



Studies of thermal decomposition of palladium(II) complexes with olefin ligands

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ABSTRACT

$\text{PdCl}_2(\text{VTMS})_2$ (**1**), $\text{PdCl}_2(\text{PTMSA})_2$ (**2**), $\text{PdCl}_2(\text{DMB})_2$ (**3**) and $\text{PdCl}_2(\text{DADMS})_2$ (**4**), where VTMS—trimethyl(vinyl)silane, DADMS—diallyldimethylsilane, PTMSA—1-phenyl-2-(trimethylsilyl)acetylene and DMB—2,3-dimethyl-2-butene were prepared and thermal characteristics studied by TG/DTG/DTA techniques. TG/IR method was used for the gas phase studies of ligands and complexes in the range 303–573 K. MS–EI analysis data were applied for elucidation of the metallated species in the gas phase. Thermal analysis results indicate detachment of organic ligand in the first stage of decomposition, whereas the chlorine molecule in the second stage. Metallic palladium was the final product of decomposition, what was confirmed by XRD analysis of the residues heated up to 1273 K. The metallic palladium was formed in the temperature range 478–720 K, what make the complexes (**1–4**) a promising Chemical Vapour Deposition (CVD) precursors. TG/IR spectra of all palladium(II) complexes revealed bands characteristic for appropriate ligands vibrations, what confirm the proposed mechanism of thermal decomposition. The MS results indicate the palladium fragments detachment in the temperature range 321–548 K. The organic and chlorine species were also observed.

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1. Introduction

Palladium as a metal or silver–palladium powder pastes is widely applied in production of many electronic components such as diodes, transistors, integrated or hybrid circuits, multilayer ceramic capacitors, thick film resistors and conductors. Silver–palladium alloys are employed for electrical contacts, relays and switching systems in telecommunication equipment. Besides that palladium layers are present in gas sensing electrodes, filters for hydrogen purification and, whereas complexes are used in catalysis of many chemical processes. [1–9] Palladium in a form of metallic layers can be prepared also by Chemical Vapour Deposition (CVD) of volatile coordination or organometallic precursors. [8] The part of search for CVD precursors must be focused on their thermal properties, which are important for CVD operational parameters and selection of the most promising precursor. Besides that data from the thermal studies are used for determination of the precursors vaporization temperature, conditions of the transport in the gas phase, and the decomposition mechanism on a substrate surface.

Palladium(II) dimeric precursors with bridging (η^3 -allyl) ligands: $\text{Pd}(\eta^3\text{-methyl-2-allyl})(\text{acac})$; (acac -acetylacetonate), $[\text{Pd}(\eta^3\text{-methyl-2-allyl})\text{Cl}]_2$ or $\text{Pd}(\eta^3\text{-allyl})(\text{hfacac})$; (hfacac -hexafluoroacetylacetonate) have been used for CVD. [10–12] Besides that,

other palladium(II) complexes with different allyl ligands e.g. ethylene, butane, pentene, cyclooctene, styrene, isobutylene and cyclohexene were characterized structurally. [13] These complexes revealed dimeric structures with π -bonded olefin molecules, whereas in palladium(II) acetylene complexes, an alkene ligands were coordinated asymmetrically via triple bond. [14,15] For CVD purposes MS spectra of many palladium(II) allylic complexes were analyzed in search for metallated volatile particles and many of them revealed the lack of such fragments. [16,17] In the MS spectra of di- μ -chlorodiallylpalladium(II) and di- μ -chlorodi(4-methoxy-1-methylpent-2-enyl)dipalladium(II) complexes, fragments with palladium and chlorine atoms were registered. [18–20] These properties suggest their future usage as precursors for CVD of palladium layers. Moreover thermal studies of the latter complexes suggested three stages decomposition mechanism resulting in metallic palladium. [14,16] To the best of our knowledge, the thermal properties of palladium(II) complexes with silylated olefin ligands have not been studied. Our previous studies suggested, that the presence of trimethylsilyl group improves the complex volatility. [18,19] Therefore the purpose of this work was to study the thermal properties of new Pd(II) complexes with the following olefin ligands: 2,3-dimethyl-2-butene (DMB), 1-phenyl-2-(trimethylsilyl)acetylene (PTMSA), diallyldimethylsilane (DADMS), trimethylvinylsilane (VTMS), which can be tested as CVD precursors. Volatile species evolved during thermal decomposition will be characterized by TGA–IR and mechanism of decomposition process will be discussed.

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2. Experimental

2.1. Materials

PdCl₂, inorganic salts and solvents of analytical grade were purchased from POCh Gliwice (Poland), whereas trimethyl(vinyl)silane-(CH₃)₃SiCH₂ (VTMS)–97%, diallyldimethylsilane-CH₂=CHCH₂)₂Si(CH₃)₂ (DADMS)–98%, 1-phenyl-2-(trimethylsilyl)acetylene-C₆H₅C≡CSi(CH₃)₃ (PTMSA)–97%, 2,3-dimethyl-2-butene-(CH₃)₂C=C(CH₃)₂ (DMB)–98% from Aldrich.

2.2. Instrumentation

Thermal analysis (TG, DTG, DTA) was performed on a SDT 2960 TA analyzer. Decomposition processes were studied in a dynamic atmosphere of dry nitrogen flowing at 60 ml/min, heating rate 5 °/min and heating range up to 1273 K, or heating rate 2.5 °/min, and heating range up to 723 K. Samples (4–11 mg) were placed in platinum crucible and measured against reference material–Al₂O₃. Gaseous products of the thermal decomposition were detected by a FT IR Bio–Rad Excalibur spectrometer equipped with a TA analyzer equipment, heated to 493 K, for gases evolved from a SDT 2960 TA analyzer. Powder X-ray diffraction data for residues of the thermal analysis were obtained with a Philips X'PERT diffractometer using Cu Kα radiation. Variable temperature mass spectra (VT–MS) were measured in the temperature range 303–573 K with a Finnigan MAT 95 mass spectrometer using EI technique. ¹H and ¹³C NMR spectra in benzene-d₆ were collected with a Varian Gemini 200 MHz spectrometer using TMS as the standard. IR spectra in the range 4000–400 cm⁻¹ were recorded on a PerkinElmer 2000 FT IR spectrometer using KBr discs. Palladium was determined gravimetrically, after complex mineralization, whereas C, H, by elemental analysis performed on Vario Macro CHN Elementar Analysensysteme GmbH. [17]

2.3. Synthesis

2.3.1. Synthesis of dichlorobis(benzonitrile)palladium(II) (PdCl₂(C₆H₅CN)₂)

Bezonitrile 20 ml (0.2 mol) was added to 0.5 g (2.82 mmol) of palladium(II) chloride. The reaction mixture was heated (T=383 K), stirred for 2 h and filtered. Next, 80 ml petroleum ether at room temperature was added to the filtrate and the yellow precipitate was isolated and washed with petroleum ether. [13,20] ¹H NMR (benzene-d₆, ppm) 7.3–7.5 (C₆H₅), ¹³C NMR (benzene-d₆, ppm) 112 (CCN), 116 (CN), 129, 132, 133 (C₆H₅). IR (cm⁻¹) 2230 ν(CN), 1492 ν(C=C_{aromatic}), 1449 ν(C=C_{aromatic}), 768 ν(CH_{aromatic}), 648 ν(CH_{aromatic}), 388, 358 ν(Pd–Cl).

2.3.2. Synthesis of palladium(II) complexes

Described procedure is a general way of complexes synthesis with studied ligands: Freshly prepared PdCl₂(C₆H₅CN)₂ (0.05 g, 1.3 × 10⁻⁴ mol) was dissolved in 20 ml of benzene in the Schlenk tube and trimethyl(vinyl)silane (VTMS) (275 μl, 1.9 × 10⁻⁴ mol) was added via septum and the reaction mixture was stirred for 12 h at room temperature. Afterwards mixture was filtered and solvent removed under vacuum at 273 K, living brown oily product of PdCl₂(VTMS)₂, which was unstable on the air. All obtained products had an oily consistence. They have been purified by dissolving in hexane. Unreacted olefins and solvent were removed on vacuum line. The composition was conformed by the CHN elemental analysis results and IR spectra analysis. In the IR spectra bands from solvent and free ligand stretching vibrations have not been observed. The reaction between olefin or initial complex with obtained product has not been noticed in the IR and NMR spectra. The results of these analysis confirmed purity of the product without solvent and ligand.

Results of spectroscopic and analytical data for new complexes isolated in that way are listed below.

2.3.2.1. PdCl₂(VTMS)₂ (**1**). Elemental analysis calc/found % for C₁₀H₂₄Cl₂Si₂Pd: C 31.62/31.9, Pd 28.01/27.68, H 6.40/6.67; MS: (T=474 K, m/z) [CSi(CH₃)]⁺ (57) R.I. 100%, Cl₂ (71) R.I. 78%, [Pd[(CH₃)₃SiCH=CH]⁺ (207) R.I. 44%, [PdCl[(CH₃)₃Si]⁺ (221) R.I. 40%; ¹H NMR (benzene-d₆, ppm) 7.2 (HCCSi), 6.1, 6.8 (HC=C), 0.08 (CH₃); ¹³C NMR (benzene-d₆, ppm) 142.1 (HCSi); 127.9 (CH₂), -0.38, -1.4, -2.3 (CH₃); IR (cm⁻¹) 3075, 3047 ν(=CH₂), 1511, 1540 ν(C=C), 848 ν(Si–C), 398, 365 ν(Pd–Cl). [21–25]

2.3.2.2. PdCl₂(PTMSA)₂ (**2**). Elemental analysis calc/found % for Cl₂C₂₂H₂₈Si₂Pd: C 50.23/50.81, Pd 20.23/20.6, H 5.36/5.42; MS: (T=321 K, m/z) [Si(CH₃)₃]⁺ (73) R.I. 44%, [PdSi(CH₃)₃]₂⁺ (315) R.I. 7%, [PdSiC]⁺ (147) R.I. 98% [C₆H₅CCH₂]⁺ (103) R.I. 100%; ¹H NMR (benzene-d₆, ppm) 7.30, 7.36, 7.49 (CH_{aromatic}), 0.07 (CH₃), ¹³C NMR (benzene-d₆, ppm) 131, 127, 121 (CH_{aromatic}), 96 (C≡CSi), 50 (CSi), 3.2 (CH₃); IR (cm⁻¹) 2963 ν(CH₃), ν(CH_{aromatic}), 1986 ν(C≡C), 851 ν(Si–C), 332, 354 ν(Pd–Cl). [21–25]

2.3.2.3. PdCl₂(DMB)₂ (**3**). Elemental analysis calc/found % for Cl₂C₁₂H₂₄Pd: C 41.69/41.2, Pd 30.78/30.5, H 6.99/6.38; MS: (T=548 K, m/z) [C₄H₉]⁺ (57) R.I. 100%, Cl₂ (71) R.I. 62%, [PdC₄H₆Cl]⁺ (195) R.I. 34%, [PdCl[(CH₃)₂C=C(CH₃)H]⁺ (212) R.I. 79%, [Pd₃[(CH₃)₂C=C(CH₃)₂]₂]⁺ (487) R.I. 10%; ¹H NMR (benzene-d₆, ppm) 2.2. (CH₃); ¹³C NMR (benzene-d₆, ppm) 128 (C=C), 23 (CH₃); IR (cm⁻¹) 2996 ν(CH₃), 1510, 1540 ν(C=C), 311, 354 ν(Pd–Cl). [21–25]

2.3.2.4. PdCl₂(DADMS)₂ (**4**). Elemental analysis calc/found % for Cl₂C₁₆H₃₂Si₂Pd: C 41.96/42.21, Pd 23.23/24.56, H 7.04/7.47; MS: (T=389 K, m/z) [CH₂=CH–CH₂]⁺ (41) R.I. 38%, Cl₂ (71) R.I. 58%, [Si(CH₃)₃]⁺ (73) R.I. 35%, [CH₂CHCH₂Si(CH₃)₃]⁺ (99) R.I. 40%, [PdCH₂CHCH₂]⁺ (173) R.I. 72%, [Pd(CH₂CHCH₂)SiH(CH₃)₂]⁺ (207) R.I. 63%, [PdCl₂]⁺ (247) R.I. 38%. [Pd₂CH₂CHCH₂Si]⁺. (369) R.I. 41%; ¹H NMR (benzene-d₆, ppm) 7.30, 7.36, 7.49 (=CH), 0.07 (CH₃), ¹³C NMR (benzene-d₆, ppm) 134 (CH), 113 (CH₂), 22 (CH₂), -4.2 (SiCH₂); IR (cm⁻¹) 3016, 3049 ν(=CH₂), 1510 ν(C=C), 885 ν(Si–C), 398, 343 ν(Pd–Cl) [21–25].

3. Results and discussion

3.1. Thermal analysis

Thermal properties of the studied compounds are important for the assessment of their usage in CVD of palladium layers. The onset of decomposition process and temperature of metallic palladium formation are the two factors which determine CVD procedure parameters, hence these are determined by analysis of thermoanalytical curves. Results of DTA, TG and DTG curves analysis for two sets of thermograms registered up to 773 K and 1273 K are listed in Table 1.

DTA curve of complex (**1**) revealed two endothermic effects over 298–343 K and 398–463 K (Fig. 1, heating range 773 K), whereas third one exhibit slightly marked endothermic process (max. 682 K) and mass loss 11.1% on TG curve.

Analysis of the DTG curve indicates three processes with maxima at 320, 442 K and 682 K and TG mass loss 8.0%, 38.8% and 11.1% respectively. In the case of PdCl₂(VTMS) (**1**) in the first step two methyl group from VTMS ligand were detached. The results of the thermal analysis have been verified by TG–IR analysis of gaseous products of the complexes decomposition (over 290–470 K), where bands from methyl C–H stretching (2800–2900 cm⁻¹) were observed. In the second step the rest of VTMS molecules evolves. Summary mass loss for three effects

Table 1
Palladium(II) complexes thermoanalytical data.

Compound	Heat effect		Temperature range (K)		DTG _{max} (K)		Mass loss (%)		Evolved moiety
	a*	b*	a*	b*	a*	b*	found	calcd	
PdCl ₂ (VTMS) ₂ (1)	endo	endo	298–343	300–340	320	329	53.7	53.3	2VTMS
	endo	endo	398–463	430–500	442	465			
	endo	endo	650–720	680–740	682	695			
PdCl ₂ (PTMSA) ₂ (2)	endo	endo	330–375	360–410	352	385	66.7	66.4	2C ₆ H ₅ C≡CSi(CH ₃) ₃
	exo	endo	450–543	490–595	472	525			
	endo	endo	590–632	650–760	629	732			
	endo	exo	634–723	810–830	687	863			
PdCl ₂ (DMB) ₂ (3)	endo	endo	345–423	410–460	417	426	49.5	48.6	2(CH ₃) ₂ C=C(CH ₃) ₂
	endo	endo	430–523	460–520	438	476			
	endo	endo	608–748	680–770	693	730			
PdCl ₂ (DADMS) ₂ (4)	endo	endo	298–318	290–320	310		59.7	59.7	2DADMS
	endo	endo	323–388	400–480	350	303			
	exo	endo	408–471	590–740	427	445			
	endo		650–700		673	668			
	endo		710–750		721				

(a*) heating range 773 K, heating rate 2.5 °/min, (b*) heating range 1273 K, heating rate 5 °/min

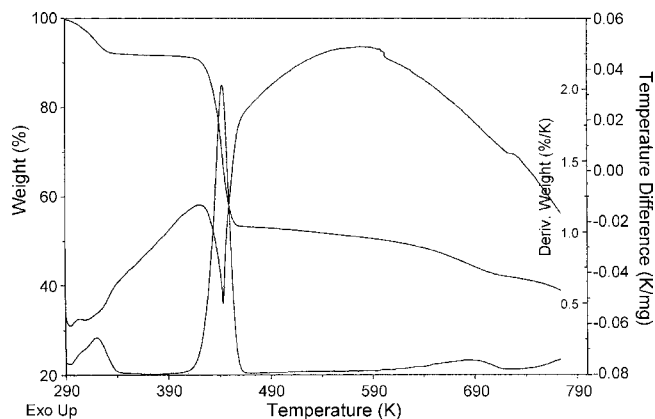


Fig. 1. TGA-DTA traces of PdCl₂(VTMS)₂ (1), heating range 773 K.

(57.9%) correspond to the detachment of two VTMS molecules and partial dissociation of chlorine (difference between 57.9 and 53.3%).

Detachment of chlorine is evident on the thermogram registered up to 1273 K (Fig. 2), where two peaks on DTG (max. 695 K and 842 K) correspond to 25.2% mass loss on TG curve, leaving metallic palladium (lack of mass loss on TG above 700 K).

This thermogram is even more informative about detachment of VTMS, because summary mass loss for the two first stages is

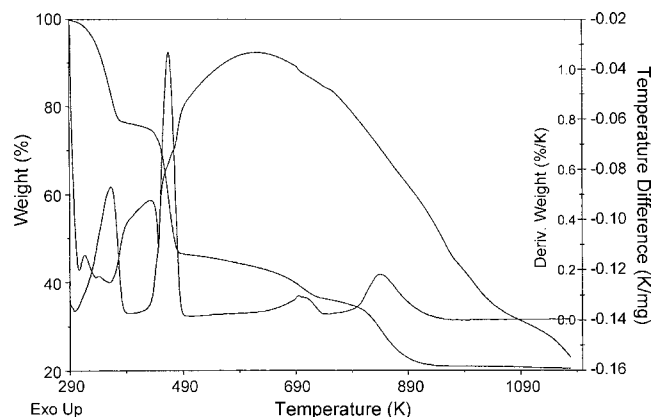


Fig. 2. TGA-DTA curves of PdCl₂(VTMS)₂ (1), heating range to 1273 K.

very close to calculated for two VTMS molecules (cal. 53.3%, found 53.7%). Palladium was formed above 641 K what is evident from DTG curve. The process of chlorine detachment was conformed by MS spectrum, where the chlorine isotope pattern signal (*m/z* 71, R.I. 78%) was observed at *T* = 474 K.

The differences of TG curves for compound (1) (Figs. 1 and 2) result from various conditions during thermal decomposition processes. In both cases the decomposition processes were studied in a dynamic atmosphere of dry nitrogen flowing at 60 ml/min, but in the first case the heating rate was 2.5 °/min, and heating range up to 773 K, whereas in the second the heating rate was 5 °/min, heating range up to 1273 K. The different measurement conditions caused various shape of the TG and DTA curves. [26] Similar phenomenon has been observed on the thermograms of all studied (1–4) complexes.

Thermogram of (2) (Fig. 3) exhibits four DTG peaks with maxima at 352, 472, 631 and 687 K, which on TG curve reveal three stages with 14.1, 26.6, and 13.2% sample mass loss. The total mass loss (66.7%) corresponds with the detachment of PTMSA (cal. 66.4%). Further TG analysis indicates reduction of the sample mass (13.2%), what originate from Cl₂ molecule dissociation (cal.13.5%).

The palladium metal was formed above 720 K. Analysis of the DTA curve is more informative from the thermogram measured at higher heating rate (5 °/min), than for 2.5 °/min, where the curve does not present distinct exo- or endotherms. On both curves at the beginning (up to 441 K) only change of sample heat capacity can be

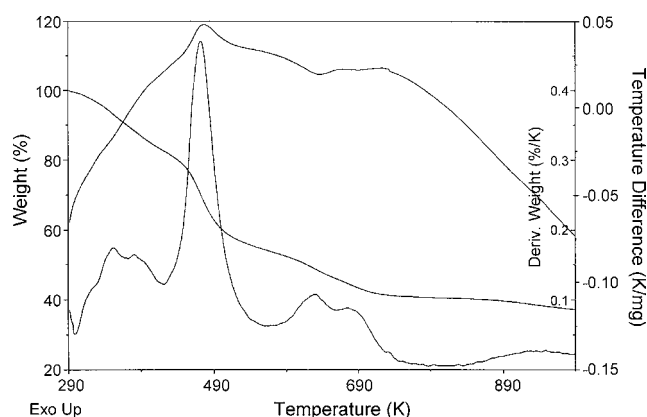


Fig. 3. TGA-DTA curves of PdCl₂(PTMSA)₂ (2).

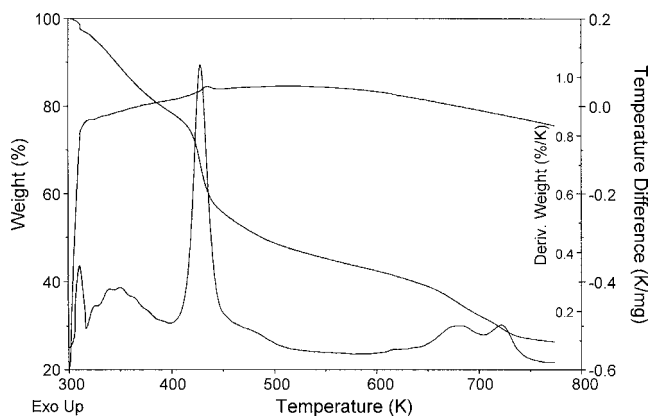


Fig. 4. TGA-DTA curves of $\text{PdCl}_2(\text{DADMS})_2$ (**4**).

noted. First exotherm revealed maximum at 472 K, whereas the second weak endotherm maximum at 629 K (1273 K range) was found. Such behavior is different from the compound (**1**), what can be explained by the ligand structure and coordination way of PTMSA.

Compound (**3**) reveals different DTG curve in comparison to (**1**), because two peaks in the range 345–450 K are poorly separated and only total mass loss can be calculated (49.5%), which can be assigned to 2 DMB molecules detachment (cal. 48.6%). Second DTG peak corresponds to 9.7% mass loss, what can be related to half chlorine molecule (cal. 10.1%) dissociation, followed by metallic palladium formation at 685 K.

Thermogram of (**4**) (Fig. 4) over 873 K presents on TG curve continuous mass loss, starting from 304 K to 471 K, whereas the first exothermic stage can be observed on DTA curve (305 K).

The mass loss corresponds to 59.5% (cal. 59.7%), which is in good accordance with the DADMS dissociation. Further sample mass reduction is connected with the chlorine molecule detachment (found 14.7%; cal. 15.5%) and palladium formation at 690 K. For all complexes detachment of chlorine was conformed by MS results, where peaks characteristic for chlorine isotope pattern with high relative intensity [Cl_2 m/z (71)] were detected in the range 389–548 K.

Metallic palladium was the final product of the thermal decomposition for complexes (**1–4**), what is evident from TG calculations from thermograms measured to 1273 K (cal./found Pd%: (**1**) 28.4/29.8, (**2**) 32.9/32.4, (**3**) 20.1/20.1, (**4**) 23.5/23.9). Besides that XRD studies of the residues in the crucible were performed and observed diffractogram lines (0.2230, 0.1940, 0.1370, 0.1170, 0.1097 nm) correspond to metallic palladium (Powder Diffraction File) [27].

First stage onset temperatures suggest lower stability of complex (**1**) and (**4**), whereas all of them decompose to palladium at temperatures over 478–720 K, what can be promising parameter for CVD of palladium. However both compounds (**1** and **4**) can be tested as CVD precursors for metallic palladium because of the initial decomposition temperatures below 300 K. Noted temperatures of palladium formation reveals the following order $\text{PdCl}_2((\text{DAMDS})_2$ (**4**) < $\text{PdCl}_2(\text{VTMS})_2$ (**1**) < (**3**) $\text{PdCl}_2(\text{DMB})_2$ < $\text{PdCl}_2(\text{PTMSA})_2$ (**2**).

When data for (**1**) are related to complexes: (**2**), (**3**) and (**4**) (Figs. 3 and 4) it is evident that compound (**1**) and (**4**) have similar onset of the first effect ca. 298 K.

Reported $\text{Pd}(\eta^3\text{-allyl})_2$ and $\text{Pd}(\eta^3\text{-methyl-2-allyl})_2$, $\text{Pd}(\eta^3\text{-allyl})(\text{Cp})$ complexes were studied as precursors of thin films of palladium by CVD method. [8] It has been observed that $\text{Pd}(\eta^3\text{-allyl})_2$ and $\text{Pd}(\eta^3\text{-methyl-2-allyl})_2$ complexes revealed slight palladium layers contamination by C (<1%) (deposition process at 523 K under medium vacuum 10^{-4} Torr). [10,11,28] Better volatility revealed $\text{Pd}(\eta^3\text{-allyl})(\text{acac})$, $\text{Pd}(\eta^3\text{-methyl-2-allyl})(\text{acac})$, $\text{Pd}(\eta^3\text{-$

$\text{allyl})(\text{hfacac})$ and $\text{Pd}(\eta^3\text{-methyl-2-allyl})(\text{hfacac})$. The high purity palladium films (>99% Pd) from those complexes by using different reactive gases, have been obtained. [10,11–28]. The decomposition temperatures were relatively high: 603–643 K and vacuum 10^{-2} Torr. [28] Studied compounds (**1–4**) decomposed to metallic palladium over 478–720 K, what in comparison to the above referenced palladium complexes [10,11,28] make them promising CVD precursors. Important parameters for CVD of metallic palladium such as low initial temperature of the thermal decomposition process (298 K for **1** and **4**) and ambient pressure of the measurement are also in favor of the studied complexes.

3.2. TG-IR spectra

Analysis of the IR spectra of the gases evolved during the thermal decomposition of $\text{PdCl}_2(\text{VTMS})_2$ (**1**) suggests the presence of trimethyl(vinyl)silane ($\nu(\text{=CH})$ – 2966 cm^{-1} , $\nu(\text{C=C})$ – 1511, 1540 cm^{-1} , $\nu(\text{Si-C})$ – 847 cm^{-1}) in the gas phase over 290–470 K. Below 290 K and above 470 K these bands were not observed, what indicates the absence of VTMS in the gas phase. The latter is in agreement with the mass loss observed on TG curve (52.66%) and endotherm on DTA curve. IR spectra of the uncoordinated VTMS revealed bands at 2956 $\nu(\text{=CH})$, 1405 $\nu(\text{C=C})$, 836, 851, 859 $\nu(\text{Si-C})$ cm^{-1} . Observed coordination shift of the $\nu(\text{=CH})$ – 2966 cm^{-1} band towards higher frequency, in the gas phase, in comparison to the spectrum of free VTMS, suggests shorter double bonds distances in the gas phase. TG/IR spectra of the $\text{PdCl}_2(\text{PTMSA})_2$ (**2**) below 730 K exhibit characteristics bands: $\nu(\text{CH}_{\text{aromatic}})$ – 3071 cm^{-1} , $\nu(\text{C=C})$ – 2300 cm^{-1} , $\nu(\text{Si-C})$ – 851 cm^{-1} , which are sifted towards higher frequencies in comparison to IR spectrum of free PTMSA ($\nu(\text{C=C})$ – 2185 cm^{-1} , $\nu(\text{Si-C})$ – 820 cm^{-1}) except $\nu(\text{CH}_{\text{aromatic}})$ – 3080 cm^{-1} . These bands indicate 1-phenyl-2(trimethylsilyl)acetylene presence in the gaseous phase during thermal decomposition. Above 730 K in the TG/IR spectra in the region 600–1100 cm^{-1} and 1800–2600 cm^{-1} absorption bands from $\text{C=CSi}(\text{CH}_3)_3$ fragments were not observed, what can be related to the completion of ligand detachment process.

For $\text{PdCl}_2(\text{DMB})_2$ (**3**) in the temperature above 380 K alkene absorption bands $\nu(\text{CH}_3)$ – 3080 cm^{-1} and $\nu(\text{C=C})$ – 1648 cm^{-1} were registered. [21–25] These fragments were noted also in MS, ($T=548$ K, $[\text{C}_4\text{H}_9]^+$ (57) R.I. 100%) and can be assigned to ligands fragmentation. The IR spectra of the free DMB revealed bands at ($\nu(\text{CH}_3)$ = 2970, 3000 cm^{-1} , $\nu(\text{C=C})$ = 1675 cm^{-1} , which upon coordination were shifted towards higher frequencies.

In the TG/IR spectra of (**4**) the characteristic bands for diallyldimethylsilane above 300 K ($\nu(\text{=CH})$ – 2966 cm^{-1} , $\nu(\text{C=C})$ – 1650 cm^{-1} , $\nu(\text{Si-C})$ – 815 cm^{-1}) have been detected, whereas in free DADMS bands at ($\nu(\text{=CH})$ – 2900, 3000, 3180 cm^{-1} , $\nu(\text{C=C})$ – 1620 cm^{-1} , $\nu(\text{Si-C})$ – 895 cm^{-1}) were noted. The presence of these bands indicate the beginning of the DADMS detachment above 300 K.

Comparing the results of the TG/IR spectra analysis of all palladium(II) complexes it can be noted, that the ligand molecules were detached in the first stage of the thermal process followed by release of the chlorine molecule in the second stage.

3.3. Mass spectra analysis

Variable temperature EI-MS spectra were recorded in the range 303–573 K in order to detect the metallated species in the gas phase, which is the major feature determining usage of complexes as CVD precursors. These fragments should be stable during transport in the gas phase in CVD equipment and adsorb on the substrate surface. In MS spectrum of (**1**) (at 474 K) the following most intensive ions: $[\text{CSi}(\text{CH}_3)]^+$ R.I. 100%, Cl_2 R.I. 78%, $[\text{Pd}[(\text{CH}_3)_3\text{SiCH=CH}]]^+$ R.I. 44%, $[\text{PdCl}[(\text{CH}_3)_3\text{Si}]]^+$ R.I. 40% were detected. Below this tempera-

ture low intensive peaks containing only organic fragments (VTMS R.I. 16% and $[\text{CSi}(\text{CH}_3)]^+$ R.I. 100%) were observed. The presence of organic and chlorine species indicate detachment of VTMS and chlorine molecules and complex decomposition in the temperature range 358–474 K. MS spectra of (**2**) in the range 321–521 K exhibit the following peaks from olefinic and organometallic species: $[\text{Si}(\text{CH}_3)_3]^+$ (R.I. 44% at 321 K and 50% at 490 K), $[\text{PdSi}(\text{CH}_3)_2]^+$ (R.I. 7% at 321 K and 4% at 490 K), $[\text{PdSiC}]^+$ (R.I. 98% at 321 K and 8% at 490 K). However the spectrum at 321 K present $[\text{C}_6\text{H}_5\text{CCH}_2]^+$ R.I. 100% as the most intensive signal. Such fragments indicate simultaneous detachment and fragmentation of PTMSA over 321–490 K. It can be noted, that the intensity of metal bonded peaks exhibit reduced relative intensity along the temperature increase. The latter suggests decomposition of the organometallic fragments and metallic palladium formation, similarly to processes observed on TG and DTG curves. In the case of (**3**) at 548 K peaks which include metallated species revealed the following data: $[\text{PdC}_4\text{H}_6\text{Cl}]^+$ R.I. 34%, $[\text{PdCl}[(\text{CH}_3)_2\text{C}=\text{C}(\text{CH}_3)\text{H}]]^+$ R.I. 79%, $[\text{Pd}_3[(\text{CH}_3)_2\text{C}=\text{C}(\text{CH}_3)_2]_2]$ R.I. 10%. Besides that the intensive peaks from organic species were noted as well: $[\text{C}_4\text{H}_9]^+$ R.I. 100% and Cl_2 R.I. 62%. Below 548 K fragments with palladium species were not registered, only line from $[\text{CH}_3\text{CH}_2\text{CCl}]^+$ (R.I. 28%) ion was detected.

MS spectra of (**4**) reveal peaks from organic fragments $[\text{CH}_2=\text{CH}-\text{CH}_2]^+$ (R.I. 38% at 447 K and R.I. 40% at 389 K), $[\text{Si}(\text{CH}_3)_3]^+$ (R.I. 35% at 447 K and R.I. 52% at 389 K), $[\text{CH}_2\text{CHCH}_2\text{Si}(\text{CH}_3)_3]^+$ (R.I. 40% at 447 K and R.I. 56% at 389 K), while organometallic fragments: $[\text{PdCH}_2\text{CHCH}_2]^+$ (R.I. 72% at 389 K and 98% at 447 K), $[\text{Pd}(\text{CH}_2\text{CHCH}_2)\text{SiH}(\text{CH}_3)_2]^+$ (R.I. 63% at 389 K and 84% at 447 K) were noted over 389–447 K. Moreover at 389 K dipalladium ion ($[\text{Pd}_2\text{CH}_2\text{CHCH}_2\text{Si}]^+$) has been observed. Similar dipalladium species were noted in MS of di- μ -chlorodiallyldipalladium(II) $[\text{C}_6\text{H}_5\text{PdCl}]_2$. [15] Above results demonstrate, that compounds (**1–4**) can be used for the deposition of palladium layers by CVD, due to formation of the volatile metallated species (e.g. $[\text{PdC}_4\text{H}_6\text{Cl}]^+$, $[\text{PdSi}(\text{CH}_3)_3]^+$, $[\text{PdCH}_2\text{CHCH}_2]^+$) under reduced pressure. The MS analyses indicate fragmentation temperature: 358–474 K (**1**), 321–521 K (**2**), 395–548 K (**3**) and 389–447 K (**4**). The organometallic fragments were observed mostly at higher temperatures 474 K (**1**), 521 K (**2**), 548 K (**3**) and 447 K (**4**) what is important for the CVD. MS lines from chlorine were detected only in the case of (**1**) and (**3**) at 474 K and 548 K respectively, whereas at lower temperatures (358 K (**1**) and 395 K (**3**)) only organic fragments were noted. On the other hand MS spectra of (**2**) and (**4**) revealed organic, organometallic fragments and chlorine molecular peak. The palladium containing fragments were registered at 474 K (**1**), 321 K (**2**), 548 K (**3**) and 389 K (**4**). In the case of di- μ -chlorodiallylpalladium(II) and di- μ -chlorodi(4-methoxy-1-methylpent-2-enyl)dipalladium(II) complexes fragments containing palladium atom e.g. $[\text{C}_3\text{H}_5\text{PdCl}]^+$, $[\text{C}_3\text{H}_5\text{Pd}_2\text{Cl}]^+$, $[(\text{C}_3\text{H}_5)_2\text{Pd}_2\text{Cl}]^+$ for di- μ -chlorodiallylpalladium(II) have been registered also. [15] The MS spectra of di- μ -chlorodi(4-methoxy-1-methylpent-2-enyl)dipalladium(II) revealed only weak clusters of peaks for palladium containing ions. The ligand was decomposed during thermal process. MS spectra of other methoxyallyl complexes such di- μ -chlorodi(5-methoxyhexa-2-enyl)dipalladium(II), di- μ -chlorodi(4-methoxy-1,4-diphenylbut-2-enyl)dipalladium(II) did not reveal palladium containing peaks, but the base peak was the $[\text{L}-\text{H}]^+$ ion. In conclusion it can be suggested that the mechanism of thermal decomposition in MS analysis of the complexes **1–4** are similar like for di- μ -chlorodiallylpalladium(II).

4. Conclusions

Thermal analysis of the complexes (**1–4**) indicated the metallic palladium as the final product of the thermal decomposition, what was evident from TG calculations on thermograms measured to 1273 K and XRD studies of the residues in the crucible (Powder Diffraction File) [27]. First stage onset temperatures suggest lower stability of complex (**1**) and (**4**), whereas all of them decompose to palladium at temperatures over 478–720 K, what can be promising parameter for CVD of palladium. Analysis of TG/IR spectra of all palladium(II) complexes indicate the ligand molecules detachment. The VT-MS spectra revealed fragments containing palladium species in the range 321–548 K. Noted temperatures of palladium formation reveals the following order $\text{PdCl}_2(\text{DAMDS})_2$ (**4**) < $\text{PdCl}_2(\text{VTMS})_2$ (**1**) < (**3**) $\text{PdCl}_2(\text{DMB})_2$ < $\text{PdCl}_2(\text{PTMSA})_2$ (**2**).

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tca.2009.06.002

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