoyl-2-methallyl	6.44	16.5	27
anti-1,2-Diphenylallyl	17.6	20.4	109
syn-1,2-Diphenylallyl	37.4	19.2	103

TABLE 3

THE GEOMETRICAL ISOMER OF π-ALLYLPALLADIUM CHLORIDE COMPLEXES FOUND IN THE SOLID AND PREDOMINATING IN SOLUTION

1,2,3-h^3-*(allyl)PdClL*		*Isomer found in the solid*	*% anti in solution*
Allyl	*L*		
1-Acetyl-2-methallyl	(*S*)-α-PEA	*anti*-Acetyl	70
1-Acetyl-2-methallyl	2-Picoline	*syn*-Acetyl	70
1-Acetyl-2-methallyl	4-Picoline	*anti*-Acetyl	75
1-Acetyl-2-methallyl	2,6-Lutidine	*syn*-Acetyl	[b]
1-Propionyl-2-methallyl	Dimer	*syn*-Propionyl	65
1-Propionyl-2-methallyl	(*S*)-α-PEA	*anti*-Propionyl	70
1-Benzoyl-2-methallyl	Dimer		[c]
1-Benzoyl-2-methallyl	(*S*)-α-PEA	*anti*-Benzoyl	65
1-Benzoyl-2-methallyl	2,6-Lutidine	*anti*-Benzoyl	60
1-Benzoyl-2-phenallyl	Dimer	*anti*-Benzoyl	100
1-Benzoyl-2-phenallyl	2,6-Lutidine	*anti*-Benzoyl	100
1-Acetyl-2-phenallyl	Dimer	*anti*-Acetyl	100
1-Acetyl-2-phenallyl	2,6-Lutidine	*anti*-Acetyl	100
1,2-Diphenylallyl	Dimer	*syn*-Phenyl	[c]
1,2-Diphenylallyl	4-Picoline	*syn*-Phenyl	60
1,2-Diphenylallyl	2,6-Lutidine	*syn*-Phenyl	60

[a] (*S*)-α-PEA = (*S*)-α-phenethylamine. Percentages were obtained at 29° in deuterochloroform solutions that had been allowed to stand sufficiently long to reach equilibrium. [b] Presence of superimposed resonances due to *cis*- and *trans*-amine isomers did not allow calculation of the ratio. [c] The dimer was too insoluble to allow accurate determination of isomer ratio.

σ-bonded intermediate[2,*]. The kinetic data which was obtained for this process is given in Table 2.

Both the dimers and their amine derivatives crystallize as only one of the possible isomers. Table 3 gives the form which was found in the solid for several substituted

* Formation of a 3-*h* ρ-bonded intermediate leads to the interchange of the *syn* and *anti* protons on carbon 3 and inversion of the configuration about carbon 1. It is by this mechanism that the complexes racemize. Conversely, formation of a 1-*h* σ-bonded intermediate would lead to isomerization.

allylpalladium complexes. With the slow interconversion rates observed at low temperatures, one finds that the configuration found in the solid is maintained in solution. Hence, by judicious choice of ligands and consideration of interconversion rates, one can prepare a solution which contains only a given configuration of the allyl moiety.

Stereospecific synthesis of a range of organic compounds should readily be achieved through either simple reduction or insertion reactions on the coordinated ligand. That the stereochemistry is so easily interpretable and ultimately so simply regulated points to allylic palladium complexes as a rich and conveniently tapped source of various organic reagents.

EXPERIMENTAL

Preparation of compounds

The 1,2,3-h^3-allyl dimers were prepared by reacting the appropriate unsaturated ketone with palladium chloride suspended in distilled water and acidified with hydrochloric acid according to the procedure of Moiseev *et al.*[5] Yields in excess of 85% were obtained.

Bis[1,2,3-h^3-(1-*benzoyl*-2-*phenylallyl*)*chloropalladium*]. Reaction of dypnone[6] (α-methylchalcone) with palladium chloride produced a yellow dimer which proved to be soluble in chloroform or methylene chloride. Crystallization from tetrahydrofuran gave an air-stable complex, m.p. 170° decompn.; ν(C=O) 1654 cm^{-1} in chloroform.

Bis[1,2,3-h^3-(1-*acetyl*-2-*phenylallyl*)*chloropalladium*]. The reaction of 4-phenyl-3-penten-2-one[7] with palladium chloride produced an orange-yellow dimer which proved to be soluble in chloroform or methylene chloride. Crystallization from carbon tetrachloride gave an air-stable complex, m.p. 125–127 decompn.; ν(C=O) 1680 cm^{-1} in chloroform.

Bis[1,2,3-h^3-(1-*benzoyl*-2-*methallyl*)*chloropalladium*]. Reaction of 3-methyl-1-phenyl-2-buten-1-one[8] with palladium chloride gave a yellow dimer which was only sparingly soluble in most organic solvents. Crystallization from tetrahydrofuran gave a powder decomposing above 210°; ν(C=O) 1655 cm^{-1}.

Bis[1,2,3-h^3-(1,2-*diphenylallyl*)*chloropalladium*]. The reaction of α-methylstilbene with palladium chloride according to the published procedure[4] produced the yellow dimer in 92% yield. Crystallization from tetrahydrofuran gave an air-stable complex, m.p. 224° decompn.

Amine derivatives. The dimer was treated with a 5% excess of the appropriate amine in ethyl acetate solution. The solvent was removed and the residue recrystallized from carbon tetrachloride. If crystallization proved difficult, cyclohexane was added and the solution stored overnight at −10°. The amine derivatives were generally obtained in over 85% yield as air-stable pale yellow crystals.

Kinetic measurements

Interconversion rates were determined by NMR line broadening methods[2]. The apparent first order rate constant for a particular isomer converting to another was determined from the additional broadening observed due to exchange from the slow limit equation $k=\pi \cdot W$. The additional broadening, W, was determined at temperatures which gave values of W between 1 and 10 Hz; *i.e.*, values for which

the most accurate rates can be determined. The temperatures and rate constants were then used to compute the free energies of activation. These values of ΔF^* were adequate for predicting rearrangement rates at other temperatures of interest.

Thermodynamic measurements

Equilibrium percentages were determined by weighing traces of the resonances. The structure in the solid was inferred by dissolving the crystalline solid in cold (usually $-50°$ depending upon ΔF^*) $CHCl_3$ or $CHClF_2$ and observing which isomer was present and which isomer appeared on standing or warming the solution.

Instrumentation

NMR spectra were measured using a Varian HA-100 and or a Jeolco Minimar 100 spectrometer. Chemical shifts are given as ppm downfield from TMS at 100 MHz.

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