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CARBON-13 NMR SPECTRA OF π-ALLYL PALLADIUM CHLORIDE DIMERS FROM CYCLOHEXENE AND METHYLCYCLOHEXENES

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Although there have been a number of ^{1}H NMR studies on π-allyl palladium chloride dimers, we have only found the ^{13}C NMR spectra of a few simple chain compounds in the literature.[1] The π-allyl palladium chloride dimer complexes were prepared from cyclohexene and methylcyclohexenes by the method of Trost,[2] and the natural-abundance 25.15 MHz ^{13}C FT-NMR spectra were measured using the ^{1}H noise decoupling technique. ^{13}C signals were assigned by comparing signal shifts due to differences in structures between closely related compounds and by use of the ^{1}H off-resonance decoupling technique. The carbon chemical shifts obtained are listed in the Table together with those of the free ligands. Although each of π-allyl palladium complexes, 4, 5 and 7 is allowed to exist in two stereoisomers, it was impossible to determine the stereochemistry of the complexes obtained here.

For the carbon chemical shifts of the π-allyl palladium moiety, the resonances for the tertiary central carbons of endo-cyclic complexes appeared at a field slightly higher than those of exo-cyclic complexes. On the other hand, the resonances for the secondary terminal carbons of endo-cyclic complexes appeared at a field lower than those of exo-cyclic isomers. The resonances for the primary terminal carbons appeared at a field higher than those for the secondary terminal carbons. The carbons in the π-allyl palladium moiety show the NMR signals in the limited region of magnetic fields depending on their own situations. The chemical shifts of complexes are compared with those of corresponding cyclohexenes. Only the chemical shifts for primary terminal carbons are compared with those of corresponding methylenecyclohexanes. The signals for the tertiary central carbons of endo-cyclic complexes revealed upfield shifts by 12.31-18.54 ppm, while those of exo-cyclic complexes by 7.95-16.27 ppm. The signals for the secondary terminal carbons of endo-cyclic complexes show upfield shifts by 42.71-48.47 ppm and those of exo-cyclic compounds by 49.51-52.54 ppm. The primary terminal carbons of exo-cyclic complexes are shielded by 47.08-50.91 ppm relative to the corresponding carbons of the free ligands. Such upfield shifts of carbon resonances of these π-allyl ligands are generally observed in the ^{13}C NMR spectra of the π-allylic type transition metal complexes.[3] The bonding of the π-allyl metal complexes involves the two components; forward donation from the olefin π orbital to a vacant hybrid orbital of the metal and the interaction of the π* orbital with a filled metal orbital, which returns electron density to the ligand, but only to the terminal carbon atoms.[4] This results in the significant upfield shifts of the terminal carbons in the π-allyl palladium moiety.

For the carbons of the rest of the molecule, the signals of C-3 and C-5 of endo-cyclic complexes are usually shifted downfield, while that of C-4 is shifted upfield relative to the corresponding carbons of the free ligand. Such an upfield shift of C-4 signal infers that this carbon is closer to the palladium atom than C-3 and C-5, and the nonbonding paramagnetic shielding effect of a palladium atom which is a function of $(r_{M-C})^{-3}$,[5] plays a major role in shift to the higher field by complex formation. The exception is the case of C-4 of 1,4-dimethyl cyclohexene. The deformation of the six-membered ring due to the replacement of the hydrogen on C-4 with the methyl group may result in a net deshielding of this carbon. In exo-cyclic complexes, the carbon signals other than the π-allyl palladium moiety were impossible to assign to the specific carbon atoms. The carbon resonances for the substituted methyl groups revealed no appreciable shift by complex formation.

REFERENCES

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3. B. E. Mann, Adv. Organometal. Chem. 12, 135 (1974)
4. P. M. Maitlis, "The Organic Chemistry of Palladium" (Edited by P. M. Maitlis, F. G. A. Stone and R. West), Vol 1, p. 205. Academic Press, New York, 1971
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TABLE

^{13}C Chemical Shifts of π-Allyl Palladium Chloride Dimers[a]

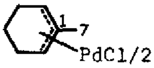
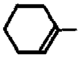
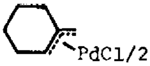
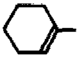
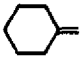
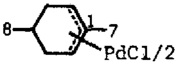
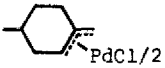
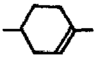
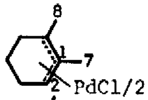
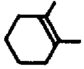
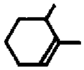
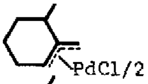
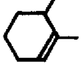
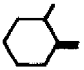
No.			C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8
(1)			101.74	78.81	28.81	19.41	28.81	78.81		
			127.28	127.28	25.54	23.11	23.11	25.54		
		Δδ[b]	-25.54	-48.47	3.27	-3.70	5.70			
(2)			116.18	77.90	29.06	20.08	29.06	77.90	22.56	
			133.96	121.34	25.54	23.35	24.02	30.33	22.69	
		Δδ	-17.78	-43.44	3.52	-3.27	5.04		-0.13	
(3)			126.01	68.80	(26.93)[c]	(17.59)	(21.05)	(28.81)	58.24	
			133.96	121.34	25.54	23.35	24.02	30.33	22.69	
			149.97	35.55	28.45	26.51	28.45	35.55	106.65	
		Δδ	-7.95	-52.54					-48.41	
(4)			114.99	78.20	35.91	31.48	35.91	78.20	(22.44)	(20.99)
			133.53	120.91	34.15	28.51	30.39	31.54	23.60	21.90
		Δδ	-18.54	-42.71	1.76	2.97	5.52			
(5)			123.10	71.40	(35.24)	27.47	(29.49)	(31.36)	55.87	21.59
			133.53	120.91	34.15	28.51	30.39	31.54	23.60	21.90
			149.43	36.58	34.82	32.39	34.82	36.58	106.78	22.02
		Δδ	-10.43	-49.51		-1.04			-50.91	-0.31

TABLE — Continued.

			C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8
(6)			113.33	75.71	29.00	20.87	36.34	90.70	(22.14)	(19.29)
			125.64	31.91	23.72	23.72	31.91	125.64	19.17	19.17
			138.03	121.76	25.96	22.02	31.85	33.67	20.02	19.65
		Δδ	-12.31	-46.05	5.28	-2.85	4.43	-34.94		
(7)			121.76	71.71	(26.81)	(16.01)	(29.30)	20.99	57.27	18.74
			138.03	121.76	25.96	22.02	31.85	33.67	20.02	19.65
			154.18	36.88	28.87	26.08	36.22	37.73	104.35	18.68
		Δδ	-16.27	-50.05				-12.68	-47.08	-0.91

a. ^{13}C FT-NMR spectra were obtained at 25.15 MHz with a JEOL JNM-MH-100 spectrometer equipped with a JNM-MFT-100 Fourier transform accessory. Samples were observed in 5-mm spinning tubes at 30±5% (w/v) solutions in $CDCl_3$ at 27°C. All chemical shifts are expressed in δ (ppm downfield from internal TMS). Each observed chemical shift is estimated to be accurate to ±0.06 ppm. FT measurement conditions were as follows: spectral width, 6250 Hz; acquisition time, 0.65 sec; pulse flipping angle, 45°; number of data points, 8192.

b. The chemical shift of the complex minus that of the free ligand. Positive values represent shifts of lower field.

c. The values in parentheses may be interchanged.