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# Binuclear palladium(I) and platinum(I) dimers stabilized by aromatic ligands: synthesis, structural characterization and reactivity with carbon monoxide

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#### Abstract

Reaction of PdCl<sub>2</sub> with excess of GaCl<sub>3</sub> in aromatic solvents leads to binuclear compounds of the general formula  $[Pd_2X_2(arene)_2]$ , where arene  $= C_6H_6$ ,  $X^- = Ga_2Cl_7^-$  (1); arene  $= C_7H_8$ ,  $X^- = GaCl_4^-$  (2). The solid-state structures of compounds 1 and 2 have been determined by X-ray crystallography. Two molecules of the arene are bound to the dipalladium unit. The compounds 1 and 2 do not react with triphenyl phosphine. Reaction of carbon monoxide with 1 in benzene solution yields  $[Pd_2(GaCl_4)_2(C_6H_6)_2]$  (3), for which the crystal structure has also been determined. The compound  $[Pt_2(GaCl_4)_2(C_{10}H_{10})_2] \cdot 2C_6H_6$  (4), which was obtained by reaction of  $K_2[PtCl_4]$  with GaCl<sub>3</sub> and naphthalene in a benzene solution, has a similar structure in the solid state.

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# 1. Introduction

Palladium complexes play an outstanding role in organic synthesis as catalysts of hydrogenation [1-3], oxidation [4], carbonylation [5–7], hydrosilylation [8], arylation [9] of a wide range of organic compounds. Another unique property of palladium complexes is their ability to display allylic coordination, and some palladium complexes have been used as catalysts in allylic substitution reactions [10,11].

The common oxidation states of palladium in organometallic chemistry are 0 and +2. It was proposed that palladium(I) complexes are intermediates in a number of reactions [12], but until 1971 only two palladium(I) compounds had been obtained [13].

Recently, Olmstead and co-workers have found that  $Pd_6Cl_{12}$  forms stable supramolecular aggregates with

\* Corresponding author. E-mail address: larsa@inorg.kth.se (L. Kloo). arenes [14]. The formal oxidation state of palladium in these aggregates is +2. On the other hand, the binuclear palladium(I) complexes  $[(\eta$ -arene)PdX]<sub>2</sub> (where X<sup>-</sup> = AlCl<sub>4</sub><sup>-</sup>, Al<sub>2</sub>Cl<sub>7</sub><sup>-</sup>; arene = benzene, toluene) were prepared by reaction of PdCl<sub>2</sub> with AlCl<sub>3</sub> and Al in arene solutions [15]. Crystal structures of the benzene complexes were determined [15,16]. It was also observed that these compounds are active catalysts for ethylene dimerization [17].

It was found in our lab [18] that low-valent di- and trimercury cations are stable in benzene solution of GaCl<sub>3</sub>. It was proposed that this may be the consequence of a soft-base stabilization provided by the interaction between the aromatic molecules and sub-valent cations.

In the last years, Heaton and co-workers reported that homoleptic dinuclear carbonyl platinum cluster  $[{Pt(CO)_3}_2]^{2+}$  can be prepared in strongly acidic media, such as concentrated sulfuric acid [19]. The low-valent Group 10 homoleptic carbonyls have turned

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out to be excellent catalysts for the carbonylation of olefins [20-22].

The main objective of this work is the stabilization of subvalent cations of the platinum metals by gallium trichloride dissolved in aromatic solvents, and the subsequent investigation of the reactivity of these compounds with respect to carbon monoxide.

This article reports the syntheses and crystal structures of four new binuclear palladium(I) and platinum(I) complexes containing  $GaCl_4^-$  or  $Ga_2Cl_7^-$  groups stabilized by aromatic molecules, together with their reactivity versus carbon monoxide and triphenyl phosphine.

#### 2. Results and discussion

#### 2.1. Palladium complexes

Table 1

The reaction of PdCl<sub>2</sub> with an excess of GaCl<sub>3</sub> in aromatic solvents yields binuclear compounds of the general formula [Pd<sub>2</sub>X<sub>2</sub>(arene)<sub>2</sub>], where  $X^- = GaCl_4^-$ 

or  $Ga_2Cl_7^-$ ; arene =  $C_6H_6$ ,  $C_7H_8$ . The predominant reducing agent with respect to the added Pd<sup>II</sup> is the arene.

The products crystallize as dark red, almost black solids. The solid-state structures of the compounds  $[Pd_2(Ga_2Cl_7)_2(C_6H_6)_2]$  (1),  $[Pd_2(GaCl_4)_2(C_7H_8)_2]$  (2) and  $[Pd_2(GaCl_4)_2(C_6H_6)_2]$  (3) have been determined by single crystal X-ray diffraction (Table 1).

The compounds 1-3 contain a  $Pd_2^{2+}$  unit as the central structural feature. The short distance between palladium atoms strongly suggests that the  $Pd_2^{2+}$  unit is stabilized by metal-metal bonding. The dipalladium unit is coordinated by two parallel arene molecules in a sandwich configuration (Fig. 1). The coordination sphere is completed by  $Ga_2Cl_7^-$  (1) and  $GaCl_4^-$  (2 and 3) anions, which are bound to the Pd atoms via one chlorine atom. In all compounds described in this work, this complex resides on an inversion center, thus yielding a symmetric arrangement whose halves are crystallographically equivalent. The type of ligand has hardly any influence on the geometry of the complex: the Pd-Pd distance in the toluene complex is 257.2 pm and thus

# Crystallographic data and experimental details of the X-ray studies of $[Pd_2(Ga_2Cl_7)_2(C_6H_6)_2]$ (1), $[Pd_2(GaCl_4)_2(C_7H_8)_2]$ (2), $[Pd_2(GaCl_4)_2(C_6H_6)_2]$ (3) and $[Pt_2(GaCl_4)_2(C_10H_{10})_2] \cdot 2C_6H_6$ (4)

Compound	1	2	3	4	
Sum formula	C <sub>6</sub> H <sub>6</sub> Cl <sub>7</sub> Ga <sub>2</sub> Pd	C <sub>7</sub> H <sub>8</sub> Cl <sub>4</sub> GaPd	C <sub>6</sub> H <sub>6</sub> Cl <sub>4</sub> GaPd	C <sub>16</sub> H <sub>16</sub> Cl <sub>4</sub> GaPt	
Cell constants	a = 925.50(2)  pm	a = 767.19(2)  pm	a = 1397.42(2)  pm	a = 2386.95(2)  pm	
	b = 939.70(3)  pm	b = 1670.76(5)  pm	b = 1107.29(2)  pm	b = 987.67(1)  pm	
	c = 946.50(2)  pm $\alpha = 83.807(1)^{\circ}$	c = 930.83(3)  pm	c = 1444.58(3)	c = 1964.79(2)  pm	
	$\beta = 70.294(1)^{\circ}$ $\gamma = 77.317(1)^{\circ}$	$\beta = 91.017(1)^{\circ}$	$\beta = 101.9312(7)^{\circ}$	$\beta = 96.0285(3)^{\circ}$	
Cell volume (pm <sup>3</sup> )	$755.53(3) \times 10^{6}$	$1192.94(6) \times 10^{6}$	$2186.98(7) \times 10^{6}$	$4606.41(8) \times 10^{6}$	
Z	2	4	8	8	
$\rho$ (calc.) (g cm <sup>-3</sup> )	2.515	2.283	2.406	1.993	
Crystal system, space group	triclinic, P1	monoclinic, $P2_1/c$	monoclinic. $C2/c$	monoclinic, $P2_1/c$	
Temperature (K)	100	297	297	120	
Radiation		Mo K $\alpha$ , $\lambda = 71.073$ pm			
Absorption coefficient $\mu$ (cm <sup>-1</sup> )	59.2	46.1	50.3	77.1	
Absorption correction	numerical				
$\theta$ Range	$4.21^{\circ} < \theta < 27.45^{\circ}$	$4.19^{\circ} < \theta < 27.48^{\circ}$	$4.56^{\circ} < \theta < 27.49^{\circ}$	$4.13^{\circ} < \theta < 27.47^{\circ}$	
Number of measured reflec-	17 021	13614	13 778	41 121	
Number of unique reflec-	3436	2700	2487	10 422	
$R_{\rm c}$ (%)	3 31	6 14	5 70	13.1	
Number of refined para- meters	163	118	109	420	
Ratio reflections/parameters	21	23	23	25	
Residuals	w $R_2 = 4.93\%$ (all reflections)	$wR_2 = 8.21\%$ (all reflections)	$wR_2 = 7.59\%$ (all reflections)	$wR_2 = 23.7\%$ (all reflections)	
	$R_1 = 2.32\%$ (all reflections)	$R_1 = 5.15\%$ (all reflections)	$R_1 = 7.59\%$ (all reflections)	$R_1 = 9.25\%$ (all reflections)	
	$R_1 = 2.09\%$ (3222 observed re-	$R_1 = 3.56\% (2169 \text{ ob-}$	$R_1 = 7.30\%$ (2235 ob-	$R_1 = 8.34\%$ (9056 ob-	
	flections)	served)	served)	served)	
Difference electron density	0.61/-0.62	0.44/-0.50	0.92/-1.00	4.34/-4.89	



Fig. 1. View of 1 (A), 3 (B) and 2 (C).

lies in between those in the two benzene complexes in which it is 256.2 (1) and 258.4 (3). The shortest Pd-C distance in this complex is 221.6 pm and is thus the same as in the benzene complexes (221.0 pm in 1 and 222.1 in 3).

The synthesis and structure of the similar aluminium compounds,  $[Pd_2(AlCl_4)_2(C_6H_6)_2]$  and  $[Pd_2(Al_2Cl_7)_2(C_6H_6)_2]$ , were described by Allegra and co-workers [15]. These compounds were prepared by reaction of PdCl<sub>2</sub> with AlCl<sub>3</sub> and Al in benzene solutions. The first compound was obtained using a 1:1 molar ratio of PdCl<sub>2</sub> and AlCl<sub>3</sub> (Pd-Al), the second one with a molar ratio of 1:1.6. In the case of **2** in this work, the corresponding Pd-Ga ratio was 1:4.5, but the resulting complex,  $[Pd_2(GaCl_4)_2(C_7H_8)_2]$ , contains only GaCl<sub>4</sub><sup>-</sup> groups. It seems that an excess of gallium trichloride does not give compounds with Ga<sub>2</sub>Cl<sub>7</sub><sup>-</sup> groups.

Compounds 1 and 3 are isotypic with the respective aluminum compounds published earlier [15,16]. The Pd-Pd distance in these complexes agrees with the distances published previously. It is interesting to note, that the benzene rings in 1 showed severe rotational disorder at room temperature, which made a data collection at 100 K necessary. The structure of 3, while containing the same arene ligand, does not exhibit this phenomenon. Additionally, the coordination of the Pd-Pd dumbbell is slightly different: in 3 a two-fold axis of the benzene rings are exactly aligned with the Pd-Pd bond, whereas they are slightly tilted in 1 (Fig. 2).



Fig. 2. Orientation of benzene ligands in 3 (A) and 1 (B).

It is important to note that  $PdCl_2$  reacts with  $GaCl_3$  in ethyl benzene or mesitylene, but instead of the formation of dipalladium cluster metallic palladium is observed. It seems likely that the aromatic molecules are important in stabilizing the  $Pd_2^{2+}$  units through softbase interactions [18]. However, just as for the subvalent  $Hg_m^{2+}$  cations, the stabilization only appears for relatively weak soft bases, e.g. benzene and toluene. Stronger bases tend to stabilize the  $Pd_2^{I+} \rightarrow Pd_{(s)}^{0+} + Pd^{II}$ .

On the other hand, complex formation using 1,2,4trichlorobenzene as solvent is not observed. This strongly indicates that the predominant reduction of Pd<sup>II</sup> occurs via oxidation (i.e. chlorination) of the arenes giving products such as chlorobenzenes. The use of an already chlorinated solvent consequently retards any reduction of Pd<sup>II</sup>. We can, therefore, conclude that these compounds are extremely sensitive to small changes in electronic and steric effects caused by the arenes.

The reaction between  $PdCl_2$ ,  $GaCl_3$  and ferrocene in THF solution was also studied. The products of this reaction are metallic palladium and blue crystals (Eq. (1)). The X-ray analysis of the latter has shown that it is  $[(C_5H_5)_2Fe][GaCl_4]$ , whose crystal structure was recently determined by Scholz and co-workers [23].

$$PdCl_{2} + 2GaCl_{3} + 2(C_{5}H_{5})_{2}Fe$$
  

$$\rightarrow Pd^{0}_{(s)} + 2[(C_{5}H_{5})_{2}Fe][GaCl_{4}]$$
(1)

### 2.2. Platinum complexes

 $PtCl_2$  does not react with  $GaCl_3$  in benzene, toluene or mesitylene even under heating. However,  $K_2[PtCl_4]$ readily reacts with  $GaCl_3$  in these aromatic solvents to give a dark brown solution. After several minutes the solution separates into two phases. The upper layer is yellow while the lower one is dark brown. <sup>195</sup>Pt NMR spectra of upper layer (benzene system) show the absence of platinum compounds in any detectable amounts. The existence of liquid phase separation have previously been observed in systems with mononuclear mercury compounds  $Hg(arene)_2(MCl_4)_2$  where M = Al, Ga [24], and in the saturated solution of  $Hg_2Cl_2$  and GaCl<sub>3</sub> in benzene [18].

Reaction of  $K_2[PtCl_4]$  with GaCl<sub>3</sub> and naphthalene in benzene solution yields  $[Pt_2(GaCl_4)_2(C_{10}H_{10})_2] \cdot 2C_6H_6$ (4) and KGaCl<sub>4</sub> [25]. The crystal structure of 4 has been determined (Table 1, Fig. 3).

The structure of 4 deviates significantly from those presented so far. It consists of a central  $Pt_2(GaCl_4)_2$  unit which is coordinated by two molecules of naphthalene. In this structure, two crystallographically independent complexes are present.

Additionally, the structure contains two molecules of benzene per complex, which probably serve as 'separators' between the rather bulky naphthalene ligands (Fig. 4). The Pt-Pt distances are 254.4 and 254.2 pm, respectively. The shortest Pt-C distances in these complexes are 217.2 pm in both complexes.

# 2.3. Reactivity towards PPh<sub>3</sub> and CO

All attempts to substitute any of the ligands in 1 and 2 by triphenyl phosphine (PPh<sub>3</sub>) were unsuccessful. Even in the presence of excess of PPh<sub>3</sub>, PdCl<sub>2</sub> and GaCl<sub>3</sub> in benzene or toluene yield 1 and 2, respectively.

The reaction of 1 and 2 with carbon monoxide was also studied. After bubbling CO gas through the benzene solution of 1 for 2 h red crystals formed after a delay. The solid-state crystal structure of this compound was unexpected. It was found that the compound is the binuclear cluster,  $[Pd_2(GaCl_4)_2(C_6H_6)_2]$  (3), and it does not contain any CO ligands (Table 1, Fig. 1 (B)). After exposure to CO the solution becomes sensitive to air with the formation of metallic palladium. This is in

Fig. 3. View of 4.



Fig. 4. Packing diagram of 4.

contrast to the initial solution, which is stable with respect to disproportionation.

Carbon monoxide was bubbled through the solution of  $PdCl_2$  and  $GaCl_3$  in toluene for 4 h, but only compound **2** was isolated in the solid state.

Bubbling of CO through the arene (benzene, toluene, mesitylene) solutions of  $K_2[PtCl_4]$  and GaCl<sub>3</sub> and subsequent evaporation led to a red or brown oil and KGaCl<sub>4</sub>. A comparison of the <sup>195</sup>Pt NMR spectra of the solutions before and after CO exposure shows that CO reacts with the platinum compounds. There is one peak at -137 ppm in the <sup>195</sup>Pt NMR spectrum of benzene solution of  $K_2[PtCl_4]$  and GaCl<sub>3</sub>. After bubbling of CO through this solution the peak shifts to -293 ppm. No detailed information could give clues to the species present in solution. <sup>13</sup>C NMR spectra were recorded but they proved to be inconclusive; indicating a mixture of products.

#### 3. Conclusions

The complexes described above represent a development of the chemistry of the organometallic soft-base stabilized binuclear palladium(I) and platinum(I) complexes. The compound  $[Pt_2(GaCl_4)_2(C_{10}H_{10})_2] \cdot 2C_6H_6$  is the first example of a platinum complex of this type. It was found that the  $[Pd_2X_2(arene)_2]$  compounds are stable with respect to substitution with PPh<sub>3</sub> or CO.

# 4. Experimental

# 4.1. Starting materials

GaCl<sub>3</sub> (Aldrich Chemical Company, 99.99%,  $H_2O < 100$  ppm) and PdCl<sub>2</sub> (Aldrich Chemical Company, 99.9+%) were used as received. K<sub>2</sub>[PtCl<sub>4</sub>] was obtained according to Ref. [26]. All solvents were dried prior to use. Carbon monoxide 99.9995% quality was used.

### 4.2. NMR spectroscopy

NMR spectra were obtained on a Bruker AMX 500 spectrometer. The spectra were recorded at 300 K in the appropriate arene solution. The <sup>195</sup>Pt NMR spectra were recorded at 107.1 MHz and referenced versus an aqueous solution of  $K_2$ [PtCl<sub>4</sub>]. The <sup>13</sup>C NMR spectra were recorded at 125.7 MHz.

#### 4.3. Structure determinations

Due to the extreme sensitivity towards humidity, crystals of all compounds were sealed inside glass capillaries in a nitrogen atmosphere. Data were collected on a Bruker Nonius KappaCCD diffractometer. Numerical absorption corrections were applied [27]. The positions of the Pd (Pt), Ga and Cl atoms could be determined using Direct Methods (SHELXS-97). The positions of the C atoms were determined in subsequent difference Fourier syntheses. H atoms were placed at calculated positions. All parameters were refined against  $F^2$  using full-matrix least-squares (SHELXL-97). Further details are to be found in Table 1.

# 4.4. Synthesis

All experiments were performed in a glove box under an inert atmosphere of deoxygenated and dried nitrogen ( < 1 ppm H<sub>2</sub>O).

Elemental analyses of 1 and 2 show very small abundance of carbon (1.2% for 1). The results most likely are caused by decomposition through evaporation of the arene, which is readily lost on storage (in contrast to the immediate crystallographic analysis performed).

# 4.4.1. Synthesis of $[Pd_2(Ga_2Cl_7)_2(C_6H_6)_2]$ (1)

Benzene (2 ml) was added to the solid mixture of anhydrous GaCl<sub>3</sub> (0.441 g, 2.505 mmol), and PdCl<sub>2</sub> (0.062 g, 0.352 mmol). The reaction flask was wrapped in aluminium foil and set aside for 24 h. Dark red crystals formed; yield 90.4 mg, 45%.

#### 4.4.2. Synthesis of $[Pd_2(GaCl_4)_2(C_7H_8)_2]$ (2)

Prepared in a manner similar to that for compound 1, but using toluene (2 ml), anhydrous  $GaCl_3$  (0.223 g, 1.267 mmol), and  $PdCl_2$  (0.050 g, 0.282 mmol). Red

crystals were grown within 24 h at room temperature (r.t.). Yield: 110.9 mg, 96%.

# 4.4.3. Synthesis of $[Pd_2(GaCl_4)_2(C_6H_6)_2]$ (3)

The compound 1 (0.050 g, 0.044 mmol) was dissolved in benzene (20 ml) under heating. The carbon monoxide was bubbled through the solution for 2 h at r.t. The color of solution turned from red to brown. The solution was stored without cap and set aside for 1 week. Red crystals formed.

# 4.4.4. Synthesis of $[Pt_2(GaCl_4)_2(C_{10}H_{10})_2] \cdot 2C_6H_6(4)$

Benzene (2 ml) was added to the solid mixture of anhydrous GaCl<sub>3</sub> (0.043 g, 0.240 mmol), K<sub>2</sub>[PtCl<sub>4</sub>] (0.050 g, 0.120 mmol), and naphthalene (0.061 g, 0.480 mmol). The mixture was stirred for 15 min. The darkbrown solution was set aside for 2–3 weeks. Red crystal plates formed and were washed twice by benzene. Yield: < 1%. Since both the yield and reproducibility of this compound were extremely low, elemental analysis could not be carried out.

#### 5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC Nos. 195958, 195959, 195960 and 195961 for compounds 1–4, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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