



Synthesis and characterization of binuclear palladium(I) compounds and the influence of competing arenes

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ABSTRACT

The binuclear palladium(I) compounds, $[\text{Pd}_2(\text{Ga}_2\text{Cl}_7)_2(\text{C}_7\text{H}_8)_2]$ (**1**), $[\text{Pd}_2(\text{GaCl}_4)_2(\text{C}_9\text{H}_{12})_2] \cdot \text{C}_9\text{H}_{12}$ (**2**) and $[\text{Pd}_2(\text{Ga}_2\text{Cl}_7)_2(\text{C}_6\text{H}_5\text{Cl})_2]$ (**3**), have been prepared from palladium(II) chloride in gallium(III) chloride-arene reaction media. All isolated crystalline solids (**1**, **2** and **3**) have been structurally characterized by single crystal X-ray diffraction and Raman spectroscopy. The results from quantum chemical calculations on the interaction energies of the arenes and the dipalladium unit of these compounds is also presented.

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1. Introduction

Gallium halide-arene mixtures have been shown to be powerful tools, capable of both reducing metal centers and acting as halide scavengers [1]. It is the special properties of gallium(III) halides to be extremely soluble in arenes (up to 50 mol% in benzene), the ability to accept halide ions from metal halides and the reducing ability of GaX_3 -arene mixtures that make them suitable for the preparation of low-valent clusters and compounds of the transition metals [2]. In the formation of binuclear transition metal compounds with coordinating arenes these properties are central, along with the nature of the arene-ring substituents and transition metal centers, affecting the structure of the metal-arene compounds formed.

The first binuclear palladium compounds having arenes as ligands were prepared in an AlCl_3/Al mixture by Allegra et al. [3]. In these reactions, elemental aluminum was proposed as the reducing agent, reducing palladium(II) to palladium(I). It was later shown in our group that a GaCl_3 /arene mixture not including metallic gallium enable the formation of binuclear palladium(I) compounds under mild conditions. It is believed that the reduction of the palladium(II) center occurs via oxidation (i.e. halogenation) of the arenes [4a]. A number of binuclear arene-supported palladium(I) compounds have been prepared in this way in our lab [4].

Furthermore, in recent years several one- and two-dimensional chains and networks of polynuclear palladium compounds, so called 'sandwich compounds', coordinating different polycyclic aromatic hydrocarbons (PAHs) have been reported by Kurosawa and co-workers [5]. Most of these compounds have been prepared through the use of the substitutionally labile homoleptic acetonitrile dipalladium compound $[\text{Pd}_2(\text{CH}_3\text{CN})_6][\text{BF}_4]_2$.

Palladium, along with its neighboring Group 10 metals, plays a central role in the field of catalysis [6]. The Group 10 metals are indispensable for organic synthesis, playing a part as catalysts in reactions such as carbonylation [7], isomerization [8] and dimerization [9]. Palladium catalysed carbon-carbon bond forming reactions have been especially significant to the development of organic chemistry and are valuable in industry. The catalytic properties of palladium explain the general interest in palladium clusters and compounds, exhibiting changes in coordination and oxidation state.

The aim of this study has been to use the exceptional reductive ability of the gallium (III) halide-arene mixtures in quest for new polynuclear palladium compounds supported by simple arenes or polyaromatic hydrocarbons, such as naphthalene, anthracene or biphenyl.

In this work we report the syntheses and crystal structures of three new binuclear palladium(I) compounds; $[\text{Pd}_2(\text{Ga}_2\text{Cl}_7)_2(\text{C}_7\text{H}_8)_2]$ (**1**), $[\text{Pd}_2(\text{GaCl}_4)_2(\text{C}_9\text{H}_{12})_2] \cdot \text{C}_9\text{H}_{12}$ (**2**), $[\text{Pd}_2(\text{Ga}_2\text{Cl}_7)_2(\text{C}_6\text{H}_5\text{Cl})_2]$ (**3**), one of which was solely recovered from a mixed arene reaction medium, highlighting the effects of arene competition with respect to coordination to the Pd_2^{2+} unit.

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2. Results and discussion

The binuclear palladium–toluene compound was obtained from the straightforward room-temperature reaction of palladium(II) chloride and an excess of gallium(III) chloride (molar ratio 1:4.4) in toluene, red/brown crystals in moderate yield were acquired. The single crystal structure determination proved the compound to be $[\text{Pd}_2(\text{Ga}_2\text{Cl}_7)_2(\text{C}_7\text{H}_8)_2]$ (**1**).

In the search for suitable solvents for dissolving PHAs, naphthalene, anthracene and biphenyl a number of solvents were tested. Toluene as well as benzene, were tested but only the previously known $[\text{Pd}_2(\text{GaCl}_4)_2(\text{C}_6\text{H}_6)_2]$, $[\text{Pd}_2(\text{Ga}_2\text{Cl}_7)_2(\text{C}_6\text{H}_6)_2]$ and $[\text{Pd}_2(\text{GaCl}_4)_2(\text{C}_7\text{H}_8)_2]$ compounds were formed, except for the new $[\text{Pd}_2(\text{Ga}_2\text{Cl}_7)_2(\text{C}_7\text{H}_8)_2]$ (**1**). This indicates that these simple aromatic solvents outcompete or simply outnumber the three PAHs in terms of coordination to the Pd_2^{2+} unit. From the reaction of PdCl_2 and GaCl_3 in a biphenyl-saturated mesitylene solution deeply red/brownish crystals were collected. These crystals were of the general composition $[\text{Pd}_2(\text{GaCl}_4)_2(\text{C}_9\text{H}_{12})_2] \cdot \text{C}_9\text{H}_{12}$ (**2**). The solubility of biphenyl and naphthalene in mesitylene, as well as in toluene and benzene, was shown to be good. However, anthracene shows a generally low solubility.

Chlorobenzene was also used as solvent for the reaction of PdCl_2 and GaCl_3 with naphthalene, anthracene and biphenyl, respectively. Chlorobenzene was anticipated to be a good solvent for the palladium reaction, because of its weak base character. It was also expected to retard the oxidation (i.e. chlorination) of the arene solvent and the following reduction of palladium(II) to palladium(I), because of the already present chlorine substituent. Chlorobenzene showed similar solubility for naphthalene, biphenyl and anthracene as mesitylene, toluene and benzene. The reaction between PdCl_2 and GaCl_3 in chlorobenzene resulted in brown/black needle-shaped crystals of $[\text{Pd}_2(\text{GaCl}_4)_2(\text{C}_6\text{H}_5\text{Cl})_2]$ (**3**) within weeks. It might well be that the reaction is slower, but it is evident that chlorobenzene instead of the targeted PAHs coordinate to the dipalladium unit. Fig. 1 shows the molecular structures of **1**, **2** and **3**. The results of the structural determinations are summarized in Table 1.

Just as for the dipalladium–toluene compound, $[\text{Pd}_2(\text{GaCl}_4)_2(\text{C}_7\text{H}_8)_2]$ earlier isolated in our group [4a], compound **1** displays a central dipalladium unit enclosed by two sandwiching toluene molecules. Each of the sandwiching toluenes shows a η^5 -coordination to the two palladium atoms of the dipalladium unit. As a result of packing effects, the methyl groups of the two toluene molecules are oriented in opposite direction, like a *trans*-arrangement. Each of the palladium atoms in the dipalladium unit is bound to one of the chloride atom of the Ga_2Cl_7^- anion forming the halogen bridge to gallium.

In the formation of some arene coordinated f-block compounds a deviation in the arene substituents out of the aromatic plane have been observed [1c]. This phenomenon also occurs in structures **1**, **2** and **3**, see Table 3. An approximately 6.0° deviation in the angle α is observed for the methyl group of the toluene compound (**1**). The chlorine atom of the chlorobenzene compound (**3**) is tilting 8.4° out of the aromatic plane and the methyl groups of the mesitylene compound (**2**) between 6.3° and 8.9° . The deviations in angle of the substituting groups on the aromatic ring have been noted, by Hubig et al. [10], to be correlated with the degree of charge transfer from the arene donor to the coordinated acceptor. In accordance with the discussion by Hubig et al. the deviation angles measured; 6.0° (**1**), 6.3 – 8.9° (**2**) and 8.4° (**3**) indicate an increasing σ -character in the coordination of the metal unit to the arenes, opposed to the pure π -character that would be expected for a compound with zero deviation angle. An increasing σ -character with increasing deviation angle implies an increase

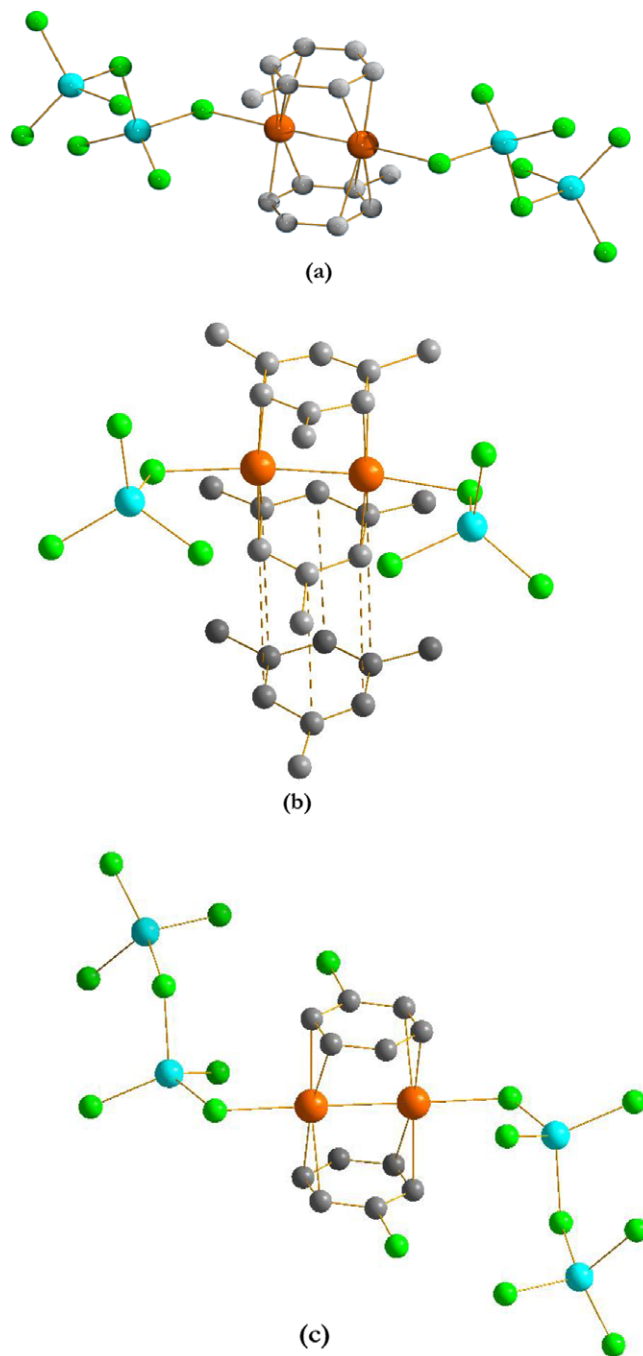


Fig. 1. The molecular structure of **1** (a), **2** (b) and **3** (c).

in the charge transfer from the arene donor to the coordinated acceptor. The deviation angles measured for the three compounds are however relatively small as to why they can still be expected to exhibit high π -character.

The crystallographic data of **2** show a third, non-coordinated mesitylene molecule at a distance of 3.9 \AA from the aromatic plane of the closest coordinating mesitylene molecule. This mesitylene is interacting via π -stacking (or π - π interaction), Fig. 1b. A similar structural feature, has previously been reported for the diplatinum species $[\text{Pt}_2(\text{GaCl}_4)_2(\text{C}_{10}\text{H}_8)_2] \cdot 2\text{C}_6\text{H}_6$ containing naphthalene [4a]. This occurrence might be of a stabilizing nature or simply an effect of packing in the crystal structure.

Table 1Crystallographic data and structure refinement of the X-ray studies of $[\text{Pd}_2(\text{Ga}_2\text{Cl}_7)_2(\text{C}_7\text{H}_8)_2]$ (**1**), $[\text{Pd}_2(\text{GaCl}_4)_2(\text{C}_9\text{H}_{12})_2]\cdot\text{C}_9\text{H}_{12}$ (**2**) and $[\text{Pd}_2(\text{Ga}_2\text{Cl}_7)_2(\text{C}_6\text{H}_5\text{Cl})_2]$ (**3**).

Compound	$[\text{Pd}_2(\text{Ga}_2\text{Cl}_7)_2(\text{C}_7\text{H}_8)_2]$	$[\text{Pd}_2(\text{GaCl}_4)_2(\text{C}_9\text{H}_{12})_2]\cdot\text{C}_9\text{H}_{12}$	$[\text{Pd}_2(\text{Ga}_2\text{Cl}_7)_2(\text{C}_6\text{H}_5\text{Cl})_2]$
Sum formula	$\text{C}_{14}\text{H}_{16}\text{Cl}_{14}\text{Ga}_4\text{Pd}_2$	$\text{C}_7\text{H}_{36}\text{Cl}_8\text{Ga}_2\text{Pd}_2$	$\text{C}_{12}\text{H}_{10}\text{Cl}_6\text{Ga}_4\text{Pd}_2$
M_r	1172.25	996.45	1213.14
<i>Lattice parameters</i>			
<i>a</i> (pm)	916.06(9)	1844.1(2)	915.08(13)
<i>b</i> (pm)	1887.0(3)	1667.1(2)	1844.85(14)
<i>c</i> (pm)	955.30(8)	2367.0(2)	947.84(13)
β (°)	97.615(8)		99.00(1)
Space group	$P2_1/n$	<i>Pbca</i>	$P2_1/n$
Cell volume (pm ³)	$1636.8(3) \times 10^6$	$7277.1(12) \times 10^6$	$1580.4(3) \times 10^6$
<i>Z</i>	4	8	2
Total number of reflections	16,937	35,967	17,850
Number of independent reflections, R_{int}	3686, 0.041	6558, 0.084	3612, 0.046
Number of L.S. parameters	155	361	154
R_1	0.030	0.070	0.046
wR_2	0.061	0.159	0.114
<i>S</i>	1.11	1.16	1.08
Residual electron density, peak/hole	0.50/−0.49	0.70/−0.66	1.92/−1.95

Table 2

Palladium–palladium bond lengths in selected dipalladium–arene compounds.

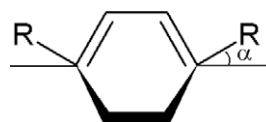
Compound	Pd–Pd [Å]	Reference
$[\text{Pd}_2(\text{GaCl}_4)_2(\text{C}_6\text{H}_6)_2]$	2.584	[4a]
$[\text{Pd}_2(\text{Ga}_2\text{Cl}_7)_2(\text{C}_6\text{H}_6)_2]$	2.562	[4a]
$[\text{Pd}_2(\text{GaCl}_4)_2(\text{C}_7\text{H}_8)_2]$	2.572	[4a]
$[\text{Pd}_2(\text{Ga}_2\text{Cl}_7)_2(\text{C}_7\text{H}_8)_2]$	2.561	This work
$[\text{Pd}_2(\text{GaCl}_4)_2(\text{C}_9\text{H}_{12})_2]\cdot\text{C}_9\text{H}_{12}$	2.538	This work
$[\text{Pd}_2(\text{Ga}_2\text{Cl}_7)_2(\text{C}_6\text{H}_5\text{Cl})_2]$	2.567	This work

The crystal determination of **3** is somewhat ambiguous, since obtaining high-quality diffraction data proved difficult. The crystallographic results indicate that coordination is not completely uniform. A possible explanation to this observation might be that the crystal structure includes a small amount of coordinated benzene, as to solely chlorobenzene. The Pd–Pd distance in **3** is however almost the same as that of the corresponding benzene compound, $[\text{Pd}_2(\text{Ga}_2\text{Cl}_7)_2(\text{C}_6\text{H}_6)_2]$ (2.562 Å), and the Pd–C distances between 2.2 and 2.4 Å also shows good conformity with previous results. The C–Cl distance in the chlorobenzene sandwiching ligands are 1.675 Å, which is in agreement with, the C–Cl distance expected for chlorobenzene [11].

The palladium–palladium distance in **1**, 2.561 Å, is comparable to that in the benzene analogue, but it is slightly longer than that for the toluene analogue $[\text{Pd}_2(\text{GaCl}_4)_2(\text{C}_7\text{H}_8)_2]$ (2.572 Å), as seen in Table 2. The Pd–Pd distances indicate that the dipalladium units are stabilized by direct metal–metal bonding. It also seems that the slight difference in palladium–palladium distance between compounds with the Ga_2Cl_7^- and the GaCl_4^- halogen bridging ligands have negligible effects on the overall geometry of the compounds. The Pd–C distances in **1** vary from 2.2 to 2.5 Å, which is comparable to the palladium–carbon distances in $[\text{Pd}_2(\text{GaCl}_4)_2(\text{C}_7\text{H}_8)_2]$.

The palladium–palladium distance in **2**, 2.538 Å, is slightly shorter than those of **1** and **3** and the other compounds in Table 2. This shortening of the Pd–Pd bond might be induced by the coordinating mesitylenes. The mesitylenes in **2** each show a η^4 -coordination to the two palladium atoms of the dipalladium unit. The mesitylenes are oriented in a parallel fashion, with the substituting methyl groups in an eclipsed conformation. The Pd–C distances in **2** are between 2.2 and 2.4 Å. The reaction of PdCl_2 with GaCl_3 in biphenyl-saturated mesitylene was carried out in an excess of GaCl_3 and resulted in the formation of **2** containing the GaCl_4^- ligand.

It has previously been suggested from spectroscopic studies of the GaCl_3 -mesitylene system that only the monomeric GaCl_3

Table 3The deviation angle of the substituent groups from the aromatic plane in **1–3**.

Compound	α [°]
$[\text{Pd}_2(\text{Ga}_2\text{Cl}_7)_2(\text{C}_7\text{H}_8)_2]$	6.0
$[\text{Pd}_2(\text{Ga}_2\text{Cl}_7)_2(\text{C}_6\text{H}_5\text{Cl})_2]$	8.4
$[\text{Pd}_2(\text{GaCl}_4)_2(\text{C}_9\text{H}_{12})_2]\cdot\text{C}_9\text{H}_{12}$	6.3–8.9

species is spectroscopically evident in solution, and that a strong gallium(III)-mesitylene complex is formed between the two entities [12]. The formation of this relatively stable gallium(III)-mesitylene complex might disfavor the formation of a mesitylene-stabilized dipalladium compound. This can pose as an explanation to why **2** has not been isolated from a simple mesitylene solution, indicating the effect of dissolved biphenyl in the reaction. And in a paradox way, the intended ligand sees itself outcompeted by the solvent as ligand to Pd_2^{2+} ; possibly through coordination to $\text{GaCl}_3/\text{Ga}_2\text{Cl}_6$, thus increasing mesitylene activity relative to the pure GaCl_3 -mesitylene reaction medium.

Mesitylene, unlike benzene or toluene, has also been shown to have a tendency of being strongly coordinating to the Pd_2^{2+} unit, leading to disproportionation into Pd^0 and Pd^{II} [4a]. However, mesitylene has been reported to stabilize Hg_2^{2+} , in $[\text{Hg}_2(\text{AlCl}_4)_2(\text{C}_6\text{H}_{12})_2]$ [13], and it is in this work shown to stabilize Pd_2^{2+} in $[\text{Pd}_2(\text{GaCl}_4)_2(\text{C}_9\text{H}_{12})_2]\cdot\text{C}_9\text{H}_{12}$. It thus seems that there is a small overall difference in the strength of the soft base donors mesitylene, toluene and benzene.

In order to investigate the interactions between the different arenes and the dipalladium unit, two simple theoretical models were constructed; $\text{Pd}_2\text{Cl}_2(\text{arene})_2$ and $\text{Pd}_2(\text{GaCl}_4)_2(\text{arene})_2$ (arene = benzene, toluene, mesitylene or chlorobenzene). Quantum chemical calculations on these models at hybrid density functional level show the $\text{Pd}_2\text{Cl}_2(\text{arene})_2$ model to be the most informative model because of its simplicity and ease of interpretation. Using the $\text{Pd}_2\text{Cl}_2(\text{arene})_2$ model the interaction energy between chlorobenzene and the dipalladium unit in $\text{Pd}_2\text{Cl}_2(\text{chlorobenzene})_2$ was calculated to be nearly three times that of benzene. The interaction between chlorobenzene and the dipalladium unit in compound $[\text{Pd}_2(\text{Ga}_2\text{Cl}_7)_2(\text{C}_6\text{H}_5\text{Cl})_2]$ might be of electrostatic nature. Toluene on the other hand shows quite similar interaction energy to that of benzene, while mesitylene is interacting slightly stronger, 1.5 times that of benzene. These relatively small differences in the

interaction energies calculated are in agreement with the small differences in the observed deviation angles of the arene substituents out of the aromatic plane for the different compounds. There thus seems to be a small overall difference in the stability of the three different compounds isolated. The Pd–Pd bond distances were also calculated, 2.629–2.631 Å and are somewhat longer than those measured for **1**, **2** and **3**. The calculated Pd–Pd bond distance along with calculated Raman frequencies are shown in Table S1 in Supplementary information.

The synthesis of **1**, **2** and **3** were performed using an excess of GaCl₃. It was indicated by variations in concentration that an equilibrium of anions GaCl₄[−] and Ga₂Cl₇[−] govern these reactions and that which compound is formed is a matter of packing effects in the solid compound formed. It was earlier suggested by Allegra et al. that an excess of AlCl₃, molar ratio 1:1.6 of PdCl₂ to GaCl₃, would generate [Pd₂(Al₂Cl₇)(C₆H₆)₂], while a 1:1 molar ratio would result in [Pd₂(AlCl₄)(C₆H₆)₂] [**3**]. In this work a 1:4.4 molar ratio of GaCl₃ leads to the formation of compounds with Ga₂Cl₇[−] ligands for **1** and **3** and GaCl₄[−] for **2**.

Raman spectra of **1** in toluene show a band at 152 cm^{−1} that might be assigned to the symmetric Pd–Pd stretch. Quantum chemical calculations on the toluene sandwich compound (**1**) show this palladium–palladium vibration band at 159 cm^{−1}, Table S1 in Supplementary information. The bands at 356 cm^{−1} and 384 cm^{−1} are assigned to chlorogallates(III), GaCl₄[−], Ga₂Cl₇[−] and Ga₃Cl₁₀[−], see Supplementary information Fig. S1. The Raman spectra of the product solution of [Pd₂(GaCl₄)₂(C₉H₁₂)₂].C₉H₁₂ (**2**) shows a band at 360 cm^{−1} that can be assigned to the chlorogallate(III) GaCl₄[−], see Fig. S2 in Supplementary information. Because of the low solubility of the crystals of **2** in mesitylene, it proved difficult to dissolve in detectable amounts. Compound **3** decomposed during Raman detection, wherefore no results from these measurements are presented.

3. Conclusion

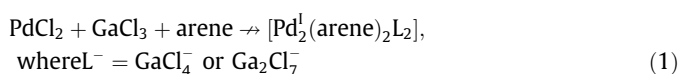
In summary, the syntheses performed resulted in the formation of three new arene-stabilized binuclear palladium(I) compounds. [Pd₂(Ga₂Cl₇)₂(C₇H₈)₂] was synthesized from PdCl₂ in a toluene reaction mixture with GaCl₃ in large excess. It was found that mesitylene coordinates more easily to the dipalladium core than biphenyl when mixed in the reaction with palladium(II) chloride and gallium(III) chloride, a reaction which resulted in the formation of [Pd₂(GaCl₄)₂(C₉H₁₂)₂].C₉H₁₂. Moreover, the chlorobenzene compound, [Pd₂(Ga₂Cl₇)₂(C₆H₅Cl)₂], was isolated. The results from calculations show chlorobenzene to be the strongest interacting arene to the dipalladium unit, of the arenes used within this work.

4. Experimental

4.1. Synthesis

All reactions were performed under an inert atmosphere of deoxygenated and dried nitrogen in a glove box. The starting materials; GaCl₃ (Sigma–Aldrich, anhydrous 99.99%), PdCl₂ (Sigma–Aldrich, 99.999%), naphthalene (Avocado, 98.0%), anthracene (Avocado, 95.0%), biphenyl (Sigma–Aldrich, 99.5%) were used as received. The solvents; toluene (Sigma–Aldrich, 99.9%), mesitylene (Fluka, 98.0%) and chlorobenzene (Sigma–Aldrich, anhydrous, 99.8%) were dried over molecular sieves prior to use.

The following general reaction scheme represents the synthetic approach used for the synthesis of **1**, **2** and **3**:



4.1.1. Synthesis of [Pd₂(Ga₂Cl₇)₂(C₇H₈)₂] (**1**)

Toluene (1 ml) was added to the solid mixture of PdCl₂ (0.025 g, 0.141 mmol) and GaCl₃ (0.11 g, 0.614 mmol). The mixture was gently shaken and unreacted starting material was removed after a few hours. The reaction flask was wrapped in aluminum foil and left at room-temperature. Within days dark red crystals of **1** (yield ~ 69%) were formed.

4.1.2. Synthesis of [Pd₂(GaCl₄)₂(C₉H₁₂)₂].C₉H₁₂ (**2**)

Compound **2** was prepared by the addition of a 1 ml saturated solution of biphenyl in mesitylene to the solid mixture of PdCl₂ (0.025 g, 0.141 mmol) and GaCl₃ (0.11 g, 0.614 mmol). After a few hours unreacted solid material was removed and the deep red reaction mixture was wrapped in aluminum foil. Deeply red, almost black crystals of **2** appeared within a few weeks (yield 21%).

4.1.3. Synthesis of [Pd₂(Ga₂Cl₇)₂(C₆H₅Cl)₂] (**3**)

The synthesis of **3** was performed in a similar manner to that of **1**. Chlorobenzene (1 ml) was added to anhydrous solid PdCl₂ (0.025 g, 0.141 mmol) and GaCl₃ (0.11 g, 0.614 mmol). The reaction vessel was left in an aluminum foil wrapped vessel for a few weeks, after which a few red/brownish crystals had formed. The approximate yield for the reaction was merely 6%.

4.2. Crystal structure determination

The isolated compounds experience sensitivity to moisture and oxygen. Therefore all crystals were selected under a protecting atmosphere, and inserted into glass capillaries prior to crystal structure determination. Diffraction data was collected on a Bruker–Nonius KappaCCD diffractometer. For **2**, a linear decomposition correction was applied [14]. Structural models were obtained using direct methods and H atoms were placed at calculated positions [15]. Table 1 summarises the details of the structure determinations.

4.3. Raman spectroscopy

Raman spectroscopic analyses on the products **1**, **2** and **3** were carried out on a BioRad FTS 6000 spectrometer. The Raman spectrometer was equipped with a Raman accessory, 2W Nd:YAG laser (λ = 1064 nm), a quartz beam splitter and a liquid nitrogen-cooled solid state Ge detector. A resolution of 4.0 cm^{−1} was used in all measurements. The samples were studied in sealed standard NMR-tubes at room-temperature.

4.4. Quantum chemical calculations

The calculations were made using GAUSSIAN 03 (rev. C02) [16]. Calculations were made using the hybrid density functional B3PW91. Basis sets for H, C and Cl were of '6-311G' quality supplemented with diffuse and polarization functions. Quasi-relativistic effective core potentials (28 electrons, MWB) were used for Ga and Pd together with contracted [4s4p]/(2s2p) and [8s7p6d]/(6s5p3d) valence functions, respectively [17–19].

Acknowledgement

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Appendix A. Supplementary data

CCDC 757219 (1), 757218 (2) and 757220 (3) contains the supplementary crystallographic data for this paper. These data

can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2010.03.011.

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