BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 44, 2703—2705 (1971)

The Electronic Character of the π-Allylic Group of π-Allylic Palladium Complexes

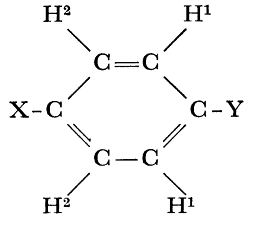
Yasutaka Takahashi, Hiroyuki Akahori, Shizuyoshi Sakai, and Yoshio Ishii
Department of Synthetic Chemistry, Faculty of Engineering, Nagoya University, Chikusa, Nagoya

(Received January 7, 1971)

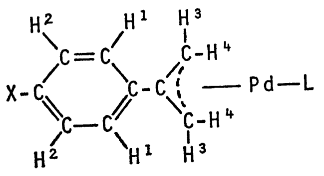
The substituent constants of the 2- and 1-positions of the π-allylic group of acetylacetonato (a) and cyclopentadienyl (b) derivatives of π-[2-(*p*-substituted phenyl)allyl]-(I) and π-(*p*-substituted cinnamyl)-palladium complexes(II) were estimated from their NMR spectra. The differences in the chemical shift ($\Delta\nu$, Hz) between the *p*-phenylene ring protons H^1 and H^2 of the complexes was found to be dependent upon the ligand and the substituent X. The plot of $\Delta\nu$ against the substituent constant σ_p^+, of X gave a fairly good linear relationship, and from the intercept of the straight line at $\Delta\nu=0$, the substituent constants of the 1-and 2-positions of the π-allylic group in the IIa or IIb complex and the Ia or Ib complex were estimated: σ_p: at the 1-position, 0.27 (IIa) or 0.24 (IIb), and at the 2-position, 0.21 (Ia) or 0.03 (Ib).

Up to now, little evidence suggesting the electronic character of the π-allylic group in π-allylic palladium complexes has been reported. Robinson and Shaw[1] found that 4-methoxy-substituted π-allylic palladium complexes were converted to the corresponding 4-ethoxy derivatives by ethanolysis, in which a carbonium-ion intermediate stabilized with the π-allylic group was assumed. This result suggests that the π-allylic group has an olefinic character even after coordinating with the metal ion. Nesmeyanov and Gubin,[2] on the other hand, suggested that the palladium ion in π-cyclopentadienyl-π-allylpalladium was to be regarded as an electron-attracting atom from an investigation of the electrophilic reaction and from the polarographic study. Bis(π-allylpalladium chloride) is also known to react with a nucleophilic reagent such as alkoxide, acetate, and the malonate anion.[3] The latter two results are evidence that the electron density of the π-allylic group is rather poor. These apparently contradictory observations stimulated us to estimate the electronic character of the π-allylic group.

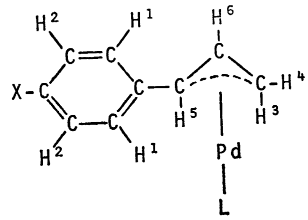
In the NMR spectra of *p,p'*-disubstituted benzene derivatives, the differences in the chemical shifts, $\Delta\nu$, of *p*-phenylene-group protons depend upon the electronic characters of the X and Y substituents, becoming zero when they are equal.



If Y is a π-allylic palladium moiety, its electronic character may be determined from the relation of $\Delta\nu$ to a substituent constant of X. Furthermore, the electron-donating or -withdrawing character of another ligand bonded to a metal may be evaluated at the same time. From this point of view, the NMR spectra of I and II complexes were measured. The results will be presented and discussed in this paper.



(I)



(II)

[L=acac (a), Cp (b), Cl (C); X=Br, Cl, H, CH_3, and CH_3O]

Experimental

The acetylacetonato and cyclopentadienyl derivatives of π-(*p*-substituted cinnamyl)palladium complexes (IIa and IIb) were prepared by the reaction of bis[π-(*p*-substituted cinnamyl)palladium chloride] with thallium acetylacetonate and cyclopentadienide[4] respectively, according to the methods in the literature.[5,6] Bis[π-{2-(*p*-substituted phenyl)-allyl}palladium chloride] complexes were prepared by the reaction of sodium chloropalladite and *p*-substituted α-methylstyrenes in the presence of cupric acetate in acetic acid. The complexes prepared are summarized as follows:

Sub-stituent	Yield (%)	Mp(°C)		Analysis C(%)	H(%)	Pd(%)
Br	93.5	260(d)[a]	Found	31.96	2.31	31.4
			Calcd	31.99	2.39	31.49
Cl[b]	70.4	220(d)	Found	36.66	2.69	36.1
			Calcd	36.83	2.75	36.25
H[b]	78.9	200(d)	Found	41.82	3.42	41.2
			Calcd	41.73	3.50	41.08
CH_3	74.8	260(d)	Found	43.81	3.86	38.7
			Calcd	43.99	4.06	38.97
CH_3O	69.1	230—2	Found	41.56	3.90	36.9
			Calcd	41.55	3.84	36.81

a) Decomposed, b) These compounds have previously been prepared by Hüttel *et al.*[7] and by Volger.[8]

---

[1] S. D. Robinson and B. L. Shaw, *J. Chem. Soc.*, **1963**, 4806.

[2] A. N. Nesmeyanov and S. P. Gubin, *Tetrahedron Lett.*, **1964**, 2881.

[3] J. Tsuji, H. Takahashi, and M. Morikawa, *Kogyo Kagaku Zasshi*, **69**, 138 (1966).

[4] H. Meister, *Angew. Chem.*, **69**, 533 (1957).

[5] Y. Takahashi, T. Inagaki, H. Mori, S. Sakai, and Y. Ishii, *Kogyo Kagaku Zasshi*, **73**, 760 (1970).

[6] P. M. Maitlis, A. Efrarty, and M. L. Games, *J. Organometal. Chem.*, **2**, 284 (1965).

[7] R. Hüttel, J. Kratzer, and M. Bechter, *Chem. Ber.*, **94**, 766 (1961).

[8] H. C. Volger, *Rec. Trav. Chim. Pays-Bas*, **88**, 225 (1969).

These complexes were converted to acetylacetonato (Ia) or cyclopentadienyl derivatives (Ib) by treatment with thallium acetylacetonate or cyclopentadienide respectively.

The NMR spectra were measured on JEOL, MH-60 in $CDCl_3$ (or CCl_4), using TMS as the internal standard, and were calibrated by the signal due to $CHCl_3$ contaminated in $CDCl_3$. The $\Delta\nu$ values observed in chloroform were consistent with those observed in carbon tetrachloride.

Results and Discussion

Acetylacetonato (Ia or IIa) and π-cyclopentadienyl derivatives (Ib or IIb) were prepared from the reactions of the corresponding chloro-bridged complexes (Ic or IIc) with thallium cyclopentadienide and acetylacetonate in benzene, and their NMR spectra were measured in $CDCl_3$ except for the case of IIb (CCl_4). The observed spectra of two representative complexes Ib (X=Cl) and IIa (X=Cl) are shown in Figs. 1 and 2 respectively. The spectral data for Ia and Ib are summarized in Tables 1 and 2. In the case of complex IIa, the resonance of the methyl group in the acetylacetonato-ligand appeared as two singlets because of the anisotropic effect of the phenyl ring in the π-cinnamyl moiety.[5] Allylic protons were observed distinctly as three doublets and a multiplet assignable to H^{3-5} and H^6 respectively; these results are consistent with the general features of the NMR spectra for a rigid π-allyl complex. In the case of complex IIb, the NMR spectra for the rigid π-allyl structure were also observed. These observations seem, therefore, to support the assumption that there is no fluxinal behaviour including the Pd-

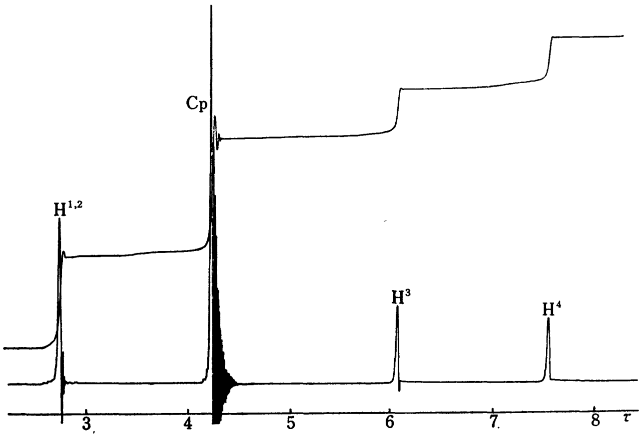
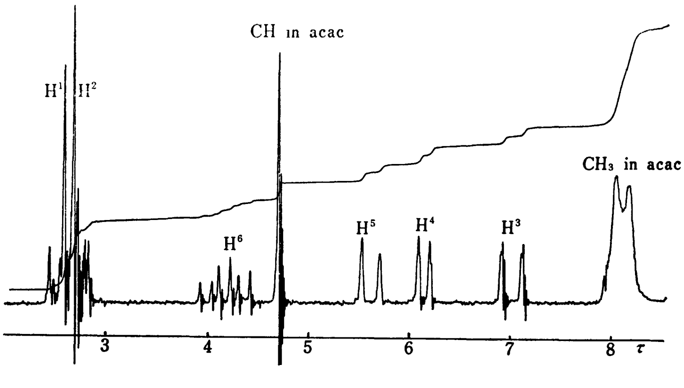
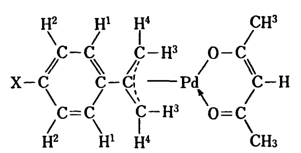


Fig. 1. NMR spectrum of complex Ib (X=Cl) in $CDCl_3$ at 25°.



Eig. 2. NMR spectrum of complex IIa in $CDCl_3$ at 25°.

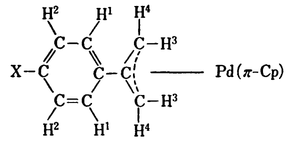
TABLE 1. NMR SPECTRA OF π-{2-(p-SUBSTITUTED PHENYL)ALLYL}ACETYLACETONATOPALLADIUM COMPLEX (Ia)



X	τ_3	τ_4	τ_{CH_3}	τ_{CH}	τ_X	τ_1	τ_2	$\Delta\nu_{2-1}$
Br	6.94	5.85	7.93	4.54	—	2.51	2.51	0.0
Cl	6.97	5.89	7.96	4.56	—	6.51	2.64	8.0
H	6.98	5.84	7.94	4.56	—	—	—	*ca.* 8
CH_3	6.99	5.83	7.94	4.56	7.58	2.48	2.78	17.5
CH_3O	7.01	5.83	7.94	4.57	6.06	2.46	3.05	35.5

τ (ppm), $\Delta\nu$ (Hz)

TABLE 2. NMR SPECTRA OF π-{2-(p-SUBSTITUTED PHENYL)ALLYL}CYCLOPENTADIENYLPALLADIUM COMPLEX (Ib)



X	τ_3	τ_4	τ_{Cp}	τ_X	τ_1	τ_2	$\Delta\nu_{2-1}$
Br	7.57	6.08	4.25	—	2.76	2.67	−6.5
Cl	7.59	6.10	4.27	—	2.76	2.76	2.0
H	7.59	6.10	4.30	—	—	—	*ca.* 2
CH_3	7.62	6.10	4.29	7.70	2.82	3.02	11.5
CH_3O	7.68	6.13	4.35	6.26	2.85	3.35	30.0

τ (ppm), $\Delta\nu$ (Hz)

ligand bond dissociation or the σ-π interconversion of the π-allylic moiety in the solution of complex IIa.

The chemical-shift difference between H^1 and H^2, $\Delta\nu$, decreased in the order of the *p*-substituent, X: $CH_3O>CH_3>H>Cl>Br$. The plot of $\Delta\nu$ against the substituent constant, σ_p^+, of X gave a moderately good linear relationship, as is shown in Fig. 3, but the constant other than σ_p^+ did not. The intercept of the straight lines at the axis, $\Delta\nu=0$, were designated as 0.21 (Ia) and 0.03 (Ib). In *p*-substituted toluenes and acetophenones, an analogous correlation between $\Delta\nu$ and σ_p^+ was also found,[9] as is shown in Figs. 4 and 3 respectively. The intercept (-0.30) of the straight line for toluenes at $\Delta\nu=0$, which might be the substituent-constant of the methyl group, was consistent with its σ_p^+ value as it appeared in the literature.[10] Therefore, the results obtained for complex Ia or Ib might be considered to indicate the substituent constant of the 2-position of the π-allylic group of complex Ia or Ib respectively. These results suggest that the substituent constant of the 2-position of the π-allylic group varies with other ligand bonded to the palladium ion, and that cyclopentadienyl group gave a smaller σ_p^+ value than the acetylacetonato group, indicating that the former is a better electron donor than the latter. These results are in accordance with the fact that the $CpRh(CH_2{=}CH_2)_2$ complex is more basic than the $(acac)Rh(CH_2{=}CH_2)_2$.[11]

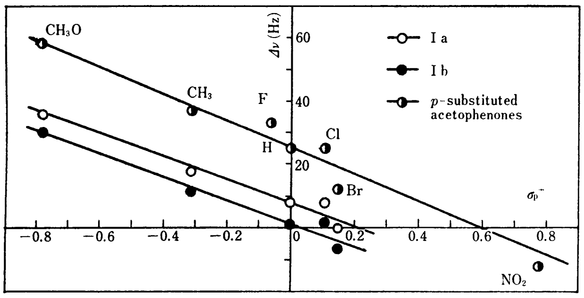


Fig. 3. The relation of $\Delta\nu$ of *p*-phenylene group of complexes Ia and Ib, and of *p*-substituted acetophenones.

In the cases of π-(*p*-substituted cinnamyl)palladium acetylacetonate (IIa) and cyclopentadienide (IIb), linear relationship between $\Delta\nu$ and σ_p^+ of X were also found; the results are illustrated in Fig. 4. The intercepts of the straight lines (σ_p^+ values of the 1-position of the π-allylic group) at $\Delta\nu=0$ were independent of the ligand; 0.27 (IIa) and 0.24 (IIb), unlike as in the observations in the case of I complexes. The relatively large σ_p^+ values estimated for the complexes II indicate that the 1-position of the π-allylic group is so electron-poor to be susceptible to nucleophilic reactions.

In the NMR spectrum of *p*-methoxy- and *p*-methyl-substituted α-methylstyrenes, $\Delta\nu$ was found to be 32.0 or 13.5 Hz respectively. The line through the points for the methoxy and methyl groups was assumed (parallel with other lines), and the σ_p^+ value for the isopropenyl group was evaluated as 0.05, smaller than that for Ia, IIa, and IIb, and nearly equal to that of Ib. Therefore, except for complex Ib, π-allylic palladium group may be concluded to behave as an electron-attracting substituent, consistent with the qualitative observations of Nesmeyanov and Gubin.[2]

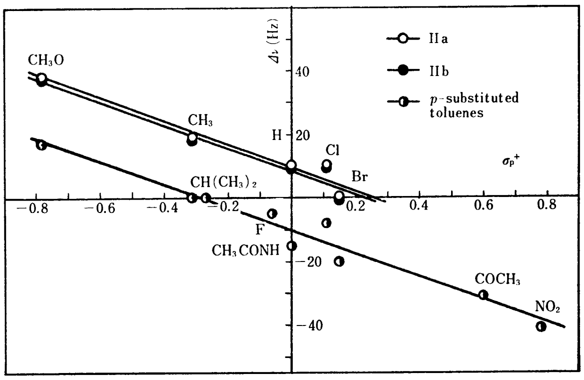


Fig. 4. The relation of $\Delta\nu$ of *p*-phenylene group of complexes IIa and IIb, and of *p*-substituted toluenes to substituent constant σ_p^+.
The σ_p^+ value of acetyl group was eastimated from the result of Fig. 1.

The different dependences of the σ_p^+ of the 1- and 2-position of the π-allylic group on the ligand are closely related to the bonding nature of the π-allylic ligand to the metal ion. Kettle and Mason[12] reported from their theoretical calculations that two lower levels of the molecular orbital (ϕ_1 and ϕ_2) of the allylic radical could be more strongly overlapped with the atomic orbital of palladium than its highest orbital ϕ_3. It may be assumed that ϕ_1 is overlapped with the metal orbital with bonding-manner, and ϕ_2 with backbonding-manner. The bonding of the 1-position of allylic radical with metal is governed by both ϕ_1 (donation) and ϕ_2 (backdonation), but that of the 2-position is governed only by ϕ_1, indicating that the 1-position of the allylic group in the complex is "softer" than the 2-position. Therefore, the substituent constant of the 2-position might be directly reflected by the electron density of the metal atom, that is, the ligand on it, but that of the 1-position is independent of it as a result of compensation between ϕ_1 and ϕ_2.

Throughout, the anisotropic effects of the π-allylic and other ligands have been ignored. Furthermore, the effect of the solvent is very important. The $\Delta\nu$ value of complex IIb (X=Cl) was observed to be 10.5 Hz in CCl_4, but changed to zero Hz in hexadeuterobenzene. In our previous paper[5] concerning the NMR spectra of a substituted π-cinnamylpalladium complex, the specific solvation of benzene molecules to palladium atom had been suggested. However the above observation can not be explained as a result of such a solvation of benzene; a different kind of factor have to account for it. We can not, at present, give a clear explanation.

---

[9] The $\Delta\nu$ values for *p*-substituted toluenes and acetophenones in the literature "NMR Data Tables for Organic Compound," Vol. 1, by F. A. Bovey, Interscience Publishers (1967) and of our measurement were used ignoring the solvent effect.

[10] H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, **79**, 1913 (1957).

[11] R. Cramer, *J. Amer. Chem. Soc.*, **89**, 5377 (1967).

[12] S. F. A. Kettle and R. Mason, *J. Organometal. Chem.*, **5**, 573 (1966).