Carbon-13 NMR Spectra of π-Allyl Palladium Chloride Complexes

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The ^{13}C NMR spectra of thirteen acyclic and cyclohexenyl π-allyl palladium chloride dimers are examined and their chemical shifts are compared with those of the corresponding olefins. The signals for the central carbons of the π-allyl palladium moiety were displaced upfield by 8.0—25.5 ppm and those for the terminal carbons by 34.9—55.9 ppm compared to the corresponding carbons of the corresponding olefins.

In recent years, considerable effort has been directed towards the elucidation of the molecular structures of organic compounds using ^{13}C NMR spectroscopy. However, its application to organometallic compounds has so far been limited. Although there have been a number of ^{1}H NMR studies on π-allyl palladium chloride dimers, the ^{13}C NMR spectra of only a few simple chain compounds are to be found in the literature.[1] Here ^{13}C NMR spectra of π-allyl palladium chloride dimers of simple acyclic olefins and substituted cyclohexenes are reported. The carbon chemical shifts are compared with those of the corresponding olefins.

Results and Discussion

The π-allyl palladium chloride complexes of acyclic olefins were prepared from the corresponding allylic chlorides[2] and those of cyclic olefins from the corresponding olefins.[3] Natural abundance 25.15-MHz ^{13}C FT-NMR spectra were obtained using the ^{1}H noise-decoupling technique. The spectra were obtained in $CDCl_3$ as a primary solvent. Since 2- (**4**) and 1-phenyl-π-allyl palladium chloride (**5**) were not sufficiently soluble in this solvent, DMSO-d_6 was also used. The signals were assigned by comparing the signal shifts due to the structural differences between closely-related compounds and by using the ^{1}H off-resonance decoupling technique. The carbon chemical shifts obtained are listed in the table together with those of the corresponding olefins. The butenyl palladium chloride complex (**3**) and **5** are assumed to be composed predominantly of *syn*-isomers.[4] Although each of the cyclohexenyl palladium chloride complexes, **9**, **10**, and **12**, can exist as 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 the *endo*-cyclic complexes appeared at fields slightly higher than those of the *exo*-cyclic complexes, while the resonances for the secondary terminal carbons of the *endo*-cyclic complexes appeared at fields lower than those of the *exo*-cyclic isomers. The carbon resonances for the acyclic compounds appeared at fields lower than those of the corresponding cyclic complexes.

The ^{13}C chemical shift of π-allyl palladium complexes were compared with those of the corresponding olefins. The chemical shifts of **3** and **5** were compared with those of the corresponding internal olefins and only the chemical shifts for the primary terminal carbons were compared with those of the terminal olefins. For cyclic π-allyl palladium complexes, the ^{13}C chemical shifts were compared with those of the corresponding cyclohexenes. Only the primary terminal carbons were compared with those of the corresponding methylenecyclohexanes. In order to evaluate the solvent shifts by DMSO, the ^{13}C spectra of the π-allyl (**1**), 2-methylallyl (**2**), **3** and cyclohexenyl palladium chloride complexes (**6**) were also measured in the DMSO-d_6 solvent. The carbon resonances for the central carbons moved downfield by 6.4—7.6 ppm and those of the terminal carbons by 4.1—4.7 ppm. It has been reported that the bridged π-allyl palladium chloride dimers in DMSO are converted to form solvent adducts[5] and that the ^{1}H resonances of the allyl part of the adducts moved downfield compared to the parent bridged dimers.[6] A similar trend was observed for the ^{13}C NMR spectra. If the averaged values of such solvent shifts are applied to the ^{13}C chemical shifts of **4** and **5**, the values for $CDCl_3$ can be estimated. These values are tabulated in the table.

The signals for the secondary central carbons revealed upfield shifts of 14.4—25.5 ppm, while those of the tertiary carbons shifts of 8.0—19.3 ppm. For the terminal carbons, the signals for the primary position moved upfield by 47.1—55.9 ppm, for the secondary ones by 42.7—52.5 ppm and for the tertiary one by 34.9 ppm. Such upfield shifts of the carbon resonances of these π-allylic ligands are generally observed in the ^{13}C NMR spectra of π-allylic-type transition metal complexes.[7] The bonding of the π-allyl metal complexes involves two components: forward donation from the φ_1 orbital to an empty metal d orbital, which causes the electron density to decrease around all three carbon atoms, and interaction of the φ_2 and φ_3 orbitals, which increases the electron density only for the terminal carbon atoms of the π-allylic ligand.[8] This results in larger upfield shifts for the terminal carbons in the π-allyl palladium moiety than for the central carbon atoms.

The ^{13}C NMR spectra of 1-phenylcyclohexene revealed that the resonances corresponding to the carbons of the phenyl group, excepting that of the substituted carbons moved downfield for the π-allylic complex **13**, especially those corresponding to the para- and ortho-related carbons. This implies that the electrons, as a whole, are shifted by the complex formation from the ligand to the metal.

For the carbons of the remaining π-cyclohexenyl ligands, the C-3 and C-5 signals of the *endo*-cyclic

Table 1. Carbon-13 chemical shifts for π-allyl palladium chloride dimers and free ligands

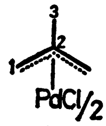
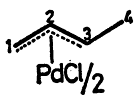
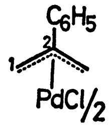
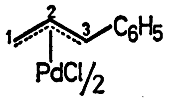
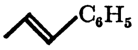
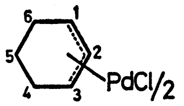
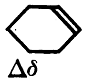
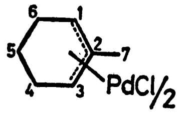
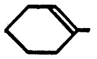
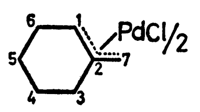
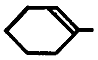
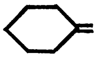
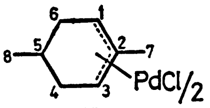
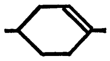
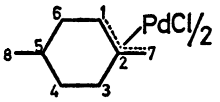
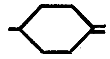
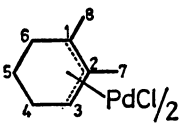
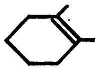
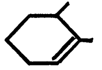
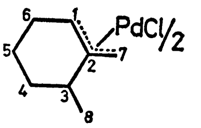
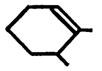
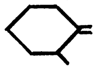
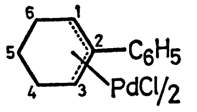
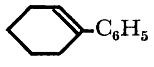
No.	Compound	Solvent	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C_6H_5–
1		$CDCl_3$	62.91	111.08							
		DMSO-d_6	67.58	118.67							
		CH_2Cl_2	63.2	111.9[a]							
		neat	115.4	135.7	18.7[b]						
	Δδ[c]		−52.1	−22.0							
2		$CDCl_3$	61.88	126.92	22.75						
		DMSO-d_6	66.49	134.14	22.75						
		CH_2Cl_2	61.7	127.9	23.1[a]						
			109.8	141.2	23.3[d]						
	Δδ		−47.9	−14.3	−0.6						
3		$CDCl_3$	58.30	111.39	81.42	18.01					
		$CDCl_3$	59	111	81	18[e]					
		DMSO-d_6	62.43	117.82	86.27	17.29					
			17.3	125.8[d]							
		neat	112.8	140.2[b]							
	Δδ		−54.5	−14.4	−44.4	0.7					
4		DMSO-d_6	63.87	132.86							s-C[f]; 135.52 o-C; 126.55 m-C; 128.85 p-C; 129.94
		$CDCl_3$	[59.5]	[125.9][g]							
		$CDCl_3$	112.36	141.36	21.78						s-C; 143.36 o-C; 125.58 m-C; 128.25 p-C; 127.46
	Δδ		−53.0	−15.5							
5		DMSO-d_6	64.18	112.60	86.57						s-C; 136.87 o-C; 128.01 m-C; 128.62 p-C; 128.01
		$CDCl_3$	[59.8]	[105.6]	[82.1]						
		$CDCl_3$	18.26	128.95	131.37						s-C; 138.05 o-C; 125.98 m-C; 128.50 p-C; 126.56
		$CDCl_3$	115.63	128.50	40.34						s-C; 143.79 o-C; 128.50 m-C; 128.68 p-C; 126.13
	Δδ		−55.9	−22.9	−49.3						
6		$CDCl_3$	78.81	101.74	78.81	28.81	19.41	28.81			
		DMSO-d_6	83.42	108.17	83.42	28.27	18.56	28.27			
		$CDCl_3$	127.28	127.28	25.54	23.11	23.11	25.54			
	Δδ		−48.5	−25.5		5.7	−3.7	3.3			
7		$CDCl_3$	77.90	116.18	77.90	29.06	20.08	19.06	22.56		
		$CDCl_3$	121.34	133.96	30.33	24.02	23.35	25.54	22.69		
	Δδ		−43.3	−17.8		5.0	−3.3	3.5	−0.1		
8		$CDCl_3$	68.80	126.01	(28.81)[h]	(21.05)	(17.59)	(26.93)	58.24		

TABLE 1. (Continued)

No.	Compound	Solvent	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C_6H_5–
		$CDCl_3$	121.34	133.96	30.33	24.02	23.35	25.54	22.69		
		$CDCl_3$	35.55	149.97	35.55	28.45	26.51	28.45	106.65		
	Δδ		−52.5	−8.0					−48.4		
9		$CDCl_3$	78.20	114.99	78.20	35.91	31.48	35.91	(22.44)	(20.99)	
		$CDCl_3$	120.91	133.53	31.54	30.39	28.51	34.15	23.60	21.90	
	Δδ		−42.7	−18.5		5.5	3.0	1.8			
10		$CDCl_3$	71.40	123.10	(31.36)	(29.49)	27.47	(35.24)	55.87	21.59	
		$CDCl_3$	120.91	133.53	31.54	30.39	28.51	34.15	23.60	21.90	
		$CDCl_3$	36.58	149.43	36.58	34.82	32.39	34.82	106.78	22.02	
	Δδ		−49.5	−10.4			−1.0		−50.9	−0.3	
11		$CDCl_3$	90.70	113.33	75.71	29.00	20.87	36.34	(22.14)	(19.29)	
		$CDCl_3$	125.64	125.64	31.39	23.72	23.72	31.91	19.17	19.17	
		$CDCl_3$	33.67	138.03	121.76	25.96	22.02	31.85	20.02	19.65	
	Δδ		−34.9	−12.3	−46.1	5.3	−2.9	4.4			
12		$CDCl_3$	71.71	121.76	20.99	(29.30)	(16.01)	(26.81)	57.27	18.74	
		$CDCl_3$	121.76	138.03	33.67	31.85	22.02	25.96	20.02	19.65	
		$CDCl_3$	36.88	154.18	37.73	36.22	26.08	28.87	104.35	18.68	
	Δδ		−50.1	−16.3	−12.7				−47.1	−0.9	
13		$CDCl_3$	75.96	117.39	75.96	29.36	19.96	29.36			s-C; 136.75 o-C; 126.13 m-C; 128.56 p-C; 128.56
		$CDCl_3$	124.43	136.69	27.54	23.23	22.38	26.02			s-C; 142.63 o-C; 124.98 m-C; 128.13 p-C; 126.49
	Δδ		−48.5	−19.3		6.1	−2.4	3.3			s-C; −5.9 o-C; 1.2 m-C; 0.4 p-C; 2.1

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a) These values are taken from Ref. 1a. b) These values are taken from G. B. Savitsky, P. D. Ellis, K. Namikawa, and G. E. Maciel, *J. Chem. Phys.*, **49**, 2395 (1968). c) The value for the complex minus that for the olefin. Positive values represent shifts toward lower field. d) These values are taken from J. B. Stothers, "Carbon-13 NMR Spectroscopy," Academic Press, New York (1972), p. 70. The solvent used was not indicated. e) These values are taken from Ref. 1e. f) Substituted. g) The values in brackets are estimated. See text. h) The values in parenthesis may be interchanged.

complexes are usually shifted downfield, while the C-4 signal is shifted upfield relative to the corresponding carbons of the corresponding olefins. Such a downfield shift of the C-3 and C-5 signals implies that these carbons are closer to the palladium atom than C-4 and the nonbonding paramagnetic shielding effect of a palladium atom which is a function of $(r_{M-C})^{-3}$,[9] plays a major role in the shift to lower field for complex formation. The exception is the case of C-4 for complex **9**. The deformation of the six-membered ring due to the replacement of the hydrogen at the C-4 position with the methyl group may result in a net decrease in the shielding of this carbon. In the *exo*-cyclic complexes, it was impossible to assign the carbon signals other than that for the π-allyl palladium moiety to specific carbon atoms. The resonances for the substituted methyl groups revealed no appreciable shift due to complex formation.

Experimental

NMR Spectra. ^{13}C FT-NMR spectra were obtained at 25.15 MHz using a JEOL JNM-MH-100 instrument equipped with a JNM-MFT-100 Fourier transform accessory; the instrument was controlled by a JEC-6 spectrum computer. The samples were in 5-mm spining tubes in 20±10% solutions of $CDCl_3$ or DMSO-d_6 at 26 °C. The solvents provided the internal lock signal. Measurement conditions were as follows: pulse width, 27.5 μs (*ca.* 45°); reptition time, 4 s; spectral width, 6250 Hz; data points, 8192; and acquisition time, 0.65 s. Noise-modulated proton decoupling was carried out at a nominal power of 20 W. All chemical shifts are expressed in δ (ppm downfield from internal Me_4Si). Each observed chemical shift is estimated to be accurate to within ±0.06 ppm.

Materials. π-Allylic palladium complexes, **1**—**5** were prepared by the method of Dent *et al.*[2a] or Hüttel *et al.*[2b] The complexes, **6**—**13** were prepared by the method of Trost and Strege.[3] For the synthesis of the new compounds (**9**—**13**), the following general procedure was used; sodium acetate (6.0 g, 0.073 mol), sodium chloride (4.2 g, 0.072 mol), cupric chloride (4.6 g, 0.034 mol) and palladium chloride (1.0 g, 0.006 mol) were stirred for 2 h at 95 °C in 62 ml of glacial acetic acid and 1.3 ml of acetic anhydride. The solution was cooled and 0.013 mol of the corresponding cyclohexene in 4 ml of acetic acid was added. The solution was heated for several hours. The reaction temperature and time were as follows: **9** from 1,4-dimethylcyclohexene, 60 °C, 4 h; **10** from 1,4-dimethylcyclohexene, 60 °C, 27 h; **11** from 1,2-dimethylcyclohexene, 55 °C, 5 h; **12** from 2,3-dimethylcyclohexene, 60 °C, 44 h; and **13** from 1-phenylcyclohexene, 55 °C, 24 h. The solution was cooled to room temperature and filtered. After an aqueous work-up and extraction with benzene, the crude yellow oil was purified by chromatography on SiO_2 with chloroform as the eluting solvent. The addition of pentane to the purified yellow oil and refrigeration (at 5 °C) for 2 days induced crystallization giving pure yellow crystals. Since compounds **10** and **11** were obtained in a mixture with **9** and **12**, respectively, separation was performed using SiO_2 chromatography with benzene. Compound **10** was only partially separated (80% purity). Compound **9**; yield, 0.36 g (26%); mp 82—86 °C (dec) (Found: C, 38.01; H, 5.02 %. Calcd for $C_{16}H_{26}Pd_2Cl_2$: C, 38.26; H, 5.18%); ^{1}H NMR ($CDCl_3$); δ 4.86 (bs, 2H), δ 2.07 (s, 3H), δ 0.91 (d, J=6.8 Hz, 3H), δ 1.5—2.3 (5H): compound **10**; yield, 0.22 g (16%); mp 114—118 °C (dec) (Found: C, 38.19; H, 5.15%. Calcd for $C_{16}H_{26}Pd_2Cl_2$: C, 38.26, H, 5.18%); ^{1}H NMR ($CDCl_3$); δ 4.16 (bs, 1H), δ 3.62 (bs, 1H), δ 2.63 (bs, 1H), δ 0.92 (d, J=6.8 Hz, 3H), δ 1.5—2.2 (7H): compound **11**, yield, 0.65 g (46%); mp 79—81 °C (dec) (Found; C, 37.91; H, 5.02%. Calcd for $C_{16}H_{26}Pd_2Cl_2$: C, 38.26; H, 5.18%); ^{1}H NMR ($CDCl_3$); δ 5.23 (bs, 1H), δ 2.08 (s, 3H), δ 1.23 (s, 3H), δ 1.0—2.3 (6H): compound **12**; yield, 0.60 g (43%); mp 98—100 °C (dec) (Found; C, 38.49; H, 5.08%. Calcd for $C_{16}H_{26}Pd_2Cl_2$: C, 38.26; H, 5.18%); ^{1}H NMR ($CDCl_3$); δ 4.43 (bs, 1H), δ 3.76 (bs, 1H), δ 2.67 (bs, 1H), δ 1.23 (d, J=6.5 Hz, 3H), δ 1.2—2.2 (7H): compound **13**, yield, 0.28 g (17%); mp 188—190 °C (dec) (Found; C, 48.29; H, 4.07%. Calcd for $C_{24}H_{26}Pd_2Cl_2$: C, 48.18; H, 4.35%); ^{1}H NMR ($CDCl_3$); δ 7.27 (m, 5H), δ 5.30 (bs, 2H), δ 1.0—2.3 (6H).

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