[Pt$_2$(GaCp*)$_2$(μ$_2$-GaCp*)$_3$]: structure and bonding situation of the first homoleptic platinum complex with terminal and bridging Cp*Ga ligands

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A new homoleptic diplatinum complex [Pt$_2$(GaCp*)$_2$(μ$_2$-GaCp*)$_3$] (Cp* = pentamethylcyclopentadienyl) exhibiting a central unit of two platinum atoms coordinated by five Cp*Ga groups acting as terminal as well as bridging ligands, was synthesized by the reaction of tris(ethylene)platinum(0) with an excess of (Cp*Ga)$_6$ and was characterized by structural and quantum chemical methods.

In the past decade, the synthesis and structural chemistry of low-valent group 13 compounds and particularly their potential as ligands for the synthesis of novel group 13 element transition metal complexes and clusters, as well as the use of those latter compounds as precursors to new materials, have attracted widespread interest.[1] However, recent studies concerning this subject have almost exclusively focused on the coordination of ER species (E = Al, Ga, In) to metal carbonyl fragments.[2] When in 1998 Uhl *et al*. reported the synthesis of [Ni{InC-(SiMe$_3$)$_3$}$_4$], the first analogue of a mononuclear, binary carbonyl complex with exclusively terminal ER groups,[3] it was recognised as the starting point of a very fruitful new development in coordination chemistry. However, since then only three (!) other related *homoleptic* complexes have been reported by Uhl *et al*., [M{EC(SiMe$_3$)$_3$}$_4$] (M = Ni, E = Ga; M = Pt; E = In),[4] and Jutzi *et al*., [Ni(GaCp*)$_4$].[5] We were attracted by the unique properties of ECp* compounds[1e] and have shown recently, that ECp* ligands stabilise reactive 14e L$_2$Pt centres produced by reductive alkane elimination to yield complexes of the type [(dcpe)Pt(ECp*)$_2$] [E = Al, Ga; dcpe = 1,2-bis(dicyclohexylphosphino)ethane].[6] Herein we describe the first example of the so far unknown series M$_a$(ER)$_b$ which extends the analogy between CO and ER ligands: [Pt$_2$(GaCp*)$_2$(μ$_2$-GaCp*)$_3$] **1**. The ER ligands are often compared to carbon monoxide or phosphine ligands, but regarding **1**, no truly analogous *neutral* homoleptic diplatinum carbonyl or phosphine complexes are known. Compounds of the type [Pt$_2$(PPh$_3$)$_2$(μ$_2$-dmpm)$_3$] [dmpm = bis(dimethylphosphino)-methane] bridged by a phosphine chelate ligand, may be regarded as closest congeners, at least from a topological point of view.[7]
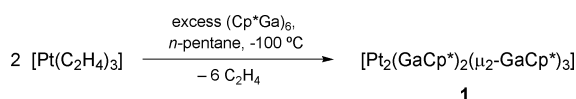
The synthesis of **1** is outlined in Scheme 1. When tris(ethylene)platinum(0)[8] in pentane solution was treated with a 4.8-fold amount of Cp*Ga[2b] per equivalent of the platinum compound at −100 °C, a reddish brown solution was formed immediately. After warming up to room temperature and evaporation of all volatile components *in vacuo*, a dark red crude crystalline material was collected (quantitative yield based on NMR spectroscopy). After recrystallization from benzene large ruby-red octahedral shaped crystals were gathered in a yield of 70%. Compound **1** was characterised by ¹H NMR, ¹³C NMR and IR spectroscopy, elemental analysis† and single crystal X-ray

diffraction.‡ The ¹H NMR spectrum in benzene-d$_6$ exhibits two resonances at δ 2.15 and 2.03, respectively, with a ratio of two to three, that can be assigned to the methyl groups of the terminal and bridging Cp*Ga units, thus showing that there is no exchange between this positions on the NMR time scale. The ¹³C NMR data show similar features.† Neither ⁷¹Ga nor ¹⁹⁵Pt NMR resonances have, as yet, been identified, most likely because of extensive quadrupolar line broadening effects caused by the Ga nuclei. A single crystal X-ray diffraction study was performed, the results of which confirm the structural predictions based on analytical and spectroscopic data.

Compound **1** crystallizes in the monoclinic space group $P2_1/c$ (Z = 4). The molecular structure of **1** (Fig. 1) consists of a central unit of two platinum atoms Pt(1) and Pt(2) with a quite short platinum–platinum bond length of 2.582(1) Å, compared to the common range for Pt⁰–Pt⁰ bonds of *ca*. 2.65–2.80 Å, *e.g.* in {[Pt(dtbpe)]$_2$} [2.765(1) Å, dtbpe = 1,2-bis(di-*tert*-butyl-phosphino)ethane] or neutral platinum clusters like [Pt$_3$(PCy$_3$)$_3$(CO)$_3$] [2.656(2) Å, Cy = cyclohexyl].[9] For the shortest Pt–Pt distances in platinum metal values in the range 2.742–2.848 Å have been reported.[10] The Pt$_2$ unit of **1** is surrounded by two terminal Cp*Ga ligands [Ga(1) and Ga(2)], and three bridging Cp*Ga ligands [Ga(3)–Ga(5)]. All Cp*
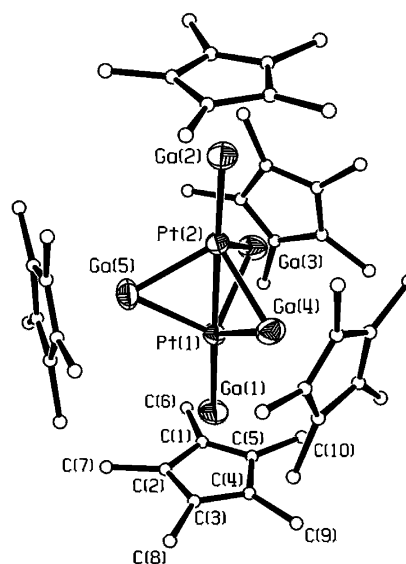
Fig. 1 Molecular structure of **1**. Selected bond lengths (Å) and angles (°): Pt(1)–Pt(2) 2.582(1), Pt(1)–Ga(1) 2.326(2), Pt(2)–Ga(2) 2.331(1), Pt(1)–Ga(3) 2.450(1), Pt(1)–Ga(4) 2.465(1), Pt(1)–Ga(5) 2.464(1), Pt(2)–Ga(3) 2.472(1), Pt(2)–Ga(4) 2.463(1), Pt(2)–Ga(5) 2.470(1), Ga(1)–Ga(3) 4.160, Ga(3)–Ga(4) 3.593, Ga(1)–C(1–5) 2.294(7)–2.310(7), Ga(4)–C(31–35) 2.313(7)–2.338(7), Cp*$_{centroid}$–Ga(1) 1.968, Cp*$_{centroid}$–Ga(2) 1.969, Cp*$_{centroid}$–Ga(3) 2.013, Cp*$_{centroid}$–Ga(4) 2.001, Cp*$_{centroid}$–Ga(5) 2.021; Ga(1)–Pt(1)–Pt(2) 178.93(2), Ga(2)–Pt(2)–Pt(1) 178.60(2), Pt(1)–Ga(3)–Pt(2) 63.28(2), Pt(1)–Pt(2)–Ga(3) 57.95(2), Pt(2)–Pt(1)–Ga(3) 58.77(2), Ga(1)–Pt(1)–Ga(3) 121.12(3), Ga(3)–Pt(1)–Ga(4) 93.95(3).

Scheme 1

2 [Pt(C$_2$H$_4$)$_3$] $\xrightarrow[\text{− 6 C}_2\text{H}_4]{\substack{\text{excess (Cp*Ga)}_6, \\ \text{n-pentane, -100 °C}}}$ [Pt$_2$(GaCp*)$_2$(μ$_2$-GaCp*)$_3$]

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moieties are bound to the Ga centres in a nearly ideal symmetric η^5 mode with average values for the Cp*$_{centroid}$–Ga distances of 1.969 Å for the terminal Cp*Ga units and 2.013 Å for the bridging ligands, both values being close to the free ligand of 2.081 Å (gas phase, monomer).[1a] Such distances are an indirect measure for the polarity of the Ga–Pt bond, which appears to be low compared to [(CO)$_n$M–GaCp*] complexes, especially for the bridging Cp*Ga ligands.[2a,6] The coordination pattern of the five Cp*Ga units at the central Pt(1)–Pt(2) core results in a diplatinum centred trigonal-bipyramidal structure (idealized D_{3h} symmetry) with an essentially linear Cp*Ga–Pt–Pt–GaCp* arrangement. The structure can also be described in terms of two face-sharing PtGa$_4$ tetrahedra. At least formally we can imagine an (unstable ?) intermediate species [Pt(GaCp*)$_4$] similar to the corresponding stable [Ni(GaCp*)$_4$] adding one reactive [PtGaCp*] fragment to yield **1**. This tendency of the heavier d-metals to form oligonuclear complexes rather than mononuclear species is well known from classical metal carbonyl chemistry. The terminal Pt–Ga distances of 2.326(2) and 2.331(1) Å are the shortest Pt–Ga bonds known and compare with average terminal Pt–Ga bond lengths of 2.369 Å in [(dcpe)Pt-(GaCp*)$_2$].[6] The bridging Cp*Ga units exhibit an average Pt–Ga bond length of 2.464 Å, with values in the range 2.450(1)–2.472(2) Å. The shortest Pt–Ga distances of the intermetallic alloy systems PtGa and Pt$_2$Ga$_3$ amount to 2.60 and 2.45 Å, respectively.[11] A final comparison can be drawn to the complex [(dcpe)Pt(GaR$_2$)(R)] (R = CH$_2$Bu^t), which exhibits the only other known Pt–Ga bond in molecular compounds [2.438(1) Å].[12] The Ga–Ga distances of compound **1** are in the range 3.593–3.691 Å for the bridging Cp*Ga units and 4.160–4.197 Å for the distances between terminal and bridging Cp*Ga ligands, which both are regarded as non-bonding. These values can be compared to the situation in (Cp*Ga)$_6$ with Ga–Ga distances in the range 4.073–4.173 Å as a consequence of very weak bonding interactions in the solid state.[1a]

We examined the bonding situation in **1** with the aid of quantum chemical methods. To this end we first optimized the geometry of the model compound [Pt$_2$(GaCp)$_2$(μ_2-GaCp)$_3$] **1M** where the Cp* ligands of **1** are replaced by Cp at the gradient-corrected DFT (BP86) level of theory.[13] The calculated bond lengths of **1M** are Pt–Ga$_{terminal}$ 2.308 Å, Pt–Ga$_{bridge}$ 2.368 Å and Pt–Pt 2.829 Å. The theoretical value for the Pt–Ga$_{bridge}$ bond is significantly shorter than the experimental value of **1**, and the calculated Pt–Pt distance is much too long. Therefore we optimized the geometry of the real compound **1** at the same level of theory.[13] The calculation took three weeks cpu-time on a fast workstation and gave interatomic Pt–Pt distances which are in better agreement with experiment. The theoretical (average) values for **1** are Pt–Ga$_{terminal}$ 2.393 Å, Pt–Ga$_{bridge}$ 2.558 Å and Pt–Pt 2.676 Å. Calculated bond lengths of donor–acceptor bonds are usually longer than experimental values obtained from X-ray structure analysis, since solid state effects tend to shorten the interatomic distances.[15] Analysis of the Pt–Pt bond with the help of the NBO[16a] and AIM[16b] methods suggests weak attractive interactions only. A detailed bonding analysis will be reported in a full paper.

Though to our knowledge no intermetallic Pt$_2$Ga$_5$ bulk phase has been reported, the synthesis of heterobimetallic compounds such as **1** might provide prospects for molecular pathways to new intermetallic materials and nanophases as a valid target for further studies, following our work on single molecule sources for OMCVD of alloy thin film materials, which we have been performing for a number of years.[1d]

Notes and references

† *Spectroscopic data* for **1**: δ_H(298 K, 250.1 MHz, C$_6$D$_6$) 2.03 [s, 45H, CH$_3$, (μ_2-Cp*Ga)], 2.15 [s, 30H, CH$_3$, (Cp*Ga, terminal)]; δ_C(298 K, 62.9 MHz, C$_6$D$_6$) 10.58 [CH$_3$, (Cp*Ga, terminal)], 12.35 [CH$_3$, (μ_2-Cp*Ga)],

112.56 [ring atoms, (μ_2-Cp*Ga)], 114.35 [ring atoms, (Cp*Ga, terminal)]. IR (KBr, cm^{-1}) 2957m (sh), 2903s, 2849s, 1480m, 1445m (sh), 1418s, 1375s, 1260w, 1063w, 1020w, 797m, 585m, 473w. Elemental Anal. Calc. for C$_{50}$H$_{75}$Ga$_5$Pt$_2$, C, 42.44; H, 5.34. Found: C, 42.78; H, 5.49%. Slow decomp. beginning at 50 °C.

‡ *Crystallographic data* for **1** (ruby-red octahedra, 0.35 × 0.30 × 0.28 mm): C$_{50}$H$_{75}$Ga$_5$Pt$_2$, M = 1414.9, monoclinic, a = 14.9284(12), b = 20.1058(15), c = 18.9613(15) Å, β = 100.730(1)°, U = 5591.7(8) Å^3, T = 203 K, space group $P2_1/c$, Z = 4, μ(Mo-Kα, λ = 0.71073 Å) = 7.384 mm^{-1}, 34742 reflections measured, 12822 unique (R_{int} = 0.0639) which were used in all calculations. The final $wR(F^2)$ was 0.0758 (all data); measurements: Bruker-axs-SMART-diffractometer; programs used: SHELXS-86 and SHELXL-97. CCDC 182/1841. See http://www.rsc.org/suppdata/cc/b0/b008133g/ for crystallographic files in .cif format.

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13 The calculations were carried out at BP86[14a] with the RI (resolution of identity) approximation[14b] using the following basis sets for the atoms. A quasi-relativistic small-core ECP with a valence double-zeta basis augmented by one set of f-functions was used for Pt.[14c] All-electron DZ+P basis sets have been employed for Ga and the carbon atoms of the Cp ring.[14d] Minimal basis sets have been used for the methyl groups of Cp*.[14e] Auxiliary basis sets for all atoms have been taken from the literature.[14b] The calculations have been carried out with the program package Turbomole.[14f,g] The geometry optimizations were carried out with C_s symmetry constraints.

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