

Reaction between palladium(II) and gallium(III) halogenides in arenes: influence of halogen nature on the formation of binuclear palladium(I) clusters

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Abstract

Palladium(II) bromide reacts with gallium(III) bromide in the presence of arenes yielding binuclear palladium(I) complexes $[\text{Pd}_2(\text{GaBr}_4)_2(\text{arene})_2]$, where arene = benzene (**1**), toluene (**2**) and *p*-xylene (**3**). Reaction of palladium(II) chloride with gallium(III) chloride in *p*-xylene leads to the analogous palladium(I) compound $[\text{Pd}_2(\text{GaCl}_4)_2(\text{p-xylene})_2]$ (**4**); the X-ray structures of **1–4** were determined.

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1. Introduction

Since the discovery of the first compound containing a direct single palladium–palladium bond [1], a large number of these complexes have been synthesised and structurally characterized. The structure, chemistry and catalytic properties of clusters with Pd–Pd bonds were recently reviewed [2,3]. These compounds take part in a wide range of catalytic reactions: isomerization of double C–C bonds [4,5], hydrogenation of multiple bonds [6–8], hydrogen-transfer reduction [9–11] and carbonylation [12–15].

Dipalladium clusters having arenes as ligands were prepared for the first time by Allegra et al., and crystal structures of two benzene compounds $[\text{Pd}_2\text{X}_2(\text{benzene})_2]$ ($\text{X}^- = \text{AlCl}_4^-$ or Al_2Cl_7^-) were determined [16,17]. Later it

was found [18], that they could be used as catalysts for ethylene dimerization. We have recently reported the synthesis and structures of three palladium(I)–gallium(III) compounds $[\text{Pd}_2\text{X}_2(\text{arene})_2]$, where arene = benzene or toluene, $\text{X}^- = \text{Ga}_2\text{Cl}_7^-$ or GaCl_4^- , together with the first example of a corresponding diplatinum(I) complex $[\text{Pt}_2(\text{GaCl}_4)_2(\text{C}_{10}\text{H}_{10})_2] \cdot 2\text{C}_6\text{H}_6$, containing naphthalene molecules as stabilizing arene ligands [19].

There is no information in the literature about the existence of palladium–gallium compounds with bridging halogens X^- , where $\text{X}^- = \text{Br}^-$ or I^- . In this work, we report results from the investigation of the reaction between palladium(II) and gallium(III) halogenides in the presence of arenes. The syntheses and crystal structures of four new palladium(I)–gallium(III) compounds $[\text{Pd}_2(\text{GaX}_4)_2(\text{arene})_2]$ ($\text{X}^- = \text{Cl}^-$, Br^-) we described; three of them are the first examples of compounds with bridging bromide ions between palladium and gallium.

2. Results and discussion

Heating a mixture of palladium(II) bromide and gallium(III) bromide in the presence of arene (benzene,

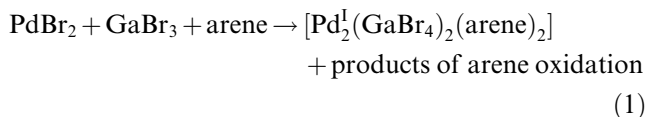
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toluene or *p*-xylene) leads to dark red solutions. After two weeks, red crystals of the general composition $[\text{Pd}_2(\text{GaBr}_4)_2(\text{arene})_2]$ can be isolated at moderate yields.

The time of heating required for reaction depends on the nature of the arene and increases from *p*-xylene to benzene. This fact is in agreement with the assumption [19], that reduction of Pd(II) is mediated by the oxidation of arenes, probably their halogenation. The over-all process may be represented as follows:



Crystal structures of compounds **1–3** are shown in Fig. 1 and crystallographic data are summarized in Table 1. The common features of these compounds are the presence of two arene ligands sandwiching the dipalladium core, together with GaBr_4^- groups coordi-

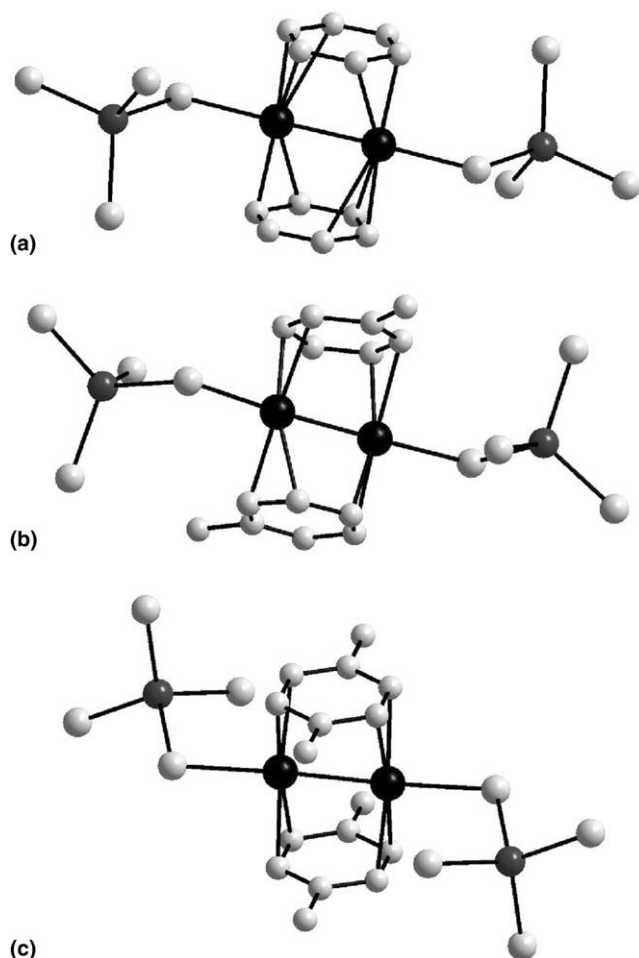


Fig. 1. View of **1** (a), **2** (b) and **3** (c).

nating to the palladium atoms in the direction of the Pd–Pd bond vector.

The complex $[\text{Pd}_2(\text{GaCl}_4)_2(\textit{p}\text{-xylene})_2]$ was obtained in the same manner as **3**, but without heating. The reaction between palladium(II) chloride and gallium(III) chloride in aromatic solvents proceeds more easily than that between the corresponding bromides, probably because of the higher ability of gallium chloride to attack aromatic rings.

The distances observed between the palladium atoms confirm the existence of a direct, single Pd–Pd bond. Recently, we reported crystallographic data for three palladium(I) complexes derived from the $\text{PdCl}_2\text{–GaCl}_3$ system. Pd–Pd distances in compounds of this type are presented in Table 2. A comparison of the bromide complexes with the isostructural chloride ones shows that Pd–Pd bonds are slightly longer in the bromide compounds (largest difference is 2 pm for the benzene clusters).

All attempts to obtain binuclear palladium(I) compounds containing GaI_4^- or Ga_2I_7^- -groups by reaction of palladium(II) iodide with gallium(III) iodide in the presence of arenes (benzene, toluene, *p*-xylene) were unsuccessful. Instead, the main product of this reaction in *p*-xylene is the mononuclear palladium(II) compound, $\text{Pd}[\text{GaI}_4]_2$. It may be a consequence of gallium(III) iodide being a weaker Lewis acid than gallium(III) bromide, thus failing to stabilize binuclear palladium(I) clusters. Details of the synthesis and crystal structure of this compound together with its bromide analogue are reported in a separate work [20].

The reaction between palladium(II) bromide and gallium(III) bromide in ethylbenzene, mesitylene or 1,2-dichlorobenzene was also studied. The main product of the reaction was metallic palladium. It is interesting to note that a small quantity of a red solid was formed in the case of the ethylbenzene reaction. However, this compound turned out to be amorphous.

Reactions of polycyclic arenes, such as naphthalene, anthracene and chrysene, with palladium(II) bromide and gallium(III) bromide in benzene or 1,2-dichlorobenzene solutions lead to green or brown solutions and a dark, almost black, oil.

Raman spectra of $[\text{Pd}_2(\text{GaBr}_4)_2(\text{C}_7\text{H}_8)_2]$ in toluene contain a strong band at 216 cm^{-1} . This band can be assigned to the symmetric stretch vibration of tetrahedral GaBr_4^- coordinated to the dipalladium unit. Previously, a strong band at 210 cm^{-1} was assigned to the free GaBr_4^- ion [21]. Raman spectra of the *p*-xylene complex **3** only display a weak band at 228 cm^{-1} . On the other hand, these spectra are almost identical to spectra of concentrated solutions of GaBr_3 in *p*-xylene (the latter contain an additional band at 202 cm^{-1}). In general, the Raman spectra of crystals of **3** contain very broad bands due to fluorescence.

Table 1

Crystallographic data and experimental details of the X-ray studies of [Pd₂(GaBr₄)₂(C₆H₆)₂], [Pd₂(GaBr₄)₂(C₇H₈)₂], [Pd₂(GaBr₄)₂(C₈H₁₀)₂] and [Pd₂(GaCl₄)₂(C₈H₁₀)₂]

Compound	[Pd ₂ (GaBr ₄) ₂ (C ₆ H ₆) ₂]	[Pd ₂ (GaBr ₄) ₂ (C ₇ H ₈) ₂]	[Pd ₂ (GaBr ₄) ₂ (C ₈ H ₁₀) ₂]	[Pd ₂ (GaCl ₄) ₂ (C ₈ H ₁₀) ₂]
Sum formula	C ₆ H ₆ Br ₄ GaPd	C ₇ H ₈ Br ₄ GaPd	C ₈ H ₁₀ Br ₄ GaPd	C ₈ H ₁₀ Cl ₄ GaPd
Cell constants	<i>a</i> = 1426.51(4) pm <i>b</i> = 1146.1(4) pm <i>c</i> = 1500.16(6) pm β = 100.067(1)°	<i>a</i> = 776.33(2) pm <i>b</i> = 1729.56(5) pm <i>c</i> = 967.69(3) pm β = 90.687(1)°	<i>a</i> = 849.22(2) pm <i>b</i> = 1564.95(4) pm <i>c</i> = 1087.54(3) pm β = 100.205(2)°	<i>a</i> = 841.76(3) pm <i>b</i> = 1543.70(5) pm <i>c</i> = 1037.07(4) pm β = 101.134(1)°
Cell volume	2414.7(1)	1299.23(6)	1422.46(6)	1322.23(8)
Z	8	4	4	4
ρ_{calc}	3.157	3.006	2.811	2.310
Crystal system, space group	monoclinic, C2/c	monoclinic, P2 ₁	monoclinic, P2 ₁ /c	monoclinic, P2 ₁ /c
Temperature (K)	223	299	299	299
Radiation		Ag K α , λ = 56.085 pm	Ag K α , λ = 56.085 pm	
Absorption coefficient	90.1	83.8	76.6	21.8
Absorption correction		numerical	numerical	
θ range	4.03 < θ < 21.37	4.05 < θ < 21.34	4.05 < θ < 21.37	4.05 < θ < 21.36
Number of measured reflections	15756	13035	11830	11532
Number of unique reflections	2748	5752	3205	2992
<i>R</i> _{int}	0.0513	0.0620	0.0388	0.0355
Number of refined parameters	109	236	127	127
Ratio reflections/parameters	25	24	25	24
	<i>R</i> ₁ = 0.0316 (2330 obs. reflections)	<i>R</i> ₁ = 0.0443 (5339 obs. reflections)	<i>R</i> ₁ = 0.0326 (2644 obs. reflections)	<i>R</i> ₁ = 0.0300 (2492 obs. reflections)
Residuals	<i>wR</i> ₂ = 0.0715	<i>wR</i> ₂ = 0.116	<i>wR</i> ₂ = 0.0713	<i>wR</i> ₂ = 0.0750
Goodness-of-fit	1.045	1.029	1.066	1.055
Difference electron density	0.90/−0.97	1.17/−0.97	0.82/−1.06	1.36/−0.43

Table 2

Selected bond lengths (pm) in dipalladium–arene clusters

Compound	Pd–Pd	Reference
[Pd ₂ (GaCl ₄) ₂ (C ₆ H ₆) ₂]	258.4	[19]
[Pd ₂ (GaBr ₄) ₂ (C ₆ H ₆) ₂]	260.4	This work
[Pd ₂ (GaCl ₄) ₂ (C ₇ H ₈) ₂]	257.2	[19]
[Pd ₂ (GaBr ₄) ₂ (C ₇ H ₈) ₂]	257.8	This work
[Pd ₂ (GaCl ₄) ₂ (C ₈ H ₁₀) ₂]	256.2	This work
[Pd ₂ (GaBr ₄) ₂ (C ₈ H ₁₀) ₂]	257.8	This work
[Pd ₂ (Ga ₂ Cl ₇) ₂ (C ₆ H ₆) ₂]	256.2	[19]

3. Conclusions

In the present work, the preparation and single-crystal structural analyses of dipalladium clusters [Pd₂(GaBr₄)₂(arene)₂], where arene = benzene, toluene and *p*-xylene, have been reported. It was found, that not only the nature of the arene ligands affects the formation of palladium(I) complexes, but also the Lewis acidity of the gallium(III) halide in the PdX₂–GaX₃–arene (X[−] = Cl[−], Br[−], I[−]) systems.

4. Experimental

4.1. Starting materials

GaCl₃ (Aldrich Chemical Company, 99.99%, H₂O < 100 ppm), GaBr₃, GaI₃, PdCl₂ (Alfa Aesar Company,

99.999%), PdBr₂ (Aldrich Chemical Company, 99%) and PdI₂ (Alfa Aesar Company, 99.9%) were used as received.

4.2. Structure determinations

Due to the extreme sensitivity towards humidity and oxygen, crystals of all compounds were sealed inside glass capillaries in a dry nitrogen atmosphere. Diffraction data were collected on a Bruker–Nonius KappaCCD diffractometer. Numerical absorption corrections were applied [22]. The structures were solved using direct methods [23] and refined on *F*² with anisotropic thermal parameters for all non-H atoms [24]. H atoms were refined on calculated positions using a riding model. Crystals of **2** were refined as inversion twins. Table 1 summarizes the results of the structure determinations. CCDC 213088 (**1**), CCDC 213089 (**2**), CCDC 213090 (**3**) and CCDC 213091 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

4.3. Raman spectroscopy

Raman spectra were recorded with a Bio-Rad FTS 6000 spectrometer equipped with a low-power Nd:YAG

laser ($\lambda = 1064$ nm) and a liquid-nitrogen-cooled, solid state Ge diode detector. A resolution of 4 cm^{-1} was used.

4.4. Synthesis

All experiments were performed in a glove box under an inert atmosphere of deoxygenated and dried nitrogen ($<1\text{ ppm H}_2\text{O}$).

4.4.1. Synthesis of $[Pd_2(GaBr_4)_2(C_6H_6)_2]$ (**1**)

Benzene (3 ml) was added to the solid mixture of $PdBr_2$ (0.030 g, 0.113 mmol) and $GaBr_3$ (0.070 g, 0.226 mmol). The mixture was heated for 4 h (80–90 °C) under stirring with repeated additions of benzene. The reaction flask was wrapped in aluminium foil and set aside for two weeks. Dark red crystals formed.

4.4.2. Synthesis of $[Pd_2(GaBr_4)_2(C_7H_8)_2]$ (**2**)

Compound **2** was prepared in a manner similar to that of compound **1**, but using toluene (3 mL) instead of benzene. Time of heating was 1–2 h. Red crystals were grown within two weeks.

4.4.3. Synthesis of $[Pd_2(GaBr_4)_2(C_8H_{10})_2]$ (**3**)

p-Xylene (2 mL) was added to the solid mixture of $PdBr_2$ (0.030 g, 0.113 mmol) and $GaBr_3$ (0.100 g, 0.323 mmol). The mixture was heated for 5–10 min at 80–90 °C without stirring. After two weeks dark red crystals formed.

4.4.4. Synthesis of $[Pd_2(GaCl_4)_2(C_8H_{10})_2]$ (**4**)

p-Xylene (2 mL) was added to the solid mixture of $PdCl_2$ (0.044 g, 0.248 mmol) and $GaCl_3$ (0.160 g, 0.909 mmol). The reaction flask was wrapped in aluminium foil and set aside for three days. Dark red crystals formed.

5. Supporting information

CIF files containing the results of the structure determinations (excluding structure factors). These material is available free of charge via the Internet at <http://pubs.acs.org>.

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