Video Article

Preparation and Use of Carbonyl-decorated Carbenes in the Activation of White Phosphorus

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Abstract

Here we present a protocol for the synthesis of two distinct carbonyl-decorated carbenes. Both carbenes can be prepared using nearly identical procedures in multi-gram scale quantities. The goal of this manuscript is to clearly detail how to handle and prepare these unique carbenes such that a synthetic chemist of any skill level can work with them. The two carbenes described are a diamidocarbene (DAC, carbene **1**) and a monoamidoaminocarbene (MAAC **2**). These carbenes are highly electron-deficient and as such display reactivity profiles that are atypical of more traditional N-heterocyclic carbenes. Additionally, these two carbenes only differ in their electrophilic character and not their steric parameters, making them ideal for studying how carbene electronics influence reactivity. To demonstrate this phenomenon, we are also describing the activation of white phosphorus (P_4) using these carbenes. Depending on the carbene used, two very different phosphorus-containing compounds can be isolated. When the DAC **1** is used, a tris(phosphaalkenyl)phosphane can be isolated as the exclusive product. Remarkably however, when MAAC **2** is added to P_4 under identical reaction conditions, an unexpected carbene-supported P_8 allotrope of phosphorus is isolated exclusively. Mechanistic studies demonstrate that this carbene-supported P_8allotrope forms via a [2+2] cycloaddition dimerization of a transient diphosphene which has been trapped by treatment with 2,3-dimethyl-1,3-butadiene.

Video Link

The video component of this article can be found at http://www.jove.com/video/52149/

Introduction

Stable carbenes have emerged as ubiquitous reagents in homogeneous catalysis[1], organocatalysis[2], materials science[3,4], and more recently main group chemistry[5-9]. In the context of the latter, stable carbenes have recently been used in the activation and functionalization of white phosphorus (P_4)[5-9]. The ability to directly convert P_4 into organophosphorus compounds has become a topical research objective in an effort to develop “greener” methods that circumvent the use of chlorinated or oxychlorinated phosphorus precursors. Despite their widespread use, the preparation and handling of carbenes and reactive compounds such as P_4 can be a daunting task. For this reason, we have written this manuscript to provide a clear and concise protocol that will allow synthetic chemists of all skill levels to synthesize and manipulate two very unique stable carbenes. Additionally, the activation of P_4 using the described carbenes is detailed.

Herein we detail a protocol for the synthesis of two electron-deficient carbonyl decorated carbenes. We have chosen these carbenes because they differ only in their electrophilic properties, and not their steric parameters, making them ideal for studying the effects of carbene electronics on reactivity. The importance of carbene electronics with regard reactivity is exemplified by two similar compounds of the general formula carbene-P_2-carbene that have been reported by Bertrand and Robinson[5,8]. Bertrand’s P_2 derivative is supported by two cyclic alkyl amino carbene (CAAC) ligands, and is structurally, photophysically, and electrochemically different than Robinson’s compound which is a P_2 fragment supported by two N-heterocyclic carbenes (NHCs)[5,8]. Indeed, Bertrand’s P_2 complex is characterized as a yellow solid that features carbene-to-phosphorus double bonds in the solid state, whereas the derivative reported by Robinson is a dark red solid that contains NHC→P dative bonds. This structural difference also manifests itself electrochemically such that Robinson’s compound contains more electron-rich phosphorus centers that can undergo reversible 1- or 2-electron oxidations in contrast to Bertrand’s compound which can only undergo a single reversible oxidation[10].

Based on the studies described above, we became interested in studying the activation of P_4 using the highly electrophilic diamido- and monoamidoamino carbenes to determine if novel carbene-stabilized allotropes of phosphorus could be prepared. We focused on diamidocarbene (DAC) **1**, and monoamidoamino carbene (MAAC) **2** which differ only in their respective electrophilicities to interrogate what role carbene electronics play in P_4 activation. Interestingly when the more electrophilic DAC is used, a tris(phosphaalkenyl)phosphane (**3**) could be isolated as the exclusive product, whereas when a MAAC is used, a carbene-stabilized P_8 allotrope (**4**) can be obtained[11]. We also interrogated the mechanism for the formation (**4**), and found that it is formed via a [2+2] cylcoaddition dimerization reaction of a transient diphosphene. The existence of this diphosphene was confirmed by trapping it with 2,3-dimethyl-1,3-butadiene to furnish the [4+2] cycloaddition adduct **5**. The protocol for synthesizing these carbonyl-decorated carbenes and their corresponding P_4 activated compounds is described herein.

Protocol

1. Synthesis of Diamidocarbene (Compound 1)

1. Connect an oven-dried 100 ml Schlenk flask to a high performance vacuum manifold, evacuate it and flush with nitrogen. Add a stir bar to the flask and cap with a rubber septum. Weigh out N,N'-dimesitylformamidine[12] (1.5 g, 5.35 mmol) and add it to the flask while flushing with nitrogen.
    1. Add (via dry, deoxygenated syringes) 30 ml of dry, degassed dichloromethane (DCM) followed by triethylamine (1.1 ml, 8.0 mmol, 1.5 equiv.). Cool the resulting solution to 0 °C in an ice bath.
    2. Add dropwise (via a dry, deoxygenated syringe) dimethylmalonyl dichloride (0.75 ml, 5.60 mmol, 1.05 equiv.) to the cooled solution. Upon addition, allow the solution to stir at 0 °C for 1 hr under an atmosphere of nitrogen. Once the solution has stirred for 1 hr, remove all the volatile materials under vacuum.
    3. Add a solvent mixture of dry, degassed hexanes:DCM (2:1 by volume, 24 ml total volume) to the residue in the reaction flask. Let the mixture triturate for 10 min.
    4. Meanwhile, attach a filter tube equipped with a medium porosity glass frit to the top of an oven-dried 100 ml Schlenk flask (see **Figure 1**). To the filter tube, add enough oven-dried Celite to create a filter plug approximately 2 inches tall. Seal the filter tube with a rubber septum, and pull vacuum, on the system by attaching the Schlenk flask to the vacuum manifold.

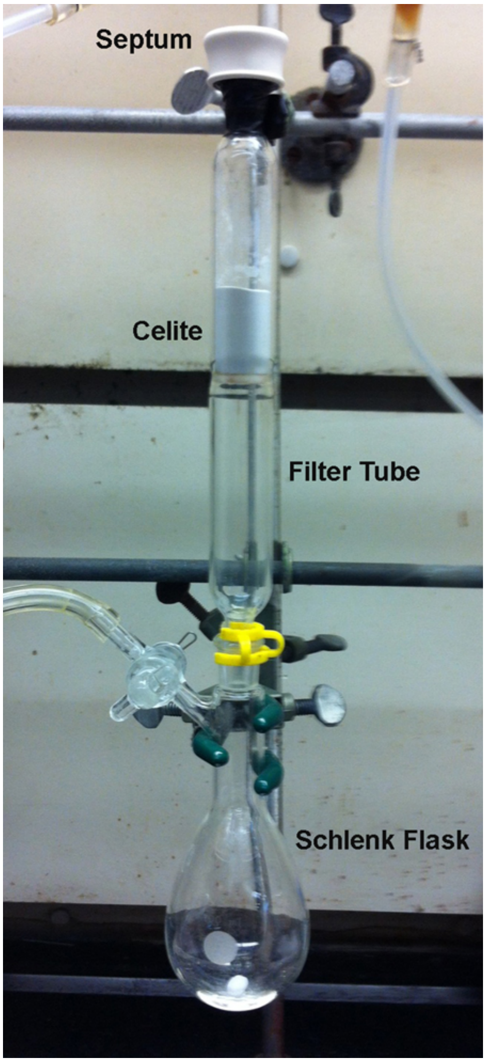


Figure 1. Filtration apparatus assembly for removal of [$HNEt_3$][Cl] from carbene precursors 1-HCl and 2-HCl. This apparatus is also used to remove NaCl formed during the synthesis of carbenes 1 and 2.

5. Filtration apparatus assembly for removal of [$HNEt_3$][Cl] from carbene precursors 1-HCl and 2-HCl. This apparatus is also used to remove NaCl formed during the synthesis of carbenes 1 and 2.
6. Once the filtration apparatus has been assembled and is under vacuum, transfer the white suspension in the reaction flask via cannula into the filter tube. Be sure to periodically pull vacuum on the collection Schlenk flask to ensure that all of the solution filters through the Celite.

   7. Wash the Celite by adding a solvent mixture of dry, degassed hexanes:DCM (2:1, volume, 18 ml total volume) using a syringe through the rubber septum. Again, periodically pull vacuum on the collection Schlenk flask to ensure that all of the solution filters through the Celite.
   8. Disconnect the collection Schlenk flask from the filter tube under a flush of nitrogen, then seal the collection Schlenk flask with a glass stopper. Remove all of the solvent from the collection Schlenk flask under vacuum to afford the precursor for diamidocarbene 1 (1-HCl) as an air/moisture sensitive white powder in approximately 92% yield (2.04 g). The product can be verified by ^{1}H and ^{13}C NMR spectroscopy ($CDCl_3$)[13,14]. Transfer compound 1-HCl into a glove box for storage prior to the next step.

2. To prepare the diamidocarbene 1, first transfer an oven-dried 100 ml Schlenk flask equipped with a stir bar and a glass stopper into a nitrogen-filled glove box.
   1. Weigh out carbene precursor 1-HCl (0.600 g, 1.45 mmol) and sodium hexamethyldisilazide (NaHMDS, 0.267 g, 1.46 mmol) and place both solids into the Schlenk flask.

3. Add dry, degassed benzene (25 ml) to the two solids in the Schlenk flask and then stopper the flask. At this point, the Schlenk flask can be removed from the glove box.
4. Stir the solution of the carbene at RT for 30 min. Throughout the reaction, the solution will become a turbid yellow-orange color. During this time, set up a filtering apparatus similar to the one described above (using a 1 inch plug of Celite) for the synthesis of 1-HCl.
5. Filter the carbene solution (to remove precipitated NaCl) as described for the precursor 1-HCl. Once the solution has been filtered, remove all of the volatiles using vacuum to afford the crude carbene 1 as a yellow-orange powder. Further purify carbene 1 by washing the solid with cold hexanes (~10 ml) to afford analytically pure compound as an air/moisture sensitive white powder in approximately 85% yield (0.462 g). Verify the product by ^{1}H and ^{13}C NMR spectroscopy (C_6D_6)[13].

2. Synthesis of Monoamidocarbene (Compound 2)

1. Connect an oven-dried 250 ml Schlenk flask to a high performance vacuum manifold, evacuate it and flush with nitrogen. Add a stir bar to the flask and cap with a rubber septum. Weigh out N,N'-dimesitylformamidine (3.00 g, 10.70 mmol) and add it to the flask while flushing with nitrogen.
   1. Add (via dry, deoxygenated syringes) 125 ml of dry, degassed DCM followed by triethylamine (2.25 ml, 16.05 mmol, 1.5 equiv.). Cool the resulting solution to 0 °C in an ice bath.
   2. Add dropwise (via a dry, deoxygenated syringe) 3-chloropivaloyl chloride (1.54 ml, 11.77 mmol, 1.1 equiv.) to the cooled solution. Upon addition, allow the solution to stir at 0 °C for 30 min under an atmosphere of nitrogen. Then gradually warm the solution to RT, and then remove all the volatile materials under vacuum. After the solvent is removed, a white solid residue will remain.
   3. Add toluene (200 ml) to the white solid and allow the suspension to triturate for 1 hr. Then filter the mixture over a 1 inch plug of Celite using a medium porosity glass fritted Büchner funnel.
   4. Transfer the toluene solution to a 500 ml round bottom flask equipped with a stir bar. Connect a reflux condenser to the flask and heat the solution to reflux (110 °C) for 16 hr. Over the course of the reaction, a white precipitate will form.
   5. After 16 hr allow the suspension to cool to RT. During this time, more solid will precipitate from the solution. Collect the solid via vacuum filtration and wash the solid with cold toluene (3 x 20 ml).
   6. Dry the obtained white solid using vacuum to afford the precursor for monoamidocarbene 2 (2-HCl) as an air stable white powder in approximately 91% yield (3.32 g). The product can be verified by ^{1}H and ^{13}C NMR spectroscopy ($CDCl_3$)[15]. Transfer compound 2-HCl into a glove box for storage prior to the next step.

2. To prepare the monoamidocarbene 2, first transfer an oven-dried 100 ml Schlenk flask equipped with a stir bar and a glass stopper into a nitrogen-filled glove box.
   1. Weigh out carbene precursor 2-HCl (0.500 g, 1.25 mmol) and NaHMDS (0.241 g, 1.32 mmol) and place both solids into the Schlenk flask.
   2. Add dry, degassed benzene (45 ml) to the two solids in the Schlenk flask and then stopper the flask. At this point, the Schlenk flask can be removed from the glove box.
   3. Stir the solution of the carbene at RT for 30 min. During the reaction, the solution will become a turbid yellow color. Meanwhile, set up a filtering apparatus similar to the one described above for the synthesis of 1-HCl using a 1 inch plug of Celite.
   4. Filter the carbene solution (to remove precipitated NaCl) as described for carbene 1. Once the solution has been filtered, remove all of the volatiles using vacuum to afford the crude carbene 2 as a tan powder. Further purify carbene 2 by washing the solid repeatedly with pentane to afford analytically pure compound as an air/moisture sensitive white powder in approximately 62% yield (0.309 g). Verify the product by ^{1}H and ^{13}C NMR spectroscopy (C_6D_6)[15].

3. Synthesis of a Tris(phosphaalkenyl)phosphane (Compound 3)

Caution Statement: White phosphorus is extremely pyrophoric as well as toxic and should be handled cautiously in a glovebox whenever possible.

1. To make a tris(phosphaalkenyl)phosphane (compound 3), weigh out diamidocarbene 1 (0.100 g, 0.266 mmol, 3 equiv.) and white phosphorus (P_4, 0.011 g, 0.089 mmol, 1 equiv.) inside of a nitrogen-filled glove box with the lights turned off. Turn off as many lights in the lab during these first few steps as P_4 is light sensitive.
2. Add the two solids to a 20 ml glass vial that is wrapped in aluminum foil. Add dry, degassed diethyl ether (Et_2O, 10 ml) to the solids and then cap the vial. Stir the slurry in the dark for 2 hr. During the course of the reaction, a bright red-orange precipitate will form.

3. Isolate the red solid via filtration using a 10 ml medium porosity glass fritted Büchner funnel. Wash the red solid with Et_2O (4 x 5 ml) and then dry it under vacuum to afford compound 3 as an analytically pure air stable compound in approximately 82% yield, 0.092 grams (based on P_4). Verify the product by ^1H and ^{31}P NMR spectroscopy (C_6D_6)[11].

4. Synthesis of a Carbene-stabilized P_8 Allotrope (Compound 4)

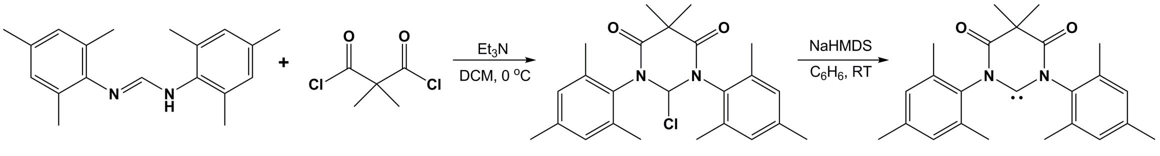
1. Method A
    1. To make a carbene-stabilized P_8 allotrope (compound 4), weigh out monoamidocarbene 2 (0.100 g, 0.276 mmol, 3 equiv.) and P_4 (11.4 mg, 0.092 mmol, 1 equiv.) inside of a nitrogen-filled glove box with the lights turned off. Turn off as many lights in the lab during these first few steps as P_4 is light sensitive.
    2. Add the two solids to a 20 ml glass vial that is wrapped in aluminum foil. Add dry, degassed diethyl ether (Et_2O, 10 ml) to the solids and then cap the vial. Upon addition of the ether, the fleeting dark green color rapidly changes to bright orange. Stir the slurry in the dark for 2 hr. During the course of the reaction, a bright orange precipitate will form.
    3. Isolate the orange solid via filtration using a 10 ml medium porosity glass fritted Büchner funnel. Wash the orange solid with Et_2O (4 x 2 ml) and then dry it under vacuum to afford compound 4 as and analytically pure air stable compound in approximately 51% yield, 39.5 mg (based on P_4). Verify the product by ^1H and ^{31}P NMR spectroscopy (THF-D8)[11].
2. Method B
    1. Weigh out monoamidocarbene 2 (0.100 g, 0.276 mmol, 2 equiv.) and P_4 (17.1 mg, 0.138 mmol, 1 equiv.) inside of a nitrogen-filled glove box with the lights turned off. Turn off as many lights in the lab during these first few steps as P_4 is light sensitive.
    2. Add the two solids to a 20 ml glass vial that is wrapped in aluminum foil. Add dry, degassed hexanes (10 ml) to the solids and then cap the vial. Upon addition of the ether, the fleeting dark green color rapidly changes to bright orange. Stir the slurry in the dark for 2 hr. During the course of the reaction, a bright orange precipitate will form.
    3. Isolate the orange solid via filtration using a 10 ml medium porosity glass fritted Büchner funnel, and then dry it under vacuum to afford compound 4 as and analytically pure air stable compound in approximately 75% yield, 87.7 mg (based on P_4). Verify the product by ^1H and ^{31}P NMR spectroscopy (THF-D8).[11]

5. Trapping a Transient *E*-1,2-bis(phosphaalkenyl)diphosphene via [4+2] Cycloaddition: Synthesis of Compound 5

1. To prepare compound 5, weigh out monoamidocarbene 2 (0.300 g, 0.828 mmol, 2 equiv.) and P_4 (51.3 mg, 0.414 mmol, 1 equiv.) *separately* inside of a nitrogen-filled glove box with the lights turned off. Turn off as many lights in the lab during these first few steps as P_4 is light sensitive.
2. Add the P_4 to a 20 ml glass vial, and then add dry, degassed hexanes (18 ml) to the vial. Next, add 2,3-dimethyl-1,3-butadiene (2 ml) to the P_4 suspension in hexanes.
3. While the hexane/P_4 suspension is rapidly stirring, add the carbene 2 as a solid in one portion. The suspension will instantly become bright yellow. Over a period of about 10 min, all of the solids will dissolve followed by the precipitation of a bright yellow solid. At this point, let the suspension stir for 4 hr.
4. After 4 hr, isolate the yellow solid via filtration using a 10 ml medium porosity glass fritted Büchner funnel. This yellow solid is compound 5 (> 90% purity by both ^1H and ^{31}P NMR). Concentrate the yellow supernatant solution to dryness and combine the yellow residue with the filtered yellow solid.
5. To purify compound 5, recrystallize the combined yellow solids from a 1:3 (by volume) DCM:hexanes solution (12 ml total volume) in a -30 °C freezer in the glovebox O/N. This procedure will afford 5 as analytically pure air stable yellow crystals in approximately 71% yield, 0.301 grams (based on P_4). Verify the product by ^1H and ^{31}P NMR spectroscopy (C_6D_6)[11].

Representative Results

The ability to isolate a tris(phosphaalkenyl)phosphane such as **3** or the P_8-allotrope (**4**) from white phosphorus relies on the use of an electrophilic carbene to activate the P_4 tetrahedron[11,16]. Therefore, it is critical to prepare carbenes with enhanced π-acidity, and by extension electrophilicity. **Figure 2** illustrates the synthesis of carbene precursor **1**-HCl and its subsequent deprotonation to afford the diamidocarbene **1**[13]. The synthesis of diamidocarbene **1** can be accomplished in a single day (approximately 6 hr from start to finish), and the carbene can be isolated as a white powder in 72% overall yield.



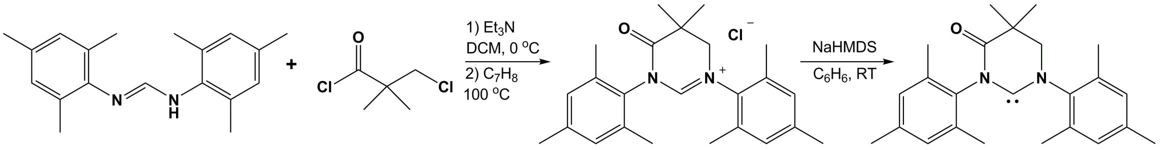
1-HCl

1

Figure 2. Synthesis of diamidocarbene **1** by coupling *N*,*N'*-dimesitylformamidine to dimethylmalonyl dichloride. Please click here to view a larger version of this figure.

By removing one of the carbonyl moieties from carbene **1**, the π-acidity of the diamidocarbene can be attenuated. To accomplish this task, monoamidocarbene **2** can be prepared in a similar manner to carbene **1** using 3-chloropivaloyl chloride and *N*,*N'*-dimesitylformamidine[15]. **Figure**

3 describes the synthesis of **2** which can be carried out in approximately two days. The free monoamidocarbene can be isolated as a white powder in 56% overall yield.



2-HCl **2**

Figure 3. Synthesis of monoamidocarbene **2** by coupling *N*,*N'*-dimesitylformamidine to 3-chloropivaloyl chloride. To date there have been several reports that detail the activation of white phosphorus using stable carbenes. In these studies, it has been well-demonstrated that the electronic properties of the carbenes directly govern the identity of the activated phosphorus product^5. To demonstrate this phenomenon, carbenes **1** and **2**, which differ only in their respective electrophilicities, can be used to activate P_4 to afford very different products. When the more electrophilic diamidocarbene **1** is used, the tris(phosphaalkenyl)phosphane (**3**) can be prepared as a red solid in 82% yield (**Figure 4**). However, when the less electrophilic monoamidocarbene **2** is used, the P_8-allotrope (**4**) can be isolated as an orange solid in yields ranging from 51-75% yield depending on the conditions used (**Figure 4**). Please click here to view a larger version of this figure.

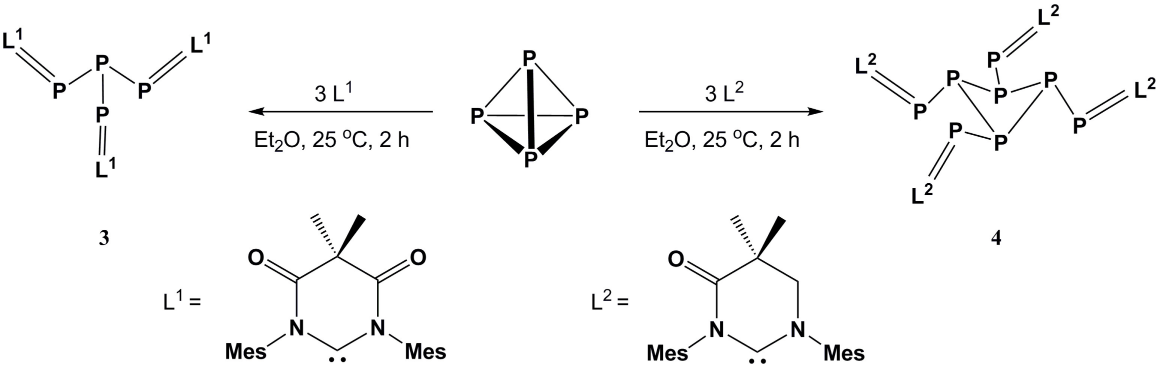
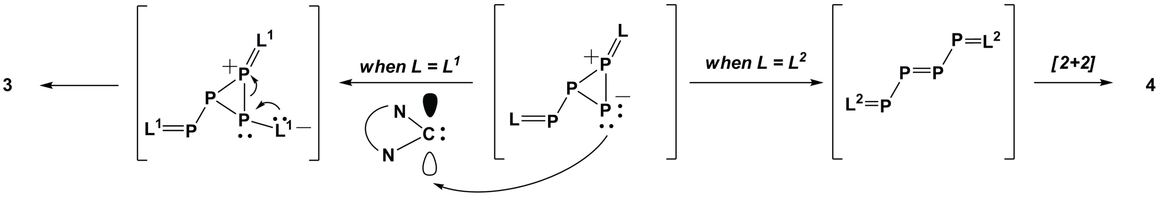


Figure 4. Synthesis of tris(phosphaalkenyl)phosphane **3** and carbene-stabilized P_8 allotrope **4** starting from carbenes **1** and **2**, respectively (Mes = 2,4,6$(CH_3)_3C_6H_2$).

A mechanism has been proposed for the formation of compounds **3** and **4** (**Figure 5**) which describes how the differing electrophilicities of carbenes **1** and **2** influences the reaction with P_4. For both carbenes, zwitterionic intermediate **A**, which features two coordinated carbene ligands has been suggested as forming initially upon activation of the P_4 tetrahedron. When the more electrophilic diamidocarbene **1** is used, intermediate **A** is sufficiently nucleophilic to add to the empty *p*-orbital of a third molecule of **1**, eventually resulting in the formation of tris(phosphaalkenyl)phosphane **3** through intermediate **B**. However, when the less electrophilic carbene **2** is used, **A** is not sufficiently nucleophilic to add a third molecule of **2**, and subsequently rearranges to afford the linear diphosphene intermediate **C**. Intermediate **C** then rapidly undergoes a [2+2] cycloaddition-dimerization to afford the P_8-allotrope **4.** It is proposed that intermediate **C** is the source of the dark green color observed in the synthesis of the **4**. Please click here to view a larger version of this figure.



B **A** **C**

Figure 5. Proposed mechanism for the formation of compounds **3** and **4**. The formation of the putative diphosphene intermediate **C** was verified by trapping with 2,3-dimethyl-1,3-butadiene to afford compound **5** (**Figure 6**). In a typical experiment, when the activation of P_4 using carbene **2** is carried out in a large excess of 2,3-dimethyl-1,3-butadiene, compound **5** can be isolated as a bright yellow solid in 71% yield. Please click here to view a larger version of this figure.

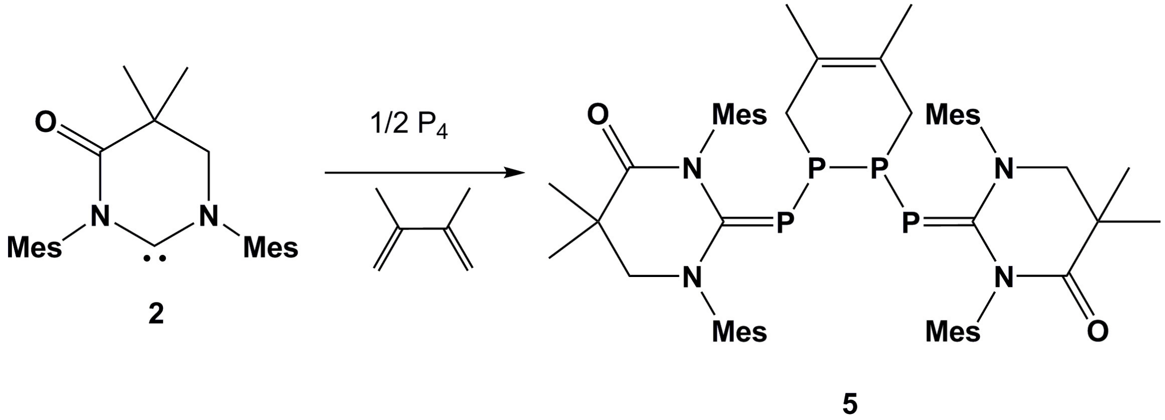


Figure 6. Synthesis of compound **5** by trapping intermediate **C** with 2,3-dimethyl-1,3-butadiene (Mes = 2,4,6(CH_3)$_3$$C_6H_2$). To demonstrate the effectiveness of these synthetic methods, we have provided ^{1}H NMR spectra for carbenes **1** and **2** as well as ^{31}P NMR spectra for compounds **3**, **4**, and **5** (see **Figures 7-11**, respectively). Please click here to view a larger version of this figure.

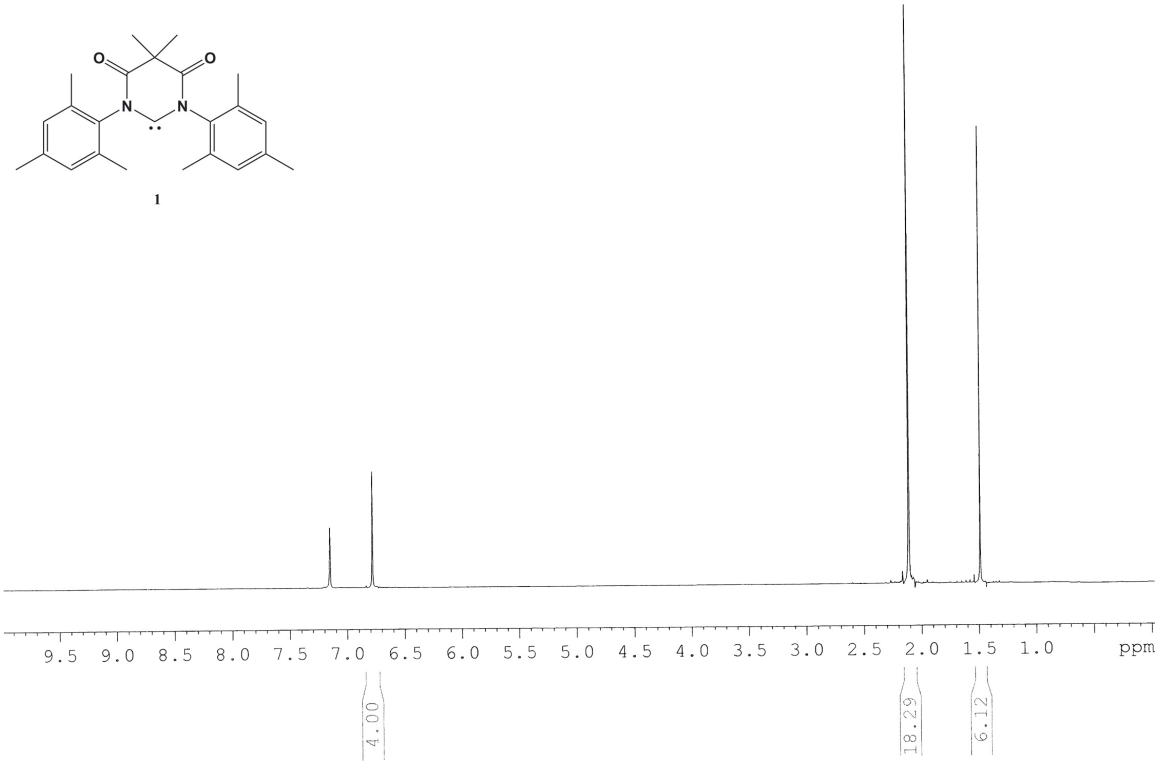


Figure 7. ^{1}H NMR (C_6D_6) of DAC **1** prepared using the described protocol.

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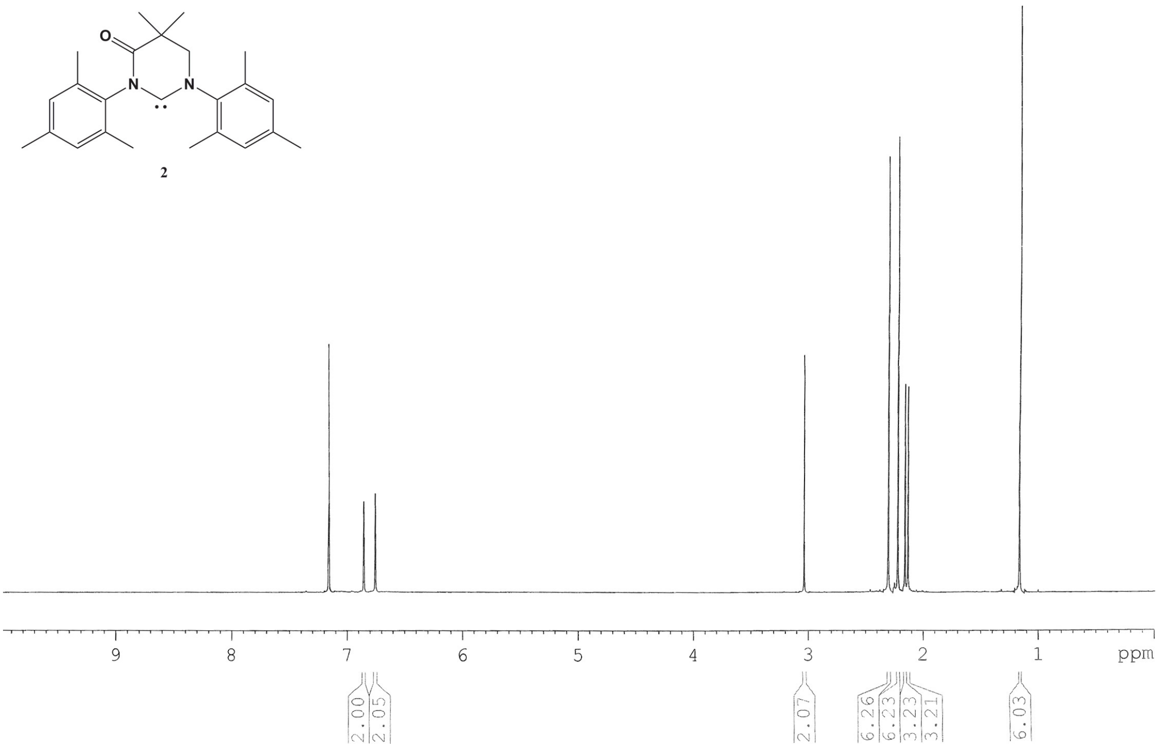

Figure 8. ^{1}H NMR (C_6D_6) of MAAC **2** prepared using the described protocol. Please click here to view a larger version of this figure.

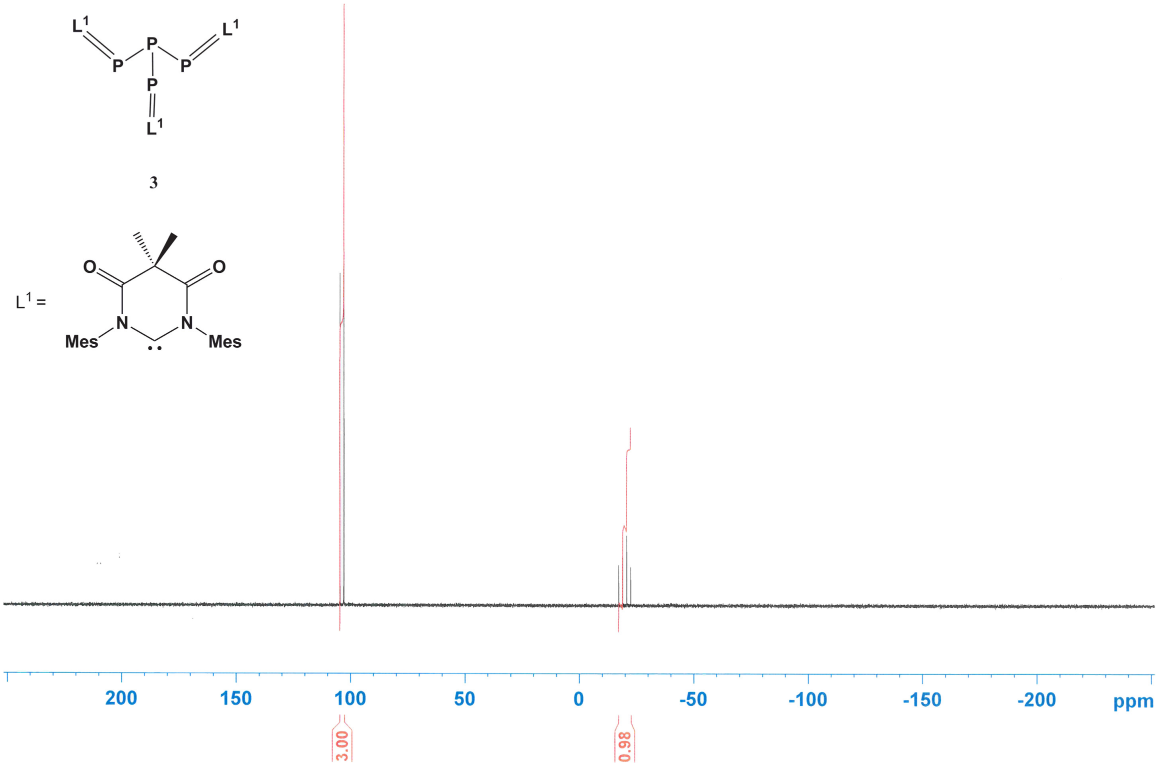

Figure 9. ^{31}P NMR (C_6D_6) of **3** prepared using the described protocol.

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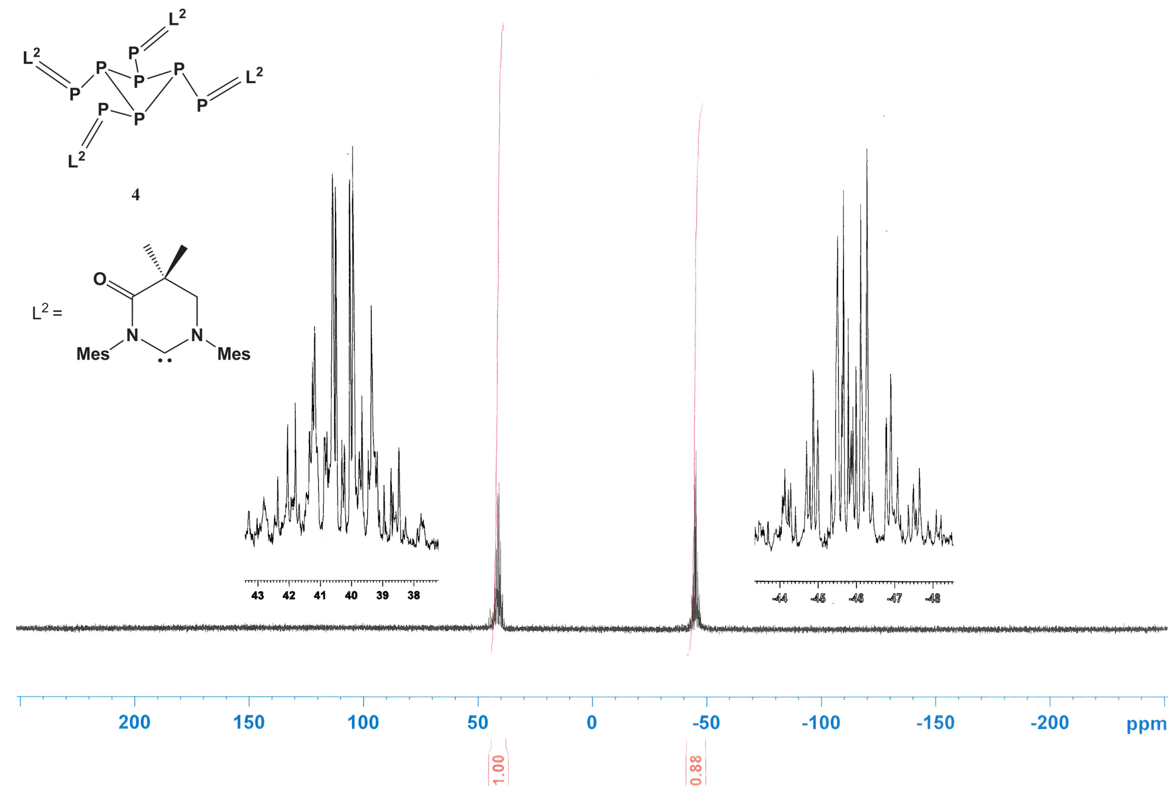

Figure 10. ^{31}P NMR (THF-D8) of **4** prepared using the described protocol. Please click here to view a larger version of this figure.

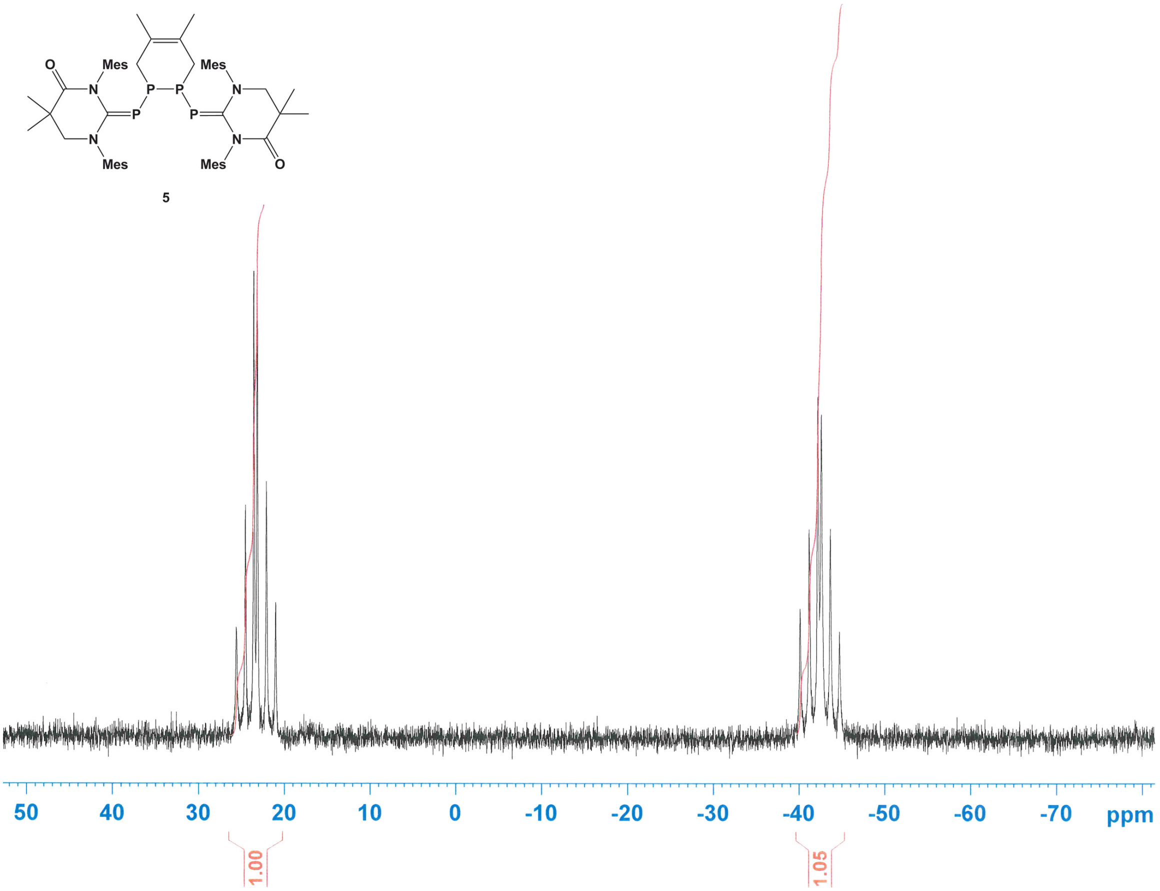

Figure 11. ^{31}P NMR (C_6D_6) of **5** prepared using the described protocol. Please click here to view a larger version of this figure.

Discussion

A straightforward procedure for generating carbonyl-decorated carbenes and their application in the activation of white phosphorus is presented here. The critical steps in the protocol for synthesizing the carbenes are: (a) make sure all solvents are properly dried before use, (b) make sure the addition of acid chlorides to the formamidine is done very slowly, (c) if the Celite is not oven-dried for a minimum of 12 hr at 180 °C, hydrolysis of the **1**-HCl as well as carbenes **1** and **2** occur. In some cases, the white phosphorous will convert to red phosphorous. For the P_4 activation reactions, it is imperative that the reactions be conducted in the dark or in foil-wrapped reaction vessels to ensure that the white phosphorus does not convert into red phosphorus.

There are no major limitations of the techniques described herein, and indeed these methods may be applied to the future synthesis of other carbenes. One significant advantage to our method of preparing the described carbenes is the utilization of NaHMDS as the base for the deprotonation of compounds **1**-HCl and **2**-HCl. NaHMDS is well-suited to the generation of carbenes as it is soluble in aromatic hydrocarbons in which the vast majority of carbenes are stable.

Disclosures

The authors have nothing to disclose.

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