The Use of Ga(C₆F₅)₃ in Frustrated Lewis Pair Chemistry

by

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A thesis submitted in conformity with the requirements for the degree of Master of Science
Department of Chemistry
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2015

Abstract

Although numerous publications have investigated the use of boron-based and aluminum-based Lewis acids in frustrated Lewis pair (FLP) chemistry, the exploration of Lewis acids of the next heaviest group 13 element, gallium, has remained limited in this context. In this work, the reactivity of Ga(C₆F₅)₃ in FLP chemistry is probed. In combination with phosphine bases, Ga(C₆F₅)₃ was shown to activate CO₂, H₂, and diphenyl disulfide, as well as give addition products with alkynes. Moreover, the potential for synthesizing gallium arsenide using Ga(C₆F₅)₃ as a source of gallium was investigated. In an effort to synthesize GaAs from a safe precursor, adduct formation of Ga(C₆F₅)₃ with a primary arsine as well as with a tertiary arsine was examined.
Acknowledgments

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<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Å</td>
<td>Ångstrom ($10^{-10}$ m)</td>
</tr>
<tr>
<td>Abs coeff</td>
<td>Absorption coefficient, $\mu$ (mm$^{-1}$)</td>
</tr>
<tr>
<td>atm</td>
<td>Atmosphere (1.013 x $10^5$ Pa)</td>
</tr>
<tr>
<td>bm</td>
<td>Broad multiplet</td>
</tr>
<tr>
<td>bs</td>
<td>Broad singlet</td>
</tr>
<tr>
<td>calcd.</td>
<td>Calculated</td>
</tr>
<tr>
<td>C</td>
<td>Celsius</td>
</tr>
<tr>
<td>Cy</td>
<td>Cyclohexyl (-C$<em>6$H$</em>{11}$)</td>
</tr>
<tr>
<td>C=C</td>
<td>Double bond</td>
</tr>
<tr>
<td>d</td>
<td>Doublet</td>
</tr>
<tr>
<td>d (calc)</td>
<td>Density calculated (g cm$^{-3}$)</td>
</tr>
<tr>
<td>dd</td>
<td>Doublet of doublets</td>
</tr>
<tr>
<td>dm</td>
<td>Doublet of multiplets</td>
</tr>
<tr>
<td>E</td>
<td>Group 13 element (B, Al, Ga)</td>
</tr>
<tr>
<td>EA</td>
<td>Elemental analysis</td>
</tr>
<tr>
<td>Et</td>
<td>Ethyl (-CH$_2$CH$_3$)</td>
</tr>
<tr>
<td>eq.</td>
<td>Equivalents</td>
</tr>
<tr>
<td>FLP</td>
<td>Frustrated Lewis Pairs</td>
</tr>
<tr>
<td>g</td>
<td>Grams</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Definition</td>
</tr>
<tr>
<td>--------------</td>
<td>------------</td>
</tr>
<tr>
<td>Hz</td>
<td>Hertz (s(^{-1}))</td>
</tr>
<tr>
<td>i</td>
<td>ipso</td>
</tr>
<tr>
<td>J</td>
<td>Coupling constant (Hz)</td>
</tr>
<tr>
<td>K</td>
<td>Kelvin</td>
</tr>
<tr>
<td>LA</td>
<td>Lewis acid</td>
</tr>
<tr>
<td>LB</td>
<td>Lewis base</td>
</tr>
<tr>
<td>LEC</td>
<td>Liquid encapsulated Czochralski growth method</td>
</tr>
<tr>
<td>LED</td>
<td>Light emitting diode</td>
</tr>
<tr>
<td>m</td>
<td>meta</td>
</tr>
<tr>
<td>m</td>
<td>Multiplet</td>
</tr>
<tr>
<td>MBE</td>
<td>Molecular beam epitaxy</td>
</tr>
<tr>
<td>Me</td>
<td>Methyl (-CH(_3))</td>
</tr>
<tr>
<td>Mes</td>
<td>Mesityl (-C(_6)H(_2)(CH(_3))(_3))</td>
</tr>
<tr>
<td>mg</td>
<td>Milligram (10(^{-3}) g)</td>
</tr>
<tr>
<td>MHz</td>
<td>Megahertz (10(^6) Hz)</td>
</tr>
<tr>
<td>mL</td>
<td>Millilitre (10(^{-3}) L)</td>
</tr>
<tr>
<td>MOCVD</td>
<td>Metalorganic chemical vapour deposition</td>
</tr>
<tr>
<td>mol</td>
<td>Mole (6.022 x 10(^{23}))</td>
</tr>
<tr>
<td>N</td>
<td>Nine (purity)</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear magnetic resonance</td>
</tr>
</tbody>
</table>
NR  No reaction

\( o \)  ortho

\( p \)  para

Ph  Phenyl \((-\text{C}_6\text{H}_5)\)

POV-Ray  Persistence of Vision Raytracer

ppm  Parts per million

q  Quartet

R  Substituent

reflns  Reflections

s  Singlet

t  Triplet

T  Temperature

\(^t\text{Bu} \)  tert-butyl \((-\text{C(CH}_3)_3)\)

TGA  Thermogravimetric analysis

THF  Tetrahydrofuran \((\text{C}_4\text{H}_8\text{O})\)

tol  Toluene \((\text{C}_6\text{H}_5\text{CH}_3)\)

trityl  Triphenylmethyl \((\text{CPh}_3)\)

V  Volume \((\text{Å}^3)\)

VGF  Vertical gradient freeze

W  Watt
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>wt</td>
<td>Weight</td>
</tr>
<tr>
<td>X</td>
<td>Anion (Cl, Br, I)</td>
</tr>
<tr>
<td>Z</td>
<td>Formula units</td>
</tr>
<tr>
<td>Δ</td>
<td>Change or heat</td>
</tr>
<tr>
<td>δ</td>
<td>Chemical shift (ppm)</td>
</tr>
<tr>
<td>λ</td>
<td>Wavelength</td>
</tr>
<tr>
<td>°</td>
<td>Degree (deg)</td>
</tr>
<tr>
<td>%</td>
<td>Percent</td>
</tr>
<tr>
<td>{^1\text{H}}</td>
<td>Proton decoupled</td>
</tr>
</tbody>
</table>
1 Introduction

1.1 Overview of Frustrated Lewis Pairs and their Chemistry

1.1.1 Classical Lewis Acid-Base Adducts and Early Exceptions

Lewis acids and bases play an important role in numerous chemical reactions. These acids and bases are defined by their ability to either accept electrons in the case of an acid, or donate electrons in the case of a base, as was described by Gilbert Lewis in 1923. Normally, a zwitterionic adduct is formed between the Lewis acid and base pair, where the Lewis base donates a lone pair of electrons to an empty orbital of the Lewis acid, typically quenching the reactivity of the pair, as shown in Figure 1.1. However, a few exceptions to this rule were documented between that time and the early twenty first century, when this unusual behaviour was more thoroughly studied.

In 1942, H. C. Brown observed that 2,6-lutidine and trimethylborane did not form the expected Lewis adduct upon mixing, although when the same lutidine species was added to a less sterically encumbered acid, such as BF₃, quenching by adduct formation occurred. In 1959, Wittig and Benz reported that triphenylborane and triphenylphosphine did not form a classical Lewis adduct, though interestingly, when benzyne was present in the reaction mixture, formation of an o-phenylene bridged phosphonium borate species took place. In 1966, Tochtermann observed the 1,2-addition product of the Lewis basic trityl cation and Lewis acidic triphenylborane with butadiene, also in lieu of classical Lewis pair quenching. This led Tochtermann to address the behaviour of the Lewis pair as “antagonistisches Paar,” German words describing the non-ideal pairing of the Lewis acid and base due to their incapability to form an adduct. Wittig and Tochtermann reasoned that in such cases, steric congestion between...
the acid and base prevents adduct formation, thus leading to the unanticipated reactivity reported²⁻⁵. It is precisely this non-typical behaviour of Lewis acid-base pairs that will be addressed throughout the remainder of this thesis. A depiction of the mentioned exceptions can be found in Scheme 1.1.

Scheme 1.1: Early examples of unusual behaviour of Lewis pairs

1.1.2 Establishment of Frustrated Lewis Pairs

Since the early 2000s, Lewis acid-base pairs that were not found to form classic adducts have been more carefully investigated, especially by the Stephan and Erker groups⁶⁻⁸. Such pairs were named “frustrated Lewis pairs” or “FLPs” due to the frustrated nature of the unquenched acidic and basic components of the pair, sterically precluded from forming a classical adduct, as shown in Figure 1.2. Unexpected reactivity was generally observed when these FLPs were exposed to H₂, CO₂, or other small molecules, at times mimicking the roles of transition metals in catalytic reactions.⁶ The investigations of frustrated Lewis pairs have thus opened the path to new metal-free routes for synthetic chemistry.
Figure 1.2: Representation of a frustrated Lewis pair

It should be noted that it is not always a requirement for a Lewis acid and base to be precluded from forming an adduct in order to exhibit FLP chemistry.\textsuperscript{6,9} For example, 2,6-lutidine and B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3} are in equilibrium between their free form and a weak and reversible adduct, as seen in Scheme 1.\textsuperscript{9} The pair is nonetheless able to behave as an FLP, and effectuates the activation of dihydrogen or the ring-opening of THF. It was thus concluded that the classical Lewis adduct formation and FLP reaction pathways are not mutually exclusive.\textsuperscript{9}

Scheme 1.2: Classical and FLP behaviour of B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3} and 2,6-lutidine

The scope of the unprecedented reactivity of these metal-free systems was thereafter widely explored.\textsuperscript{10-24} FLP systems using B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3} as the Lewis acid and a bulky phosphine as the Lewis base were shown to be capable of effecting, for example, the activation of H\textsubscript{2}, disulfide activation, addition reactions with terminal alkynes, and the activation of CO\textsubscript{2}, as depicted in Scheme 1.3.\textsuperscript{11-14}
1.1.3 The Discovery of Dihydrogen Activation by FLPs

In 2006 during the early exploration of FLP chemistry, Stephan and co-workers observed that upon mixing B(C$_6$F$_5$)$_3$ with the bulky secondary phosphine dimesitylphosphine, the latter carries out a para-nucleophilic attack on a pentafluorophenyl ring of B(C$_6$F$_5$)$_3$. This displaces the fluoride to the Lewis acidic boron centre and thereby generating a zwitterionic phosphonium-borate compound. When given chlorodimethylsilane, a fluoride-hydride exchange occurs yielding a phosphonium borohydride salt, which upon heating to 150 °C resulted in the loss of H$_2$. Introduction of hydrogen gas to the phosphinoborane solution yielded the previous phosphonium borohydride, demonstrating the reversibility of the system, as seen in Scheme 1.4. This was the first example of metal-free reversible hydrogen activation using a frustrated Lewis pair.
Thereafter, other FLP systems were also shown to activate dihydrogen. Bimolecular systems using B(C₆F₅)₃ and bulky phosphines such as tris-tert-butylphosphine and trimesitylphosphine have shown reactivity in the splitting of H₂, as well as the use of triphenylborane instead of B(C₆F₅)₃ as the Lewis acid. However, other boranes with lower Lewis acidity were not able to cleave the dihydrogen bond when combined with the same phosphines, leading to the conclusion that the reactivity of FLPs is decided not only by steric factors but also by the electronic properties of the system.

Initially, many mechanisms were proposed for the activation of dihydrogen by FLPs, however, the accepted mechanism was later established from theoretical studies by Pápai and Grimme. They found that the preclusion of bonding between the Lewis acid and base creates an electric field within the cavity between them, in which the H₂ molecule orients itself. This causes the polarization of the molecule, leading the Lewis base to donate electrons into the σ* orbital of H-H and the Lewis acid to accept the σ electrons of H-H, thus achieving facile heterolytic cleavage of the H-H bond. In general, this proposed mechanism is also accepted for other small molecule activation by FLPs.
1.1.4 Examples of Al-based FLP Chemistry

While much work has been done in the exploration of boron-based Lewis acids for use in FLP chemistry, the aluminum analogues have been investigated as well. Generally, it was found that Al-based Lewis acids exhibited greater reactivity in FLP systems because of their higher intrinsic Lewis acidity.\(^{30-39}\)

For example, activation of hydrogen proceeds in a 2:1 fashion of Al\((C_6F_5)_3\) and phosphine, as opposed to the 1:1 ratio in the boron system, to give a bridging phosphonium aluminate salt with an Al-H-Al angle of 138.0\(^\circ\), as determined by X-ray studies.\(^{36}\) This salt could then be used to react with unactivated olefins such as ethylene and cyclohexene to produce alkylalanes upon hydride transfer.\(^{36}\)

\[
2 \text{Al}(C_6F_5)_3 + \text{H}_2 \rightarrow [\text{R}_3\text{PH}]_2 \text{Al}(C_6F_5)_3 \rightarrow [\text{R}_3\text{PH}]_2 [\text{Al}(C_6F_5)_4] + (\text{R}'\text{Al}(C_6F_5)_2)_n \\
\text{R} = \text{tBu, C}_6\text{H}_2\text{Me}_3
\]

Scheme 1.5: Examples of Al-based FLP chemistry

In a second example also portrayed in Scheme 1.5, activation of CO\(_2\) was also shown to proceed in a 2:1 ratio of Al halide to trimesitylphosphine.\(^{39}\) If the activated CO\(_2\) species was given excess ammonia borane then subsequently quenched with water, it was possible to obtain methanol in yields as high as 51\%.\(^{39}\) It is unclear exactly how methanol formation occurs, however, it was shown that the phosphonium cation, borazine and Al-methoxy species are formed before quenching the reaction with water, ultimately producing methanol.
1.2 Gallium

1.2.1 Gallium: Sources, Recovery Methods, and Uses

Gallium is regarded as a rare metal due to its low abundance of about 16 ppm in the earth’s crust.\(^{40-41}\) It is best found in bauxite, sphalerite, phosphate ores and coal, however, because of its extremely low concentrations (for example, 0.003 – 0.008 % in bauxite), it is not economically favourable to extract solely for gallium from these sources.\(^{40-41}\) Gallium is thus recovered mainly as a by-product in the production of aluminum oxide from bauxite.

During the collection of alumina from bauxite (Bayer process), gallium hydroxide is concentrated in a solution of sodium hydroxide from which aluminum hydroxide is precipitated.\(^{40-41}\) There are three main methods for recovering gallium from this caustic liquor: fractional precipitation, electrolytic extraction, and the use of chelating agents. Afterwards, gallium is usually purified to 6 N or 8 N purity (99.9999 % - 99.999999 %) by methods such as fractional crystallization and zone melting.\(^{40-41}\) Although its production is costly and difficult, it should be noted that gallium is largely recycled.

![Figure 1.3: The recovery of gallium from bauxite](image)

Though it was discovered in 1875, it was not until a century later, in the 1970s, that gallium gained attention when it was found that it could exhibit impressive semiconducting properties when combined with group 15 elements.\(^{40-41}\) Low power consumption, great operation speed, as well as resistance to radiation are demonstrated by semiconducting gallium compounds such as gallium nitride, gallium phosphide and gallium arsenide.\(^{40}\) The capability of converting electrical power into light is also observed, a feature which permits these binary compounds to be used in light emitting diodes (LEDs). Gallium arsenide is of particular interest as it has been unmatched in its applications and therefore is responsible for over 95 % of Ga consumption globally.\(^{41}\)
1.2.2 Ga(C₆F₅)₃ in the Literature

The Lewis acid Ga(C₆F₅)₃, whose reactivity in FLP systems will be examined throughout this thesis, was first synthesized in 1965 by Pohlmann in an interest to expand the library of pentafluorophenyl-substituted group 13 compounds. A Grignard reaction was done using pentafluorophenyl-magnesium bromide and gallium trichloride in diethyl ether, producing the desired tris-(pentafluorophenyl)-gallium etherate, as seen in Scheme 1.6. Removal of the coordinated ether from the compound was unsuccessful until 1992, when it was observed that iodine is capable of effectuating cleavage of the gallium-ether bond.

\[
3 \text{Mg(C}_6\text{F}_5\text{)Br} + \text{GaCl}_3 \rightarrow \text{Et}_2\text{O} \rightarrow \text{Ga(C}_6\text{F}_5\text{)₃} \cdot \text{OEt}_2 + 3 \text{MgBrCl}
\]

\[
3 \text{Zn(C}_6\text{F}_5\text{)₂} \cdot \text{tol} + 2 \text{GaCl}_3 \rightarrow \text{Toluene} \rightarrow 2 \text{Ga(C}_6\text{F}_5\text{)₃} \cdot \text{tol} + 3 \text{ZnCl}_2
\]

Scheme 1.6: Preparations of Ga(C₆F₅)₃

A later synthesis showed that group 13 and 15 metal pentafluorophenyl compounds can be obtained by transmetallation using pentafluorophenyl group 11 and 12 metal compounds in a safer, more environmentally friendly manner and without the need for an etherate solution, forming Ga(C₆F₅)₃•tol in the case of gallium. The solvent coordination in Ga(C₆F₅)₃•tol proved to be weaker than that of the ether analogue, permitting facile reactivity of the gallate. As a strong Lewis acid, Ga(C₆F₅)₃ is hygroscopic, and thus easily succumbs to hydrolysis in the presence of water.

Work by Marks and Lewis has shown that Ga(C₆F₅)₃ is useful as a cocatalyst or co-initiator in the polymerization of olefins such as styrene, propylene and isobutene.
1.3 Scope of Thesis

In light of the frustrated Lewis pair chemistry done with B(C₆F₅)₃ and Al(C₆F₅)₃, it was naturally of interest to examine the reactivity of Ga(C₆F₅)₃ in FLP systems. Theoretical predictions on the Lewis acidity of these tris-pentafluorophenyl substituted group 13 elements place the acceptor strength of Ga(C₆F₅)₃ between those of Al(C₆F₅)₃ and B(C₆F₅)₃.⁴⁹,⁵⁰ This raised the question as to whether the Ga-based Lewis acid would behave more similarly to the highly reactive Al-based FLP systems, or to the B-based FLP systems, or even in a completely distinct manner. The objective of this graduate research was thus to investigate the reactivity of Ga(C₆F₅)₃ in the context of FLP chemistry. Phosphorus-based FLP systems employing Ga(C₆F₅)₃ were examined in their ability to activate CO₂, H₂, and PhSSPh, as well as in their ability to achieve addition reactions with terminal and internal alkynes. Exploration of Ga(C₆F₅)₃ and arsine adducts was also done, in an effort to probe the possibility of using these simple adducts as safer precursors in the synthesis of gallium arsenide.
2 Phosphorus-Based FLP Chemistry of Ga(C₆F₅)₃

2.1 Introduction

In combination with sterically encumbered phosphines, the highly Lewis acidic borane, B(C₆F₅)₃, and alane, Al(C₆F₅)₃ exhibit unusual chemistry when in the presence of small molecules, due to the unquenched electronic frustration of the pair.⁶,⁷,³⁶,³⁹ A handful of these small molecule activation reactions are highlighted as follows.

Reactions of bulky phosphines and B(C₆F₅)₃ or Al(C₆F₅)₃ with terminal alkynes generally result in the formation of addition products to generate zwitterionic olefinic phosphonium borates or aluminates, as shown in Scheme 2.¹³,⁵¹

Because of the rapid nature of these reactions, it was difficult to obtain mechanistic insight on how this chemistry proceeds. It is reasoned that the Lewis acid coordinates initially with the alkyne through π-interaction, which renders the alkyne susceptible to nucleophilic attack by the phosphine.¹³ It was observed that upon using the more Brønsted basic tris-tert-butylphosphine with terminal alkynes, a deprotonation reaction was favoured, resulting in the isolation of phosphonium alkynylborate or alkynylaluminate. This reaction pathway is expected to proceed via the same initial π-interaction of the Lewis acid with the alkyne, which is thought not only to activate the alkyne for nucleophilic attack but also increases the acidity of the alkynyl proton.¹³ Subsequently, the nature of the phosphine used determines whether it behaves as a nucleophile or as a Brønsted base, ultimately allowing either an addition reaction or deprotonation to occur.
Attempts to react these FLP systems with an internal alkyne resulted in reduced reactivity, producing a mixture of products in the cases of 2-hexyne, 3-hexyne and 2-butyne, which were deemed inseperable. In turn, the use of diphenylacetylene resulted in no reactivity, prompting the conclusion that reaction of these internal alkynes with FLPs is too sterically congested to proceed in a facile fashion.

Activation of carbon dioxide was achieved by employing FLP systems of B(C₆F₅)₃ or Al(C₆F₅)₃ with PᵗBu₃. Orientation of the CO₂ molecule between the phosphine and Lewis acid resulted in the formation of P-C and O-B or O-Al bonds, as depicted in Scheme 2.2. In both instances, one equivalent of the Lewis acid is incorporated into the activation product, as opposed to the case of Al(C₆F₅)₃ in combination with other phosphines. Although the liberation of carbon dioxide from the resulting compounds was possible upon heating under vacuum, isolation of the CO₂ activation products was achieved in good yields.

\[
\text{E(C}_6\text{F}_5)_3 + \text{P}^{t}\text{Bu}_3 \text{P} \xrightarrow{\text{CO}_2} \text{P}^{t}\text{Bu}_3\text{P}^+ \text{E(C}_6\text{F}_5)_3
\]

**Scheme 2.2**: Activation of CO₂ by B(C₆F₅)₃/Al(C₆F₅)₃ and PᵗBu₃

The activation of dihydrogen by FLPs was extensively investigated since the initial report of reversible metal-free H₂ activation using B(C₆F₅)₃ and the sterically congested dimesitylphosphine. This process occurs via an intramolecular route involving a zwitterionic phosphonium borate formed by para-nucleophilic attack of the phosphine to a pentafluorophenyl group of the Lewis acid. The use of B(C₆F₅)₃ and bulky tertiary phosphines also achieves H₂ activation, albeit in an intermolecular fashion, as discussed in Chapter 1. Upon testing this reaction with the more Lewis acidic Al(C₆F₅)₃, it was observed that two equivalents of the alane were being consumed, resulting in the formation of a bridging hydride species, as shown in Scheme 2.3.
Scheme 2.3: Activation of $\text{H}_2$ by $\text{B}(\text{C}_6\text{F}_5)_3/\text{Al}(\text{C}_6\text{F}_5)_3$ and $\text{P}^t\text{Bu}_3$

The facile cleavage of diphenyl disulfide was possible by combination of the latter with $\text{B}(\text{C}_6\text{F}_5)_3$ and $\text{P}^t\text{Bu}_3$, as shown in Scheme 2.4.\textsuperscript{12} It is suspected that the Lewis acid coordinates weakly to PhSSPh in an initial activation step, however complete mechanistic studies were difficult due to the rate of the reaction. The use of $\text{Al}(\text{C}_6\text{F}_5)_3$ was not tested in the activation of disulfides.

Scheme 2.4: Activation of PhSSPh by $\text{B}(\text{C}_6\text{F}_5)_3$ and $\text{P}^t\text{Bu}_3$

A great amount of research in FLP chemistry has centered around the investigation of $\text{B}(\text{C}_6\text{F}_5)_3$, with some work being done on the analogous $\text{Al}(\text{C}_6\text{F}_5)_3$ compound. Owing to its higher intrinsic Lewis acidity, $\text{Al}(\text{C}_6\text{F}_5)_3$ was found to exhibit greater reactivity in the context of FLP chemistry in many cases.\textsuperscript{30-39} Theoretical predictions on the relative Lewis acidity of group 13 perfluorinated aryl derivatives stipulates that aluminum Lewis acids have a greater Lewis acidity than do the analogous gallium compounds, than do the analogous boron compounds.\textsuperscript{49,50} In light of these results, it was of increased interest to investigate the use of $\text{Ga}(\text{C}_6\text{F}_5)_3$ in FLP chemistry in order to determine whether this gallium-based Lewis acid would behave more similarly to the Al-FLP systems or to the B-FLP systems, or even in a completely distinct manner.
2.2 Results and Discussion

2.2.1 Adduct Formation between Ga(C₆F₅)₃ and Phosphines

Formation of adducts between Ga(C₆F₅)₃ and secondary phosphines, as well as between Ga(C₆F₅)₃ and tertiary phosphines was tested.

One equivalent of diphenylphosphine was added to a solution of Ga(C₆F₅)₃ in deuterated toluene and the reaction mixture was stirred. ¹H NMR analysis revealed a change in chemical shift of the proton coupled to phosphorus from 5.28 ppm to 6.63 ppm, indicating a more deshielded environment of the proton. The ³¹P{¹H} NMR spectrum complements this result by displaying the shift of the phosphorus atom of the compound at -26.22 ppm rather than at -40.65 ppm for the free form of the secondary phosphate. As well, the ¹⁹F{¹H} NMR spectrum reveals change in the fluorine chemical shifts of free Ga(C₆F₅)₃ to that of a tetravalent gallium centre, where the gap between the para- and meta-fluorines of the C₆F₅ groups is decreased. These results imply the formation of the zwitterionic adduct Ph₂HP-Ga(C₆F₅)₃ (2-1). Removal of the solvent was done in vacuo, leaving a crude white powder which was then dissolved in a minimal amount of pentane. Cooling of the pentane solution in the freezer overnight at -35 °C resulted in the precipitation of the product 2-1 in a 44 % yield. The procedure was repeated identically using dicyclohexylphosphine, which resulted in the formation of the adduct Cy₂HP-Ga(C₆F₅)₃ (2-2) in a 53 % yield. In turn, reaction of Ga(C₆F₅)₃ with di-tert-butylphosphine yielded 33 % of 'Bu₂HP-Ga(C₆F₅)₃ (2-3). All attempts to obtain confirmation of the identity of the above products, as well as those that follow throughout this chapter, by Mass Spectrometry or Elemental Analysis were unsuccessful due to the highly sensitive nature of the compounds to moisture. It is noteworthy that although it was possible to obtain adducts of Ga(C₆F₅)₃ and secondary phosphines, para-nucleophilic aromatic substitution of the phosphine on a pentafluorophenyl group of the gallane was not observed, presumably due to the high stability of the classical Lewis adducts formed.

Similarly, adduct formation of Ga(C₆F₅)₃ with the more bulky tertiary phosphines was probed. To a solution of Ga(C₆F₅)₃ in deuterated toluene was added one equivalent of triphenylphosphine. Immediate precipitation of a white solid occurred upon mixing. Multinuclear NMR analysis of the supernatant revealed that the starting reagents had been consumed, suggesting that adduct formation had occurred between the gallane and the tertiary phosphine.
The white precipitate was decanted, triturated with pentane and dried *in vacuo* before dissolving a sample of the powder in CD$_2$Cl$_2$. $^{31}$P{$^1$H} NMR analysis showed the presence of a singlet at -1.19 ppm, different from that of the free phosphine which would have been found at -5.21 ppm. The $^{19}$F{$^1$H} NMR spectrum indicated a smaller gap between the chemical shifts of the para- and meta- fluorine resonances of the pentafluorophenyl groups of the gallane versus that of free Ga(C$_6$F$_5$)$_3$. These findings are evidence of a different chemical environment about the phosphorus atom and of the presence of a tetravalent gallium atom respectively, implying the zwitterionic adduct formation of Ph$_3$P-Ga(C$_6$F$_5$)$_3$ (2-4), which was achieved in a 65 % yield.

Reaction of Ga(C$_6$F$_5$)$_3$ with tricyclohexylphosphine proceeded in an analogous fashion, producing the adduct Cy$_3$P-Ga(C$_6$F$_5$)$_3$ (2-5) in a 54 % yield. Upon testing this methodology using tris-tert-butylphosphine, slow cooling of the toluene solution was required to induce the precipitation of the adduct tBu$_3$P-Ga(C$_6$F$_5$)$_3$ (2-6), which was obtained in a 66 % yield. Suitable single crystals of 2-6 for X-ray diffraction were grown by vapour diffusion, and confirm the identity of the product, as shown in Figure 2.1.

![Figure 2.1: POV-Ray depiction of the molecular structure of 2-6. C: black, P: orange, Ga: purple, F: green. H atoms omitted for clarity.](image-url)

The rather elongated Ga-P bond of 2.637 Å versus reported values of gallium-phosphorus bond lengths in similar compounds in the range of 2.3 – 2.4 Å was evidence of a weak interaction between the two moieties. This suggested that adduct formation between Ga(C$_6$F$_5$)$_3$ and tBu$_3$P is weak and reversible, implying that FLP-type chemistry may still be exhibited by this system, as was seen in the case of B(C$_6$F$_5$)$_3$ and 2,6-lutidine mentioned previously. By extension, the
same reasoning was applied to the adducts 2-4 and 2-5. Although precipitation of the classical Lewis adduct was facile in the latter two cases, this was not sufficient evidence that FLP behaviour was necessarily inhibited.

2.2.2  Addition Reactions of Ga(C₆F₅)₃ and Phosphines with Alkynes

Addition reactions with terminal and internal alkynes using Ga(C₆F₅)₃ and phosphines were tested.

One equivalent of phenylacetylene was added to a deuterated benzene solution of Ga(C₆F₅)₃ and P'Bu₃. Mixing of the solution resulted in the formation of an oil. Multinuclear NMR analysis of the supernatant showed that the starting material had been consumed. The solvent was then removed in vacuo and the oil was washed in pentane overnight, resulting in the formation of a white powder. The solid was decanted and dried, and a sample was dissolved in C₆D₅Br for analysis by NMR. The presence of a doublet at 8.57 ppm with a coupling constant of 29.7 Hz in the $^1$H NMR spectrum was evidence of an olefinic proton, pointing towards the occurrence of an addition reaction of the terminal alkyne with the present FLP system. The appearance of a singlet at 40.67 ppm in the $^{31}$P {$^1$H} NMR spectrum also indicated the formation of a new species, $^3$Bu₃P(Ph)C=CHGa(C₆F₅)₃ (2-7). Single crystals were grown of the product by vapour diffusion of a toluene solution of the compound with pentane and were analysed by X-ray diffraction, as shown in Figure 2.2, and confirm the presence of the addition product. Attempts to completely isolate compound 2-7 from hydrolysis side-products and other impurities were unsuccessful.
Figure 2.2: POV-Ray depiction of the molecular structure of 2-7. C: black, P: orange, Ga: purple, F: green. H atoms omitted for clarity.

It is noteworthy that when using the Lewis acids B(C₆F₅)₃ or Al(C₆F₅)₃ in combination with P'Bu₃, deprotonation of phenylacetylene was reported to occur.¹³,⁵¹ In the case of B(C₆F₅)₃, varying amounts of the addition product were observed by NMR study of the reaction mixture, however it was not possible to isolate this species from the deprotonation product.⁵¹ The preferred pathway of deprotonation in these examples was attributed to be due to the high Brønsted basicity of tris-tert-butylphosphine, prompting it to attack the proton of phenylacetylene.¹³,⁵¹ In the case of Ga(C₆F₅)₃, there was no clear indication of the deprotonation occurring, however, this reaction pathway was not able to be completely ruled out in this system owing to its high sensitivity to moisture, which brought great difficulty in its study. It was certain, nonetheless, that an addition reaction was taking place to produce the compound 2-7, as determined by NMR analysis and X-ray crystallographic studies.

It was reasoned that Ga(C₆F₅)₃ was able to stabilize the addition product 2-7 owing to the larger radius of gallium versus boron, which in turn permits the formation of bonds with carbon atoms at a larger distance. The long Ga-C bond lengths of gallium to the ipso-carbons of the pentafluorophenyl groups, resting at 2.014 Å, 2.020 Å, and 2.030 Å, were thought to allow a more facile interaction of the gallium centre to the terminal carbon of phenylacetylene, ultimately resulting in the formation of a bond between gallium and the olefinic carbon at a distance of 1.991 Å.
Upon trying the analogous reaction with triphenyphosphine in toluene, precipitation of a varying amount of the simple adduct 2-4 was unavoidable. However, observation of the NMR spectra of the reaction mixture revealed the presence of the corresponding addition product, Ph₃P(Ph)C=C(H)Ga(C₆F₅)₃ (2.8). A thorough comparison of the NMR spectra obtained to those of the addition products formed using the analogous boron and aluminum-based FLP systems was done to confirm the presence of the addition product. Because of the high sensitivity of the system to moisture and solvent impurities, complete isolation of the product proved difficult and unsuccessful. Identical behaviour of this reaction was observed when using tricyclohexylphosphine, producing the addition product, Cy₃P(Ph)C=C(H)Ga(C₆F₅)₃ (2-9).

An attempt to achieve an addition reaction with an internal alkyne and gallium-based FLPs seemed to be successful. A 1:1:1 mixture of Ga(C₆F₅)₃, 'Bu₂HP, and diphenylacetylene in C₆D₅Br was analysed by NMR study. The ¹H NMR spectrum revealed a change in the chemical shift of the phosphorus-bound proton from 4.90 ppm of the gallane-phosphine adduct 2-3 to 4.62 ppm, and of the tert-butyl protons from 1.37 ppm to 1.04 ppm, while the ³¹P NMR spectrum showed a doublet at 18.44 ppm with a coupling constant of 360.4 Hz. These results pointed towards an addition reaction taking place with PhCCPh, Ga(C₆F₅)₃ and 'Bu₂HP to produce 'Bu₂HP(Ph)C=C(H)Ga(C₆F₅)₃ (2-10). However, similarly to the reactions with terminal alkynes, isolation of the addition product 2-10 was unsuccessful. The apparent reactivity of this gallium-based FLP system towards diphenylacetylene contrasted the lack of reactivity between PhCCPh, and B(C₆F₅)₃ based FLP systems, which were deemed too sterically crowded to achieve an addition reaction with diphenylacetylene. It was thought that due to the higher predicted Lewis acidity of Ga(C₆F₅)₃ as well as the longer bonds of gallium to the ipso-carbons of its pentafluorophenyl groups as explained above, coordination of the gallium centre to the internal alkyne was possible, achieving reaction with PhCCPh.

Other secondary phosphines were tested with diphenylacetylene and Ga(C₆F₅)₃ in an effort to obtain other addition products, however, the use of diphenylphosphine or dicyclohexylphosphine gave no apparent reaction. It was reasoned that in these cases, the difference in basicity of these phosphines versus that of di-tert-butylphosphine resulted in lack of reactivity with the internal alkyne system.
2.2.3 Activation of Carbon Dioxide by Ga(C₆F₅)₃ and P₄Bu₃

A 1:1 solution of Ga(C₆F₅)₃ and P₄Bu₃ in deuterated toluene was added to a J-Young NMR tube. Multinuclear NMR analysis showed formation of the adduct 2-6. The J-Young was then degassed and filled with carbon dioxide. Observation of the ³¹P{¹H} NMR spectrum after addition of the CO₂ gas showed the appearance of a phosphorus resonance at 44.83 ppm, similar to those of the previously reported CO₂ activation products obtained using P₄Bu₃ and B(C₆F₅)₃ (δ(P) = 46.1 ppm) or Al(C₆F₅)₃ (δ(P) = 46.65 ppm).¹⁴,³⁵ As well, the ¹³C{¹H} NMR spectrum displayed a doublet at 161.2 ppm with a coupling constant of 83.9 Hz, corresponding to the carbon of the activated CO₂ moiety bound to phosphorus. A comparison to the boron and aluminum analogues revealed similar chemical shifts of PCO₂ of 161.6 ppm and 162.6 ppm respectively.¹⁴,³⁵ These results pointed to the activation of carbon dioxide in the present system in a parallel fashion to the FLP systems using B(C₆F₅)₃ and Al(C₆F₅)₃. Isolation of the product ³Bu₃P(CO₂)Ga(C₆F₅)₃ (2-11) was achieved by allowing the toluene solution to cool at -35 °C overnight, resulting in the precipitation of the compound in an 80 % yield. Thus, the formation of the product 2-11, which paralleled those obtained using B(C₆F₅)₃ and Al(C₆F₅)₃ based FLPs, demonstrated the analogous behaviour of Ga(C₆F₅)₃ in such systems and showed no deviation from what was observed in those previous experiments.

2.2.4 Activation of Dihydrogen by Ga(C₆F₅)₃ and P₄Bu₃

A deuterated toluene solution of Ga(C₆F₅)₃ and P₄Bu₃ in a 1:1 ratio was transferred to a J-Young NMR tube. Multinuclear NMR analysis indicated the simple adduct formation of compound 2-6. The J-Young tube was then degassed and filled with dihydrogen. A precipitate began to form immediately after addition of the H₂ gas. The solution was then transferred to a vial and the solid was decanted. ³¹P{¹H} NMR analysis of the supernatant showed the presence of leftover free phosphine, indicating that the reaction might have been consuming two equivalents of the Lewis acid. Indeed, upon starting the reaction using a 2:1 ratio of Ga(C₆F₅)₃ to P₄Bu₃, it was noted that there was complete consumption of the phosphine. Trituration of the solid with pentane and subsequent drying in vacuo yielded the H₂ activation product [³Bu₃PH][H(Ga(C₆F₅)₃)₂] (2-12) in a 62 % yield. The ¹H NMR spectrum of the compound in CD₂Cl₂ showed the presence of a
doublet at 5.02 ppm with a coupling constant of 427.3 Hz, indicative of P-H coupling. This was evidence of the formation of a phosphonium species, resulting from dihydrogen splitting. As well, the presence of a broad singlet at 3.70 ppm was indicative of the presence of a hydride species. The $^{31}$P NMR spectrum also displayed a doublet at 60.82 ppm with a coupling constant of 427.3 Hz, providing more supporting evidence of the formation of a phosphonium cation from the activation of H$_2$. Further confirmation of the reaction proceeding in a 2:1 ratio of the Lewis acid to the Lewis base was able to be obtained by Elemental Analysis, as shown in Table 2.1. The EA data obtained was distinct from the calculated percentages of carbon and hydrogen in the theoretical 1:1 product, indicative of the consumption of 2 equivalents of Ga(C$_6$F$_5$)$_3$ to form 2-12, to which the data corresponded.

Table 2.1: Elemental analysis of compound 2-12

<table>
<thead>
<tr>
<th></th>
<th>Observed (2-12)</th>
<th>Calculated for C$<em>{30}$H$</em>{29}$F$_{15}$GaP</th>
<th>Calculated for C$<em>{48}$H$</em>{29}$F$_{30}$Ga$_2$P</th>
</tr>
</thead>
<tbody>
<tr>
<td>C (%)</td>
<td>43.2</td>
<td>46.5</td>
<td>42.8</td>
</tr>
<tr>
<td>H (%)</td>
<td>2.8</td>
<td>3.8</td>
<td>2.2</td>
</tr>
</tbody>
</table>

In comparison to the B(C$_6$F$_5$)$_3$ and Al(C$_6$F$_5$)$_3$ hydrogen activation products, the broad singlet corresponding to the hydride species appeared at 4.18 ppm in the case of boron, and at 4.30 ppm in the case of aluminum, whereas its presence was found at 3.70 ppm in the case of gallium. Keeping in mind that the Al-based product and the Ga-based product were identified to have been incorporating two equivalents of the Lewis acid into the hydride fragment, a direct comparison of their hydride chemical shifts was possible and gave insight to the relative Lewis acidic nature of the Al(C$_6$F$_5$)$_3$ and Ga(C$_6$F$_5$)$_3$ moieties. The more downfield shift of the bridging aluminum hydride by 0.60 ppm was indicative of a more deshielded hydride as compared to the bridging gallium hydride. In turn, this was evidence of a stronger acceptor strength of the Al-based Lewis acid versus that of gallium, supporting previously mentioned theories that Al(C$_6$F$_5$)$_3$ was found to possess a greater Lewis acidity than Ga(C$_6$F$_5$)$_3$. When comparing the dihydrogen activation product obtained to those resulting from the use of B(C$_6$F$_5$)$_3$ or Al(C$_6$F$_5$)$_3$,
it was clear that Ga(C₆F₅)₃ had more similar reactivity to the aluminum-based system than to the boron-based system.

2.2.5 Activation of Diphenyl Disulfide by Ga(C₆F₅)₃ and P'Bu₃

One equivalent of diphenyl disulfide was added to a deuterated toluene solution of Ga(C₆F₅)₃ and P'Bu₃. An oil formed immediately upon mixing of the solution. Analysis of the supernatant solution by NMR studies indicated that the starting reagents were consumed. The solvent was then removed in vacuo and the oil was triturated with pentane. A white solid resulted, which was then dried and a sample was dissolved in CD₂Cl₂ for NMR analysis. The ³¹P{¹H} NMR spectra displayed a resonance at 84.90 ppm, similar to the resonance of the phosphorus in the B(C₆F₅)₃ activated product of [₄Bu₃PSPh][PhSB(C₆F₅)₃]. Observation of the ¹H NMR spectrum revealed the presence of two phenyl moieties: one with resonances at 7.85 ppm, 7.60 ppm and 7.50 ppm corresponding to the cation as previously reported for the activation using the boron-based FLP, while the other phenyl group had resonances at 7.20 ppm and 6.88 ppm corresponding to the anion. These results pointed to the activation of the disulfide by the present gallium-based FLP system in an analogous fashion to the boron-based system. The product [₄Bu₃PSPh][PhSGa(C₆F₅)₃] (2-13) was obtained in a 93 % yield. In comparison, the ¹H NMR spectrum of [₄Bu₃PSPh][PhSB(C₆F₅)₃] displayed its ortho-phenyl resonances of the anion at 7.09 ppm, slightly less downfield than those of the gallium-based activation product at 7.20 ppm. This result compliments the theoretical predictions that Ga(C₆F₅)₃ was found to have a higher acceptor strength than B(C₆F₅)₃, causing the o-phenyl protons of the Ga(C₆F₅)₃SPh anion to be slightly more deshielded than those of the B(C₆F₅)₃SPh anion. Still, the Ga(C₆F₅)₃ FLP system effectuated cleavage of the disulfide bond of PhSSPh in a parallel fashion to the B(C₆F₅)₃ FLP system.
2.3 Conclusions

Classical Lewis adducts were formed and isolated between Ga(C₆F₅)₃ and bulky secondary phosphines, as well as of Ga(C₆F₅)₃ and even more sterically encumbered tertiary phosphines. frustrated Lewis pair chemistry was nonetheless demonstrated by these gallium-based systems. Addition reactions of Ga(C₆F₅)₃ and tertiary phosphines PᵗBu₃, PPh₃ and PCy₃ with the terminal alkyne phenylacetylene were observed, as well as the addition reaction of Ga(C₆F₅)₃ and the secondary phosphine PᵗBu₂H with the internal alkyne diphenylacetylene. The FLP Ga(C₆F₅)₃ and PᵗBu₃ were also shown to achieve small molecule activation of carbon dioxide, dihydrogen, and diphenyl disulfide in an analogous fashion to the B(C₆F₅)₃ and Al(C₆F₅)₃ based systems.

2.4 Experimental

2.4.1 General Considerations

All manipulations were done in an inert, anhydrous atmosphere of N₂ in a glovebox equipped with a -35 °C freezer. All glassware was oven-dried overnight then cooled under vacuum overnight. Solvents (toluene, pentane, benzene, dichloromethane) were dried using an Innovative Technologies solvent purification system, degassed and stored over activated molecular sieves. C₆D₅CD₃, C₆D₅Br, C₆D₆ and CD₂Cl₂ were degassed and stored over activated molecular sieves. All reagents were used as received without further purifications, unless otherwise specified. Ga(C₆F₅)₃•tol was prepared from Zn(C₆F₅)₂•tol and GaCl₃ by a known procedure. GaCl₃ was sublimed prior to use. Zn(C₆F₅)₂•tol was prepared from B(C₆F₅)₃ and ZnEt₂ by a known procedure. Phenylacetylene was distilled from CaH₂ prior to use. H₂ (grade 5.0) was dried through a Nanochem WeldAssure purifier column prior to use. CO₂ (grade 4.0) was passed through a Drierite column prior to use. Elemental analysis was conducted by ANALEST at the University of Toronto using a Perkin-Elmer CHN Analyzer.

NMR spectra were obtained on a Bruker Avance III 400 MHz, a Bruker Ultrashield 400 MHz or an Agilent 600 MHz spectrometer. The ¹H and ¹³C NMR spectra were referenced to residual solvent resonances of CD₂Cl₂ (¹H = 5.32 ppm and ¹³C = 53.84 ppm), C₆D₅CD₃ (¹H = 2.08 ppm and ¹³C = 20.43 ppm), C₆D₅Br (¹H = 6.94 ppm and ¹³C = 122.4 ppm), or C₆D₆ (¹H = 7.16 ppm
and $^{13}$C = 128.06 ppm), while $^{19}$F and $^{31}$P NMR spectra were referenced to an external standard (CFCl$_3$ for $^{19}$F, 85% H$_3$PO$_4$ for $^{31}$P). All NMR experiments were performed at 25 °C. Chemical shifts (δ) are reported in ppm while coupling constants (J) are reported in Hz as absolute values.

2.4.2 Synthesis of Ga(C$_6$F$_3$)$_3$ - Phosphine Adducts

Synthesis of Ph$_2$HP-Ga(C$_6$F$_3$)$_3$ (2-1): Ga(C$_6$F$_3$)$_3$·tol (50 mg, 0.075 mmol, 1.0 eq) was combined with PPh$_2$H (14 mg, 0.075 mmol, 1.0 eq) in 1 mL of toluene. The clear solution was stirred then the solvent was removed in vacuo. The resulting white powder was dissolved in pentane and placed in the -35 °C freezer overnight, which induced crystallization. The solid was decanted then dried in vacuo. Yield: 25 mg, 44 %. $^1$H NMR (400 MHz, CD$_2$Cl$_2$): δ($H$) = 7.54 (m, 2H, p-Ph), 7.41 (m, 8H, m-Ph, o-Ph), 6.63 (d, 1H, $^1$J(HP) = 377.1 Hz, PHPh$_2$); $^{13}$C($^1$H) NMR (126 MHz, CD$_2$Cl$_2$): δ($C$) = 149.0 (dm, $^1$J(CF) = 235.8 Hz, C$_6$F$_3$), 141.9 (dm, $^1$J(CF) = 252.4 Hz, C$_6$F$_3$), 137.3 (dm, $^1$J(CP) = 255.0 Hz, C$_6$F$_3$), 133.7 (d, $^2$J(CP) = 10.5 Hz, o-Ph), 132.7 (d, $^4$J(CP) = 2.7 Hz, p-Ph), 129.9 (d, $^3$J(CP) = 10.9 Hz, m-Ph), 121.7 (d, $^1$J(CP) = 45.9 Hz, i-Ph), 113.5 (m, i-C$_6$F$_3$); $^{19}$F($^1$H) NMR (376 MHz, CD$_2$Cl$_2$): δ($F$) = -121.96 (dd, 6F, $^3$J(FF) = 27.8 Hz, $^3$J(FF) = 11.0 Hz, o-C$_6$F$_3$), -153.64 (t, 3F, $^3$J(FF) = 19.4 Hz, p-C$_6$F$_3$), -161.74 (m, 6F, m-C$_6$F$_3$); $^{31}$P($^1$H) NMR (162 MHz, CD$_2$Cl$_2$): δ(P) = -26.19 (s); $^{31}$P NMR (162 MHz, CD$_2$Cl$_2$): δ(P) = -26.22 (d, $^1$J(HP) = 378.2 Hz).

Synthesis of Cy$_2$HP-Ga(C$_6$F$_3$)$_3$ (2-2): Ga(C$_6$F$_3$)$_3$·tol (50 mg, 0.075 mmol, 1.0 eq) was combined with PCy$_2$H (15 mg, 0.075 mmol, 1.0 eq) in 1 mL of toluene. The clear solution was stirred then the solvent was removed in vacuo. The resulting white powder was dissolved in pentane and placed in the -35 °C freezer overnight, which induced crystallization. The solid was decanted then dried in vacuo. Yield: 58 mg, 53 %. $^1$H NMR (400 MHz, CD$_2$Cl$_2$): δ($H$) = 4.60 (d, 1H, $^1$J(HP) = 362.1 Hz, PHCy$_2$), 2.19 (m, 2H, PCH(C$_3$H$_{10}$)), 1.91 (bm, 2H, C$_6$H$_{11}$), 1.73 (bm, 8H, C$_6$H$_{11}$), 1.26 (bm, 10H, C$_6$H$_{11}$); $^{13}$C($^1$H) NMR (126 MHz, CD$_2$Cl$_2$): δ($C$) = 148.9 (dm, $^1$J(CP) = 238.4 Hz, C$_6$F$_3$), 141.7 (dm, $^1$J(CF) = 251.8 Hz, C$_6$F$_3$), 137.4 (dm, $^1$J(CP) = 255.4 Hz, C$_6$F$_3$), 115.1 (m, i-C$_6$F$_3$), 30.9 (d, $^3$J(CP) = 4.2 Hz, C$_6$H$_{11}$), 30.6 (s, C$_6$H$_{11}$), 30.4 (d, $^1$J(CP) = 21.9 Hz, PCH(C$_3$H$_{10}$)), 27.2 (d, $^2$J(CP) = 12.6 Hz, C$_6$H$_{11}$), 27.1 (d, $^2$J(CP) = 10.8 Hz, C$_6$H$_{11}$), 25.7 (d, $^4$J(CP) = 1.4 Hz, C$_6$H$_{11}$); $^{19}$F($^1$H) NMR (376 MHz, CD$_2$Cl$_2$): δ($F$) = -121.89 (d, 6F, $^3$J(FF) = 26.1 Hz).
occurred immediately upon mixing. The solid was decanted, triturated with pentane thrice, then

Synthesis of Cy$_3$P-Ga(C$_6$F$_3$)$_3$ (2-5): Ga(C$_6$F$_3$)$_3$•tol (50 mg, 0.075 mmol, 1.0 eq) was combined with PCy$_3$ (21 mg, 0.075 mmol, 1.0 eq) in 1 mL of toluene. Formation of a white precipitate occurred immediately upon mixing. The solid was decanted, triturated with pentane thrice, then dried in vacuo. Yield: 35 mg, 54 %. $^1$H NMR (400 MHz, CD$_2$Cl$_2$): $\delta$(H) = 2.32 (m, 3H, PCH(C$_5$H$_{10}$)), 1.89 (bm, 6H, C$_6$H$_{11}$), 1.75 (bm, 6H, C$_6$H$_{11}$), 1.67 (bm, 3H, C$_6$H$_{11}$), 1.44 (m, 6H,
C₆H₁₁), 1.10 (m, 9H, C₆H₁₁); ¹³C{¹H} NMR (126 MHz, CD₂Cl₂): δ(C) = 149.2 (dm, ¹J(CF) = 236.5 Hz, C₆F₅), 141.4 (dm, ¹J(CF) = 250.5 Hz, C₆F₅), 137.3 (dm, ¹J(CF) = 256.9 Hz, C₆F₅), 116.8 (m, t-C₆F₅), 33.4 (d, ¹J(CF) = 17.7 Hz, PCH(C₂H₁₀)), 29.3 (s, C₆H₁₁), 27.7 (s, C₆H₁₁), 26.2 (s, C₆H₁₁); ¹⁹F{¹H} NMR (376 MHz, CD₂Cl₂): δ(F) = -120.28 (d, 6F, ³J(FF) = 26.2 Hz, o-C₆F₅), -154.75 (t, 3F, ³J(FF) = 19.5 Hz, p-C₆F₅), -162.37 (m, 6F, m-C₆F₅); ³¹P{¹H} NMR (162 MHz, CD₂Cl₂): δ(P) = 3.13 (s).

Synthesis of '⁷Bu₃P-Ga(C₆F₅)₃ (2-6): Ga(C₆F₅)₃•tol (50 mg, 0.075 mmol, 1.0 eq) was combined with P'⁷Bu₃ (15 mg, 0.075 mmol, 1.0 eq) in 1 mL of toluene. The clear solution was placed in the -35 °C freezer overnight, which resulted in precipitation of a white solid. The solid was decanted and dried in vacuo. Yield: 38 mg, 66 %. Single crystals suitable for X-ray diffraction were grown by vapour diffusion of a toluene solution of the compound with pentane at -35 °C. ¹H NMR (400 MHz, C₆D₅CD₂): δ(H) = 1.08 (d, 27H, ³J(HP) = 12.4 Hz, '⁷Bu); ¹³C{¹H} NMR (126 MHz, C₆D₅CD₂): δ(C) = 149.6 (dm, ¹J(CF) = 236.0 Hz, C₆F₅), 141.8 (dm, ¹J(CF) = 252.6 Hz, C₆F₅), 137.5 (dm, ¹J(CF) = 251.7 Hz, C₆F₅), 40.1 (bs, PCMe₃), 31.4 (bs, PCMe₃), resonances of gallium-bound carbon atoms were not observed; ¹⁹F{¹H} NMR (376 MHz, C₆D₅CD₂): δ(F) = -116.39 (s, 6F, o-C₆F₅), -152.98 (s, 3F, p-C₆F₅), -161.60 (s, 6F, m-C₆F₅); ³¹P{¹H} NMR (162 MHz, C₆D₅CD₂): δ(P) = 58.64 (s).

2.4.3 Reactions of Ga(C₆F₅)₃ and Phosphines with Alkynes

Reaction of Ga(C₆F₅)₃, '⁷Bu₃P and PhCCH: Ga(C₆F₅)₃•tol (33 mg, 0.05 mmol, 1.0 eq) was combined with P'⁷Bu₃ (10 mg, 0.05 mmol, 1.0 eq) and phenylacetylene (5 mg, 0.05 mmol, 1.0 eq) in 1 mL of benzene. Formation of an oil occurred upon mixing. The solvent was removed in vacuo and the oil was allowed to stir in pentane overnight. The resulting fine white powder was decanted and dried in vacuo. Analysis of the solid by NMR spectroscopy determined that an addition product was formed, however complete isolation from hydrolysis side-products was not achieved. Single crystals suitable for X-ray diffraction were grown by vapour diffusion of a toluene solution of the solid with pentane at -35 °C. Addition product '⁷Bu₃P(Ph)C≡C(H)Ga(C₆F₅)₃ (2-7): ¹H NMR (400 MHz, C₆D₅Br): δ(H) = 8.57 (d, 1H, ³J(HP) = 29.7 Hz, C≡C-H), 6.95 (d, 2H, ³J(HP) = 7.8 Hz, o-PhC≡C), 6.88 (t, 1H, ³J(HP) = 7.3 Hz, p-
PhC=C), 6.80 (t, 2H, $^3J_{(HH)} = 7.5$ Hz, m-PhC=C), 1.12 (d, 27H, $^3J_{(HP)} = 13.5$ Hz, PCMe$_3$); $^{13}$C$^1$H NMR (126 MHz, CD$_2$Cl$_2$): $\delta_{(C)} = 181.9$ (m, C=C-Ga), 149.1 (dm, $^1J_{(CF)} = 232.2$ Hz, C$_6$F$_3$), 141.0 (d, $^2J_{(CP)} = 16.1$ Hz, i-PhC), 140.1 (dm, $^1J_{(CF)} = 242.2$ Hz, C$_6$F$_5$), 136.7 (dm, $^1J_{(CF)} = 256.6$ Hz, C$_6$F$_3$), 41.9 (d, $^1J_{(CP)} = 25.3$ Hz, PCMe$_3$), 31.4 (s, PCMe$_3$), resonances of P-C=C and phenyl-carbons and pertaining to the addition product were indiscernible, and resonances of gallium-bound carbon atoms were not observed; $^{19}$F$^1$H NMR (376 MHz, C$_6$D$_2$Br): $\delta_{(F)} = -121.52$ (dd, 6F, $^3J_{(FF)} = 29.4$ Hz, $^3J_{(FF)} = 10.6$ Hz, o-C$_6$F$_5$), $-157.17$ (t, 3F, $^3J_{(FF)} = 20.5$ Hz, p-C$_6$F$_5$), $-162.36$ (m, 6F, m-C$_6$F$_3$); $^{31}$P$^1$H NMR (162 MHz, C$_6$D$_2$Br): $\delta_{(P)} = 40.67$ (s).

**Reaction of Ga(C$_6$F$_3$)$_3$, Ph$_3$P and PhCCH:** Ga(C$_6$F$_3$)$_3$*tol (33 mg, 0.05 mmol, 1.0 eq) was combined with PPh$_3$ (13 mg, 0.05 mmol, 1.0 eq) and phenylacetylene (5 mg, 0.05 mmol, 1.0 eq) in 1 mL of toluene. Formation of a white precipitate determined to be the simple adduct of Ph$_3$P-Ga(C$_6$F$_3$)$_3$ occurred immediately upon mixing. The supernatant was separated and the solvent was removed from the latter in vacuo. The resulting colourless oil was triturated thrice with pentane, inducing the appearance of a white powder. Analysis of the solid by NMR spectroscopy determined that an addition product was formed, however complete isolation from hydrolysis side-products was not achieved. **Addition product Ph$_3$P(Ph)=C(H)Ga(C$_6$F$_3$)$_3$ (2-8):** $^1$H NMR (400 MHz, CD$_2$Cl$_2$): $\delta_{(H)} = 8.40$ (d, 1H, $^3J_{(HP)} = 37.7$ Hz, C=C-H), 7.77 (m, 3H, PPh), 7.59 (m, 6H, PPh), 7.44 (m, 6H, PPh), 7.02 (t, 1H, $^3J_{(HH)} = 7.5$ Hz, p-PhC=C), 6.85 (t, 2H, $^3J_{(HH)} = 7.7$ Hz, m-PhC=C), 6.72 (d, 2H, $^3J_{(HH)} = 8.1$ Hz, o-PhC=C); $^{13}$C$^1$H NMR (126 MHz, CD$_2$Cl$_2$): $\delta_{(C)} = 148.9$ (dm, $^1J_{(CF)} = 240.9$ Hz, C$_6$F$_3$), 140.1 (dm, $^1J_{(CF)} = 252.2$ Hz, C$_6$F$_5$), 136.5 (dm, $^1J_{(CF)} = 252.2$ Hz, C$_6$F$_5$), 136.4 (d, $^2J_{(CP)} = 18.5$ Hz, o-PhP), 135.0 (d, $^4J_{(CP)} = 3.0$ Hz, p-PhP), 134.9 (d, $^3J_{(CP)} = 9.6$ Hz, m-PhP), 130.2 (d, $^2J_{(CP)} = 12.4$ Hz, i-PhC), 130.1 (d, $^3J_{(CP)} = 4.2$ Hz, o-PhC), 128.5 (d, $^4J_{(CP)} = 2.3$ Hz, m-PhC), 128.1 (d, $^5J_{(CP)} = 1.8$ Hz, p-PhC), 119.6 (d, $^1J_{(CP)} = 84.5$ Hz, P=C=C), resonances of gallium-bound and phosphorus-bound carbon atoms were not observed; $^{19}$F$^1$H NMR (376 MHz, CD$_2$Cl$_2$): $\delta_{(F)} = -122.55$ (dd, 6F, $^3J_{(FF)} = 29.3$ Hz, $^3J_{(FF)} = 10.4$ Hz, o-C$_6$F$_5$), $-158.84$ (t, 3F, $^3J_{(FF)} = 19.5$ Hz, p-C$_6$F$_5$), $-164.20$ (m, 6F, m-C$_6$F$_3$); $^{31}$P$^1$H NMR (162 MHz, CD$_2$Cl$_2$): $\delta_{(P)} = 21.79$ (s).
Reaction of Ga(C₆F₅)₃, Cy₃P and PhCCH: Ga(C₆F₅)₃tol (33 mg, 0.05 mmol, 1.0 eq) was combined with PCy₃ (14 mg, 0.05 mmol, 1.0 eq) and phenylacetylene (5 mg, 0.05 mmol, 1.0 eq) in 1 mL of toluene. Formation of a white precipitate determined to be the simple adduct of Cy₃P-Ga(C₆F₅)₃ occurred immediately upon mixing. The supernatant was separated and the solvent was removed from the latter in vacuo. The resulting colourless oil was triturated thrice with pentane, inducing the appearance of a white powder. Analysis of the solid by NMR spectroscopy determined that an addition product was formed, however complete isolation from hydrolysis side-products was not achieved. Addition product Cy₃P(Ph)C=C(H)Ga(C₆F₅)₃ (2-9): ¹H NMR (400 MHz, CD₂Cl₂): δ(H) = 8.17 (d, 1H, ¹J(HP) = 31.6 Hz, C=C-H), 7.05 (m, 5H, PhC=C), resonances of cyclohexyl-protons pertaining to the addition product were indiscernible; ¹³C{¹H} NMR (126 MHz, CD₂Cl₂): δ(C) = 149.0 (dm, ¹J(CF) = 230.2 Hz, C₆F₅), 140.1 (dm, ¹J(CF) = 250.5 Hz, C₆F₅), 136.7 (dm, ¹J(CF) = 256.8 Hz, C₆F₅), 137.8 (d, ²J(CP) = 15.7 Hz, i-PhC), 129.7 (d, ¹J(CP) = 46.1 Hz, P-C=C), 129.6 (d, ³J(CP) = 3.7 Hz, o-PhC), 128.3 (d, ⁴J(CP) = 1.9 Hz, m-PhC), 128.2 (d, ⁵J(CP) = 1.1 Hz, p-PhC), resonances of cyclohexyl-carbons pertaining to the addition product were indiscernible, and resonances of gallium-bound carbon atoms were not observed; ¹⁹F{¹H} NMR (376 MHz, CD₂Cl₂): δ(F) = −122.5 (dd, 6F, ³J(FF) = 28.9 Hz, ²J(FF) = 10.5 Hz, o-C₆F₅), −158.95 (t, 3F, ³J(FF) = 19.4 Hz, p-C₆F₅), −164.24 (m, 6F, m-C₆F₅); ³¹P{¹H} NMR (162 MHz, CD₂Cl₂): δ(P) = 21.22 (s).

Reaction of Ga(C₆F₅)₃, tBu₂HP and PhCCCH: Ga(C₆F₅)₃tol (33 mg, 0.05 mmol, 1.0 eq) was combined with P'tBu₂H (7 mg, 0.05 mmol, 1.0 eq) and diphenylacetylene (9 mg, 0.05 mmol, 1.0 eq) in 1 mL of bromobenzene. Analysis of the crude reaction mixture by NMR spectroscopy determined that an addition product was formed, however complete isolation from hydrolysis side-products was not achieved. Addition product tBu₂HP(Ph)C=C(H)Ga(C₆F₅)₃ (2-10): ¹H NMR (400 MHz, C₆D₅Br): δ(H) = 4.62 (d, 1H, ¹J(HP) = 356.7 Hz, PH₂Bu₂), 1.04 (d, 18H, ³J(HP) = 15.2 Hz, PCH₃), resonances of phenyl-protons pertaining to the addition product were indiscernible; ¹⁹F{¹H} NMR (376 MHz, C₆D₅Br): δ(F) = −119.8 (d, 6F, ³J(FF) = 23.2 Hz, o-C₆F₅), −152.32 (t, 3F, ³J(FF) = 20.5 Hz, p-C₆F₅), −159.88 (m, 6F, m-C₆F₅); ³¹P{¹H} NMR (162 MHz, C₆D₅Br): δ(P) = 18.47 (s); ³¹P NMR (162 MHz, C₆D₅Br): δ(P) = 18.44 (d, ¹J(HP) = 360.4 Hz).
2.4.4 Small Molecule Activation Reactions Using Ga(C₆F₅)₃ and P³Bu₃

Synthesis of [¹Bu₃P(CO₂)Ga(C₆F₅)₃] (2-11): Ga(C₆F₅)₃\*tol (33 mg, 0.05 mmol, 1.0 eq) was combined with P³Bu₃ (10 mg, 0.05 mmol, 1.0 eq) in 1 mL of toluene. The reaction mixture was transferred to a J-Young NMR tube. The J-Young NMR tube was degassed and filled with CO₂ to a pressure of approximately 4 atm. After 30 minutes, the clear solution was transferred to a vial and placed in the -35 °C freezer overnight, which resulted in precipitation of a white powder. The solid was decanted and dried in vacuo. Yield: 33 mg, 80 %. \(^1\)H NMR (400 MHz, CD₂Cl₂): \(\delta(H) = 1.62\) (d, 27H, \(^3\)J(HP) = 14.3 Hz, \(^1\)Bu); \(^1\)³C\(^1\)\(^1\)H} NMR (126 MHz, CD₂Cl₂): \(\delta(C) = 161.17\) (d, \(^1\)J(CF) = 236.8 Hz, C₆F₅), 141.2 (d, \(^1\)J(CF) = 254.7 Hz, C₆F₅), 137.0 (d, \(^1\)J(CF) = 254.7 Hz, C₆F₅), 40.7 (d, \(^1\)J(CP) = 19.5 Hz, PCMe₃), 30.6 (s, PCMe₃), resonances of gallium-bound carbon atoms were not observed; \(^1\)⁹F\(^1\)\(^1\)H} NMR (376 MHz, CD₂Cl₂): \(\delta(F) = -124.20\) (dd, 6F, \(^3\)J(FF) = 27.5 Hz, \(^3\)J(FF) = 11.0 Hz, \(o\)-C₆F₅), −155.98 (t, 3F, \(^3\)J(FF) = 19.5 Hz, \(p\)-C₆F₅), −163.11 (m, 6F, \(m\)-C₆F₅); \(^3\)¹P\(^1\)\(^1\)H} NMR (162 MHz, CD₂Cl₂): \(\delta(P) = 44.83\) (s).

Synthesis of [¹Bu₃PH][H(Ga(C₆F₅)₃)] (2-12): Ga(C₆F₅)₃\*tol (33 mg, 0.05 mmol, 2.0 eq) was combined with P³Bu₃ (5 mg, 0.025 mmol, 1.0 eq) in 1 mL of toluene. The reaction mixture was transferred to a J-Young NMR tube. The J-Young NMR tube was degassed and filled with H₂ to a pressure of approximately 4 atm. A white solid begins to precipitate immediately. The solution was then transferred to a vial, decanted and dried in vacuo. Yield: 21 mg, 62 %. \(^1\)H NMR (400 MHz, CD₂Cl₂): \(\delta(H) = 5.02\) (d, 1H, \(^1\)J(HP) = 427.3 Hz, PH), 3.70 (bs, 1H, Ga-H-Ga), 1.65 (d, 27H, \(^3\)J(HP) = 15.8 Hz, \(^1\)Bu); \(^1\)³C\(^1\)\(^1\)H} NMR (126 MHz, CD₂Cl₂): \(\delta(C) = 149.1\) (d, \(^1\)J(CF) = 241.6 Hz, C₆F₅), 141.4 (d, \(^1\)J(CF) = 251.8 Hz, C₆F₅), 136.9 (d, \(^1\)J(CF) = 251.8 Hz, C₆F₅), 38.2 (d, \(^1\)J(CP) = 26.7 Hz, PCMe₃), 30.4 (s, PCMe₃), resonances of gallium-bound carbon atoms were not observed; \(^1\)⁹F\(^1\)\(^1\)H} NMR (470 MHz, CD₂Cl₂): \(\delta(F) = -122.86\) (d, 12F, \(^3\)J(FF) = 20.5 Hz, \(o\)-C₆F₅), −155.91 (t, 6F, \(^3\)J(FF) = 19.5 Hz, \(p\)-C₆F₅), −163.66 (m, 12F, \(m\)-C₆F₅); \(^3\)¹P\(^1\)\(^1\)H} NMR (162 MHz, CD₂Cl₂): \(\delta(P) = 60.77\) (s). \(^3\)¹P\(^1\)\(^1\)H} NMR (162 MHz, CD₂Cl₂): \(\delta(P) = 60.82\) (d, \(^1\)J(HP) = 427.3 Hz).

Elemental analysis for C₄₉H₂₉F₃₀Ga₂P: calcd.: C 42.8, H 2.2; found: C 43.2, H 2.8.
Synthesis of \([tBu_3PSPh][PhSGa(C_6F_5)_3]\) (2-13): Ga(C_6F_5)_3•tol (50 mg, 0.075 mmol, 1.0 eq) was combined with P^3Bu_3 (15 mg, 0.075 mmol, 1.0 eq) and PhSSPh (16 mg, 0.075 mmol, 1.0 eq) in 1 mL of toluene. Formation of an oil occurred immediately upon mixing. The solvent was removed in vacuo, and the oil was triturated thrice with pentane, resulting in the formation of a white powder. The solid was dried in vacuo. Yield: 69 mg, 93 %.

**^1H NMR** (400 MHz, CD_2Cl_2): \(\delta(H) = 7.85 \) (m, 2H, o-PhSP), 7.60 (m, 1H, p-PhSP), 7.50 (m, 2H, m-PhSP), 7.20 (m, 2H, o-PhSGa), 6.88 (m, 3H, m-PhSGa, p-PhSGa), 1.67 (d, 27H, \(^3J(HP) = 15.9\) Hz, tBu); **^13C\{^1H\} NMR** (126 MHz, CD_2Cl_2): \(\delta(C) = 149.0 \) (d, \(^1J(CF) = 236.7\) Hz, C_6F_5), 140.5 (d, \(^1J(CF) = 251.5\) Hz, C_6F_5), 138.2 (s, PSPh), 136.7 (d, \(^1J(CF) = 250.8\) Hz, C_6F_5), 134.6 (s, GaSPh), 132.9 (s, PSPh), 131.1 (s, PSPh), 127.7 (s, GaSPh), 121.7 (s, GaSPh), 46.3 (d, \(^1J(CP) = 15.0\) Hz, PCMe_3), 30.8 (s, PCMe_3), resonances of gallium-bound carbon atoms were not observed; **^19F\{^1H\} NMR** (376 MHz, C_6D_5Br): \(\delta(F) = -121.21 \) (dd, 6F, \(^3J(FF) = 30.5\) Hz, \(^3J(FF) = 10.7\) Hz, o-C_6F_5), -122.43 (dd, 6F, \(^3J(FF) = 28.7\) Hz, \(^3J(FF) = 11.5\) Hz, o-C_6F_5), -156.43 (t, 3F, \(^3J(FF) = 20.3\) Hz, p-C_6F_5), -157.25 (t, 3F, \(^3J(FF) = 20.2\) Hz, p-C_6F_5), -162.41 (m, 6F, m-C_6F_5), -162.72 (m, 6F, m-C_6F_5); **^31P\{^1H\} NMR** (162 MHz, CD_2Cl_2): \(\delta(P) = 84.90\) (s).

### 2.4.5 Collection, Reduction, Solution, and Refinement of X-Ray Data

Single crystals were coated with Paratone-N oil and mounted under a cold nitrogen stream. Data sets were collected on a Bruker Kappa Apex II CCD diffractometer using a graphite monochromater with MoK\(\alpha\) radiation (\(\lambda = 0.71073\) Å). Data reduction was performed using the Bruker SMART software package. Data sets were corrected for absorption effects using SADABS. The structures were solved by direct methods using XS and refined by full-matrix least-squares on F2 using XL as implemented in the SHELXTL suite of programs. All nonhydrogen atoms were refined anisotropically unless noted otherwise. Hydrogen atoms were placed in calculated positions using an appropriate riding model and coupled isotropic temperature factors.
### Table 2.2: Crystallographic data for compounds 2-6 and 2-7

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3 Exploration of Ga(C$_6$F$_5$)$_3$-Arsine Adducts as Precursors for GaAs

3.1 Introduction

Gallium arsenide (GaAs) is a semiconductor of great technological importance. Because of its capacity to convert electrical signals into light as well as its high operation speed and resistance to radiation, GaAs has been unequalled in some of its applications in optoelectronics. It is used in LEDs, computers, solar cells, alloys, DVDs, aerospace and telecommunication, thus playing an essential role in the electronics sector.

The current bulk preparations of gallium arsenide in industry are problematic due to the highly toxic nature of the arsenic compounds used. In the production of GaAs single crystals, high purity gallium and arsenic are combined and treated according to either the liquid encapsulated Czochralski (LEC) growth method, the vertical gradient freeze (VGF) process, or the Bridgman-Stockbarger technique, all of which use high temperatures to melt arsenic and gallium together and induce the formation of gallium arsenide. Standard methods to produce GaAs thin films are molecular beam epitaxy (MBE), also requiring ultra pure arsenic and gallium, and the more common metalorganic chemical vapour deposition (MOCVD) process, which utilizes the vapours of pyrophoric trimethylgallium, Ga(CH$_3$)$_3$, and the highly lethal arsine gas, AsH$_3$. It is thus evident that finding an alternative synthesis of GaAs employing less harmful reagents with a reduced environmental impact is desirable.

Upon observing the facile adduct formation of Ga(C$_6$F$_5$)$_3$ with secondary and tertiary phosphines, as shown in Chapter 2, it was proposed that a gallium-arsenic bond could be achieved via the analogous adduct formation between Ga(C$_6$F$_5$)$_3$ and organoarsines. Subsequent heating of such GaAs adducts could then induce the loss of the pentafluorophenyl groups of gallium and the organic groups bound to arsenic, producing the desired gallium arsenide, as shown in Scheme 3.1. Although elevated temperatures could still be required to force the ejection of the organic groups of the gallium-arsenic adduct, the starting material (non-pyrophoric Ga(C$_6$F$_5$)$_3$ and less toxic organoarsines) are much more favourable than the extremely harmful AsH$_3$ and Ga(CH$_3$)$_3$ commonly used.
3.2 Chemistry of Ga(C₆F₅)₃ with a Primary Arsine

3.2.1 Introduction

Analogous to the Ga(C₆F₅)₃ and phosphine adducts discussed in the previous chapter, formation of a Ga(C₆F₅)₃ and primary arsine adduct was tested. Such a compound could potentially serve as a precursor to the formation of gallium arsenide in a safer manner versus previously mentioned methods. With this objective in mind, tert-butylarsine was chosen to react with Ga(C₆F₅)₃ under the supposition that after adduct formation, the subsequent loss of a single alkyl group along with three pentafluorophenyl groups would be facile upon heating.

3.2.2 Results and Discussion

As'BuCl₂ was reduced to tert-butylarsine using one equivalent of lithium aluminum hydride (LiAlH₄) in a pentane-ether solution. Lithium aluminum hydride was then removed by filtration and the colourless solution was placed under vacuum briefly to allow the ether portion to evaporate in order to avoid coordination to Ga(C₆F₅)₃ in the following step. The complete isolation of tert-butylarsine was avoided because of the highly toxic and volatile nature of the compound. Immediately after, one equivalent of Ga(C₆F₅)₃ dissolved in toluene was added. The clear pentane-toluene solution was then placed in the freezer for ten minutes, resulting in the formation of a black precipitate.
Analysis of the black precipitate was not achieved by NMR studies due to the insolubility of the compound in common solvents. Such insolubility as well as the appearance of the solid was consistent with the formation of gallium arsenide.

A sample of the supernatant was taken without further treatment for $^{19}$F NMR analysis. The $^{19}$F NMR spectrum exhibited three sets of resonances corresponding to three compounds containing pentafluorophenyl groups. The ortho-, para- and meta-fluorine signals were observed at $\delta_{(o-F)} = -123.30, -123.64, -123.88$; $\delta_{(p-F)} = -152.81, -154.04, -154.65$; and $\delta_{(m-F)} = -162.12, -162.50, -162.88$ ppm in a ratio of 2:6:1 for each group of signals, while the ortho:para:meta ratio was 2:1:2. The chemical shifts observed were different than those of free Ga(C$_6$F$_5$)$_3$ and demonstrate a decrease in the separation of the para-meta signals, pointing to the formation of tetravalent gallium. A small amount of the Ga(C$_6$F$_5$)$_3$ - arsine adduct was thus suspected to be present in solution. However, the 2:6:1 ratio between these signals indicated the presence of three separate compounds rather than C$_6$F$_5$ moieties within the same compound rendered asymmetric by inhibited rotation of the gallium-arsenic bond due to the steric bulk of the tert-butyl group of the arsine. Since the chemical shifts in the $^{19}$F NMR spectrum were also similar to those of the Ga(C$_6$F$_5$)$_3$ – phosphine adducts, it was thus hypothesized that the reduction of As$^t$BuCl$_2$ was incomplete and that consequently there existed the following three Ga(C$_6$F$_5$)$_3$ - arsine species in solution: (C$_6$F$_5$)$_3$Ga-AsH$_2^t$Bu, (C$_6$F$_5$)$_3$Ga-AsHCl$^t$Bu, (C$_6$F$_5$)$_3$Ga-AsCl$_2^t$Bu.

Despite the formation of a black insoluble precipitate believed to be gallium arsenide, there was no indication in the $^{19}$F NMR spectrum of the supernatant of pentafluorobenzene. In order to form GaAs from the (C$_6$F$_5$)$_3$Ga-AsH$_2^t$Bu adduct, it would be expected that two pentafluorophenyl groups pendant on the gallium centre combine with the two accessible hydrogens of the arsine to form two equivalents of pentafluorobenzene. It would then be feasible that the third C$_6$F$_5$ group attack a hydrogen of the tert-butyl group, releasing a third equivalent of pentafluorobenzene as well as one equivalent of isobutylene, thereby leaving gallium arsenide to precipitate. Because of the low boiling point of isobutylene and the fact that a mixture of protic solvents was present in the sample used for NMR study, it was not entirely surprising that isobutylene was not observed in the $^1$H NMR spectrum. However, the absence of pentafluorobenzene in the $^{19}$F NMR spectrum was perplexing. Evidently, more investigation is necessary to better understand the reactivity of this Ga(C$_6$F$_5$)$_3$ - arsine adduct. X-ray powder diffraction analysis could aid in identifying gallium arsenide in the black precipitate. It is
apparent nonetheless, that the combination of a primary arsine with Ga(C₆F₅)₃ resulted in a reactive system.

### 3.3  Chemistry of Ga(C₆F₅)₃ with a Tertiary Arsine

#### 3.3.1  Introduction

After observing the reactivity of the Ga(C₆F₅)₃ and primary arsine system, it was proposed to investigate a less reactive system in order to better study and characterize gallium-arsenic adducts. Triphenylarsine was selected because of its electron withdrawing phenyl groups, which reduce the basicity of the arsenic centre and therefore are expected to slow down reactivity. The use of this readily available tertiary arsine also eliminates the necessity of executing a reduction reaction, as in the case of As'BuCl₂, which is not only hazardous but also inefficient. It should also be noted that triphenylarsine is a non-volatile solid, making it less toxic and easier to handle than other arsines.

#### 3.3.2  Results and Discussion

Ga(C₆F₅)₃ was combined with triphenylarsine in toluene, resulting in the immediate precipitation of a white solid. A sample was dissolved in CD₂Cl₂ for NMR analysis. The ¹H NMR spectrum displayed aromatic signals at 7.09, 7.32 and 7.48 ppm in a 2:2:1 ratio, corresponding to the ortho-, meta-, and para- protons, respectively, of the phenyl groups pendant on the arsenic centre, which were different than the resonances observed for free triphenylarsine. In the ¹⁹F NMR spectrum, three fluorine signals with a ratio of 2:1:2 at -122.99, -153.38 and -161.89 ppm were assigned to the ortho-, para-, and meta- fluorine atoms, respectively, of the pentafluorophenyl groups of the gallium centre. The reduction in the separation of the chemical shift between the meta- and para- fluorine resonances versus the spectrum of free Ga(C₆F₅)₃ indicated that the gallium centre became tetravalent. Resonances in the ¹³C NMR spectrum were also consistent with the formation of the (C₆F₅)₃Ga-AsPh₃ adduct (3-1), as was X-ray diffraction analysis of single crystals of the product, as shown in Figure 3.1. The bond length of Ga-As in 3-1 had a value of 2.5739(7) Å, which was longer, as expected for a dative bond, than the
reported value of 2.448 Å for the Ga-As bond in gallium arsenide.\textsuperscript{57} It was speculated that the steric congestion about the gallium and arsenic centres also resulted in the longer Ga-As bond observed in compound 3-1.

**Figure 3.1:** POV-Ray depiction of the molecular structure of 3-1. C: black, As: yellow, Ga: purple, F: green. H atoms omitted for clarity.

### 3.3.3 Thermogravimetric Analysis Results and Discussion

Thermogravimetric Analysis (TGA) was performed on a sample of 3-1 in order to probe the feasibility of obtaining gallium arsenide from the adduct at elevated temperatures. The data recorded is presented in **Figure 3.2**.
Figure 3.2: TGA of the adduct 3-1. The primary axis in green shows the change in weight (%) of the sample with respect to the temperature (°C). The secondary axis in blue depicts the variation in heat flow (W/g).

A small initial decrease in sample weight % was attributed to the loss of moisture which would have accumulated during preparation of the TGA instrument. Upon heating between roughly 160 °C and 270 °C it was observed that the sample released heat and liberated a weight percentage of about 54 %. Following this, there was a small dip in heat flow, indicating that the sample absorbed thermal energy around 270 °C, then the sample released heat once more and liberated a weight percentage of about 35 %. The loss of the three pentafluorophenyl groups and triphenylarsine as a whole were associated with the aforementioned weight losses respectively. Stabilization of the sample weight percentage at elevated temperatures to about 8 % corresponded to the weight % of the element gallium in the initial sample, leading to the conclusion that elemental gallium was all that remained. In the event that gallium arsenide would have been formed, the final sample weight percentage would have been about 16 %. Therefore, it was concluded that the gallium-arsenic bond was not strong enough to withstand elevated
temperatures and produce GaAs from this triphenylarsine adduct. A more basic arsine would thus be worthwhile to investigate in an attempt to strengthen the gallium-arsenic interaction.

3.4 Conclusions

Adduct formation between Ga(C₆F₅)₃ and a primary arsine as well as with a tertiary arsine were tested in the interest of producing gallium arsenide. Tert-butylarsine proved challenging to handle because of its high toxicity, the reduction step from As'BuCl₂, and its high reactivity towards Ga(C₆F₅)₃, producing an insoluble black precipitate believed to be GaAs. In turn, triphenylarsine was easier to handle and formed a white precipitate with Ga(C₆F₅)₃ in good yield, evidenced to be the simple adduct formed between these two compounds. Thermogravimetric analysis of this compound resulted in the liberation of the substituents on gallium as well as the triphenylarsine moiety, leaving only elemental gallium at elevated temperatures.

3.5 Experimental

3.5.1 General Considerations

All manipulations were done in an inert, anhydrous atmosphere of N₂ in a glovebox equipped with a -35 °C freezer. All glassware was oven-dried overnight then cooled under vacuum overnight. Solvents (toluene, pentane, diethyl ether, dichloromethane) were dried using an Innovative Technologies solvent purification system, degassed and stored over activated molecular sieves. CD₂Cl₂ degassed and stored over activated molecular sieves. 'BuAsCl₂ was provided by Digital Specialty Chemicals. All reagents were used as received without further purifications, unless otherwise specified. Ga(C₆F₅)₃·tol was prepared from Zn(C₆F₅)₂·tol and GaCl₃ by a known procedure.¹⁴ GaCl₃ was sublimed prior to use. Zn(C₆F₅)₂·tol was prepared from B(C₆F₅)₃ and ZnEt₂ by a known procedure.¹⁴ Elemental analysis was conducted by ANALEST at the University of Toronto using a Perkin-Elmer CHN Analyzer. Thermogravimetric analysis was performed on a TA Instruments SDT Q600 using aluminum sample pans under a stream of N₂.
NMR spectra were obtained on a Bruker Avance III 400 MHz or a Bruker Ultrashield 400 MHz spectrometer. The $^1$H and $^{13}$C NMR spectra were referenced to residual solvent resonances of CD$_2$Cl$_2$ ($^1$H = 5.32 ppm and $^{13}$C = 53.84 ppm), while $^{19}$F NMR spectra were referenced to an external standard (CFCl$_3$). All NMR experiments were performed at 25 °C. Chemical shifts (δ) are reported in ppm while coupling constants (J) are reported in Hz as absolute values.

### 3.5.2 Adduct Formation between Ga(C$_6$F$_5$)$_3$ and a Primary Arsine

**In situ preparation of tert-butylarsine:** t-BuAsCl$_2$ (10 mg, 0.05 mmol, 1.0 eq) was placed in 2 mL of a 9:1 pentane : diethyl ether mixture. LiAlH$_4$ (2 mg, 0.05 mmol, 1.0 eq) was added and the solution was mixed for 3 minutes, after which LiAlH$_4$ was removed by gravity filtration. The clear solution was placed under vacuum for under one minute and capped.

**Reaction of the tert-butylarsine solution with Ga(C$_6$F$_5$)$_3$:** Ga(C$_6$F$_5$)$_3$•tol (33 mg, 0.05 mmol, 1.0 eq) was dissolved in 1 mL of toluene and combined with the t-BuAsH$_2$ pentane solution. The transparent mixture was placed in the freezer at -35 °C for 10 minutes, inducing the precipitation of a black solid. The precipitate was decanted and unsuccessfully dissolved in CD$_2$Cl$_2$. A sample of the supernatant was taken for NMR analysis after cooling of the solution at -35 °C for one week. $^{19}$F{$^1$H} NMR (376 MHz, no solvent): three species were found, believed to be (C$_6$F$_5$)$_3$Ga-AsCl$_2$t-Bu, (C$_6$F$_5$)$_3$Ga-AsHCl$t$Bu, (C$_6$F$_5$)$_3$Ga-AsH$_2$t-Bu; δ(F) = -123.30 (dd, 6F, $^3J$(_{FF}) = 25.2 Hz, $^3J$(_{FF}) = 11.1 Hz, o-C$_6$F$_5$), -152.81 (t, 3F, $^3J$(_{FF}) = 18.9 Hz, p-C$_6$F$_5$), -162.12 (m, 6F, m-C$_6$F$_5$); δ(F) = -123.64 (dd, 6F, $^3J$(_{FF}) = 26.8 Hz, $^3J$(_{FF}) = 11.9 Hz, o-C$_6$F$_5$), -154.04 (t, 3F, $^3J$(_{FF}) = 18.9 Hz, p-C$_6$F$_5$), -162.50 (m, 6F, m-C$_6$F$_5$); δ(F) = -123.88 (dd, 6F, $^3J$(_{FF}) = 26.8 Hz, $^3J$(_{FF}) = 11.9 Hz, o-C$_6$F$_5$), -154.65 (t, 3F, $^3J$(_{FF}) = 19.0 Hz, p-C$_6$F$_5$), -162.88 (m, 6F, m-C$_6$F$_5$).
3.5.3 Adduct Formation between Ga(C₆F₅)₃ and a Tertiary Arsine

**Synthesis of (C₆F₅)₃Ga-AsPh₃ (3-1):** Ga(C₆F₅)₃•tol (33 mg, 0.05 mmol, 1.0 eq) was combined with AsPh₃ (15 mg, 0.05 mmol, 1.0 eq) in 1 mL of toluene. A white precipitate was formed immediately, decanted and dried in vacuo. Yield: 34 mg, 78 %. Single crystals suitable for X-ray diffraction were grown by vapour diffusion of a solution of the compound in dichloromethane with pentane at -35 °C. ¹H NMR (400 MHz, CD₂Cl₂) \( \delta = 7.48 \) (t, 3H, \( J_{HH} = 7.5 \) Hz, p-Ph), 7.32 (t, 6H, \( J_{HH} = 7.6 \) Hz, m-Ph), 7.09 (d, 6H, \( J_{HH} = 7.5 \) Hz, o-Ph); ¹³C{¹H} NMR (100 MHz, CD₂Cl₂) \( \delta(C) = 148.9 \) (d, \( J_{CF} = 234.3 \) Hz, C₆F₅), 141.9 (d, \( J_{CF} = 255.5 \) Hz, C₆F₅), 137.3 (d, \( J_{CF} = 255.5 \) Hz, C₆F₅), 133.1 (s, o-Ph), 131.5 (s, p-Ph), 129.8 (s, m-Ph), 128.4 (s, i-Ph), resonances of gallium-bound carbon atoms were not observed; ¹⁹F{¹H} NMR (376.4 MHz, CD₂Cl₂) \( \delta(F) = -121.99 \) (d, 6F, \( J_{FF} = 19.5 \) Hz, o-C₆F₅), -153.38 (t, 3F, \( J_{FF} = 19.2 \) Hz, p-C₆F₅), -161.89 (m, 6F, m-C₆F₅); **Elemental analysis** for C₃₆H₁₅F₁₅GaAs: calcd.: C 49.3, H 1.7; found: C 48.9, H 1.8.

3.5.4 Precautions Taken while Handling Arsenic Containing Compounds

Special care was taken during the handling and disposal of compounds containing arsenic. An extra pair of nitrile gloves were used in tandem with the existing gloves of the glovebox. A Nalgene bottle was used to collect waste contaminated with arsenic such as pipettes, Kimwipes, nitrile gloves and empty vials, which was then sealed and kept segregated from other waste until proper disposal. Solid and liquid arsenic waste were individually sealed and placed in a Nalgene bottle to transport into a fumehood where it was carefully opened and diluted in a solution of 50 % bleach, 50 % water then poured into a glass waste bottle clearly labelled as arsenic waste with the contents listed. NMR tubes were rinsed thrice with the aqueous bleach solution, left to soak overnight in a fourth washing, and later rinsed with water then acetone. Once waste bottles were ready to be disposed of, they were sealed and placed in individual Ziplock bags. Gloves were frequently changed and hands were washed multiple times during clean-up.
3.5.5 Collection, Reduction, Solution, and Refinement of X-Ray Data

Single crystals were coated with Paratone-N oil and mounted under a cold nitrogen stream. Data sets were collected on a Bruker Kappa Apex II CCD diffractometer using a graphite monochromater with MoKα radiation (λ = 0.71073 Å). Data reduction was performed using the Bruker SMART software package. Data sets were corrected for absorption effects using SADABS. The structures were solved by direct methods using XS and refined by full-matrix least-squares on F2 using XL as implemented in the SHELXTL suite of programs. All nonhydrogen atoms were refined anisotropically unless noted otherwise. Hydrogen atoms were placed in calculated positions using an appropriate riding model and coupled isotropic temperature factors.

Table 3.1: Crystallographic data for compound 3-1

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4 Conclusion

4.1 Thesis Summary

This thesis has described the examination of the reactivity of Ga(C₆F₅)₃ in the context of FLP chemistry. This field remains relatively unexplored compared to the study of Al(C₆F₅)₃ based FLPs and B(C₆F₅)₃ based FLPs. The main conclusions are as follows:

Classical Lewis adduct formation between Ga(C₆F₅)₃ and secondary phosphines, as well as between Ga(C₆F₅)₃ and tertiary phosphines was realized. The tertiary phosphine - Ga(C₆F₅)₃ adducts were able to undergo addition reactions with the terminal alkyne phenylacetylene, including in the case of using PᵗBu₃, which was previously found to favour a deprotonation pathway when employing B(C₆F₅)₃ or Al(C₆F₅)₃. Addition to the internal alkyne diphenylacetylene was observed when employing the FLP PᵗBu₂HP-Ga(C₆F₅)₃. The FLP system PᵗBu₃P-Ga(C₆F₅)₃ was capable of activating carbon dioxide, dihydrogen, and diphenyl disulfide in a similar fashion to the boron-based and aluminum-based FLP systems.

The formation of Ga(C₆F₅)₃ - arsine adducts was explored. Coordination of the tertiary arsine triphenylarsine to Ga(C₆F₅)₃ yielded the adduct Ph₃As-Ga(C₆F₅)₃ which was isolated and characterized. Thermogravimetric analysis of Ph₃As-Ga(C₆F₅)₃ at high temperatures was done to probe the possibility of using the adduct as a safer precursor for synthesizing GaAs, however, it was found that elevated temperatures resulted in the cleavage of the Ga-As bond. Further investigations into the Ga(C₆F₅)₃ and primary tert-butylarsine system are necessary to draw a complete conclusion on its reactivity.
4.2 Future Work

Though the work described in this thesis examined the use of Ga(C₆F₅)₃ in FLP chemistry, there are many areas in which this chemistry can further be investigated. For instance, while addition reactions to alkynes were observed when employing a Ga(C₆F₅)₃ and phosphine FLP system, the potential for using an amine as a Lewis base in lieu of a phosphine in this reaction became of interest. The use of amines could provide a means to form olefinic ammonium gallates, which could ultimately result in the first step towards the catalytic hydroamination of internal alkynes, similarly to previous work done with terminal alkynes and B(C₆F₅)₃.²⁴ Preliminary results have indicated that Ga(C₆F₅)₃ is able to interact with the nitrogen centre of secondary amines. Nitrogen-based Ga(C₆F₅)₃ systems could thus present interesting FLP chemistry and should be explored.

It was also shown in this thesis that the formation of Ga(C₆F₅)₃-arsine adducts is viable. In the case of Ph₃As-Ga(C₆F₅)₃, heating at elevated temperatures cleaved the gallium-arsenic bond, leaving behind solely elemental gallium. It is of interest to test adduct formation between Ga(C₆F₅)₃ with a more basic tertiary arsine, such as As'Bu₃, in an attempt to strengthen the bond between gallium and arsenic. This could provide a means to obtain the semiconductor gallium arsenide from a safer precursor in comparison to its existing synthetic methods which employ the extremely toxic AsH₃ and pyrophoric Ga(CH₃)₃.

\[
\text{Ga(C}_6\text{F}_5)\text{_3}^{\text{tol}} + \text{HNR}_2 + \text{R} & \text{R} \rightarrow \text{R}_2\text{HN}^\ominus \text{R} \\
\text{Ga(C}_6\text{F}_5)\text{_3}^{\text{tol}} + \text{As'}\text{Bu}_3 & \rightarrow \text{As'}\text{Bu}_3\text{As-Ga(C}_6\text{F}_5)\text{_3} \\
& \rightarrow \text{GaAs}
\]

**Scheme 4.1:** Proposed future directions
References


(44) Lewis, S. P., US 7585991 B2, **2008**.


