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New Synthetic Routes to C-Amino Phosphorus Ylides and their Subsequent Fragmentation into Carbenes and Phosphines**

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Abstract

Phosphonio-substituted aldiminium, iminium and imidazolidinium salts are readily prepared in excellent yields by addition of phosphines to Alder's dimer, or by treatment of the corresponding chloro iminium salt with the *in situ* generated phosphine/trimethylsilyl triflate adduct. A two-electron reduction, using either potassium metal or tetrakis(dimethylamino)ethylene, leads to the corresponding C-amino phosphorus ylides. When basic phosphine fragments are used, the ylides can be isolated; otherwise they spontaneously undergo a fragmentation into carbene and phosphine. Although the reduction/fragmentation sequence occurs under mild conditions, this method is limited to the preparation of transient carbenes, due to the non-availability of sterically hindered dications, and consequently of phosphorus ylides bearing bulky carbon substituents. To overcome this difficulty, a second novel route to phosphorus ylides has been developed: The addition, at low temperature, of 2,4-di-*tert*-butyl-*ortho*-quinone to readily available C-amino phosphalkenes. Provided the phosphorus atom bears either an amino or *tert*-butyl group, a [4+1]-cycloaddition occurs, and the resulting ylides spontaneously undergo a fragmentation into a dioxaphospholane and a spectroscopically observed carbene.

Keywords

Carbene; phosphorus; ylide; phosphalkene; dications

Introduction

Despite the existence of various methods for generating transient[1] and stable carbenes,[2] there is still a need for new methodologies, which allow for the preparation of these highly reactive species under mild conditions. Among carbenes, diaminocarbenes,[3] and more recently monoaminocarbenes,[4] have attracted considerable attention, mainly because of their ligand properties. So far, most of these compounds have been prepared by deprotonation of the conjugate acid, reduction of the corresponding thione, and 1,1-elimination reactions. All these routes have advantages but also drawbacks. The latter methods involve relatively drastic conditions,[5] whereas for the former, strong anionic bases are required,[6] which, in some cases, induce side reactions including nucleophilic addition to the starting salt,[5a] and deprotonation at other sites of the molecule.[7]

Recently,[8] we reported a new route to aminocarbenes. Based on calculations by Bestmann, Schleyer et al,[9] which predicted that the P,C dissociation energy of the parent C-amino

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phosphorus ylide $\text{H}_3\text{P}=\text{C}(\text{H})(\text{NH}_2)$ is only 8.1 kcal/mol, we showed that indeed *cyclic* C-amino phosphorus ylides **A** could undergo fragmentation into carbene and phosphine at low temperature (Scheme 1). However, in the *acyclic* series, we found that on one hand, C-amino phosphorus ylides **B** bearing strongly basic nucleophilic phosphines, such as tris(dimethylamino)phosphine, are too stable to undergo fragmentation to the carbene and phosphine, and, on the other hand, phosphonium precursors **C** featuring non-basic phosphines, such as triphenylphosphine, cannot be prepared since they readily decompose into phosphine and iminium salts. Therefore, the most general method for the preparation of phosphorus ylides, the deprotonation of the corresponding phosphonium salts, cannot be used to prepare the desired labile C-amino phosphorus ylides (Scheme 1). Moreover, none of the other well-developed methods[10] can be applied when an amino substituent is present at the ylidic carbon. The addition of phosphines to alkenes and alkynes is limited to electron-poor unsaturated derivatives. Staudinger adducts are not accessible, since amino-substituted diazo derivatives are not stable. Dihalogeno triphenylphosphoranes only react with methylene derivatives activated by electron-withdrawing groups.

Here we report two original synthetic routes to stable and transient C-amino phosphorus ylides, and discuss their fragmentation into carbenes and phosphines.

Results and Discussion

We have already shown that highly thermally stable phosphonio-substituted aldiminium salts **1**[11] are readily prepared in excellent yields by addition of phosphines to Alder's dimer,[12] or alternatively by treatment of the corresponding chloro aldiminium salt with the *in situ* generated phosphine/trimethylsilyl triflate adduct.[13] Interestingly, basic phosphines, such as tricyclohexylphosphine, are not required, triphenylphosphine can be used. One can quickly realize that these onio-substituted aldiminium salts **1** are oxidized forms of the corresponding ylides **2**. Therefore, a two-electron reduction of **1** should lead to ylides **2** (Scheme 2). Furthermore, such a process should not be very difficult, since Weiss has shown that onio-substitution dramatically increases the electron affinity of a given substance.[14]

To test this hypothesis, and knowing that ylide **2a** featuring the very basic tris(dimethylamino)phosphine is stable,[8] we prepared the phosphonio-substituted aldiminium salt **1a**, and reduced it with potassium metal (Scheme 3). The reaction was carried out in tetrahydrofuran at -50°C . After evaporation of the solvent, the residue was extracted with pentane, and ylide **2a** was isolated in near quantitative yield. We then used dication **1b**,[11] featuring the less basic triphenylphosphine. Under the same experimental conditions, but with tetrakis(dimethylamino)ethylene (TDAE) as a reducing agent, we observed the quantitative formation of triphenylphosphine and alkene **3b**, the expected dimer of the (diisopropylamino) (hydrogeno)carbene (Scheme 3).

Interestingly, not only aldiminium salts can be used to prepare dications, but also C-substituted iminium salts and imidazolidinium salts, as shown by the preparation of **1c-d** (Scheme 4). Monitoring by ^{31}P and ^{13}C NMR spectroscopy the reduction reaction of **1c-d** with tetrakis(dimethylamino)ethylene and potassium metal, respectively, did not allow for the detection of the phosphorus ylides and carbenes. Again, we observed the quantitative formation of triphenylphosphine and alkene **3c** (Z/E: 20/80) and **3d**.

It is important to note that all attempts to prepare dications bearing bulky substituents at carbon failed. For example, no reaction occurred when the *N,N*-diisopropyl-*C-tert*-butyl chloroiminium salt was treated with the *in situ* generated triphenylphosphine/trimethylsilyl triflate adduct. Therefore, although the reduction of dications **1**, and the fragmentation of the ensuing C-amino-phosphorus ylides **2**, occur under very mild conditions, when a non-basic

phosphine fragment is used, the overall sequence seems limited to the generation of transient amino carbenes, because of the non-availability of sterically hindered starting dications.

Therefore, in order to generate persistent carbenes, it was necessary to design a new route, which will allow for the preparation of *C*-amino-phosphorus ylides featuring bulky substituents at carbon and a non-basic phosphorus fragment. It is known that *ortho*-quinones react with phosphines via a [4+1] cycloaddition process to give hypervalent phosphorus derivatives (Scheme 5).[15] On the other hand, *C*-alkyl and *C*-aryl substituted phosphalkenes react with *ortho*-quinones to afford [4+2] cycloadducts.[16] However, for phosphalkenes the π -orbital and the phosphorus lone pair are very close in energy, and depending on the nature of the substituents at carbon and phosphorus, either of these orbitals can be the HOMO of the system. [17] Consequently, we expected that phosphalkenes which bear a π -donor amino substituent at carbon, would react via their lone pair by a [4+1] cycloaddition process to afford the desired *C*-amino phosphorus ylides; moreover, the presence of two oxygen substituents at phosphorus was expected to allow for a facile fragmentation.

C-amino phosphalkenes can be prepared by several routes.[18] We chose the nucleophile-induced ring opening of diphosphirenium salt **4**. [19] Indeed, this synthetic strategy allows for the synthesis of phosphalkenes featuring a $C(Ni-Pr_2)[P(Ni-Pr_2)_2]$ fragment known to be a persistent carbene.[20] Moreover, starting from a single precursor, the use of various nucleophiles gives the opportunity to study the influence of the nature of the phosphorus substituent on the fate of the reaction with the quinone. Using phenyllithium, *tert*-butyllithium, and lithium diisopropyl amide, phosphalkenes **5a**, **5b** and **5c** were prepared in 82, 90 and 90 % yield, respectively (Scheme 6).

Phosphalkene **5a**, bearing a phenyl group at phosphorus, reacts with 2,4-di-*tert*-butyl-*ortho*-quinone at -78°C , giving a complex mixture, which includes the desired carbene **6**, but in only 20% yield (according to ^{31}P NMR spectroscopy) (Scheme 7). Among the other products of the reaction were the benzo-1,3,2-dioxaphospholane **7a**, the bis(quinone) adduct **8a**, and the six-membered heterocycles **9a** (as a mixture of two diastereomers). Therefore, in this case, despite the presence of the amino group at carbon, the [4+2]-cycloaddition strongly competes with the desired [4+1] process.

The observed instability and clean fragmentation of the (highly probable) phosphorus ylide intermediate was a very encouraging result. Therefore, in order to facilitate the formation of ylides versus dioxaphosphinanes **9**, we used phosphalkenes **5b** and **5c**, featuring stronger electron-donating groups at phosphorus. The reaction with 2,4-di-*tert*-butyl-*ortho*-quinone occurred at -78°C , and cleanly afforded the desired carbene **6**, along with an equimolar amount of benzodioxaphospholanes **7b** and **7c**, respectively; no traces of six-membered heterocycles were observed (Scheme 8).

Conclusion

A variety of dicationic species can be prepared by simple addition of a phosphine, which includes non-basic phosphines, to aldiminium, iminium and even imidazolidinium salts. Subsequent two-electron reductions cleanly afford the corresponding *C*-amino phosphorus ylides, which, depending on the nature of the phosphorus substituents, can either be stable or undergo fragmentation into the corresponding phosphine and carbene. However, the overall sequence seems restricted to the generation of transient amino carbenes, because of the unavailability of sterically hindered starting dications. To overcome this limitation, *C*-amino phosphorus ylides, bearing bulky substituents at carbon, can readily be synthesized by addition of *ortho*-quinones to *C*-amino phosphalkenes. Since a variety of the latter have been described in the literature, and quinones are not aggressive reagents, this new route to amino carbenes should have a broad scope of application, and be very functional group tolerant.

Experimental Part

General

All manipulations were performed under an inert atmosphere of argon using standard Schlenk techniques. Dry, oxygen-free solvents were employed. ^1H , ^{13}C and ^{31}P NMR spectra were recorded on Varian Inova 300, 500 and Bruker Avance 300 spectrometers.

Synthesis of C-Phosphonio-Aldiminium Salts **1a** and **1b**

An acetonitrile solution (15 mL) of phosphine (8.5 mmol) was added at -40°C to an acetonitrile solution (15 mL) of Alder's dimer (7.7 mmol). The suspension was stirred for 1 hour at room temperature. After evaporation of the solvent, the solid residue was washed with THF (20 mL) affording **1a** and **1b**[11] as white microcrystalline solids. **1a**: 3.81 g, 86%; mp: $201\text{--}202^\circ\text{C}$; ^{31}P NMR (CD_3CN , 25°C): +33.5; ^1H NMR (CD_3CN , 25°C): 1.61 (d, $J_{\text{HH}} = 6.2$, 6H, CHCH_3), 1.63 (d, $J_{\text{HH}} = 6.2$, 6H, CHCH_3), 2.88 (d, $J_{\text{HP}} = 11.3$, 18H, NCH_3), 4.69 (sept, $J_{\text{HH}} = 6.2$, 1H, CHCH_3), 4.77 (sept d, $J_{\text{HH}} = 6.2$, $J_{\text{HP}} = 4.1$, 1H, CHCH_3), 8.53 (d, $J_{\text{HP}} = 24.1$, 1H, CH). ^{13}C NMR (CD_3CN , 25°C): 20.8 (CHCH_3), 24.3 (CHCH_3), 37.5 (d, $J_{\text{CP}} = 4.6$, NCH_3), 63.0 (d, $J_{\text{CP}} = 7.5$, CHCH_3), 65.1 (d, $J_{\text{CP}} = 5.3$, CHCH_3), 122.2 (q, $J_{\text{CF}} = 319.6$, CF_3SO_3^-), 167.8 (d, $J_{\text{CP}} = 141.6$, CH).

Synthesis of C-Phosphonio-Iminium and Imidazolidinium Salts **1c** and **1d**

A CH_2Cl_2 solution (10 mL) of trimethylsilyltrifluoromethane sulfonate (4.66 mmol) and triphenylphosphine (2.55 mmol) was added at -78°C to a CH_2Cl_2 solution (10 mL) of *C*-phenyl-*C*-chloro-*N,N*-diisopropyliminium chloride and chloro imidazolidinium chloride (2.33 mmol), respectively. The reaction mixture was stirred for 1 hour at room temperature. After evaporation of the solvent under vacuum, the residue was washed with THF (20 mL) affording **1c** and **1d** as white solids. **1c**: 1.57 g, 90%; ^{31}P NMR (CD_3CN , 25°C): +35.7. ^1H NMR (CD_3CN , 25°C): 1.20 (d, $J_{\text{HH}} = 6.3$, 6H, CHCH_3), 1.43 (d, $J_{\text{HH}} = 6.6$, 6H, CHCH_3), 4.60 (sept d, $J_{\text{HH}} = 6.3$, $J_{\text{HP}} = 2.4$, 1H, CHCH_3), 4.90 (sept d, $J_{\text{HH}} = 6.6$, $J_{\text{HP}} = 3.6$, 1H, CHCH_3), 7.36–7.55 (m, 5H, H_{ar}), 7.75–8.02 (m, 15H, H_{ar}). ^{13}C NMR (CD_3CN , 25°C): 19.6 (CHCH_3), 24.8 (CHCH_3), 67.8 (CHCH_3), 72.8 (d, $J_{\text{CP}} = 6.3$, CHCH_3), 114.0 (d, $J_{\text{CP}} = 85.0$, C_{ar}), 122.2 (q, $J_{\text{CF}} = 321.6$, CF_3SO_3^-), 128.7 (s, C_{ar}), 129.4 (d, $J_{\text{CP}} = 10.3$, C_{ar}), 130.2 (s, C_{ar}), 132.6 (d, $J_{\text{CP}} = 14.5$, C_{ar}), 134.6 (s, C_{ar}), 136.2 (d, $J_{\text{CP}} = 10.3$, C_{ar}), 138.4 (s, C_{ar}), 183.5 (d, $J_{\text{CP}} = 53.9$, C). **1d**: (7.65 g, 91%); ^{31}P NMR (CD_3CN , 25°C): +20.7. ^1H NMR (CD_3CN , 25°C): 2.66 (s, 6H, NCH_3), 4.29 (s, 4H, NCH_2), 7.89–8.10 (m, 15H, H_{ar}). ^{13}C NMR (CD_3CN , 25°C): 38.6 (NCH_3), 55.2 (NCH_2), 113.1 (d, $J_{\text{CP}} = 88.2$, C_{ar}), 122.2 (q, $J_{\text{CF}} = 319.4$, CF_3SO_3^-), 132.7 (d, $J_{\text{CP}} = 14.6$, C_{ar}), 136.3 (d, $J_{\text{CP}} = 12.0$, C_{ar}), 138.8 (s, C_{ar}), 152.5 (d, $J_{\text{CP}} = 86.9$, C).

Reduction of C-[tris(dimethylamino)Phosphonio]-*N,N*-diisopropylamino-Aldiminium Salt **1a**

A THF solution (2 mL) of **1a** (0.30 g, 0.5 mmol) was added at -50°C to a THF suspension (1 mL) of potassium (0.04 g, 1.0 mmol). The suspension was warmed to room temperature and stirred for 30 min. After evaporation of the solvent, the residue was extracted with pentane (5 mL) affording phosphorus ylide **2a** as a yellow oil (0.10 g, 69%). The spectroscopic data for **2a** were identical to those previously reported.[8]

Reduction of C-triphenylphosphonio-*N,N*-diisopropylamino-aldiminium Salt **1b**, and C-triphenylphosphonio-*C*-phenyl-*N,N*-diisopropylamino-iminium Salt **1c**

Tetrakis(dimethylamino)ethylene (0.23 mL, 1.0 mmol) was added at -40°C to an acetonitrile solution (5 mL) of **1b** (0.68 g, 1.0 mmol) or **1c** (0.75 g, 1.0 mmol). Then the suspension was warmed to room temperature and stirred for 30 min. After evaporation of the solvent, the residue was extracted with Et_2O (10 mL). After evaporation of Et_2O , multinuclear NMR

spectroscopy indicates the quantitative formation of dimer **3b**[21] and **3c**,[22] along with two equivalents of triphenylphosphine.

Reduction of C-triphenylphosphonio-imidazolidinium Salt **1d**

A THF solution (2 mL) of **1d** (0.30 g, 0.5 mmol) was added at -50°C to a THF suspension (1 mL) of potassium (0.04 g, 1.0 mmol). The suspension was warmed to room temperature and stirred for 30 min. After evaporation of the solvent, the residue was extracted with Et_2O . (5 mL). After evaporation of Et_2O , multinuclear NMR spectroscopy indicates the quantitative formation of dimer **3d**,[23] along with two equivalents of triphenylphosphine.

Synthesis of C-Amino-Phosphaalkenes **5**

A stoichiometric amount of a hexane solution of the desired lithium reagent was added dropwise at -95°C to a THF solution (3 mL) of diphosphirenium tetrafluoroborate **4** (1.7 mmol). The mixture was stirred for 1.5 hours and then allowed to warm up to room temperature. The solvent was removed under vacuum and the product extracted with pentane. After evaporation of the pentane, **5b** and **5c**[19b] were obtained as red oils, whereas **5a** was isolated as red crystals by slow recrystallization from pentane at -30°C . **5a**: 641 mg, 82%, mp: $85-87^{\circ}\text{C}$; ^{31}P NMR (C_6D_6 , 25°C): 52.4 (d, $J_{\text{PP}} = 42.9$), 124.3 (d, $J_{\text{PP}} = 42.9$); ^1H NMR (C_6D_6 , 25°C): 1.13 (d, $J_{\text{HH}} = 6.6$, 12H, CHCH_3), 1.35 (d, $J_{\text{HH}} = 6.6$, 12H, CHCH_3), 1.42 (d, $J_{\text{HH}} = 6.9$, 12H, CHCH_3), 4.06 (sept d, $J_{\text{HH}} = 6.6$, $J_{\text{PH}} = 1.8$, 4H, CHCH_3), 4.71 (sept d, $J_{\text{HH}} = J_{\text{PH}} = 6.6$, 2H, CHCH_3), 7.04–7.21 (m, 3H, CH_{aro}), 7.67–7.72 (m, 2H, CH_{aro}); ^{13}C NMR (C_6D_6 , 25°C): 22.5 (s, CHCH_3), 23.9 (d, $J_{\text{PC}} = 5.3$, CHCH_3), 47.5 (dd, $J_{\text{PC}} = 4.6$ and 12.7, CHCH_3), 55.3 (d, $J_{\text{PC}} = 18.7$, CHCH_3), 126.8 (s, CH_{aro}), 133.3 (d, $J_{\text{PC}} = 12.1$, CH_{aro}), 147.2 (d, $J_{\text{PC}} = 62.8$, C_{aro}), 205.1 (dd, $J_{\text{PC}} = 42.7$ and 112.2, $\text{P}=\text{C}$); EI-MS: m/z 451 [M^+]. **5b**: 330 mg, 90%; ^{31}P NMR (C_6D_6 , 25°C): 54.2 (d, $J_{\text{PP}} = 24.4$ Hz), 175.7 (d, $J_{\text{PP}} = 24.4$); ^1H NMR (C_6D_6 , 25°C): 1.29 (d, $J_{\text{HH}} = 6.0$, 12H, CHCH_3), 1.30 (d, $J_{\text{HH}} = 6.5$, 12H, CHCH_3), 1.32 (d, $J_{\text{HH}} = 6.5$, 12H, CHCH_3), 1.39 (d, $J_{\text{PH}} = 10.5$, 9H, CCH_3), 4.05 (sept d, $J_{\text{HH}} = 6.0$, $J_{\text{PH}} = 2.4$, 4H, CHCH_3), 4.42 (sept d, $J_{\text{HH}} = J_{\text{PH}} = 6.5$, 2H, CHCH_3); ^{13}C NMR (C_6D_6 , 25°C): 23.4 (s, CHCH_3), 24.4 (pseudo t, $J_{\text{PC}} = 6.2$, CHCH_3), 24.6 (d, $J_{\text{PC}} = 8.3$, CHCH_3), 31.3 (d, $J_{\text{PC}} = 16.6$, CCH_3), 36.6 (d, $J_{\text{PC}} = 62.2$, CCH_3), 47.7 (d, $J_{\text{PC}} = 6.2$, CHCH_3), 55.5 (d, $J_{\text{PC}} = 18.7$, CHCH_3), 200.3 (dd, $J_{\text{PC}} = 45.6$ and 118.2 Hz, $\text{P}=\text{C}$); EI-MS: m/z 431 [M^+]. **5c**: 210 mg, 80%; ^{31}P NMR (C_6D_6 , 25°C): 160.2 (d, $J_{\text{PP}} = 17.6$ Hz), 50.2 (d, $J_{\text{PP}} = 17.6$); ^1H NMR (C_6D_6 , 25°C): 1.32 (d, $J_{\text{HH}} = 7.0$, 6H, P(II)NCHCH_3), 1.41 (d, $J_{\text{HH}} = 7.0$, 12H, P(III)NCHCH_3), 1.42 (d, $J_{\text{HH}} = 7.0$, 12H, P(III)NCHCH_3), 1.44 (d, $J_{\text{HH}} = 7.0$, 12H, CNCHCH_3), 1.46 (d, $J_{\text{HH}} = 7.0$, 6H, P(II)NCHCH_3), 3.62 (sept d, $J_{\text{HH}} = 7.0$, $J_{\text{PH}} = 6.5$, 2H, P(II)NCHCH_3), 4.14 (sept d, $J_{\text{HH}} = 7.0$, $J_{\text{P(III)H}} = 1.5$, $J_{\text{P(II)H}} = 2.0$, 4H, P(III)NCHCH_3), 4.61 (sept d, $J_{\text{HH}} = 7.0$, $J_{\text{P(III)H}} = 4.5$, 2H, CNCHCH_3); ^{13}C NMR (C_6D_6 , 25°C): 23.1–24.6 (CHCH_3), 46.6 (dd, $J_{\text{PC}} = 11.6$ and 5.5, P(III)NCHCH_3), 47.1 (d, $J_{\text{PC}} = 3.8$, P(II)NCHCH_3), 49.6 (d, $J_{\text{PC}} = 14.6$, CNCHCH_3), 177.4 (dd, $J_{\text{PC}} = 105.5$ and 47.5 Hz, $\text{P}=\text{C}$); EI-MS: m/z 474 [M^+].

Reaction of Phosphaalkene **5a** with 2,4-di-*tert*-butyl-*ortho*-quinone

A THF solution (0.3 mL) of 2,4-di-*tert*-butyl-*ortho*-quinone (98 mg, 0.44 mmol) was added at -78°C to a THF solution (0.3 mL) of **5a** (200 mg, 0.44 mmol) in an NMR tube. The NMR tube was sealed under argon and the reaction was monitored by ^{31}P NMR spectroscopy. After 1 h, the adduct **9**, as a mixture of 2 diastereomers (85%), the mono(quinone) adduct **7a** (5%), (bis(quinone) adduct **8a** (10%), and the carbene **6** (15%) are observed. Derivatives **7a**, **8a** and carbene **6** were characterized by comparison of the ^{31}P NMR data with those of authentic samples prepared as described hereafter and in ref 20a, respectively. The major isomer (80%) of the six-membered heterocycle **9** appeared as an AX system at 78.3 and 160.9 ($J_{\text{PP}} = 122.7$ Hz), whereas the minor isomer (20%) gives an AX system at 83.0 and 173.9 ($J_{\text{PP}} = 52.6$ Hz). After sulfuration of the reaction mixture with elemental sulfur, the mono sulfur adducts of **9**

were observed: ^{31}P NMR (THF, 25°C): major isomer 79.1 (d, $J_{\text{PP}} = 235.4$ Hz), 89.0 (d, $J_{\text{PP}} = 235.4$ Hz); minor isomer 78.1 (d, $J_{\text{PP}} = 215.9$ Hz), 92.1 (d, $J_{\text{PP}} = 215.9$ Hz). All attempts to isolate one of the diastereomer failed, preventing an accurate description of the ^1H and ^{13}C NMR data. The mono-sulfur adducts of **9** were further characterized by mass spectroscopy: DCM/NBA: 704 (M^+).

Reaction of Phosphaalkenes **5b,c** with 2,4-di-*tert*-butyl-*ortho*-quinone

A THF solution (0.3 mL) of 2,4-di-*tert*-butyl-*ortho*-quinone (100 mg, 0.46 mmol) was added at -78°C to a THF solution (0.3 mL) of **5b,c** (**5b**: 200 mg, 0.46 mmol; **5c**: 220 mg, 0.46 mmol;) in an NMR tube. The NMR tube was sealed under argon. According to ^{31}P NMR spectroscopy, carbene **6** along with an equimolar amount of adducts **7b** and **7c** were the only observable products. Carbene **6** and adducts **7b** and **7c** were characterized by comparison of the multinuclear NMR data with those of authentic samples reported in ref 20a and prepared as described hereafter, respectively.

Synthesis of Authentic Samples of Benzo-1,3,2-dioxaphospholane **7a**[24] and Bis(quinone) Adduct **8a**

A diethyl ether solution of dichlorophenylphosphine was added at -30°C to a diethyl ether solution of 2 equivalents of triethylamine and 1 equivalent of 2,4-di-*tert*-butylcatechol. The suspension was allowed to warm up to room temperature and then stirred for 12 hours at room temperature. According to ^{31}P NMR spectroscopy, a mixture containing the remaining dichlorophosphine (25%), the benzo-1,3,2-dioxaphospholane **7a** (50% yield), and the bis-adduct **8a** (25% yield) was obtained. **7a**: ^{31}P NMR (CDCl_3 , 25°C): 180.2. Following the same protocol, but using 4 equivalents of triethylamine and 2 equivalents of 2,4-di-*tert*-butylcatechol, **8a** was isolated as a white powder by recrystallization from diethyl ether at -20°C . **8a**: (430 mg, 80%); ^{31}P NMR (CDCl_3 , 25°C): -10.5 ; ^1H NMR (CDCl_3 , 25°C): 1.29 (s, 18H, CCH_3), 1.46 (s, 18H, CCH_3), 6.85 (m, 2H, CH_{aro}), 7.00 (m, 2H, CH_{aro}), 7.34–7.38 (m, 3H, CH_{aro}), 7.84–7.93 (m, 2H, CH_{aro}); ^{13}C NMR (CDCl_3 , 25°C): 30.0 (s, CCH_3), 31.9 (s, CCH_3), 34.6 (s, CCH_3), 35.1 (s, CCH_3), 106.5 (d, $J_{\text{PC}} = 13.8$, C_{aro}), 115.7 (s, C_{aro}), 128.4 (d, $J_{\text{PC}} = 17.2$, C_{aro}), 131.2 (d, $J_{\text{PC}} = 11.2$, C_{aro}), 131.6 (s, C_{aro}), 133.4 (d, $J_{\text{PC}} = 12.1$, C_{aro}), 139.2 (s, C_{aro}), 143.9 (s, C_{aro}), 144.5 (s, C_{aro}); DCI/ NH_3 : 549 [$\text{M} + \text{H}^+$].

Synthesis of Authentic Samples of Benzo-1,3,2-dioxaphospholanes **7b** and **7c**[25]

A diethyl ether solution of the desired dichlorophosphine was added at -30°C to a diethyl ether solution of 2 equivalents of triethylamine and 1 equivalent of 2,4-di-*tert*-butylcatechol. After stirring for 30 minutes at room temperature, the solution was filtered and the solvent removed under vacuum. Benzodioxaphospholanes **7b,c** were isolated as colorless oils. **7b**: (250 mg, 91%); ^{31}P NMR (CDCl_3 , 25°C): 208.1; ^1H NMR (CDCl_3 , 25°C): 0.91 (d, $J_{\text{PH}} = 12.9$, 9H, PCCH_3), 1.30 (s, 9H, CCH_3), 1.42 (s, 9H, CCH_3), 6.85 (d, $J_{\text{HH}} = 2.0$, 1H, CH_{aro}), 6.91 (d, $J_{\text{HH}} = 2.0$, 1H, CH_{aro}); ^{13}C NMR (CDCl_3 , 25°C): 22.0 (d, $J_{\text{PC}} = 18.5$, PCCH_3), 29.7 (s, CCH_3), 31.9 (s, CCH_3), 34.6 (s, CCH_3), 35.0 (s, CCH_3), 39.0 (d, $J_{\text{PC}} = 42.6$, PCCH_3), 107.5 (s, CH_{aro}), 116.0 (s, CH_{aro}), 133.9 (s, C_{aro}), 143.3 (d, $J_{\text{PC}} = 8.1$, C_{aro}), 145.3 (s, C_{aro}), 147.9 (d, $J_{\text{PC}} = 6.9$, C_{aro}); EI-MS: m/z 308 [M^+]. **7c**: (320 mg, 85%); ^{31}P NMR (CDCl_3 , 25°C): 153.8; ^1H NMR (CDCl_3 , 25°C): 1.25 (d, $J_{\text{HH}} = 6.6$, 12H, CHCH_3), 1.32 (s, 9H, CCH_3), 1.42 (s, 9H, CCH_3), 3.35 (sept d, $J_{\text{PH}} = 9.6$, $J_{\text{HH}} = 6.6$, 2H, CHCH_3), 6.85 (d, $J_{\text{HH}} = 2.4$, 1H, CH_{aro}), 6.90 (d, $J_{\text{HH}} = 2.4$ Hz, 1H, CH_{aro}); ^{13}C NMR (CDCl_3 , 25°C): 24.7 (d, $J_{\text{PC}} = 8.1$, CHCH_3), 25.0 (d, $J_{\text{PC}} = 8.1$, CHCH_3), 29.8 (s, CCH_3), 32.0 (s, CCH_3), 34.6 (s, CCH_3), 34.9 (s, CCH_3), 45.0 (d, $J_{\text{PC}} = 11.5$, CHCH_3), 106.8 (s, CH_{aro}), 115.2 (s, CH_{aro}), 133.4 (s, C_{aro}), 142.6 (d, $J_{\text{PC}} = 8.1$, C_{aro}), 144.1 (s, C_{aro}), 147.0 (d, $J_{\text{PC}} = 6.9$, C_{aro}).

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Scheme 1.

Scheme 2.

Scheme 3.

Scheme 4.

Scheme 5.

Scheme 6.

Scheme 7.

Scheme 8.