VIP Low-Valent Gallium

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A Simple Route to Univalent Gallium Salts of Weakly Coordinating Anions**

John M. Slattery, Alexander Higelin, Thomas Bayer, and Ingo Krossing**

Low-valent p-block chemistry has been a subject of great interest in recent years. Many of the low-valent compounds synthesized have challenged conventional bonding theories and caused significant discussion in the literature. True gallium(I) halides (GaX, X = halide) are thermodynamically unstable with respect to disproportionation, resulting in formation of gallium metal and GaX_3. However, metastable, donor-stabilized GaX solutions may be prepared in a demanding procedure by quenching GaX vapor formed at about 1000 °C in a suitable donor solvent or solvent mixture; such compounds were extensively studied by Schnöckel et al.[1] This elegant chemistry has led to significant developments in low-valent and metalloid gallium cluster chemistry.[1–3] More accessible low-valent gallium halides are the mixed-valent species Ga_2X_4, which exists as $Ga^+[GaX_4]^-$,[4] and "GaI", a compound of uncertain composition probably dominated by $Ga^+_2[Ga_2I_6]^{2-}$.[5] These materials behave as sources of gallium(I), for example, in the salts $[Ga(arene)_2][GaX_4]$ (X = Cl, Br) that were extensively studied by Schmidbaur,[6] but they also frequently undergo comproportionation or other redox reactions with the isolation of compounds containing gallium in higher oxidation states (see Ref. [5] and references therein). The presence of relatively strongly coordinating and chemically reactive halogallate counterions in these materials limits their usefulness in preparative chemistry, as they prevent investigation of the coordination chemistry of gallium(I) with very weak ligands and also appear to promote comproportionation reactions upon addition of conventional σ-donor ligands. Mixtures of subvalent gallium triflates, which can also be used as sources of low-valent gallium, are accessible by the protonation of pentamethylcyclopentadienylgallium(I) (Cp*Ga) with triflic acid.[7] However, as several species are present in these mixtures, careful control of reaction products may be difficult.

Recently, Fischer and co-workers showed that the gallium(I) salt $[Ga_2Cp^*]^+[B(Ar^F)_4]^-$ can be prepared and used as a well-defined starting material for gallium(I) chemistry.[8,9] With this salt, gallium(I) was transferred to platinum and ruthenium, forming for example $[Pt(Ga)(GaCp^*)_4]^+[B(Ar^F)_4]^-$.[10,11] However, the synthesis of $[Ga_2Cp^*]^+[B(Ar^F)_4]^-$ is not trivial, in that it involves multiple steps, and the atom efficiency of this gallium(I) source is less than perfect, as a molecule of Cp*Ga is lost for every gallium(I) delivered to a substrate. Moreover, the liberated GaCp* molecule may interfere with the desired gallium(I) chemistry.

Herein we describe a simple and high-yielding route to gallium(I) salts of weakly coordinating, perfluorinated alkoxyaluminate anions (WCAs) that promise to be excellent well-defined sources of gallium(I) free from reactive and coordinating counterions. We demonstrate the use of these salts as sources of gallium(I) by the synthesis of the first homoleptic gallium(I)–phosphine complex, a material not accessible from mixed-valent halides because of comproportionation reactions.[12a]

As salt metathesis reactions to prepare $Ga^+[WCA]^-$ salts were unsuccessful (for example, the reaction of Ag[WCA] with "GaI" led to mixtures of products), an alternative strategy, based on the oxidation of elemental gallium by silver(I), was applied [Eq. (1)].

$$[Ag]^+[Al(OC(CF_3)_3)_4]^- + Ga \xrightarrow[\text{sonication (ca. 16 h)}]{\text{arene (solvent)}} [Ga(arene)_2]^+[Al(OC(CF_3)_3)_4]^- + Ag \quad (1)$$

A solution of $Ag^+[Al(OC(CF_3)_3)_4]^-$ in a mixture of *o*-$C_6H_4F_2$ and toluene was treated with an excess of gallium metal under ultrasonic activation. Separation of the solution from the resulting silver precipitate and removal of the solvent led to a slightly off-white solid that was poorly soluble in toluene, sparingly soluble in C_6H_5F, and very soluble in *o*-$C_6H_4F_2$. The ^1H NMR spectrum of this solid in *o*-$C_6H_4F_2$ has signals attributable to toluene, and the ^{19}F NMR spectrum showed the characteristic signal for the $[Al(OC(CF_3)_3)_4]^-$ anion ($\delta = -75.6$ ppm), and no evidence of anion decomposition products. Storage of a highly concentrated, oily solution of this material in a mixture of *o*-$C_6H_4F_2$ and toluene overnight under the vapor pressure of the solvent resulted in colorless blocks that were shown by single-crystal X-ray diffraction studies to be the essentially ion-separated gallium–arene complex $[Ga(C_6H_5Me)_2]^+[Al(OC(CF_3)_3)_4]^-$ (**1**; Figure 1). The $[Ga(C_6H_5Me)_2]^+$ cation of **1** adopts a bent sandwich structure typical of $[Ga(arene)_2][GaX_4]$ (X = Cl, Br) salts extensively studied by Schmidbaur.[6]

[*] Dr. J. M. Slattery
Department of Chemistry, The University of York
Heslington, York, YO10 5DD (UK)
E-mail: js633@york.ac.uk
A. Higelin, T. Bayer, Prof. Dr. I. Krossing
Institut für Anorganische und Analytische Chemie
Albert-Ludwigs-Universität Freiburg
and
Freiburger Materialforschungszentrum FMF
Albertstrasse 21, 79104 Freiburg (Germany)
Fax: (+49) 761-203-6001
E-mail: krossing@uni-freiburg.de

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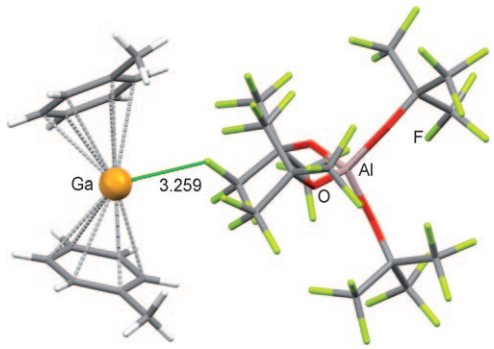

Figure 1. Molecular structure of $[Ga(C_6H_5Me)_2]^+[Al(OC(CF_3)_3)_4]^-$ (**1**). The asymmetric unit contains two independent cations and anions; only one of each is shown for clarity. Ga–F contacts are shown that are shorter than the sum of the van der Waals radii (3.34 Å).

Mass-balance calculations suggest that crystals of **1** lose one coordinated toluene molecule after storage in vacuo (ca. 10^{-3} mbar, 16 h). The analogous reaction of gallium with $Ag[Al(OC(CF_3)_3)_4]$ in *o*-$C_6H_4F_2$ leads to a gray precipitate (silver metal) and, after decantation and removal of the solvent, an off-white solid. The ^{19}F NMR spectrum of this product shows a circa 2:1 mixture of the $[Al(OC(CF_3)_3)_4]^-$ ion ($\delta = -75.5$ ppm) and the fluoride-bridged $[((F_3C)_3CO)_3Al\text{-}F\text{-}Al(OC(CF_3)_3)_3]^-$ ion ($\delta = -75.7$ ppm) in solution. Formation of the fluoride-bridged anion is the result of partial electrophilic decomposition of the $[Al(OC(CF_3)_3)_4]^-$ anion, and is often seen as a resting state in the decomposition pathway of this anion because of its increased stability towards further electrophilic attack.[13] The use of less π-basic fluorinated arenes as ligands promoted electrophilic attack of the anion by gallium(I), which is presumably driven by the formation of GaF with a very high Ga–F bond energy of 674 kJ mol^{-1}. Crystallization gave a mixture of crystals, which were analyzed by single crystal X-ray diffraction and found to contain $[Ga(o\text{-}C_6H_4F_2)_2]^+[Al(OC(CF_3)_3)_4]^-$ (**2**) and $[Ga(o\text{-}C_6H_4F_2)_2]^+[((CF_3)_3CO)_3Al\text{–}F\text{–}Al(OC(CF_3)_3)_3]^-$ (**3**; see the Supporting Information). In these $[Ga(o\text{-}C_6H_4F_2)_2]^+$ bent sandwich cations, the arenes are slightly distorted from η^6-coordination, with longer Ga–C distances for the carbons bearing fluorine substituents (see Table 1). If fluorobenzene is used as solvent in an analogous synthesis to **1**, $[Ga(C_6H_5F)_{2.5}]^+[Al(OC(CF_3)_3)_4]^-$ (**4**) is produced. The asymmetric unit of the crystal structure (see the Supporting Information) contains one $[Ga(C_6H_5F)_2]^+$ cation (**4a**$^+$) with a similar bent sandwich structure to **1**, **2**, and **3**, and also a $[Ga(C_6H_5F)_3]^+$ ion (**4b**$^+$) in which gallium is coordinated by three arenes in a similar manner to the chelating cyclophane complexes observed by Schmidbaur.[14] To the best of our knowledge, **4b**$^+$ is the first tris(arene) gallium(I) cation with three independent arene molecules (Figure 2).

Table 1: Comparison of key structural parameters ([Å] and [°]) for the $[Ga(arene)_2]^+$ complexes herein and in $[Ga(C_6H_6)_2]^+[GaCl_4]^-$.[15]

	1	(**4a**$^+$)	**2**	**3**	$[Ga(C_6H_6)_2]^+$
Ga–C (min)	2.864	2.913	2.873	2.942	3.015
Ga–C (max)	3.095	3.084	3.119	3.139	3.291
Av. Ga–cent[a]	2.633	2.669	2.684	2.696	2.847
Av. cent-Ga-cent[b]	138.8	141.7	159.0	125.5	–[c]
Closest Ga–X	3.242	3.054	3.119	3.171	3.097 (to Cl)
v.u.[d] Ga–X	0.014	0.023	0.019	0.017	0.069
Ga–X contacts[e]	1	2	2	1	3 (to Cl)

[a] Average distance from gallium to the centroids of the C_6 rings. [b] Average angle formed by the two C_6 centroids and the central gallium atom. [c] Not reported. [d] v.u. = valency units. [e] The average number of Ga···X contacts (X = F, Cl) shorter than the sum of the van der Waals radii (3.34 Å for Ga···F and 3.70 Å for Ga···Cl).

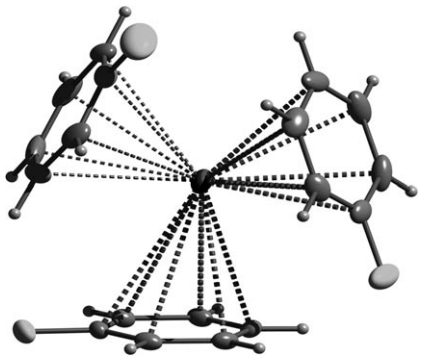

Figure 2. Molecular structure of the $[Ga(C_6H_5F)_3]^+$ (**4b**$^+$) cation in $[Ga(C_6H_5F)_{2.5}]^+[Al(OC(CF_3)_3)_4]^-$.

After dissolving **4** in several different solvents, we recorded the room-temperature ^{71}Ga NMR spectra of $Ga^+[Al(OR^F)_4]^-$ in toluene ($\delta = -520$ ppm, $h_{1/2} = 1200$ Hz), fluorobenzene ($\delta = -756$ ppm, $h_{1/2} = 600$ Hz), and 1,2-difluorobenzene ($\delta = -750$ ppm, $h_{1/2} = 400$ Hz). CD_2Cl_2 was also suitable as a solvent for several hours ($\delta = -630$ ppm, $h_{1/2} = 1300$ Hz) before the material decomposed with formation of a compound having a ^{71}Ga NMR signal at $\delta = +190$ ppm. NMR measurements in THF were also successful ($\delta = -448$ ppm); however, the sample completely polymerized within 24 h. The ^{71}Ga NMR shifts of the fluorinated $[Ga(arene)_2]^+$ cations are almost identical to the gallium(I) signal in molten Ga-$[GaX_4]$.[6]

To determine whether these salts could be used as precursors for further gallium(I) chemistry, the ligand-exchange reaction between the coordinated toluene of **1** and triphenylphosphine was examined. This seemingly simple reaction is in fact not trivial. Previous work on the reaction of gallium(I) sources, such as Ga_2X_4 (X = halide) or "GaI", with neutral donors has always led to disproportionation, comproportionation, or other redox reactions, and the isolation of higher-valent gallium species (see for example Ref. [5] and references therein). Moreover, to the best of our knowledge, no homoleptic gallium(I)–phosphine complex was known before this work apart from matrix isolation experiments. We believe that the redox reactions often seen in low-valent gallium halide chemistry were promoted by the reactivity of the halogallate anions and that salts **1**–**4** are suitably stabilized by the chemically robust alkoxyaluminate anions to circumvent this decomposition pathway.

Indeed, when a solution of **1** in *o*-$C_6H_4F_2$ was allowed to react with two equivalents of PPh_3, no evidence of dispro-

portionation was seen (for example precipitation of gallium metal), and a pale yellow solution was formed. Concentration of this solution to a viscous oil and storage for about 16 h resulted in a large crop of colorless crystals suitable for study by single-crystal X-ray crystallography. These were found to contain the gallium(I)–phosphine complex $[Ga(PPh_3)_3]^+[Al(OC(CF_3)_3)_4]^-\cdot 1.5\,C_6H_4F_2$ (**5**; see Figure 3).

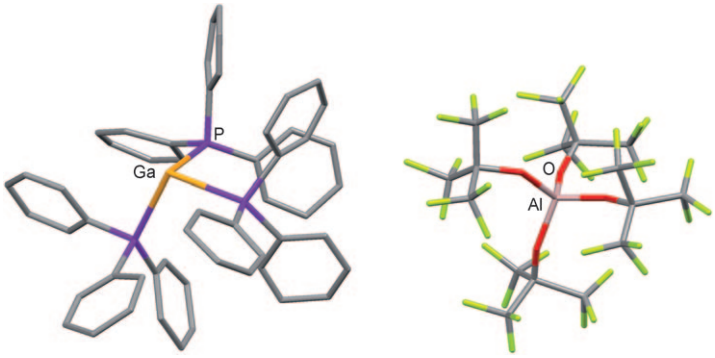

Figure 3. Molecular structure of $[Ga(PPh_3)_3]^+[Al(OC(CF_3)_3)_4]^-\cdot 1.5\,C_6H_4F_2$ (**5**). The asymmetric unit contains four independent cations and anions; only one is shown for clarity. Hydrogen atoms and *o*-$C_6H_4F_2$ molecules of crystallization are omitted for clarity.

To the best of our knowledge, this remarkable salt contains the first structurally characterized homoleptic gallium–phosphine complex in any oxidation state, and only one further gallium(I) complex that contains phosphine ligands, $[Ga_8I_8(PEt_3)_6]$, has been previously reported by Schnöckel et al.[12b] The X-ray crystal structure of **5** contains four independent cations and anions in the asymmetric unit. The bond lengths and angles of the $[Ga(PPh_3)_3]^+$ cations show a large degree of variation, both within each cation and between the independent cations, suggesting relatively flexible coordination geometries around gallium that are strongly affected by steric constraints and crystal-packing effects. In all four cations, gallium is found in a distorted trigonal pyramidal geometry with P-Ga-P angles ranging from 90.2 to 103.3° (av. 96.7)° and Ga–P lengths of 2.65 to 2.76 Å (av. 2.71 Å).

DFT calculations support this finding and suggest that a trigonal planar $Ga(PH_3)_3^+$ cation is about 233 to 272 kJ mol^{-1} higher in energy than a pyramidal cation (BP86, B3LYP, and PBE0 with SV(P) basis). The Ga–P distances in **5** are between 0.20 and 0.31 Å longer than in most gallium(III)–phosphine complexes reported in the Cambridge Crystallographic Database (average for 58 four-coordinate gallium(III)–phosphine complexes: 2.45 Å) consistent with the larger ionic radius of gallium(I). In contrast to the gallium–arene complexes **1**–**4**, the gallium center in **5** has no Ga···F contacts shorter than the sum of the van der Waals radii.

Compound **5** is more conveniently prepared by treating compound **1** with three equivalents of PPh_3. The ^{31}P NMR signal of **5** in *o*-$C_6H_4F_2$ at $\delta = -1.6$ ppm (243 and 298 K) is only slightly shifted compared to free PPh_3 ($\delta = -6.0$ ppm), but the ^{71}Ga NMR spectra show a large downfield shift compared to **1** ($\delta = -144$ ppm). Clearly, the ^{71}Ga chemical shift is sensitive to changes in coordinated ligand, but the ^{31}P chemical shift is relatively unperturbed on coordination. This result is supported by the 15 kHz solid-state ^{31}P MAS-NMR spectrum of **5**, which gives a broad singlet at $\delta = -4$ ppm, and the calculation of the ^{31}P chemical shift in $[Ga(PPh_3)_3]^+$ of $\delta = -7$ ppm ((RI-)BP86/SV(P)). This value hints at relatively weak Ga···P interactions, which are also suggested in the X-ray structure, but may also be related to ligand-exchange processes (the ^{31}P NMR signal is relatively broad).

To better understand this behavior, quantum chemical calculations were performed on the model systems $[Ga(PR_3)_n]^+$ (R = H, Ph; $n = 2$, 3) and $[Ga(arene)_2]^+$ (arene = toluene, *o*-$C_6H_4F_2$) at the (RI-)BP86/SV(P) and the (RI-)MP2/TZVPP level (only R = H; see Supporting Information for details.)[16–18] The optimized structures of the model cations match the X-ray structures well (within 0.1 Å). The ligand-exchange free energies (Table 2) suggest similar gallium–ligand binding energies for the different ligands and only a small barrier to phosphine loss from the model complex $[Ga(PH_3)_3]^+$ (MP2: 22 kJ mol^{-1}). These results suggest that phosphine ligand exchange and potentially phosphine–arene ligand exchange may be facile in this system, which could explain the broad signal seen in the ^{31}P NMR spectrum.

Table 2: Calculated gas-phase ligand-exchange free energies.[a]

Reaction	ΔH_{rxn} BP86	ΔG_{rxn} BP86	ΔG_{rxn} MP2
1 a) $[Ga(tol)_2]^+ + 3\,PH_3 \rightarrow [Ga(PH_3)_3]^+ + 2\,tol$	−4.3	+23	+93
1 b) $[Ga(tol)_2]^+ + 3\,PPh_3 \rightarrow [Ga(PPh_3)_3]^+ + 2\,tol$	−125	−53	–
2 a) $[Ga(PH_3)_3]^+ \rightarrow [Ga(PH_3)_2]^+ + PH_3$	+58	+14	+22
2 b) $[Ga(PPh_3)_3]^+ \rightarrow [Ga(PPh_3)_2]^+ + PPh_3$	+55	−13	–
3) $[Ga(tol)_2]^+ + C_6H_4F_2 \rightarrow [Ga(C_6H_4F_2)_2]^+ + 2\,tol$	+59	+55	+60

[a] Energies in kJ mol^{-1}. tol = toluene.

The inferior donor quality of *o*-$C_6H_4F_2$ follows from reaction 3 in Table 2 and suggests the superior performance of the fluorinated arene complexes as starting materials for coordination chemistry with weak Lewis bases. The calculations also allow us to examine the bonding in the $[Ga(PH_3)_3]^+$ cation (Figure 4). The lowest-energy Ga–P bonding orbital involves an overlap between a predominantly s-character orbital at gallium and all three PH_3 lone pairs. A pair of degenerate orbitals involving bonding interactions between the phosphine lone pairs and two of the gallium p orbitals lies higher in energy.

The HOMO is a gallium-based lone pair, which has mostly s-character with some p_z admixture (NBO calculations suggest an s-orbital contribution of 93%). The doubly degenerate LUMOs are relatively low in energy and composed of antibonding combinations of the gallium p_x and p_y orbitals and the phosphine lone pairs. This suggests that ligand exchange reactions with Lewis bases could take place by an associative mechanism. Indeed, optimization of a $[Ga(PH_3)_4]^+$ cation at the same level of theory suggests that an S_N2-like mechanism for PH_3 exchange in the model system

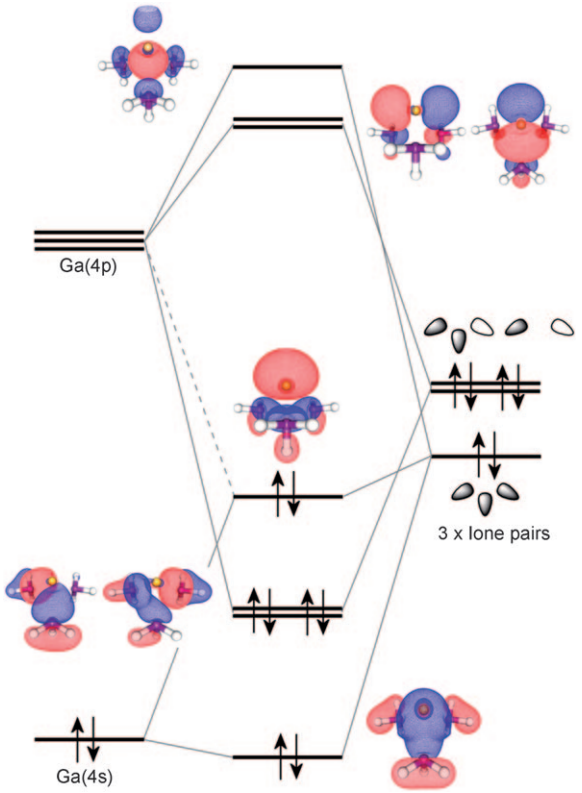

Figure 4. Molecular orbital diagram for the $[Ga(PH_3)_3]^+$ cation optimized at the MP2/TZVPP level. Relative orbital energies are shown to scale.

is low in energy ($[Ga(PH_3)_4]^+$ is essentially isoenergetic with $[Ga(PH_3)_3]^+ + PH_3$ if the BSSE is neglected). In the $[Ga(PPh_3)_n]^+$ system, steric effects are expected to significantly disfavor this mechanism.

In conclusion, a new method for the synthesis of gallium(I) salts of weakly coordinating anions has been developed. This method is simple, involves easily accessible starting materials and synthetic procedures, and provides gallium(I) salts in very high yields. The gallium–arene salts described herein enable the exploration of new coordination chemistry at gallium(I) that was inaccessible using previous starting materials. Further work is in progress to investigate the use of these salts as sources of gallium(I) for further coordination chemistry and catalysis. In this respect, the similarity between the gallium complex **5** and Wilkinson's catalyst $[(Ph_3P)_3RhCl]$ should be noted. The ability to use the redox behavior of a main group element, for example, the Ga^I/Ga^{III} redox couple, in catalysis rather than transition metals such as rhodium is an intriguing possibility that could reduce costs.

Experimental Section

All manipulations were performed using grease-free Schlenk or drybox techniques and a dinitrogen or argon atmosphere. See the extensive Supporting Information (155 pages) for detailed experimental procedures and synthetic details. CCDC 756309 (**1**), 756307 (**2**), 756306 (**3**), 758076 (**4**), and 756308 (**5**) contain 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. All quantum-chemical calculations were performed using TURBO-MOLE.[18] See the Supporting Information for calculational details, XYZ coordinates, energies, and vibrational frequencies.

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