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Preliminary communication

New cluster ions in the FD- and FAB-mass spectra of π-allylpalladium chloride complexes

C. Akira Horiuchi *, Eiichi Miki, Takeo Takada, and J. Yasuo Satoh
Department of Chemistry, Rikkyo (St. Paul's) University, Toshima-Ku, Tokyo 171 (Japan)

Mikio Tanaka
Laboratory of Chemistry, Nippon Medical School, Nakahara-Ku, Kawasaki 211 (Japan)

Mitsuo Hayashi, Tamotsu Yamamoto,
Research Laboratories, Toyo Jozo Co., Ltd. Ohito-Cho, Shizuoka 410-23 (Japan)

Yoshio Koike, Toshio Takayama,
Department of Applied Chemistry, Kanagawa University, Yokohama 221 (Japan)

and Sukekatsu Nozaki
Faculty of Pharmaceutical Science, Josai University, Sakado, Saitama 350-02 (Japan)

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Abstract

The field desorption (FD) and fast atom bombardment (FAB) mass spectra of steroidal and terpenoid π-allylpalladium chloride complexes have been recorded. The molecular ions and cluster ions (those containing two or more metal atoms) with lower intensity than the molecular ions have been observed under field desorption conditions. On the other hand the FABMS spectra showed the presence of $(M-\text{Cl})^+$ ions and the cluster ions $(M+M/2-\text{Cl})^+$. Cluster ions for less volatile and unstable π-allylpalladium chloride complexes are reported here for the first time.

It is known that field desorption (FD) mass spectrometry [1–4] has been widely used in obtaining molecular ion data, and that fast atom bombardment (FAB) mass spectrometry [5,6] has been used for molecular ion and fragmentation data for most samples. Recently Dean and co-workers revealed the presence of new higher mass cluster ions (those containing two or more metal atoms) that had not previously been reported for transition metal complexes [7]. However there has been no

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Table 1

Isotopes of the complex bis[chloro(7,1,2-1-η^3-pinene)palladium] (**1**) and comparison of relative isotopic intensities by theory, by field desorption, and by fast atom bombardment.

$(M-\mathrm{Cl})^+$ rel. isot. intens.				$M^{+\cdot}(C_{20}H_{30}Pd_2Cl_2)$ rel. isot. intens.				$(M+M/2-\mathrm{Cl})^+$ rel. isot. intens.			
m/z	theor.	FD	FAB	m/z	theor.	FD	FAB	m/z	theor.	FD	FAB
513	8		11	548	6	5		790	27	23	28
514	21		27	549	17	17		791	44	38	46
515	52		56	550	43	46	47	792	59	61	61
516	65		73	551	57	59	57	793	79	73	79
517	81		84	552	77	83	82	794	88	87	89
518	78		84	553	79	76	86	795	100	100	100
519	100		100	554	100	100	100	796	92	85	93
520	56		61	555	65	65	69	797	97	100	95
521	85		86	556	93	94	87	798	68	58	66
522	25		26	557	34	32	38	799	74	68	69
523	45		46	558	57	57	56	800	38	34	37
524	10		10	559	14	13		801	44	37	42
525	14		15	560	23	26		802	17	14	17
								803	19	11	17

information on the less volatile and unstable π-allylpalladium complexes. We have investigated the stereospecificity of nucleophilic substitutions on steroidal π-allylpalladium complexes [8]. As a first step in this research project, we reported the synthesis of π-allylpalladium chloride complexes [9,10] and the oxidation of steroidal palladium complexes by chromium(VI) oxide [11]. In a previous paper, we reported the solvent effects on the ^{1}H NMR spectra of steroidal π-allylpalladium chloride complexes [12]. Here, we report on new cluster ions observed in the FD and FAB mass spectra of π-allylpalladium chloride complexes.

Samples. The π-allylpalladium chloride complexes were prepared by published procedures [9].

Instrumentation. Field desorption. A Hitachi M-80 double-focusing mass spectrometer equipped with a Hitachi M-003 data processing system was used in this study. The complexes were dissolved in chloroform and placed on a carbon emitter (The emitter currents: 15–25 mA; the emitter potential: 3 kV; the cathode potential: −4 kV; the ion accelerating potential: 3 kV).

Fast atom bombardment. A JMS-SX102 mass spectrometer equipped with a JMA-DA 6000 data system was used in this study. Xenon was used to produce the primary beam. The complexes were placed on a stainless-steel plate tip as a solution in *m*-nitrobenzyl alcohol (The emisson currents: 10 mA; the gun at high voltage: 5 kV; the ion accerating volt: 10 kV).

A series of π-allylpalladium complexes, where the ligand (L) = pinene, 1,4-dimethylcyclohexene, cycloheptene, or cholestene, were analyzed by FD- and FAB-MS.

Table 1 compares the experimental values of relative isotopic intensities obtained by FD and FAB with the theoretical ones for the complex **1**. The experimental intensities for most masses agree with the theoretical values, i.e. within a relative error of 10%. It seems that this result is a close match and strong evidence for the composition. As seen in Table 2, a number of high-mass cluster ions are observed in

Table 2

Major ions observed in the FD and FAB spectra of the complexes (**1**–**8**).

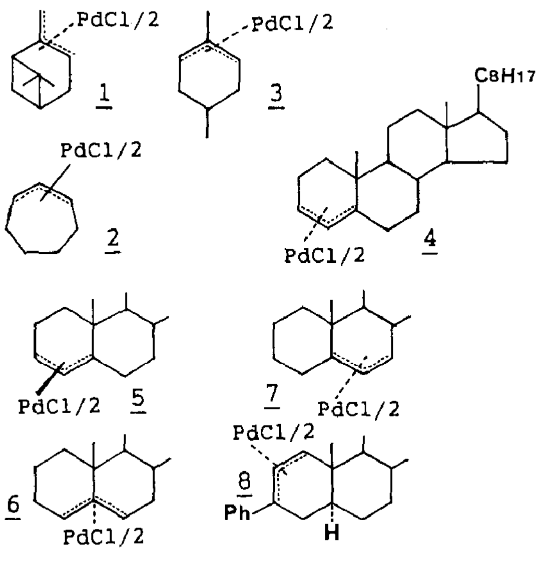
Complex	FD m/z (relative intensity)			FAB m/z (relative intensity)		
	M^+	$(M-\mathrm{Cl})^+$	$(M+M/2-\mathrm{Cl})^+$	$M^{+\cdot}$	$(M-\mathrm{Cl})^+$	$(M+M/2-\mathrm{Cl})^+$
1	554(100)	519(–)	795(14)	554(22)	519(100)	795(75)
2	473(100)	438(–)	675(58)	473(–)	438(100)	675(8)
3	501(–)	466(–)	716(100) [a]	501(38)	466(100)	716(53)
4	1022(100)	987(–)	1497(100)	1022(–)	987(100)	1497(76)
5	1022(–)	987(–)	1497(–)	1022(–)	987(100)	1497(8)
6	1022(100)	987(–)	1497(20)	1022(–)	987(100)	1497(37)
7	1022(100)	987(–)	1497(8)	1022(–)	987(94)	1497(100)
8	1174(100)	1139(–)	1725(–) [b]	1174(14)	1139(100)	1725(62)

[a] $(C_{32}H_{52}Pd_4Cl_3)^+$ at m/z 967(213). [b] Spectra were scanned up to $m/z \sim 1500$.

both FD and FAB mass spectra. The $M^{+\cdot}$ ion is observed for six complexes in the FD mass spectra, except for the unstable complexes 3 and 5. The $(M-\mathrm{Cl})^+$ and $M^{+\cdot}$ ions for 3, and $(M-\mathrm{Cl})^+$ for 5 are observed in the FAB mass spectra. All of the π-allylpalladium complexes exhibit a strong peak corresponding to $(M-\mathrm{Cl})^+$ in the FAB mass spectra. This peak may arise from the loss of chlorine as a radical.

Thus, it was found that these results confirm the utility of FD mass spectrometry, a more gentle technique, as a useful tool for less volatile and unstable π-allylpalladium complexes. In addition, when FDMS is unable to provide molecular, $M^{+\cdot}$, peak information, FAB fragmentation patterns $(M-\mathrm{Cl})^+$ can provide such. It could be that the formation of the cluster ions is due to dissociation of gas phase cluster species or fragment ion-molecular ion reactions [13].

This is the first time that new cluster ions for less volatile unstable π-allylpalladium chloride complexes have been observed in FD and FAB mass spectrometry.



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