Platinum–Gallium Compounds

One-Step Synthesis of a Platinum(0)–Gallium(III) Chrysene Complex**

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Recent investigations of gallium(III) halide–aromatic solvent systems with respect to platinum-group metal halides have shown them to be very efficient reducing media.[1,2] Another attractive feature of gallium(III) halides is their aptitude to abstract halide ions from other metal halides, which facilitates metal–metal bond formation. Taking advantage of these properties, we have prepared and crystallographically characterized a series of dipalladium(I) and diplatinum(I) complexes $[M_2(\eta^6\text{-arene})_2(GaX_4)_2]$ (arene = benzene, its alkylated derivatives, or naphthalene; $X = Cl^-$ or Br^-).[1,2]

The reactions of $GaCl_3$ with $PtCl_2$ and polycyclic aromatic hydrocarbons (PAH), such as anthracene, tetracene, or pentacene, turned out to be complicated, probably because of the interaction between the strong Lewis acid $GaCl_3$ and the PAHs; only dark oily products have so far been obtained from these systems. In spite of this, the reaction of platinum(II) and gallium(III) chlorides in the presence of chrysene in 1,2,4-trichlorobenzene leads to the formation of a dark violet solution, from which red crystals can be isolated within a few weeks. An X-ray single-crystal structure determination revealed that the crystalline product is the Pt–Ga compound **1**.[3] The formation of this complex can be described schematically with Equation (1).

$$2\,PtCl_2 + 12\,GaCl_3 + 4\,\text{chrysene} \xrightarrow{+4e^-} [Pt_2Ga_2Cl_2(\mu\text{-}Cl)_2(\text{chrysene})_4](Ga_3Cl_{10})_2 + 4GaCl_4^- \quad (1)$$

The main structural feature of compound **1** is a centrosymmetric $(PtGaCl_2)_2$ unit, where each Pt center is coordinated by two chrysene molecules (Figure 1). This structural unit can be derived from the structure of Ga_2Cl_6 by replacing one terminal Cl substituent on each Ga atom by the Pt-containing group. The geometry is thus that of two edge-sharing tetrahedra. The Ga–Cl bond lengths are 213.6 pm for the terminal Cl substituents and 230.0 and 240.5 pm for the two bridging Cl substituents. They are thus of the same order of magnitude as in Ga_2Cl_6, and are much shorter than would be expected for gallium(I), thus suggesting a +3 oxidation state for Ga. The Ga–Pt distance (233.6 pm) is similar to Ga–Pt bond lengths in related compounds.[4–8] The overall charge

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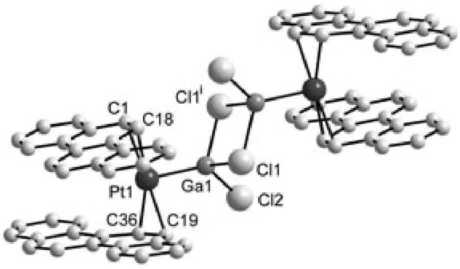

Figure 1. Structure of the cation $[Pt_2Ga_2Cl_2(\mu\text{-}Cl)_2(chrysene)_4]^{2+}$. Selected bond lengths [pm]: Pt1–Ga1 233.6(2), Pt1–C1 222(2), Pt1–C18 221(2), Pt1–C19 223(2), Pt1–C36 219.4(14), Ga1–Cl2 213.6(4), Ga1–Cl1 240.5(4), Ga1–Cl1^{i} 230.0(4). Symmetry operation: I: $2-x$, $1-y$, $1-z$.

of +2 of this unit is unequivocally determined by the fact that there are two $[Ga_3Cl_{10}]^-$ anions present in the structure. The formal oxidation state of Pt in this structure is thus zero.

Each platinum atom is connected to two planar chrysene molecules. The Pt–C bond lengths in **1** (219.4–223.2 pm) are comparable to those in a diplatinum(I) naphthalene complex (219.9–225.8 pm),[1] but they are shorter than those in some other platinum(II) complexes containing arene ligands (for example, 233–234 pm in the 9,10-dihydro-9,10-ethenoanthracene complex).[9]

It should be emphasized that the isolation of compound **1** demonstrates the diversity of reaction routes based on platinum or palladium halides in combination with aluminum or gallium halides in arene-based media. Indeed, only compounds with a dimetallic M_2^{2+} (M = Pd, Pt) core have so far been isolated from these systems.[1,2,10] In the only platinum complex isolated from related systems the platinum center is coordinated by naphthalene. In spite of that, the chrysene complex **1** has a unique structure. The shortest distance between the benzene rings of adjacent chrysene ligands is 358.8 pm, which may indicate a π–π interaction between the chrysene ligands, possibly providing additional stability to **1**.

The crystal packing of **1** is shown in Figure 2. Organic layers of coordinated chrysene molecules are separated by inorganic layers composed of gallium and chlorine atoms, which belong to the central part of the cation and the $[Ga_3Cl_{10}]^-$ anions. The shortest distance between chrysene ligands of adjacent molecules is 360 pm.

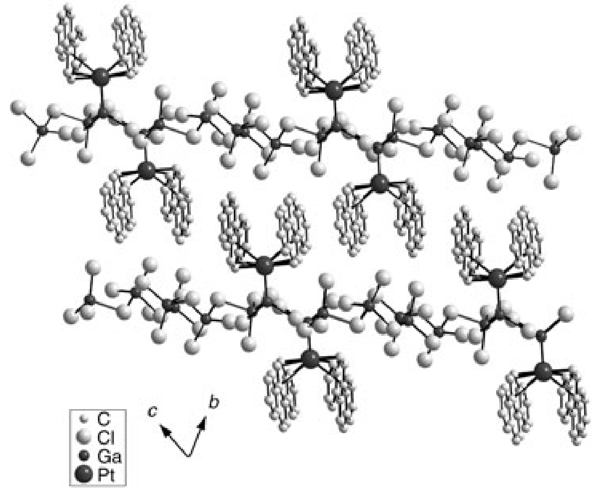

Figure 2. View of the crystal packing of **1**.

Compound **1** is the first platinum–chrysene compound whose structure has been confirmed by X-ray diffraction.[3] It should be noted that among platinum-group metals only ruthenium–chrysene compounds have been described previously.[11–13] In contrast to these compounds, which have an η^6-type coordination, the chrysene in **1** is coordinated in an η^2-mode. Moreover, in the case of the ruthenium complexes exterior ring(s) of chrysene are bound to the metal atom(s), while in **1** the inner ring is coordinated to platinum.

Another remarkable feature of **1** is the presence of a direct platinum–gallium bond whose length is 233.6(2) pm. The platinum–gallium distance is comparable to those in platinum(0)–gallium(I) complexes described in the literature.[4–8] This is remarkable, since electron bookkeeping based on the structure of **1** (vide supra) suggests a platinum(0)–gallium(III) interaction, which means two electrons less on the metal centers available for covalent interaction. In spite of this essentially the same Pt–Ga separation is observed.

To get some further insight into the oxidation states of the atoms involved, X-ray photoelectron spectroscopy (XPS) data were collected for **1**. The binding energies (BE) for **1** are presented in Table 1. Charge-transfer to the ligands has an important impact, and the binding energy of the Pt 4f(7/2) electrons in **1** more resembles that of a formal oxidation state of +2 [for example, the BEs of Pt 4f(7/2) in $K_2[Pt^{II}Cl_4]$ and $[Pt^0(PPh_3)_4]$ are 73.4 and 71.6 eV, respectively].[14] Thus, the XPS results do not provide the clear-cut information about formal oxidation states hoped for.

Table 1: The XPS data of **1**.

Line	C 1s	Pt 4f(7/2)	Cl 2p(3/2)	Ga 2p(3/2)	Ga 3d
BE [eV]	284.7 285.6	72.9	199.7 200.4	1120.0	22.2

To shed some further light on the formal oxidation states of the metal centers in **1**, quantum chemical calculations were performed for a series of model compounds. $[(C_6H_6)_2Pt-Ga_2Cl_5]^+$ was chosen as a simplified model of **1** as it essentially represents the cation in **1** terminated by an extra chloride ion, instead of a second $(C_6H_6)_2Pt$ entity, and chrysene molecules replaced by more simple η^2-coordinated benzene molecules. The Natural Bond Order (NBO) charge of platinum in the geometrically optimized model was calculated to be +0.27 at the B3LYP level. This is larger than that found in the isolated, neutral $(C_6H_6)_2Pt$ entity (+0.14) but significantly smaller than that in a formal platinum(II) compound such as $[PtCl_4]^{2-}$ (+0.48). The corresponding $[(C_6H_6)_2Pt]^{2+}$ unit, which thus contains two electrons less, displays a Pt charge of +0.73. The corresponding NBO charge of the gallium atom directly connected to platinum is +1.04 and of the one furthest away

+1.17. Both values are close to those found in compounds with formal gallium(III) (viz. +1.12 in $[GaCl_4]^-$). These results confirm the assignment of both gallium atoms in **1** as gallium(III). The optimized Pt–Ga distance obtained is 241.8 pm, which is slightly longer than the experimentally obtained. The closest Pt–C distances range from 228 to 232 pm.

Susceptibility measurements of **1** show the compound to be diamagnetic, thus ruling out a qualitative electron transfer from platinum to the chrysene ligands to give a formal platinum(II) center and anionic arene ligands. Logically, therefore, the platinum centers must be formally assigned as platinum(0).

The bonding situation in known compounds with a platinum(0)–gallium(I) interaction closely resembles that in $[Ni(CO)_4]$. The platinum(0) center is surrounded by neutral phosphine and/or cyclopentadienylgallium(I) entities in a quasi-tetrahedral fashion,[4–8] and the bonding can be described in terms of a perturbed T_d symmetry involving both σ- and π-bonding.[15–17] In a series of such compounds, quantum chemical calculations have been used to assign the NBO charge on Pt to about −0.6. Gallium typically displays an NBO charge from +0.5 to +0.7, substantially lower than in the model of **1**.

The bonding situation in **1** is clearly different, and the platinum(0)–gallium(III) interaction is best described as dative, similar to that between Cl^- and gallium(III), and the similar Pt–Ga separation observed must be simply a coincidence.

The presence of hydride ligands bound to platinum and/or gallium atoms can also formally be proposed. However, neither chemical, structural, or spectroscopic, nor theoretical results give any support to the presence of hydride ligands in **1**.[18] As a bonus, it should be noted that the title compound contains the first example of a structurally characterized decachlorotrigallate anion, whose existence has only been shown by spectroscopic techniques until now.[19]

The nature of the reducing agent in this system is not clear, although two possibilities can be proposed. First of all, chrysene can be oxidized by gallium(III) chloride (presumable products are chlorinated chrysenes and/or products of chrysene polymerization) and thereby chrysene may act as the reductant. However, the Pt:Ga:chrysene molar ratio is 1:2:1, which means that no excess of chrysene was used. The solvent, 1,2,4-trichlorobenzene, can also be chlorinated, but, as noted earlier,[1] chlorinated benzene–$GaCl_3$ systems are inert with respect to the reduction of platinum-group metal chlorides.

The reactions between $PtBr_2$ and $GaBr_3$, $PtCl_2$ and $AlCl_3$, and $PtBr_2$ and $AlBr_3$ in the presence of chrysene in 1,2-dichlorobenzene were also studied. In spite of the formation of deeply colored solutions, no crystals could be isolated. Attempts to obtain the analogous palladium compounds were unsuccessful, both in the gallium and aluminum halide systems.

In conclusion, this work describes the one-step synthesis of a platinum(0)–gallium(III) compound from readily available $PtCl_2$. The complex, with two Pt–Ga bonds, contains platinum chrysene units and Ga_3Cl_{10} groups, the latter of which have been crystallographically confirmed for the first time.

Experimental Section

General: $GaCl_3$ (Aldrich, 99.99%), $GaBr_3$ (Alfa Aesar, 99.999%), $PtCl_2$ (Aldrich, 99.9+%), $PtBr_2$ (Alfa Aesar, 99.9%) $AlCl_3$ (Alfa Aesar, 99.985%), $AlBr_3$ (Alfa Aesar, 99.998%), $PdCl_2$ (Alfa Aesar, 99.999%), $PdBr_2$ (Aldrich, 99%), and chrysene (Aldrich, 98%) were used as received. 1,2,4-Trichlorobenzene (Aldrich, 99%) and 1,2-dichlorobenzene (Fluka Chemika, ≥99%) were dried over molecular sieves. All experiments were performed in a glove box under an inert atmosphere of deoxygenated and dried nitrogen (< 1 ppm H_2O and O_2).

XPS spectra were recorded with a Kratos Axis Ultra electron spectrometer fitted with a monochromatic $Al_{K\alpha}$ source operating at 180 W. The BE scale was referenced to the C1s line of *p*-quaterphenyl (284.7 eV). The uncertainty in the BE values is ±0.1 eV, and ±10% in atomic ratios. Processing of the spectra was accomplished with Kratos software. Special care (glove bag) was taken during transfer of the air-sensitive samples for analysis by ensuring a dry nitrogen atmosphere. The samples were pre-cooled and XPS analyses were carried out at liquid-nitrogen temperature.

NMR spectra were obtained on a Bruker AMX 500 MHz spectrometer. The spectra were recorded at 300 K in 1,2,4-trichlorobenzene solution under an inert atmosphere.

1: 1,2,4-Trichlorobenzene was added to a solid mixture of $PtCl_2$ (30 mg, 0.113 mmol), $GaCl_3$ (40 mg, 0.226 mmol), and chrysene (26 mg, 0.113 mmol). The mixture was stirred for 15 min. A red crystalline product was obtained after 4–5 weeks. Crystals of **1** are unstable: 2–3 weeks after their formation most of the crystals had decomposed, even in the dark and when in contact with the mother liquor.

Quantum chemical calculations were performed at the Hartree–Fock and hybrid density functional level (B3LYP) using the Gaussian98 program package.[20] Basis sets for H, C, and Cl were of 6-31G quality supplemented with additional diffuse and polarization functions. Valence basis sets for Ga and Pt were fully noncontracted of (7s6p6d) and (8s7p6d1f) quality, respectively. Quasi-relativistic effective core potentials replaced 18 and 60 electrons for Ga and Pt, respectively.[21] Natural Bond Order populations were evaluated using the integrated Gaussian NBO version 3.1.

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[3] Crystal structure determination of **1**: triclinic, space group $P\bar{1}$, $a = 1237.9(2)$, $b = 1216.62(11)$, $c = 1618.5(2)$ pm, $\alpha = 62.750(4)$, $\beta = 83.700(6)$, $\gamma = 89.62(2)°$, $V = 2151.3(6) \times 10^6$ pm^3, $\rho_{calcd} = 2.09$ g cm^{-3}, $2\theta_{max} = 35.5°$, $Ag_{K\alpha}$ radiation, $\lambda = 56.090$ pm, $T = 299$ K. The diffraction data were collected on a Bruker-Nonius KappaCCD diffractometer. All non-H atoms were refined with anisotropic temperature parameters. Numerical absorption corrections were applied. The structure was solved with SHELXS-97 and refined on F^2 with SHELXL-97. Final R values: $R_1 = 0.0687$, $wR_2 = 0.153$; GOF = 1.180 for 5381 unique reflections and 478 parameters. Max./min. residual electron density 1.47/−1.48. CCDC-252705 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.

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[18] From a chemistry point of view, the co-existence of gallium(III) and a hydride in the cation of **1** is highly unlikely. Both the Lewis acidity and reduction propensity of gallium(III) would most likely lead to direct reaction. The X-ray structure analysis supplied no indications of the presence of hydride ligands in **1**. A solution of **1** in 1,2,4-trichlorobenzene shows no hydrides in the negative chemical-shift region in the ^{1}H NMR spectrum. In addition, the introduction of hydrides into the theoretical model to give $[(C_6H_6)_2Pt(H_2)Ga_2Cl_5]^+$, with a formal platinum(II)and hydrides initially placed as bridging atoms along the Pt−Ga bond (which is the structurally most elusive position), gave rise to an extraction of one hydride by the $[Ga_2Cl_5]^+$ entity to give a neutral Ga_2Cl_5H molecule that is well separated from platinum, thus highlighting the expected Lewis acidity of gallium(III).

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