Author for correspondence:
Douglas W. Stephan
e-mail: dstephan@chem.utoronto.ca

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Halogenated triphenylgallium and -indium in frustrated Lewis pair activations and hydrogenation catalysis

Maotong Xu[1], Josephine Possart[2], Alexander E. Waked[1], Julie Roy[1], Werner Uhl[2] and Douglas W. Stephan[1]

[1]Department of Chemistry, University of Toronto, 80 St George Street, Toronto, Ontario, Canada M5H 3H6
[2]Institut für Anorganische und Analytische Chemie, Universität Münster, Corrensstraße 28–30, 48149 Münster, Germany

(iD) WU, 0000-0002-7178-5517; DWS, 0000-0001-8140-8355

The Lewis acids $Ga(C_6F_5)_3$, $In(C_6F_5)_3$ and $Ga(C_6Cl_5)_3$ are prepared and their Lewis acidity has been probed experimentally and computationally. The species $Ga(C_6F_5)_3$ and $In(C_6F_5)_3$ in conjunction with phosphine donors are shown to heterolytically split H_2 and catalyse the hydrogenation of an imine. In addition, frustrated Lewis pairs (FLPs) derived from $Ga(C_6F_5)_3$ and $In(C_6F_5)_3$ and phosphines react with diphenyldisulfide to phosphoniumgallates or indates of the form $[tBu_3PSPh][PhSE(C_6F_5)_3]$ and $[tBu_3PSPh][(\mu\text{-}SPh)(E(C_6F_5)_3)_2]$ (E = Ga, In). The potential of the FLPs based on $Ga(C_6F_5)_3$, $In(C_6F_5)_3$ and $Ga(C_6Cl_5)_3$ and phosphines is also shown in reactions with phenylacetylene to give pure or mixtures of the products $[tBu_3PH][PhCCE(C_6X_5)_3]$ and $R_3P(Ph)C=C(H)E(C_6X_5)_3$. A number of these species are crystallographically characterized. The implications for the use of these species in FLP chemistry are considered.

This article is part of the themed issue 'Frustrated Lewis pair chemistry'.

1. Introduction

While classic Lewis acids and Lewis bases usually form strong adducts [1], in 2006, we disclosed that the intramolecular Lewis acid/Lewis base pair
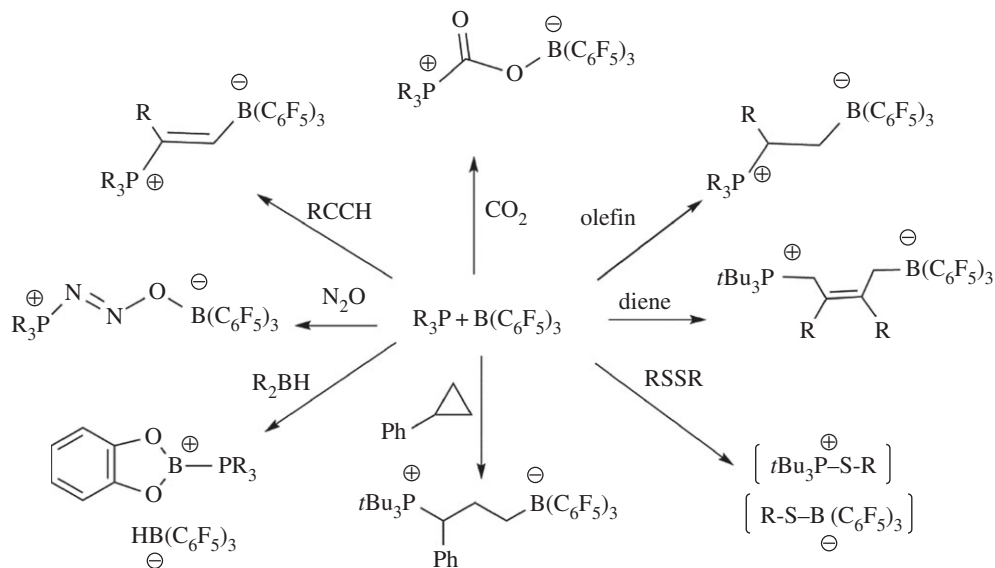
Scheme 1. Representative reactivity of phosphine/borane FLPs with small molecules.

$(Mes_2P)C_6F_4(B(C_6F_5)_2)$ cleanly cleaves the dihydrogen molecule under mild conditions [2]. Subsequently, we showed this ability to heterolytically split H_2 could be generalized to combinations of phosphines and boranes where steric demands precluded dative bond formation [3]. This finding swiftly led to the discovery of the first metal-free hydrogenation catalysts that involve main group species activating H_2 and delivering it to a variety of unsaturated organic substrates [4–10].

In the intervening decade, these findings have garnered considerable attention, and indeed, frustrated Lewis pair (FLP) chemistry has broadened dramatically [8–10]. Indeed, a broad range of polar and non-polar unsaturated substrates have been shown to undergo FLP hydrogenations. Moreover, asymmetric FLP catalysts have been developed leading to highly selective metal-free hydrogenations [11–18]. FLPs have been shown to react with a variety of other small molecule substrates, including olefins and alkynes, CO_2, N_2O, SO_2, RNSO and NO [8,10,19,20]. Recently, this unique reactivity has been extended to C–H bond activation as well as to provide new strategies for organic and radical chemistry [21]. The concept of FLP chemistry has also been applied in transition-metal chemistry, applied to develop synthetic models for hydrogenases, unveiled new strategies for polymer syntheses and found analogies in the mechanisms of surface reaction chemistry [8] (scheme 1).

While much of the above FLP chemistry exploits boron-based Lewis acids, the Al-based Lewis acid $Al(C_6F_5)_3$ has also been explored in FLP reactions with alkynes [22], olefins [23–25], H_2 [26], CO_2 [27–30] and N_2O [31]. At the same time, the Fontaine [32] and Uhl [33–37] groups have explored the FLP chemistry of intramolecular Al/P systems, of the form $R_2PCH_2AlMe_2$ and $RHC=C(PR'_2)(AlR''_2)$, respectively.

Ga and In Lewis acids have been used as homogeneous catalysts in a number of organic transformations [38]. For example, gallium triflate catalyses Friedel–Crafts alkylations and acylations, epoxyolefin cyclizations, Mukaiyama aldol condensations and ketone reductions [38–46]. Indium(III) Lewis acids have also been shown to effectively promote Diels–Alder reactions between various dienes and dienophiles in water, as well as Michael reactions between amines and α,β-ethylenic compounds [47]. Despite these applications of gallium and indium Lewis acids, the application of these heavier group 13 reagents in FLP chemistry has received less attention [48–50]. In such efforts, Gandon and co-workers [48] have exploited Ga species to effect the hydroarylation and hydrogenation of olefins, while Aldridge and co-workers [49] have described

the catalytic reduction in CO_2. In related work, the Ozin group [51] has recently described the activation of H_2 and CO_2 at the surface of heterogeneous nanocrystalline hydroxylated indium oxide $(In_2O_{3-x}(OH)_y)$ as a catalyst [51–53]. These authors propose that the activation of these molecules occurs via an FLP-like mechanism, in which proximal surface separated Lewis acidic indium and Lewis basic InOH sites act to activate H_2. These advances notwithstanding, the paucity of gallium and indium applications in FLP chemistry has inspired us to probe the Lewis acidity of gallium and indium derivatives with perhalogenated substituents. In addition, we have investigated the FLP reactivity of these species in the reactions with H_2, disulfides and alkynes.

2. Results and discussion

The Lewis acids $E(C_6F_5)_3 \bullet tol$ (E = Ga **1**, In **2**) and $E(C_6F_5)_3 \bullet OEt_2$ (E = Ga **3**, In **4**) were prepared using a modification of a patented preparation [54] (scheme 2). This involved the reaction of $Zn(C_6F_5)_2 \bullet tol$ with $GaCl_3$ or $InCl_3$. This afforded the direct isolation of **1** and **2** while recrystallization of the product from ether afforded **3** and **4**. In the case of **2**, the nature of the toluene adduct was confirmed crystallographically (figure 1). The structural data affirm an η^1-interaction with toluene with an In–C distance of 2.634(2) Å. The In–C bond lengths to the C_6F_5 rings were found to range from 2.155(2) to 2.168(2) Å. The geometry at indium is pseudo-tetrahedral with C–In–C angles of 119.46(7)°, 110.80(7)° and 115.94(7)° between the aryl rings, while the C–In–C angles between the aryl rings and the coordinated toluene carbon atom are 105.84(7)°, 101.65(7)° and 100.06(7)°. These data are similar to those previously reported for the Al analogue [55].
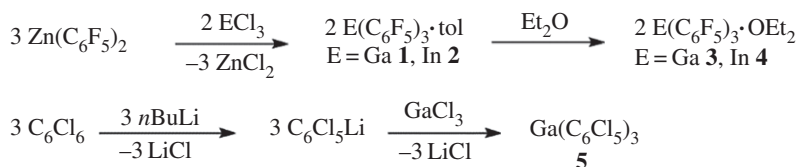
Recrystallization of **1** from diethyl ether afforded crystals of the corresponding ether adduct $Ga(C_6F_5)_3 \bullet OEt_2$ **3**. An X-ray crystallographic study of **3** reveals a structure that, as expected, shows a pseudo-tetrahedral geometry at gallium, with a Ga–O bond length of 2.018(2) Å (figure 2).

The species $Ga(C_6Cl_5)_3$ **5** was prepared in a fashion analogous to that described by Ashley *et al.* [56] for the preparation of the boron analogue. Treatment of C_6Cl_6 with *n*BuLi in *n*-hexane was followed by addition to a solution of $GaCl_3$ at −78°C. Warming to room temperature and stirring overnight followed by workup and Soxhlet extraction afforded **5** in 86% yield (scheme 2). Electron ionization mass spectrometric data for **5** were consistent with the constitution of this species although it was shown to decompose at 280°C. This compound proved challenging to characterize spectroscopically due to the quadrupolar nature of Cl atoms; nonetheless, its subsequent reactivity provided further support for its formulation (*vide infra*).
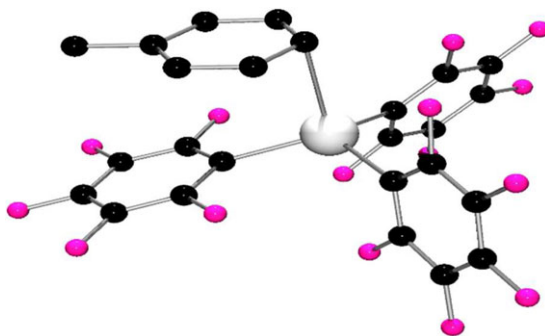
Efforts to garner some information about the relative Lewis acidity were undertaken by employing the Gutmann–Beckett method [57,58]. When a 1 : 1 ratio of **1** and Et_3PO were mixed in dichloromethane, the ^{31}P NMR resonance of coordinated Et_3PO was shifted 17.9 ppm downfield of free Et_3PO. The analogous reaction with **2** and Et_3PO resulted in a downfield shift of 18.7 ppm in the ^{31}P NMR spectrum. Both values are smaller than those seen for the corresponding experiment using $B(C_6F_5)_3$ ($\Delta\delta = 26.6$ ppm). This is consistent with the diminished Lewis acidity of **1** and **2** in comparison to $B(C_6F_5)_3$ [59]. Applying the same test to **5** was unsuccessful as a very weak adduct was formed with Et_3PO as evidenced by the observation of only a very broad resonance in the ^{31}P NMR spectrum. Similarly, Ashley *et al.* [56] reported that $B(C_6Cl_5)_3$ did not form an adduct with Et_3PO.

To further address the issue of relative Lewis acidity, the fluoride ion affinities (FIAs) were computed at the B3LYP/Def2TZVP(GD3BJ) level of theory [60–62] (table 1). For the series of species $E(C_6F_5)_3$, the computed FIAs are consistent with the greater Lewis acidity of the Al species and a decrease for the series of Al, Ga and In species. The perchlorinated species is computed to have a significantly lower FIA. It is important to note that these calculations reflect the electronic features at Ga and fail to account for the increased steric demands of the C_6Cl_5 rings.

Compounds **1** and **2** form adducts with the tertiary phosphine tBu_3P. In the case of **1** and tBu_3P, storage of the mixture at −35°C resulted in precipitation of a white solid, **6**. The ^{19}F NMR spectrum of this product showed a decreased gap between the resonances attributed to the *meta*

$$3\ Zn(C_6F_5)_2 \xrightarrow[-3\ ZnCl_2]{2\ ECl_3} 2\ E(C_6F_5)_3{\cdot}tol \xrightarrow{Et_2O} 2\ E(C_6F_5)_3{\cdot}OEt_2$$
$$E = Ga\ \mathbf{1},\ In\ \mathbf{2} \qquad\qquad E = Ga\ \mathbf{3},\ In\ \mathbf{4}$$

$$3\ C_6Cl_6 \xrightarrow[-3\ LiCl]{3\ nBuLi} 3\ C_6Cl_5Li \xrightarrow[-3\ LiCl]{GaCl_3} Ga(C_6Cl_5)_3$$
$$\mathbf{5}$$

Scheme 2. Synthesis of **1–5**.

Figure 1. Molecular structure of **2**. H-atoms have been omitted for clarity. C, black; In, grey; F, pink.
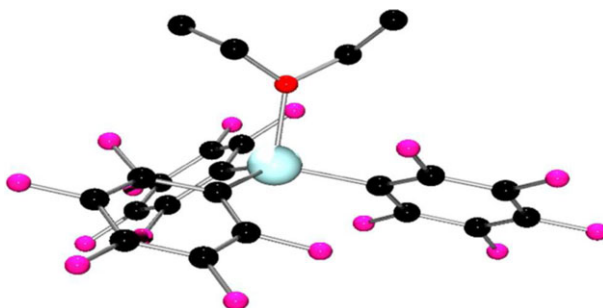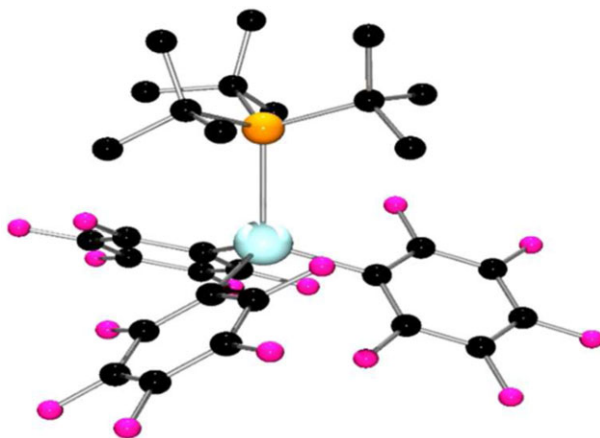

Figure 2. Molecular structure of **3**. H-atoms have been omitted for clarity. C, black; Ga, turquoise; O, red; F, pink.

Table 1. Computed fluoride ion affinities.

Lewis acid	FIA (kJ mol^{-1})
$B(C_6F_5)_3$	426
$Al(C_6F_5)_3$	535
$Ga(C_6F_5)_3$	445
$In(C_6F_5)_3$	413
$Ga(C_6Cl_5)_3$	385

and *para* fluorine atoms, which is indicative of four rather than three coordinate group 13 Lewis acid centres which contain C_6F_5 ligands. The ^{31}P NMR spectrum displayed a signal at 58.6 ppm. These data support the formulation of the product **6** as the adduct $(tBu_3P)Ga(C_6F_5)_3$. Crystals of **6** suitable for X-ray diffraction were grown by vapour diffusion of *n*-pentane into a toluene

Figure 3. Molecular structure of **6**. H-atoms have been omitted for clarity. C, black; P, orange; Ga, turquoise; F, pink.
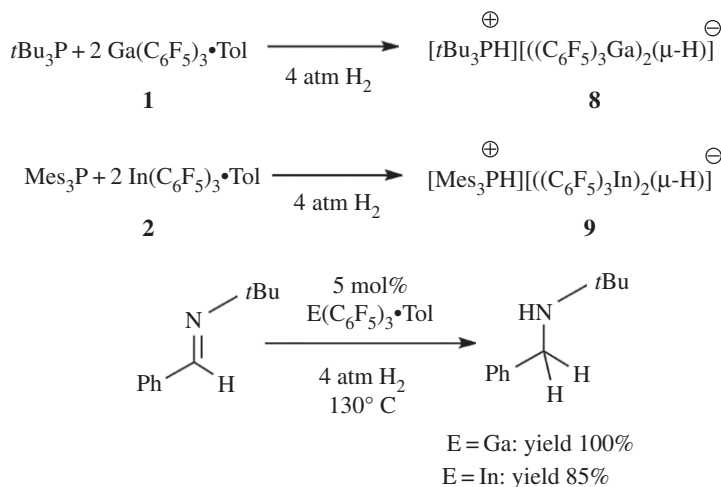

Scheme 3. Stoichiometric/catalytic reactions of **1** or **2** with H_2.
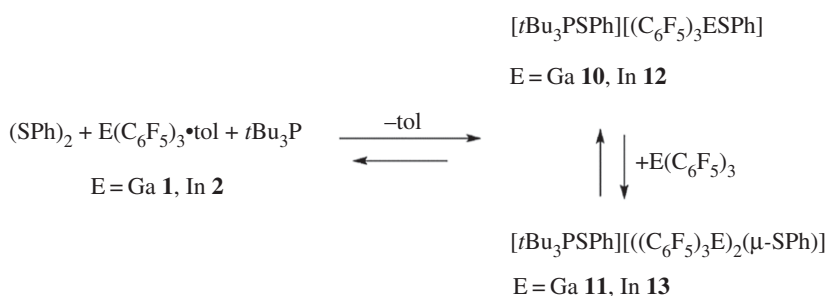
solution (figure 3). X-ray crystallographic data confirmed the proposed formulation and revealed a Ga–P bond length of 2.635(4) Å. This is significantly longer than the typical covalent Ga–P bond distances of approximately 2.4 Å [63].

The analogous reaction of **2** with tBu$_3$P afforded a clear colourless solution that showed ^{19}F resonances consistent with the quaternization of the indium centre, while the ^{31}P NMR spectrum showed a shift in the resonance to 67.1 from 62.0 ppm for the free tBu$_3$P. These data confirmed the formation of the product (tBu$_3$P)In(C$_6$F$_5$)$_3$ **7**. While this species is observable in solution, attempts to isolate it afforded consistently impure product.

The quintessential reaction of FLPs is the reaction of such combination of Lewis acid and base with H_2 [3]. Exploring this reactivity with **1** and **2** was thus undertaken. The reaction of **1** with tBu$_3$P in a 2 : 1 ratio in toluene under 4 atm of H_2 afforded the species [tBu$_3$PH][(Ga(C$_6$F$_5$)$_3$)$_2$(μ-H)] **8** (scheme 3). The ^{1}H NMR spectrum shows a doublet with a coupling constant of 427 Hz at 5.02 ppm, and the ^{31}P NMR spectrum displayed the corresponding doublet at 60.8 ppm, consistent with the protonated phosphonium cation. The ^{19}F NMR spectrum showed three resonances at −122.9, −155.9 and −163.7 ppm, corresponding to the C$_6$F$_5$ rings, consistent with the formation of a four coordinate gallium centre. In this case, the bridging hydride was observed
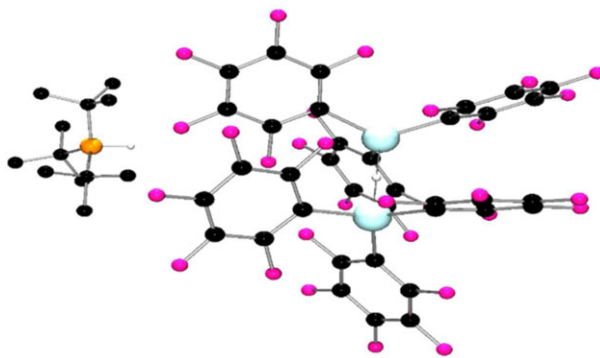
Figure 4. Molecular structure of **8**. H-atoms have been omitted for clarity. C, black; P, orange; Ga, turquoise; H, grey; F, pink.

$$[t\text{Bu}_3\text{PSPh}][(\text{C}_6\text{F}_5)_3\text{ESPh}]$$

$$E = \text{Ga } \mathbf{10}, \text{In } \mathbf{12}$$

$$(\text{SPh})_2 + \text{E}(\text{C}_6\text{F}_5)_3 \bullet \text{tol} + t\text{Bu}_3\text{P} \xrightarrow{\quad -\text{tol}\quad}$$

$$E = \text{Ga } \mathbf{1}, \text{In } \mathbf{2}$$

$$\uparrow \downarrow \; +\text{E}(\text{C}_6\text{F}_5)_3$$

$$[t\text{Bu}_3\text{PSPh}][((\text{C}_6\text{F}_5)_3\text{E})_2(\mu\text{-SPh})]$$

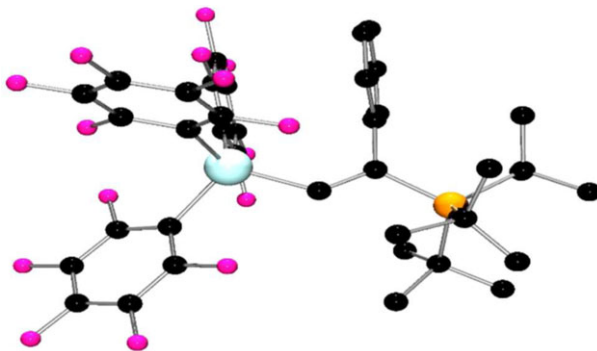$$E = \text{Ga } \mathbf{11}, \text{In } \mathbf{13}$$

Scheme 4. Reactions of **1** or **2** with diphenyl disulfide.

at 3.70 ppm as a broad singlet, presumably as a result of the quadrupolar gallium nuclei (^{69}Ga and ^{71}Ga, $I = 3/2$). Elemental analysis and X-ray crystallography confirmed the formation of **8** (figure 4). The structure is directly analogous to the aluminium analogue [26], with a Ga–H–Ga angle of 175(2)° and an average Ga–H distance of 1.68(1) Å in the anion.

In the case of **2**, addition of 1 equivalent of Mes$_3$P in toluene under 4 atm of H$_2$ at 25°C resulted in complete consumption of In(C$_6$F$_5$)$_3$. The ^{31}P NMR spectrum revealed the presence of two approximately equimolar species in solution: one new species exhibiting a doublet at −27.4 ppm with a coupling constant of 478 Hz, and a second resonance attributed to free Mes$_3$P at −36.5 ppm. The corresponding ^{1}H NMR spectrum showed a doublet at 8.24 ppm with a coupling constant of 478 Hz, characteristic of the [Mes$_3$PH]$^+$ cation. The ^{19}F NMR spectrum showed three resonances at −117.4, −155.9 and −162.5 ppm, consistent with the formation of a four coordinate indium centre. Interestingly, when a 1:2 ratio of Mes$_3$P and In(C$_6$F$_5$)$_3$•tol was used, complete consumption of both starting materials was observed. These results were consistent with the formulation of **9** as [Mes$_3$PH][(In(C$_6$F$_5$)$_3$)$_2$(μ-H)] (scheme 3). The bridging hydride was observed in the ^{1}H NMR spectrum at 4.82 ppm as a broad singlet, presumably because of the proximity to ^{113}In and ^{115}In, both of which are quadrupolar with a nuclear spin of 9/2.

This demonstration of the activation of H$_2$ probed questions about the potential utility of **1** and **2** in catalytic hydrogenation. To this end, attempts were undertaken to hydrogenate *N*-benzylidene-*tert*-butylamine (*t*BuN=CHPh). A bromobenzene solution of **1** or **2** was added to 20 equivalents of imine substrate. To the resulting solutions, 4 atm of H$_2$ was added and the mixtures were heated at 130°C overnight. ^{1}H NMR data revealed that **1** catalysed the complete reduction in the imine to the amine, while **2** afforded 85% conversion.

Analogous participation in the heterolytic activation of disulfides has been previously reported for FLPs derived from phosphine and B(C$_6$F$_5$)$_3$. In similar reactions, **1** or **2** were combined with diphenyl disulfide and *t*Bu$_3$P. The ^{19}F NMR spectrum showed resonances attributable to two
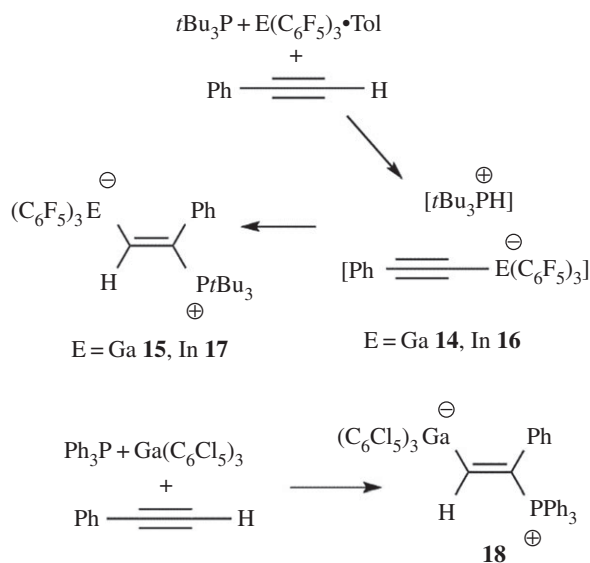
Figure 5. Molecular structure of **15**. H-atoms have been omitted for clarity. C, black; P, orange; Ga, turquoise; F, pink.

species suggesting the formation of the anions in [tBu$_3$PSPh][PhSE(C$_6$F$_5$)$_3$] (E = Ga **10**, In **12**) and [tBu$_3$PSPh][(µ-SPh)(E(C$_6$F$_5$)$_3$)$_2$] (E = Ga **11**, In **13**) (scheme 4) in ratios of 1 : 0.34 and 1 : 0.22, respectively. In the reaction of In(C$_6$F$_5$)$_3$, the ^{31}P NMR data showed a single resonance at 84.6 ppm attributable to the cation [tBu$_3$PSPh] [64]. Measuring the ^{19}F spectrum at 60°C shows that the two sets of peaks from the two species coalesce into a single resonance, while at −60°C, the ratio of the indium products was altered to 1 : 0.45. These data suggest the presence of equilibria between these anions. Varying the ratios of **2** to diphenyl disulfide and tBu$_3$P to 0.5 : 1 : 1 showed that the resonances attributable to **12** dominated, while the peaks attributed to **13** were enhanced when five equivalents of **2** was used instead. These data stand in contrast with the corresponding reaction of B(C$_6$F$_5$)$_3$ that yields only [tBu$_3$PSPh][PhSB(C$_6$F$_5$)$_3$] [64].

A classical reaction of FLPs involves either FLP addition to a terminal acetylene or deprotonation of the alkyne to give the phosphonium alkynylborate. The analogous reaction of **1** with an equimolar amount of tBu$_3$P and phenylacetylene in toluene resulted in the formation of an oil at room temperature after 15 min. The ^{31}P NMR spectrum indicated the presence of a minor amount of (tBu$_3$P)Ga(C$_6$F$_5$)$_3$ adduct as evidenced by the signal at 58.8 ppm. In addition, a major species **14** gave rise to a doublet at 59.9 ppm with $^1J_{PH} = 429$ Hz attributable to the cation [tBu$_3$PH]. Meanwhile, a new singlet peak appeared at 40.7 ppm in the ^{31}P NMR spectrum attributable to a new species **15**. This latter peak correlated to a doublet ($J = 30$ Hz) in the ^{1}H NMR spectrum. This latter observation is reminiscent of the previous report [22] describing the reaction of Al(C$_6$F$_5$)$_3$, (o-tol)$_3$P and phenylacetylene which was shown to give the addition of the FLP to the alkyne affording the zwitterionic product (o-tol)$_3$P(Ph)C=C(H)Al(C$_6$F$_5$)$_3$, which gave a doublet in the ^{1}H NMR at 8.05 ppm with $^3J_{PH} = 43$ Hz [22]. Thus, compounds **14** and **15** are proposed to be the analogous species [tBu$_3$PH][PhCCGa(C$_6$F$_5$)$_3$] and tBu$_3$P(Ph)C=C(H)Ga(C$_6$F$_5$)$_3$, respectively (scheme 5). On warming the mixture to 40°C overnight, partial conversion of **14** to **15** was observed as evidenced by the ^{31}P NMR spectra. These data suggest that **14** is the kinetic product and this slowly transforms to the thermodynamic product **15**. The formulation of compound **15** was confirmed by single-crystal X-ray diffraction (figure 5). The structure shows addition of phosphine and gallium to the alkyne in an E-fashion, with phosphine adding to the substituted carbon of the alkyne. The phenyl ring is oriented parallel to one of the C$_6$F$_5$ rings with a distance of 3.6 Å, suggesting π–π stacking interaction between the two rings. The *trans*-orientation of the Ga and P fragments stands in contrast with the *cis*-addition previously observed by the Uhl group in [PhCH=C(P(C$_6$H$_3$Me$_2$)$_2$)(EtBu$_2$)(PhCH=CH)] (E = Al [33], Ga [50]).

In the analogous reaction of **2** with tBu$_3$P and phenylacetylene, stirring for 20 min at room temperature and removing all the volatiles afforded a white solid. The ^{1}H NMR spectrum revealed a characteristic doublet at 3.64 ppm ($^1J_{PH} = 432$ Hz) and the ^{31}P NMR spectrum also contained a doublet at 57.9 ppm ($^1J_{PH} = 432$ Hz). The ^{19}F NMR spectrum showed three resonances at −116.3, −157.0 and −162.1 ppm, consistent with the formation of a four

**Scheme 5.** Reactions of **1** or **2** with phosphine and alkyne.
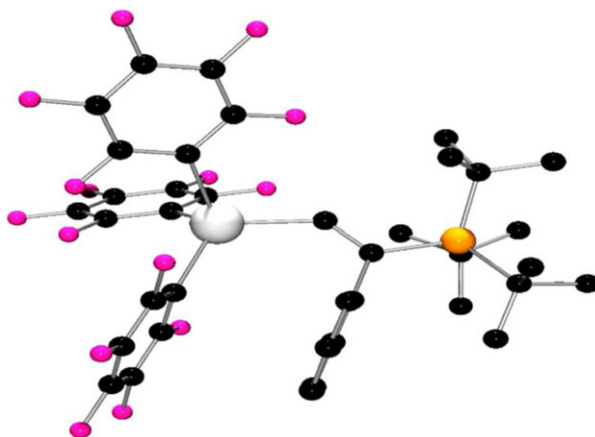
Figure 6. Molecular structure of **17**. H-atoms have been omitted for clarity. C, black; P, orange; In, grey; F, pink.

coordinate indium centre. These results suggest the formation of the simple deprotonation $[tBu_3PH][PhCCIn(C_6F_5)_3]$ **16** (scheme 5). However, another set of ^{19}F resonances was also observed, suggesting the formation of the addition product $tBu_3P(Ph)C=C(H)In(C_6F_5)_3$ **17**. This addition product is formed typically in about 15–20% of the total yield. While separation of these products proved challenging, crystals of **17** were obtained from a solution in an NMR tube. The subsequent crystallographic study confirmed the formulation of **17** (figure 6). The structure of **17** is analogous to **15** with an In–C distance of 2.204(4) Å and a new P–C bond length of 1.850(4) Å. It is interesting to note that the initially formed ratios of **14**:**15** and **16**:**17** are 1:1.5 and 1:4.5, respectively, reflecting the greater Lewis acidity of **1** over **2**.

In our efforts to examine the reactivity of **5**, reactions with phosphine and H_2 were challenged by product solubility difficulties. However, the reaction of **5** with PPh_3 and phenylacetylene at room temperature gave a yellow solution, from which crystals were isolated in 30% yield. The ^1H NMR spectrum showed a doublet at 8.85 ppm with $^3J_{PH} = 41$ Hz and a $^{31}P\{^1H\}$ signal at 20.2 ppm. Mass spectral data showed a peak corresponding to the mass ion consistent with the formulation of **18** as $Ph_3P(Ph)C=C(H)Ga(C_6Cl_5)_3$ (figure 7). This was further supported by the determination of the crystal structure of **18**, which showed the addition of phosphine and gallium
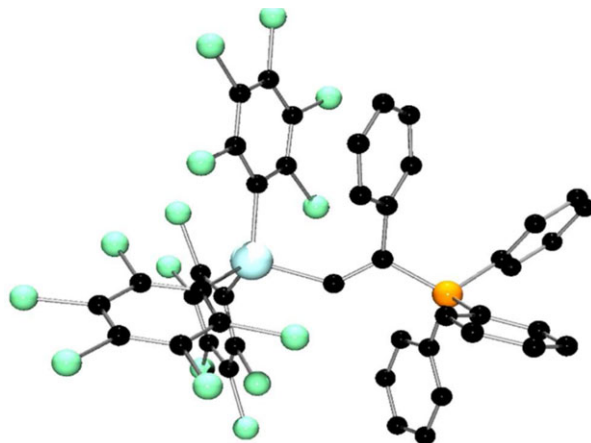
Figure 7. Molecular structure of **18**. H-atoms have been omitted for clarity. C, black; P, orange; Ga, turquoise; Cl, green.

to the alkyne in an analogous fashion to **15** and **17**. The newly formed Ga–C bond to the linker was found to be 2.020(3) Å, while the P–C bond to the olefin carbon is 1.810(3) Å.

It is noteworthy that combinations of $B(C_6F_5)_3$ and $Al(C_6F_5)_3$ and tBu_3P in reactions with phenylacetylene lead exclusively to the deprotonation products $[tBu_3PH][PhCCB(C_6F_5)_3]$ and $[tBu_3PH][PhCCAl(C_6F_5)_3]$. A proposed mechanism for these reactions [65] involves an initial π-interaction of the alkyne with the Lewis acid. This prompts increased acidity of the alkynyl proton. The present results imply the decreased Lewis acidity of the gallium and indium Lewis acids prompting competitive addition of phosphine to the β-carbon. In addition, the longer Ga–C and In–C bond lengths diminish the steric congestion about the alkyne, allowing addition to compete with deprotonation.

3. Conclusion

The Lewis acids $Ga(C_6F_5)_3$, $In(C_6F_5)_3$ and $Ga(C_6Cl_5)_3$ were prepared and shown to exhibit lesser Lewis acidity than the boron and aluminium species $B(C_6F_5)_3$ and $Al(C_6F_5)_3$. Nonetheless, these species participate in FLP chemistry in conjunction with phosphine donors. These species are shown to heterolytically split H_2, catalyse the hydrogenation of an imine, effect the heterolytic cleavage of diphenyldisulfide and effect reactions with alkynes. Interestingly, the larger size of gallium and indium results in hydride- and thiolate-bridged anions, while the lower Lewis acidity prompts the formation of mixtures of deprotonation and addition products in the reactions with phenylacetylene. These data extend the range of Lewis acids that effect FLP chemistry and current efforts are directed at exploring further aspects of gallium and indium species in hydrogenation chemistry.

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