Synthesis of a C(sp²)-bridged phosphine-borane by ionic coupling

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Abstract:

*The vinyl carbenoid H₂C=CBr(Li) has been used as key precursor to prepare a geminal C(sp²)-bridged phosphine-borane. Starting from bromoethene, two sequences of lithiation/electrophilic trapping, with ClPiPr₂ and FBMe₂ respectively, affords iPr₂P–C(=CH₂)–BMe₂ **3** [Mes = 2,4,6-(H₃C)₃C₆H₂]. This new phosphine-borane **3** was characterized by multi-nuclear NMR and mass spectroscopy. It adopts a monomeric open structure without P→B interaction. A few crystals of a secondary product **4** have been analysed by X-ray diffraction, revealing an unusual dimeric structure.*

Since the landmark discovery by Stephan *et al* of H₂ activation by the phosphine-borane Mes₂P–(*o*-C₆F₄)–B(C₆F₅)₂ in 2006,^[1] the synergy between Lewis acid and Lewis basic moieties has attracted huge interest, both for small molecule activation / metal-free catalysis^[2] and as ambiphilic ligands for transition metals.^[3] Over the years, a wide library of ambiphilic compounds has been developed, in particular with phosphines as Lewis basic sites. A number of spacers varying in size and rigidity have been investigated, and P^ΛE compounds of type **I–IV** (E = B, Al, Si, Sn...-based Lewis acids) featuring a one-atom spacer (Λ = C, N, O) are an important subclass of ambiphilic derivatives (Figure 1).^[4–11]

Figure 1. Schematic representation of known one-atom-bridged ambiphilic derivatives P^ΛE (Λ = C, N, O) with selected examples.

The nitrogen-bridged compound **IIIa** reported by Brey *et al* in 1966 was one of the first ambiphilic phosphine to be synthesized.^[4] About 2 decades later, Karsch *et al* prepared the CH₂-bridged phosphine-alane **Ia** and substantiated its head-to-tail dimeric structure.^[5a] Later on, **Ia** was shown by Zargarian and Fontaine to display ambiphilic behaviour upon coordination to transition metals.^[5b–d] Since 2006, increasing interest has been devoted to such P^ΛE compounds, in particular to C(sp²)-bridged derivatives of type **II**,^[7–10] and most recently, to O-bridged species of type **IV**.^[11]

Figure 2. Selected examples of C(sp²)-bridged ambiphilic compounds with the synthetic routes to access them.

Among one-atom-bridged ambiphilic derivatives, vinyl phosphines of type **II** occupy a forefront position (Figure 2). The short and rigid C(sp²) spacer imparts geometric constraints (preventing the formation of strong intramolecular P→E interactions) and at the same time preorganizes the Lewis pair. The first C(sp²)-bridged Lewis pairs, namely **IIa,b**, were prepared in the early 2010's by Erker, Uhl, Slootweg and Lammerstma.^[7,8] Besides boron and aluminum, other Lewis acid moieties have then been incorporated in compounds of type **II**, in particular heavier group 13 elements (such as Ga, **IIc**)^[8h] and early transition metals (such as Zr, **IId**).^[9] One of the main challenge in this chemistry

lies in the synthesis of the target compounds, the introduction of Lewis acid and Lewis basic moieties on a C(sp²) center raising chemo and regio-selectivity issues. Most compounds of type **II** have been prepared by hydro or carbo-elementation of phosphino-alkynes (addition of H–B, H–Al or Me–Zr bonds across C≡C triple bonds),^[7-9] the positioning of the Lewis acid *gem* to the phosphino group being the main challenge. Westcott introduced recently another route, a formal 1,1-phosphaboration of C≡C triple bonds, based on the Rh-catalyzed addition of a phosphino-borane to a terminal alkyne (**IIe**).^[10]

Ionic couplings have proven very efficient to access ambiphilic compounds, as introduced and extensively developed by our group for *ortho*-phenylene bridged species by sequential reactions of chlorophosphines and Al, B, Si...-based electrophiles.^[12] Surprisingly, this synthetic methodology has been overlooked to access compounds of type **II**, the only example being the synthesis of **IIe** starting from **IIc** *via* Al/Mg followed by Mg/Ga exchange, as reported by Uhl.^[8h] This prompted us to explore the ionic coupling methodology for the preparation of C(sp²)-bridged phosphine-boranes and here we report our first results in this area.

Our synthetic route involves 1-bromo-1-lithioethene as key precursor. This vinyl carbenoid has rarely been used in synthesis, except its reaction with aldehydes and ketones as reported by Novikov and Sampson.^[13,14] Starting from bromoethene, H₂C=C(Br)Li can in fact be easily generated upon treatment with *n*BuLi at –110°C. Then, electrophilic trapping with a chlorophosphine was expected to provide straightforward access to β -bromo vinylphosphines.^[15] To this end, chlorodiisopropylphosphine was added dropwise to 1-bromo-1-lithioethene at –110°C (Scheme 1). The reaction mixture was stirred at this temperature for 45 minutes and then warmed up to room temperature. ³¹P NMR monitoring shows complete conversion of *i*Pr₂PCl into a new product with a resonance signal at δ 33.4 ppm. After filtration over celite, concentration, extraction with pentane and distillation under reduced pressure, the targeted 1-bromo-1-diisopropylphosphinoethene **2** was isolated as a colorless oil (47% yield). The two ethylenic protons display diagnostic patterns in ¹H NMR spectroscopy. They both appear as doublet of doublet (δ 6.05 and 6.26 ppm) with a small ²J_{HH} coupling constant (0.9 Hz) and sizable couplings to phosphorus (³J_{HP} = 35 and 15 Hz for the H atom *trans*, respectively *cis*, to P).^[16] In the ¹³C NMR spectrum, the signal for the BrC(=CH₂)P quaternary carbon atom is a doublet at δ 136.97 ppm with a large ¹J_{CP} coupling constant of 60 Hz.

Scheme 1. Synthesis of the β -bromo vinylphosphine **2** from bromoethene **1**.

Then a halogen/lithium exchange was performed by addition of *n*BuLi to a diethylether solution of β -bromo vinylphosphine **2** at –40°C. The formed organolithium species H₂C=C(P*i*Pr₂)Li precipitated as a white solid. The reaction mixture was filtered and the residual solid was washed with diethylether at low temperature. The organolithium species was suspended in toluene and the boron electrophile FBMe₂ (0.75 eq.) was added at –78°C (Scheme 2). After warm up to room temperature and stirring overnight, ³¹P NMR control revealed the clean formation of a new product at δ 13.3 ppm. First evidence for C–B coupling was given by mass spectrometry (desorption chemical ionization with NH₃) with the presence a signal at *m/z* = 393.3, as expected for [**3**+H]⁺. The ¹¹B NMR resonance signal for **3** appears at δ 72.5 ppm, very close to that of the corresponding *ortho*-phenylene-bridged phosphine-borane (75.0 ppm)^[17] and in the typical zone for triarylboranes. Accordingly, the new phosphine-borane **3** adopts a monomeric open form without P→B interaction.

After workup (filtration followed by extraction with pentane), it was obtained as a yellow pasty solid (90% yield). The ^1H NMR spectrum displays only one set of signals for the two mesityl groups indicating free rotation of the B–Mes bonds at the NMR timescale (δ 6.77 ppm for the *meta* CH_{arom} groups; δ 2.16 and 2.32 ppm for the *para* and *ortho* Me groups, respectively). The two ethylenic protons appears as doublet of doublet at δ 6.04 ($^3J_{\text{HP}} = 8$ Hz, $^2J_{\text{HH}} = 4$ Hz) and 6.40 ppm ($^3J_{\text{HP}} = 13$ Hz, $^2J_{\text{HH}} = 4$ Hz), while the corresponding ^{13}C NMR signal appears as a doublet at δ 140.90 ppm with a small $^2J_{\text{CP}}$ coupling constant (4 Hz) (Figure 3). Most diagnostic of the C–B coupling is the low-field chemical shift of the $\text{BC}(\text{=CH}_2)\text{P}$ quaternary carbon atom at δ 158.61 ppm. Due to the quadrupolar moment of boron, this signal is a broad doublet, with a $^1J_{\text{CP}}$ coupling constant of 38 Hz.

Scheme 2. Synthesis of the phosphine-borane **3** by lithiation/electrophilic trapping of **2**.

Figure 3. Ethylenic/aromatic region of the ^1H (top) and ^{13}C (down) NMR spectra of **3**.

Attempts to grow crystals of **3** suitable for X-ray diffraction analysis unfortunately failed, but a few crystals of a minor product **4** were incidentally obtained at -20°C in pentane.^[18] As shown in Figure 4, this compound is a 1,4-diphosphorus 6-membered ring with two exocyclic BMes_2 groups. The ring adopts a chair conformation and the molecule has a C_2 axis of symmetry. The ylid-type carbon atoms C_1 are in trigonal planar environment [sum of bond angles = $359.9(6)^\circ$] with relatively small endocyclic PCC bond angles [$109.2(2)^\circ$] to accommodate the chair conformation. The $\text{P1}-\text{C1}$ bond length [$1.757(2)$ Å] is in the average of those reported for phosphorus ylids $\text{R}_3\text{P}=\text{CR}'_2$ (1.751 Å).^[19] The exocyclic boryl substituent is coplanar to the ylid plane, suggesting some π overlap between the carbon lone pair and the vacant orbital at boron. Consistently, the $\text{C1}-\text{B}$ bond is rather short [$1.482(4)$ Å] and has some double-bond character (the mean distance of $\text{B}=\text{C}$ bond is about 1.492 Å).^[19] Although no sign of conversion of **3** into **4** was detected, compound **4** is formally a dimer of the phosphine-borane **3**. The way it is formed remains unclear at this stage. It is possible that some impurity promotes the nucleophilic Michael-type addition of the phosphorus atom to the terminal vinylic carbon atom of another molecule. The structure of **4** can be described as a superposition of the three mesomeric forms **4a**, **4b** and **4c** (Figure 5) to account for the stabilization of the carbanion centres by the phosphonium and boryl substituents. Dimerization of ambiphilic compounds is inherent to their electronic duality and well-precedented, but this usually involves direct interaction between the Lewis acid and basic moieties. For example, phosphine-alanes such as **1** are known to form head-to-tail 6-membered ring dimers as the result of intermolecular $\text{P} \rightarrow \text{Al}$ interactions.^[5,20]

Figure 4. Molecular structure of **4** as determined by X-ray diffraction analysis; ellipsoids are shown at 50% probability; the *iPr* and Mes groups are simplified for clarity [symmetry code : (i) 1.5-*x*, 1.5-*y*, 1-*z*]. Selected bond distances (Å) and angles (°): P1–C1 1.757(2), C1–C2 1.537(4), C2–P1 1.813(3), C1–B1 1.482(4), B1–C3 1.618(4), B1–C12 1.615(5), C2–P1–C1 108.1(1), P1–C1–C2 109.2(2), C1–C2–P1 115.1(2), C1–B1–C12 125.7(3), C12–B1–C3 115.6(2), C3–B1–C1 118.7(3).

Figure 5. Mesomeric forms of compound **4**.

In conclusion, a new synthetic methodology has been developed to access C(sp²)-bridged phosphine-boranes of type **II**. The sequential formation of C–P and C–B bonds by ionic couplings, as previously used to prepare *ortho*-phenylene-bridged phosphine-boranes, also works for the one-atom C(=CH₂) spacer. Starting from the vinyl carbenoid H₂C=C(Br)Li as key precursor, the η^2 -bromo vinylphosphine **2** and η^2 -boryl vinylphosphine **3** were successively prepared. The new phosphine-borane **3** was characterized by multi-nuclear NMR and mass spectroscopy. It adopts a monomeric *open* structure without P→B interaction.

This ionic coupling strategy complements the hydroboration and phosphino-boration routes used so far to prepare phosphine-boranes of type **II**. There is no selectivity issue (the geminal position of P and B is intrinsically *priori* easily tuned by varying the P and B electrophiles. Future work will seek to generalize this methodology to a range of C(sp²)-bridged ambiphilic compounds and to explore their behavior both in small molecule activation and as ligands for transition metals.

Experimental Section

General comments: All reactions and manipulations were carried out under an atmosphere of dry argon using standard Schlenk techniques or a glovebox. All solvents were sparged with argon and dried using an MBRAUN Solvent Purification System (SPS). All solvents were degassed using freeze pump technique. ¹H, ¹³C, ³¹P and ¹¹B NMR spectra were recorded on a Bruker Avance III HD 500 (equipped with a prodigy probe), Avance III HD 400, Avance II 300 and Avance I 300 spectrometers. Chemical shifts are expressed with a positive sign, in parts per million, calibrated to residual ¹H and ¹³C solvent signals. External BF₃·OEt₂ and 85% H₃PO₄ were used as reference for ¹¹B and ³¹P NMR respectively. Mass spectra were recorded on a Waters LCT mass spectrometer. Vinyl bromide was

prepared following a literature procedure.^[21] All others reagents were purchased on Sigma-Aldrich or Fluorochem and used as received.

Synthesis of 2: 1-Bromo-1-lithioetene was prepared as described^[13] by lithiation of vinylbromide (1 mL, 14.2 mmol) in THF:ether:pentane solution (4:1:1v, 120 mL) at -110°C with *n*BuLi (1.6 M in hexanes, 3.35 mL, 5.4 mmol). The chlorodiisopropylphosphine (0.74 mL, 4.6 mmol) was added dropwise over 5 minutes. After 45 minutes at low temperature, the mixture was brought to room temperature overnight. The mixture was filtered over a plug of Celite under argon, and the volatiles were removed *in vacuo*. The obtained oil was extracted with pentane (20 mL, twice), and the volatiles were removed from the filtrate. The oil was then trap-to-trap distilled (0.05 mbar, 60°C). **2** was obtained as colorless oil (563 mg, 47%). The compound is stored in a sealed vial at -20°C . **³¹P{¹H} NMR** (121 MHz, C₆D₆, 293K, δ): 33.4 (s). **¹H NMR** (300 MHz, C₆D₆, 293K, δ): 1.01 (dd, 6H, $^3J_{\text{HH}} = 7$ Hz, $^3J_{\text{HP}} = 10$ Hz, CH_{3*i*Pr}), 1.06 (pseudo t, 6H, $^3J_{\text{HH}} = 7$ Hz, $^3J_{\text{HP}} = 13$ Hz, CH_{3*i*Pr}), 1.84 (heptd, $^2J_{\text{HP}} = 5$ Hz, $^3J_{\text{HH}} = 7$ Hz, 2H, CH_{*i*Pr}), 6.05 (dd, 1H, $^3J_{\text{HP}} = 35$ Hz, $^2J_{\text{HH}} = 0.9$ Hz, CH₂), 6.26 (dd, 1H, $^3J_{\text{HP}} = 15$ Hz, $^2J_{\text{HH}} = 0.9$ Hz, CH₂). **¹³C{¹H} NMR** (75 MHz, C₆D₆, 293K, δ): 19.75 (d, $^2J_{\text{CP}} = 21$ Hz, CH_{3*i*Pr}), 20.10 (d, $^2J_{\text{CP}} = 11$ Hz, CH_{3*i*Pr}), 25.68 (d, $^1J_{\text{CP}} = 11$ Hz, CH_{*i*Pr}), 134.94 (d, $^2J_{\text{CP}} = 36$ Hz, CH₂), 136.97 (d, $^1J_{\text{CP}} = 60$ Hz, P-C-Br).

Synthesis of 3: *n*BuLi (1.6 M in hexanes, 0.56 mL, 0.9 mmol) was added dropwise to a solution of **2** (200 mg, 0.9 mmol) in diethylether (2 mL) at -40°C . After 1h30 at low temperature, a white precipitate appeared. The supernatant was removed by filtration. *** Warning: When exposed to air, the organolithium species *i*Pr₂PC(=CH₂)Li turned to react violently. It must be carefully neutralized. *** The solid was washed twice with Et₂O (2 mL) at low temperature. To a suspension of the solid in toluene (7.5 mL) at -78°C was added dropwise a solution of fluorodimesitylborane (0.75 eq., 181 mg, 0.67 mmol) in toluene (7.5 mL). The reaction mixture was allowed to warm to room temperature overnight. The mixture was filtered and the volatiles were removed *in vacuo*. The yellow residue was extracted twice with pentane (5 mL), and the volatiles were removed *in vacuo*. **3** was obtained as a yellow pasty solid (236 mg, 90%). MS (DCI-NH₃): exact mass (monoisotopic) calcd. for [M+H]⁺ (C₂₆H₃₉PB)⁺: 393.3; found: 393.3. **³¹P{¹H} NMR** (202.5 MHz, C₆D₆, 293K, δ): 13.3 (s). **¹¹B NMR** (96.3 MHz, C₆D₆, 293K, δ): 72.5 (br s). **¹H NMR** (500 MHz, C₆D₆, 293K, δ): 1.04 (dd, 6H, $^3J_{\text{HP}} = 10$ Hz, $^3J_{\text{HH}} = 7$ Hz, CH_{3*i*Pr}), 1.06 (dd, 6H, $^3J_{\text{HP}} = 14$ Hz, $^3J_{\text{HH}} = 7$ Hz, CH_{3*i*Pr}), 1.79 (hept.d, $^2J_{\text{HP}} = 2$ Hz, $^3J_{\text{HH}} = 7$ Hz, 2H, CH_{*i*Pr}), 2.16 (s, 6H, CH_{3*Mes* para}), 2.32 (s, 12H, CH_{3*Mes* ortho}), 6.04 (dd, 1H, $^3J_{\text{HP}} = 8$ Hz, $^2J_{\text{HH}} = 4$ Hz, CH), 6.40 (dd, 1H, $^3J_{\text{HP}} = 13$ Hz, $^2J_{\text{HH}} = 4$ Hz, CH), 6.77 (s, 4H, CH_{*Mes*}). **¹³C{¹H} NMR** (125.8 MHz, C₆D₆, 293K, δ): 18.73 (d, $^2J_{\text{CP}} = 9$ Hz, CH_{3*i*Pr}), 20.67 (d, $^2J_{\text{CP}} = 18$ Hz, CH_{3*i*Pr}), 21.27 (s, CH_{3*Mes* para}), 22.53 (br d, $^1J_{\text{CP}} = 18$ Hz, CH_{*i*Pr}), 23.97 (br s, CH_{3*Mes* ortho}), 128.75 (s, CH_{*arom*}), 138.61 (s, C_{*arom* para}), 140.50 (br s, C_{*arom* ortho}), 140.90 (d, $^2J_{\text{CP}} = 4$ Hz, CH₂), 142.59 (br, B-C_{*arom*}), 158.61 (d br, $^1J_{\text{CP}} = 38$ Hz, P-C-B).

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Table of Contents

The geminal phosphine borane $i\text{Pr}_2\text{P}-\text{C}(=\text{CH}_2)-\text{BMes}_2$ was prepared by sequential C-P and C-B ionic couplings, starting from bromoethene. It adopts an *open* monomeric structure without $\text{P} \rightarrow \text{B}$ interaction. A by-product was shown by X-ray diffraction analysis to adopt a dimeric structure differing from known head-to-tail dimers.