B(C₆F₅)₃ Enabled Synthesis of a Cyclic *cis*-Arsaphosphene

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Abstract: The synthesis and characterization of an (arsino)phosphaketene, As(PCO){[N(Dipp)](CH₂)₂} (Dipp = 2,6-diisopropylphenyl) is reported along with its subsequent reactivity with B(C₆F₅)₃. When reacted in a stoichiometric ratio, B(C₆F₅)₃ drives the insertion of the P=C bond of the phosphaketene into one of the As–N bonds of the arsino functionality affording an acid-stabilized, seven membered, cyclic arsaphosphene. In contrast, when catalytic amounts of B(C₆F₅)₃ are employed, dimeric species, which form via a formal [2+2] cycloaddition of the cyclic arsaphosphene, are generated. The cyclic arsaphosphene product represents the first example of such a compound in which the two substituents are arranged in a *cis*-configuration.

The chemical behavior of phosphaketenes (R–P=C=O), heavy analogues of isocyanates (R–N=C=O), remains largely unexplored due to the technical difficulties associated with their synthesis.^{1,2} Pioneering work in this field by Appel et al. allowed for the preparation and isolation of Mes*–P=C=O (Mes* = 2,4,6-(*t*Bu)₃C₆H₃), a stable monomeric phosphaketene.³ The steric bulk of the Mes* substituent stabilizes this highly reactive species in contrast to the *tert*-butyl analogue which was found to quickly dimerize.^{3,4}

More recently, the synthetic accessibility of [Na(dioxane)_x][PCO] has allowed for the synthesis of a variety of phosphaketenes through salt-metathesis protocols.^{2,5–7} A key contribution in this area was reported by the Bertrand group, with the isolation of a phosphino-phosphinidene by decarbonylation of a phosphino-phosphaketene.⁸ The reactivity of phosphaketenes towards Lewis bases has been studied extensively, and in selected cases it has been demonstrated that Lewis basic reagents are capable of displacing carbon monoxide with reactivity akin to that of the transition metals.⁹ By contrast the reactivity of such species towards Lewis acids is less well explored.

Given the lack of information available regarding the reactivity of phosphaketene compounds towards Lewis acids, we were prompted to establish whether Lewis acidic reagents could be employed to catalytically activate such species, and if so, what the outcome of such transformations would be. Stoichiometric reactions between Lewis acids and Na(PCO) have previously been reported and their outcome shown to be strongly dependent on the steric profiles of the acids employed.¹⁰

Boron trihalides (BX₃) are archetypal examples of Lewis acids, however the moisture sensitive and reactive nature of

three-coordinate boranes makes them difficult to handle. This led to the synthesis of tris(pentafluorophenyl)borane (BCF) in the 1960s, as a route to electrophilic boranes that would not be prone to hydrolytic cleavage.¹¹ The reactivity of B(C₆F₅)₃ remained unexplored until the 1980s, when it was reported to transfer a perfluoroaryl group to xenon upon reaction with XeF₂ to generate [C₆F₅Xe][F₂B(C₆F₅)₂].¹² This perfluoroaryl borane was reported by Yamamoto as an effective catalyst for the addition of silyl enol ethers to aldehydes, alkyl chlorides, and α,β-unsaturated ketones.¹³ Other reactions that B(C₆F₅)₃ facilitates include: addition of ketene silyl acetals to *N*-benzylimines, hydrosilylation of carbonyls, transfer hydrogenation of imines, transfer hydrosilylation of aldehydes, olefins, and imines, and Diels-Alder-type reactions.^{13,14} Similar reactivity has also been observed with substituted perfluoroaryl borane HB(C₆F₅)₂.¹⁵

Herein, we discuss the synthesis of an arsanyl-phosphaketene which, upon reaction with B(C₆F₅)₃, was found to yield an arsaphosphene in a rare *cis*-configuration. Moreover, when catalytic amounts of B(C₆F₅)₃ were employed we found that dimeric species, which form via a formal [2+2] cycloaddition of the cyclic arsaphosphene, are generated.

In a similar fashion to the previously reported chloro-diazaphospholane PCl{[N(Dipp)](CH₂)₂}¹⁶ AsCl{[N(Dipp)](CH₂)₂}₂ (**1**) could be prepared from the ring closing reaction of *N,N*-diisopropylphenylethane-1,2-diamine with AsCl₃ in the presence of base. Related 1,3-diaza-2-arsacyclopentanes have previously been reported in the literature.¹⁷ Further reactivity of **1** with [Na(dioxane)_{3.6}][PCO] afforded the (arsino)phosphaketene As(PCO){[N(Dipp)](CH₂)₂} (**2**) in high yield (Scheme 1).

The ³¹P{¹H} NMR spectrum of **2** in C₆D₆ shows a singlet resonance at –256.9 ppm, consistent with previous reports of phosphaketenes.² The molecular structure of **2** was confirmed crystallographically, revealing a P–As bond length of 2.4518(5) Å. The N–As–P bond angles of 102.49(5)° and 97.06(4)° are similar to Bertrand's phosphino-phosphaketene,⁸ suggesting that the As-based lone pair is stereochemically inert. The remaining metric parameters are unexceptional (see SI).

Scheme 1. Synthesis of **2** on reaction of **1** with [Na(dioxane)_{3.6}][PCO].

Treatment of **2** with one equivalent of B(C₆F₅)₃ in C₆D₆ resulted in an orange solution, with a dramatic downfield ³¹P{¹H} NMR shift of 225.3 ppm. Furthermore, the ¹¹B{¹H} NMR resonance at 0.6 ppm and reduced *para-meta* gap in the ¹⁹F{¹H} NMR spectra are consistent with a four-coordinate boron environment. X-ray crystallography further confirmed the

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formulation of *cyclo*-AsPC[N(Dipp)]₂(O)(BCF) (**3-BCF**) (Scheme 2; Figure 1).

Scheme 2. Synthesis of **3-BCF**.

The As=P bond length (2.1607(7) Å) is substantially shorter than that observed for **2** (2.4518(5) Å) and consistent with an As=P double bond (2.16 Å).¹⁷ By way of comparison, species with single As–P bonds such as, for example, the arsine-stabilized [P₄]²⁺ cage reported by Burford, Weigand and co-workers have notably longer bond distances (2.332(2)–2.335(2) Å),¹⁸ whereas species with As=P bonds such as Escudié's trans-arsaphosphene (2.141(5) Å) compare more favorably with **3-BCF**.¹⁹ The C=O bond length in **3-BCF** is 1.278(3) Å, which is in line with partial double bond character between the carbon and oxygen (C–O: 1.38 Å; C=O: 1.24 Å).^{17,20} Interestingly, the B...O interatomic distance is 1.545(3) Å, which along with the rather obtuse C–B–C bond angles (105.39(18)°–115.71(19)°), suggests minimal pyramidalization at the boron center. These crystallographic measurements, together with observed broadening in the ¹¹B{¹H} and ¹⁹F{¹H} NMR spectra suggest that the B(C₆F₅)₃ moiety is only loosely associated with the carbonyl and therefore undergoes fluxional disassociation in solution.

Figure 1. Single crystal X-ray structure of **3-BCF**.

A related ring expansion has been reported by Gandleman when investigating the Lewis acidity of nitrenium cations towards metal phosphides, to yield cyclic ylides.²¹ However, in our case the rearrangement is thought to proceed by donation of the phosphaketene to an equivalent of B(C₆F₅)₃, followed by nucleophilic attack on the phosphaketene carbon by nitrogen. The difference in reactivity between the phosphino-phosphaketene and arsanyl-phosphaketene is presumed to be due to the diminished basicity at arsenic when compared to phosphorus, as well as a weaker As–N bond.

To the best of our knowledge, compound **3-BCF** represents the first example of an arsaphosphene in which the two substituents are in a *cis*-configuration. This is enforced due to its cyclic structure. The ring expansion reaction which gives rise to **3-BCF** represents a novel route toward the formation of arsaphosphenes. To date, three major routes towards diphosphenes and arsaphosphenes have been reported: a) elimination of chlorine via Li, Mg, or K based reductions of chlorophosphines/ arsenines;²² b) elimination of hydrochloride via the reaction of DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) or Li compounds with chloroarsine and primary phosphines;²³ c) elimination of halosilane starting from haloarsine and silylphosphines.^{23a,24} Heavier group 15 analogues of alkenes are extremely rare and only a handful of diphosphenes with asymmetric substitution patterns are known.²⁵

VT NMR experiments were performed to probe the fluxional coordination of B(C₆F₅)₃ in **3-BCF**. At elevated temperature, free B(C₆F₅)₃ could be observed in the ¹⁹F{¹H} NMR spectrum, along with a new species in the ³¹P{¹H} NMR spectrum with a broad resonance at –3.1 ppm. Given the evidence of B(C₆F₅)₃ dissociation, the catalytic ring expansion of **2** to yield a *cis*-arsaphosphene was explored.

The reaction of **2** with 10 mol% B(C₆F₅)₃ yielded a new product, **4**, which has a ³¹P{¹H} NMR resonance at –3.1 ppm. The conversion to **4** is > 99% after 12 h but 24 h was required to reach completion when only 5 mol% B(C₆F₅)₃ was used (Scheme 3). X-ray crystallography confirmed the molecular structure of **4** to be the bridged cyclic diarsadiphosphine [AsPC(O)[N(Dipp)]₂(CH₂)₂]₂. To date, this transformation is the first report of catalysis (main-group or otherwise) using a phosphaketene as a feedstock.

Scheme 3. Catalytic synthesis of **4**.

Figure 2. Single crystal X-ray structure of **4**.

From the molecular structure of **4** (Figure 2) the formation of a distorted four membered [AsPAsP] ring with internal angles summing to 327.3° was confirmed. In addition, the observed C=O bond lengths of 1.221(5) Å and 1.227(5) Å, are considerably shorter than the one observed for **3-BCF**. Moreover, the As–P bonds ranged from 2.3405(14) to 2.3845(13) Å, all of which are significantly longer than the P=As bond observed for **2** but in line with P–As single bonds.

It was found that the addition of two equivalents of $\text{B}(\text{C}_6\text{F}_5)_3$ to **4** resulted in clean formation of **3-BCF**, whereas addition of a base, such as THF, to **3-BCF** afforded **4** (Scheme 4).

Scheme 4. Interconversion between **3-BCF** and **4**.

In an effort to induce decarbonylation, a toluene solution of **4** was heated to 110°C for 24 h. This reaction resulted in the formation of a further new product, **5**, with a $^{31}\text{P}\{^1\text{H}\}$ NMR resonance at -39.0 ppm (Scheme 5).

Scheme 5. Thermal isomerization of **4** to **5**.

X-ray crystallography studies confirmed that **5** is an isomer of compound **4** involving head-to-head, rather than head-to-tail, dimerization of the cis-arsaphosphene moiety present in **3** (Figure 3). The molecular structure reveals that no decarbonylation takes place even upon extended heating. The C=O bond distances in **5** are 1.221(4) and 1.223(3) Å, similar to those observed in **4**. In addition, the average As–P bond distance is 2.354(av) Å, and the P–P and As–As bond distances are 2.2057(9) Å and 2.5182(4) Å, respectively. When **4** is heated in the presence of dienes, alkenes or isocyanates there was no evidence for cycloaddition products, suggesting that the isomerization mechanism is intramolecular and does not involve dissociation into separated monomer units.

In order to explore the mechanisms of the above reactions in more detail, we have conducted a detailed survey of the potential energy surface using density functional theory. The optimized structure of the (arsino)phosphaketene, **2**, is shown on the left in Figure 5, and is in excellent agreement with the X-ray data. Similarly, the optimized framework of **3** is very similar to that in **3-BCF**, except for the C=O bond length which is shorter (1.23 Å) in the absence of the Lewis acid. The

interconversion of **2** and **3** is almost thermo-neutral ($\Delta E = -1.1$ kcal/mol), and the pathway connecting the two is highly asynchronous. The early part of the reaction coordinate involves nucleophilic attack of one of the nitrogen atoms on the phosphaketene carbonyl, leading to a zwitterionic intermediate, **I**, that lies in a very shallow minimum 19.0 kcal/mol above the reactant. Compared to the reactant, the new C–N bond is almost fully formed (1.67 Å) while the P–C, C–O and As–N bonds are considerably elongated (1.77 Å, 1.19 Å and 2.00 Å, respectively vs. 1.66 Å, 1.19 Å and 1.83 Å in **2**). Conversely the As–P bond length of 2.30 Å in **I** is rather shorter than that in **2** (2.44 Å), consistent with developing As=P double bond character. Intermediate **I** lies in a very shallow minimum on the surface, separated from reactants and products by **TS1** and **TS2**, respectively. **TS1**, **I** and **TS2** are very similar in structure and, given the low barriers to both forward and reverse reactions, it seems very unlikely that metastable **I** could ever be isolated. It is therefore reasonable to conclude only that the rate-limiting step of the reaction involves a structure with substantial zwitterionic character. The dimeric species **4** and **5** both correspond to stable local minima on the potential energy surface, with the latter marginally more stable, consistent with the observation that it is formed only on prolonged heating of **4**. Both dimers **4** and **5** are considerably more stable than the isolated monomer, **3**, ($\Delta G = 16.1$ and 18.1 kcal/mol per monomer unit, respectively), suggesting that in the absence of a BCF unit dimerization should be spontaneous. The strongly exothermic nature of the dimerization step is also consistent with the assertion made above that the interconversion of **4** and **5** does not involve dissociation to monomers.

Figure 3. Single crystal X-ray structure of **5**.

The introduction of $\text{B}(\text{C}_6\text{F}_5)_3$ into the (*in silico*) reaction results in a substantial perturbation to the potential energy surface (red line), with the intermediate and products binding more strongly to the BCF unit than the reactants. As a result, the conversion of **2-BCF** to **3-BCF** now becomes significantly exothermic ($\Delta E = -20.9$ kcal/mol), and the zwitterionic intermediate, **I-BCF**, is only marginally higher in energy than the reactants. Consistent with this greater exothermicity, **I-BCF** is somewhat 'later' in the sense that the N–C bond is almost fully formed (1.49 Å) and the As–N bond more elongated (2.24 Å)

compared to the corresponding values of 1.62 Å and 2.17 Å in **1** itself. The differing strength of interaction with BCF across the surface correlates with the increasing Lewis basicity of the carbonyl oxygen. The reactant, **2**, has a substantial contribution from a resonance structure with a triple C–O bond (hence the very short C–O bond length of 1.17 Å) and, therefore, a formal positive charge on the oxygen. Its Lewis basicity is therefore comparatively weak, the O–B bond in **2·BCF** is long (1.67 Å) and the structure of the P=C=O unit is only weakly perturbed from the free phosphaketene, **2**. In contrast, the BCF unit binds rather more strongly to the ketone group in the product (**3·BCF**), causing a more substantial elongation of the C=O bond (1.28 Å vs 1.23 Å). This is, at least in part, due to the intrinsically greater basicity of the ketone group, but a careful comparison of the structures of **3** and **3·BCF** suggests that conjugation of the P=As bond may also play a role (Scheme 6). The N–As–P–C unit in **3·BCF** is strikingly planar: the torsion angle is less than 1° in the X-ray structure and only 4° in the DFT counterpart. In contrast, BCF-free **3** reveals a much more puckered geometry with a dihedral angle of 15°. Subtle changes in bond lengths also point to greater conjugation in the BCF adduct: the N–As, As–P and P–C bonds in **3/3·BCF** are 1.85/1.82 Å, 2.18/2.20 Å and 1.87/1.85 Å, respectively. The basicity of the C=O group in **3** is therefore enhanced by a greater contribution from resonance structure II in Scheme 6.

(**2·BCF**→**TS1·BCF**→**3·BCF**) is now clearly rate-limiting. The transition structure is also much ‘earlier’ in the BCF catalyzed reaction, with an N–C distance of 2.50 Å in **TS1·BCF** vs 1.97 Å in **TS1**.

Scheme 6. Resonance stabilization of **3·BCF**.

The stabilization of the product by BCF is also sufficient to bring **3·BCF** below either of the dimeric products, **4** or **5**, effectively trapping the monomeric product and blocking dimerization. We note that the C=O bonds in **4** and **5** appear to be very similar to those in **3** (C–O = 1.21–1.22 Å in all cases) and so it is not immediately obvious why BCF does not also bind to the dimeric products to give adducts such as **4·BCF** or even **4·2(BCF)**. These species would undoubtedly be very sterically hindered, and this must play a role in preventing BCF binding, but the As–P bonds are saturated in **4** and **5**, so there is also no enhancement of the basicity through the equivalents of resonance structure II in Scheme 6. We have not attempted to separate these steric and electronic contributions, but it is clear that both may contribute to the apparently reduced ability of the dimers to bind BCF. While not as fully developed as in the product **3**, the double bond character in the C=O bond of **1** is certainly enhanced relative to the reactant, and as a result the region of the surface around the intermediate is also stabilized relative to reactants. The qualitative changes in the potential energy surface are therefore consistent with the catalytic effect of BCF.

Figure 4. Computed potential energy surfaces for the interconversion of **2**, **3**, **4** and **5**. Energy is given per monomeric unit.

Whilst **TS1** and **TS2** are of very similar energy in the BCF-free reaction, the stronger binding of BCF to **1**, **TS2** and **3** means that the initial nucleophilic attack step

Scheme 7. Photolysis of **4** (and **5**) to afford **6** and **7**.

In a further effort to decarbonylate **4**, we have found that irradiation first induces an isomerization to **5**, which was

detected by ^{31}P NMR spectroscopy. This is followed closely by the formation of two new products, **6** and **7** (Scheme 7). The first of these products appears as a singlet at 64.4 ppm in both the $^{31}\text{P}\{^1\text{H}\}$ NMR and ^{31}P NMR spectrum whereas **7** appears as a doublet at -10.8 ppm in the ^{31}P NMR spectrum ($^1J_{\text{P-H}} = 177$ Hz). Although this reaction mixture proved to be inseparable, crystals of **6** and **7** suitable for X-ray diffraction studies could be obtained (see Supporting Information for further details).

These reactions indicate that photolysis of **4** and **5** does not induce decarbonylation, but rather formal loss of elemental arsenic, to yield a diphosphene and a cyclic secondary phosphine. While these rearrangements highlight the facile loss of elemental As, the lack of clean conversion to single products precluded any further studies.

In contrast to the failure to eliminate CO from **4** or **5**, decarbonylation of **2** is possible by thermal treatment in benzene solution. The postulated intermediate, an arsino-phosphinidene ($\text{P-As}\{\text{N}(\text{Dipp})\}(\text{CH}_2)_2$), dimerises to form $[\text{AsP}\{\text{N}(\text{Dipp})(\text{CH})\}_2]_2$ (**8**). In contrast to previous observations on related species, the reaction does not generate a diphosphene, but rather involves insertion of a phosphorus atom into the As–N bond (Scheme 8). Insertion into the As–N bond, observed in the formation of **8** and also in the initial formation of **3-BCF** from **2**, therefore appears to be a general feature of the chemistry of these systems. In this sense the reactivity is very different from the analogous phosphine-phosphaketenes, probably reflecting the intrinsic weakness of the As–N bond. Related studies involving the reaction of **1** with $[\text{Na}(\text{dioxane})_{5.6}]\text{AsCO}$ afforded the related product $[\text{As}_2\{\text{N}(\text{Dipp})(\text{CH})\}_2]_2$ (**9**).

Scheme 8. Decarbonylation of **2** to afford **8**.

Figure 4. Single crystal X-ray structure of **8**.

To conclude, we have shown that the Lewis acid-catalysed cyclization of an (arsino)phosphaketene to a cyclic

arsaphosphene is possible using tris(pentafluorophenyl)borane. When catalytic amounts of BCF were employed the reactions give rise to a single dimeric product which can be thought of as the head-to-tail dimer of the cyclic arsaphosphene. Thermal treatment of this product results in rearrangement to the corresponding head-to-head isomer. These studies are the first example of the catalytic utilization of phosphaketenes to afford otherwise inaccessible compounds.

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Entry for the Table of Contents (Please choose one layout)

Layout 1:

COMMUNICATION

Stoichiometric and catalytic reactions between $\text{B}(\text{C}_6\text{F}_5)_3$ and an (arsino)phosphaketene, $\text{As}(\text{PCO})\{[\text{N}(\text{Dipp})](\text{CH}_2)\}_2$ (Dipp = 2,6-diisopropylphenyl) are reported. In a stoichiometric ratio, an acid-stabilized, cyclic *cis*-arsaphosphene can be isolated. In contrast, when catalytic amounts of $\text{B}(\text{C}_6\text{F}_5)_3$ are employed, dimeric species, which form via a formal [2+2] cycloaddition of the cyclic arsaphosphene, are generated.

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M. Goicoechea*

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B(C₆F₅)₃ Enabled Synthesis of a
Cyclic cis-Arsaphosphene