CHEMISTRY
AN ASIAN JOURNAL

DOI: 10.1002/asia.200600075

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

Salvador Conejero, Maoying Song, David Martin, Yves Canac, Michele Soleilhavoup, and Guy Bertrand*[a]

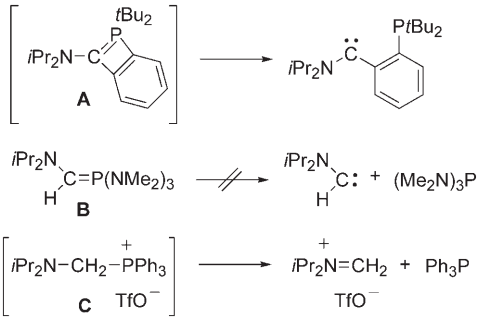
Abstract: Phosphonio-substituted aldiminium, iminium, and imidazolidinium salts are readily prepared by the addition of phosphines to the Alder dimer or by treatment of the corresponding chloroiminium salt with the phosphine/trimethylsilyl triflate adduct generated in situ. Reduction with either potassium 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 fragment into the carbene and phosphine. This method is limited to the preparation of transient carbenes, owing to the unavailability of sterically hindered dications, and consequently of phosphorus ylides with bulky carbon substituents. This difficulty is overcome by the addition of 2,4-di-*tert*-butyl-*ortho*-quinone to readily available *C*-amino phosphaalkenes at low temperature. Provided the phosphorus atom bears either an amino or *tert*-butyl group, [4+1] cycloaddition occurs, and the resulting ylides fragment into a dioxaphospholane and a spectroscopically observed carbene.

Keywords: carbenes · dications · iminium salts · phosphorus · ylides

Introduction

Despite the existence of various methods for the generation of transient[1] and stable carbenes,[2] there is still a need for new methods that allow the preparation of these highly reactive species under mild conditions. Among carbenes, diamino carbenes[3] and, more recently, monoamino carbenes[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 strong anionic bases are required for the former;[6] in some cases, side reactions are induced, 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 amino carbenes. On the basis of calculations by Bestmann, Schleyer, and coworkers,[9] who predicted that the P–C dissociation energy of the parent *C*-amino phosphorus ylide $H_3P=C(H)(NH_2)$ is only 8.1 kcal mol^{-1}, we showed that cyclic *C*-amino phosphorus ylides **A** could, indeed, undergo fragmentation into carbenes and phosphines at low temperature (Scheme 1). However, in the acyclic series, we found that on the one hand, *C*-amino phosphorus ylides **B**, which bear strongly basic nucleophilic phosphines such as tris(dimethylamino)-phosphane, are too stable to undergo fragmentation to the carbene and phosphine; on the other hand, phosphonium precursors **C**, which feature nonbasic phosphines such as triphenylphosphine, cannot be prepared as they readily decompose into phosphine and iminium salts. Therefore, the



Scheme 1. *C*-Amino phosphorus ylides are either stable (**B**) or undergo fragmentation (**A**, **C**).

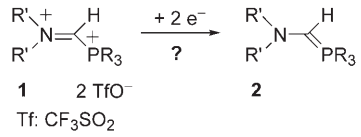
[a] Dr. S. Conejero, M. Song, Dr. D. Martin, Dr. Y. Canac, Dr. M. Soleilhavoup, Prof. G. Bertrand
UCR-CNRS Joint Research Chemistry Laboratory (UMI 2957)
Department of Chemistry, University of California
Riverside, CA 92521-0403 (USA)
Fax: (+1) 951-827-2725
E-mail: gbertran@mail.ucr.edu

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 carbon atom of the ylide function. The addition of phosphines to alkenes and alkynes is limited to electron-poor unsaturated derivatives. Staudinger adducts are not accessible as amino-substituted diazo derivatives are not stable. Dihalido triphenylphosphoranes only react with methylene derivatives activated by electron-withdrawing groups.

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

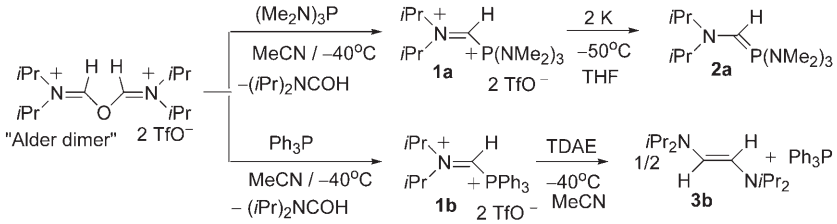
Results and Discussion

We have already shown that highly thermally stable phosphonio-substituted aldiminium salts **1**[11] are readily prepared in excellent yields by the addition of phosphines to the Alder dimer[12] or, alternatively, by treatment of the corresponding chloroaldiminium salt with the phosphine/trimethylsilyl triflate adduct generated in situ.[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, as Weiss et al. have shown that onio substitution dramatically increases the electron affinity of a given substance.[14]



Scheme 2. Two-electron reduction of onio-substituted aldiminium salts **1** to ylides **2**.

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 (diisopropylamino)(hydrogeno)carbene (Scheme 3).



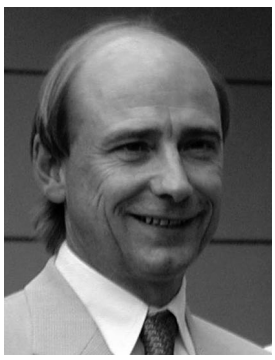
Scheme 3. Reduction of dications with different onio substituents, prepared from Alder dimer.

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). ^{31}P and ^{13}C NMR spectroscopy analysis showed that the reduction of **1c** and **1d** with tetrakis(dimethylamino)ethylene and potassium metal, respectively, did not afford the phosphorus ylides and carbenes. Again, we observed the quantitative formation of triphenylphosphane and alkene **3c** (*Z*/*E* 20:80) and **3d**.

Importantly, all attempts to prepare dications that bear bulky substituents at the carbon atom failed. For example, no reaction occurred when the *N,N*-diisopropyl-*C*-*tert*-butyl chloroiminium salt was treated with the triphenylphosphane/trimethylsilyl triflate adduct generated in situ. 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 nonbasic phosphine fragment is used, the overall sequence seems limited to the generation of transient amino carbenes, because of the unavailability of sterically hindered starting dications.

Therefore, to generate persistent carbenes, it was necessary to design a new route that would allow the preparation of *C*-amino phosphorus ylides with bulky substituents at the carbon atom and a nonbasic phosphorus fragment. It is

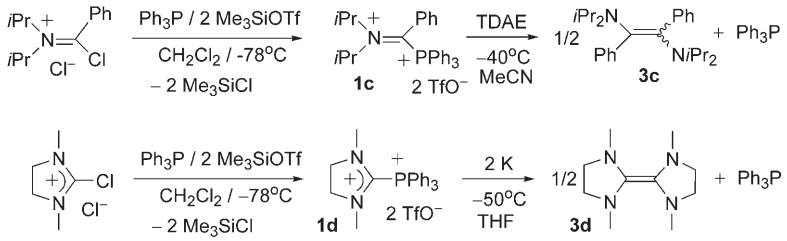
International Advisory Board Member



Guy Bertrand *received his PhD from the Univ. of Toulouse in 1979. He was a group leader in the Laboratoire de Chimie de Coordination du CNRS (1988–1998) and Director of the Laboratoire Hétérochimie of the Univ. Paul Sabatier (1999–2005). Since 2001, he is a Distinguished Prof. and the Director of the UCR/CNRS Joint Research Chemistry Laboratory at the Univ. of California, Riverside. He is a member of the French Academy of Sciences (2004). His research interests lie mainly in the field of reactive intermediates.*

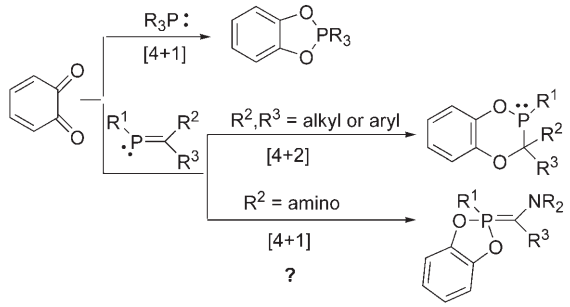
"I see the combination of Chemistry—An Asian Journal *and* Chemistry—A European Journal *as a wonderful symbol of the globalization of science, with everyone keeping their roots."*

CHEMISTRY
AN ASIAN JOURNAL



Scheme 4. Preparation of iminium and imidazolidinium dications and their reduction.

known that *ortho*-quinones react with phosphines through a [4+1] cycloaddition process to give hypervalent phosphorus derivatives (Scheme 5).[15] On the other hand, *C*-alkyl- and *C*-aryl-substituted phosphaalkenes react with *ortho*-quinones

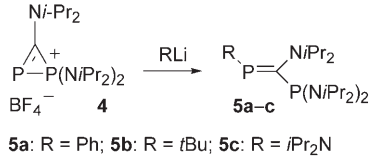


Scheme 5. Reaction of *ortho*-quinone with phosphines and phosphaalkenes.

to afford [4+2] cycloadducts.[16] However, the π orbital and lone pair of electrons of the phosphorus atom of phosphaalkenes are very close in energy; depending on the nature of the substituents at the carbon and the phosphorus atoms, either of these orbitals can be the HOMO of the system.[17] Consequently, we expected that phosphaalkenes that bear a π-donor amino substituent at the carbon atom would react through 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 the phosphorus atom was expected to allow facile fragmentation.

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

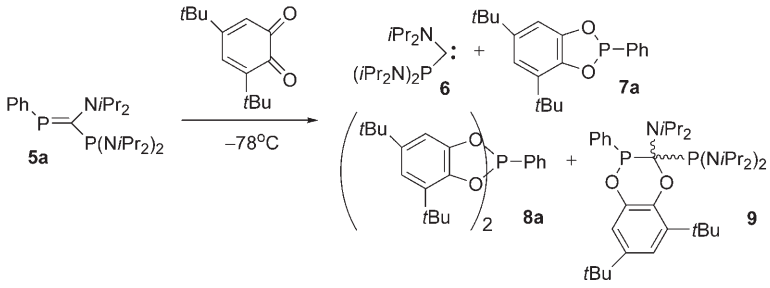
Phosphaalkene **5a**, which bears a phenyl group at the phosphorus atom, reacts with 2,4-di-*tert*-butyl-*ortho*-quinone at −78°C to give a complex mixture, which includes the desired carbene **6**, but in only 20% yield (according to ^{31}P NMR spectroscopy) (Scheme 7). Other products of the reaction include the benzo-1,3,2-dioxaphospholane **7a**, the bis(quinone) adduct **8a**, and



Scheme 6. Preparation of selected phosphaalkenes.

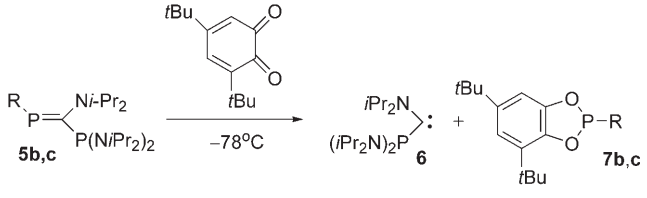
the six-membered heterocycles **9a** (as a mixture of two diastereomers). Therefore, in this case, despite the presence of the amino group at the carbon atom, the [4+2] cycloaddition strongly competes with the desired [4+1] process.

The observed instability and clean fragmentation of the (highly probable) phosphorus ylide intermediate was a very encouraging result. Therefore, to facilitate the formation of ylides versus dioxaphosphinanes **9**, we used phosphaalkenes



Scheme 7. Reaction of **5a** with 2,4-di-*tert*-butyl-*ortho*-quinone.

5b and **5c**, which feature more-strongly electron-donating groups at the phosphorus atom. 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).



Scheme 8. Reaction of **5b,c** with 2,4-di-*tert*-butyl-*ortho*-quinone.

Conclusions

A variety of dicationic species can be prepared by simple addition of a phosphine, including nonbasic 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 that bear bulky substituents at the carbon atom can be synthesized readily by the addition of *ortho*-quinones to *C*-amino phosphaalkenes. As a variety of the latter compounds 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 should tolerate a wide range of functional groups.

Experimental Section

General

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

Syntheses

1a or **1b**: A solution of the phosphine (8.5 mmol) in acetonitrile (15 mL) was added at −40 °C to a solution (15 mL) of the Alder dimer (7.7 mmol) in acetonitrile (15 mL). The suspension was stirred for 1 h at room temperature. After evaporation of the solvent, the solid residue was washed with THF (20 mL) to afford **1a** or **1b**[11] as white microcrystalline solids. **1a** (3.81 g, 86 %): M.p.: 201–202 °C; ^{31}P NMR (CD_3CN, 25 °C): $\delta = +33.5$ ppm; ^{1}H NMR (CD_3CN, 25 °C): $\delta = 1.61$ (d, $J_{HH} = 6.2$ Hz, 6H; $CHCH_3$), 1.63 (d, $J_{HH} = 6.2$ Hz, 6H; $CHCH_3$), 2.88 (d, $J_{HP} = 11.3$ Hz, 18H; NCH_3), 4.69 (sept, $J_{HH} = 6.2$ Hz, 1H; $CHCH_3$), 4.77 (sept d, $J_{HH} = 6.2$ Hz, $J_{HP} = 4.1$ Hz, 1H; $CHCH_3$), 8.53 ppm (d, $J_{HP} = 24.1$ Hz, 1H; CH); ^{13}C NMR (CD_3CN, 25 °C): $\delta = 20.8$ ($CHCH_3$), 24.3 ($CHCH_3$), 37.5 (d, $J_{CP} = 4.6$ Hz; NCH_3), 63.0 (d, $J_{CP} = 7.5$ Hz; $CHCH_3$), 65.1 (d, $J_{CP} = 5.3$ Hz; $CHCH_3$), 122.2 (q, $J_{CF} = 319.6$ Hz; $CF_3SO_3^-$), 167.8 (d, $J_{CP} = 141.6$ Hz; CH). **1b**[11] (4.87 g, 94 %).

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

Reduction of **1a**: A solution of **1a** (0.30 g, 0.5 mmol) in THF (2 mL) was added at −50 °C to a suspension of potassium (0.04 g, 1.0 mmol) in THF (1 mL). 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) to afford 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 **1b** or **1c**: Tetrakis(dimethylamino)ethylene (0.23 mL, 1.0 mmol) was added at −40 °C to a solution of **1b** (0.68 g, 1.0 mmol) or **1c** (0.75 g, 1.0 mmol) in acetonitrile (5 mL). The suspension was then 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 the Et_2O, multinuclear NMR spectroscopy indicated the quantitative formation of dimer **3b**[21] or **3c**,[22] along with triphenylphosphine (2 equiv).

Reduction of **1d**: A solution of **1d** (0.30 g, 0.5 mmol) in THF (2 mL) was added at −50 °C to a suspension of potassium (0.04 g, 1.0 mmol) in THF (1 mL). 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 the Et_2O, multinuclear NMR spectroscopy indicated the quantitative formation of dimer **3d**,[23] along with triphenylphosphine (2 equiv).

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

Reaction of **5a** with 2,4-di-*tert*-butyl-*ortho*-quinone: A solution of 2,4-di-*tert*-butyl-*ortho*-quinone (98 mg, 0.44 mmol) in THF (0.3 mL) was added at −78 °C to a solution of **5a** (200 mg, 0.44 mmol) in THF (0.3 mL) 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 two diastereomers (85%), the monoquinone adduct **7a** (5%), the bisquinone adduct **8a** (10%), and the carbene **6** (15%) were 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 or in reference [20a]. The major isomer (80%) of the six-membered heterocycle **9** appeared as an AX system at $\delta = 78.3$ and 160.9 ppm ($J_{PP} = 122.7$ Hz), whereas the minor isomer (20%) gave an AX system at $\delta = 83.0$ and 173.9 ppm ($J_{PP} = 52.6$ Hz). After sulfuration of the reaction mixture with elemental sulfur, the monosulfur adducts of **9** were observed: ^{31}P NMR (THF, 25°C): major isomer: $\delta = 79.1$ (d, $J_{PP} = 235.4$ Hz), 89.0 ppm (d, $J_{PP} = 235.4$ Hz); minor isomer: 78.1 ppm (d, $J_{PP} = 215.9$ Hz), 92.1 (d, $J_{PP} = 215.9$ Hz). All attempts to isolate one of the diastereomers failed, preventing an accurate description of the ^{1}H and ^{13}C NMR data. The monosulfur adducts of **9** were further characterized by mass spectrometry (DCM/NBA): m/z 704 [M^+].

Reaction of **5b** or **5c** with 2,4-di-*tert*-butyl-*ortho*-quinone: A solution of 2,4-di-*tert*-butyl-*ortho*-quinone (100 mg, 0.46 mmol) in THF (0.3 mL) was added at −78°C to a solution of **5b** or **5c** (**5b**: 200 mg, 0.46 mmol; **5c**: 220 mg, 0.46 mmol) in THF (0.3 mL) 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** or **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 reference [20a] or prepared as described below.

Authentic **7a**,[24] **8a**: A solution of dichlorophenylphosphine in diethyl ether was added at −30°C to a solution of triethylamine (2 equiv) and 2,4-di-*tert*-butylcatechol (1 equiv) in diethyl ether. The suspension was allowed to warm up to room temperature and then stirred for 12 h at room temperature. According to ^{31}P NMR spectroscopy, a mixture containing the remaining dichlorophosphine (25%), **7a** (50% yield), and **8a** (25% yield) was obtained. **7a**: ^{31}P NMR ($CDCl_3$, 25°C): $\delta = 180.2$ ppm. The same protocol, but with 4 equivalents of triethylamine and 2 equivalents of 2,4-di-*tert*-butylcatechol, led to the isolation of **8a** as a white powder by recrystallization from diethyl ether at −20°C. **8a** (430 mg, 80%): ^{31}P NMR ($CDCl_3$, 25°C): $\delta = -10.5$ ppm; ^{1}H NMR ($CDCl_3$, 25°C): $\delta =$ 1.29 (s, 18H; CCH_3), 1.46 (s, 18H; CCH_3), 6.85 (m, 2H; CH_{ar}), 7.00 (m, 2H; CH_{ar}), 7.34–7.38 (m, 3H; CH_{ar}), 7.84–7.93 ppm (m, 2H; CH_{ar}); ^{13}C NMR ($CDCl_3$, 25°C): $\delta = 30.0$ (s; CCH_3), 31.9 (s; CCH_3), 34.6 (s; CCH_3), 35.1 (s; CCH_3), 106.5 (d, $J_{PC} = 13.8$ Hz; C_{ar}), 115.7 (s; C_{ar}), 128.4 (d, $J_{PC} = 17.2$ Hz; C_{ar}), 131.2 (d, $J_{PC} = 11.2$ HZ; C_{ar}), 131.6 (s; C_{ar}), 133.4 (d; $J_{PC} = 12.1$; C_{ar}), 139.2 (s; C_{ar}), 143.9 (s; C_{ar}), 144.5 ppm (s; C_{ar}); MS (DCI/NH_3): m/z: 549 [M+H^+].

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

Acknowledgements

We are grateful to the NIH (R01 GM 68825) for financial support.

[1] R. A. Moss, M. S. Platz, M. Jones Jr., *Reactive Intermediates Chemistry*, Wiley, New York, **2004**.

[2] For general reviews on stable carbenes, see: a) W. Kirmse, *Angew. Chem.* **2004**, *116*, 1799; *Angew. Chem. Int. Ed.* **2004**, *43*, 1767; b) R. W. Alder, M. E. Blake, M. E. Chaker, J. N. Harvey, F. Paolini, J. Schütz, *Angew. Chem.* **2004**, *116*, 6020; *Angew. Chem. Int. Ed.* **2004**, *43*, 5896; c) Y. Canac, M. Soleilhavoup, S. Conejero, G. Bertrand, *J. Organomet. Chem.* **2004**, *689*, 3857; d) D. Bourissou, O. Guerret, F. P. Gabbaï, G. Bertrand, *Chem. Rev.* **2000**, *100*, 39; e) H. Tomioka, *Acc. Chem. Res.* **1997**, *30*, 315.

[3] For reviews on diamino carbenes, see: a) N. M. Scott, S. P. Nolan, *Eur. J. Inorg. Chem.* **2005**, 1815; b) D. Enders, T. Balensiefer, *Acc. Chem. Res.* **2004**, *37*, 534; c) J. S. Johnson, *Angew. Chem.* **2004**, *116*, 1348; *Angew. Chem. Int. Ed.* **2004**, *43*, 1326; d) V. Nair, S. Bindu, V. Sreekumar, *Angew. Chem.* **2004**, *116*, 5240; *Angew. Chem. Int. Ed.* **2004**, *43*, 5130; e) E. Peris, R. H. Crabtree, *Coord. Chem. Rev.* **2004**, *248*, 2239; f) C. M. Crudden, D. P. Allen, *Coord. Chem. Rev.* **2004**, *248*, 2247; g) V. César, S. Bellemin-Laponnaz, L. H. Gade, *Chem. Soc. Rev.* **2004**, *33*, 619; h) M. C. Perry, K. Burgess, *Tetrahedron: Asymmetry* **2003**, *14*, 951; i) W. A. Herrmann, *Angew. Chem.* **2002**, *114*, 1342; *Angew. Chem. Int. Ed.* **2002**, *41*, 1290; j) A. J. Arduengo III, *Acc. Chem. Res.* **1999**, *32*, 913.

[4] a) V. Lavallo, Y. Canac, C. Präsang, B. Donnadieu, G. Bertrand, *Angew. Chem.* **2005**, *117*, 5851; *Angew. Chem. Int. Ed.* **2005**, *44*, 5705; b) V. Lavallo, Y. Canac, A. Dehope, B. Donnadieu, G. Bertrand, *Angew. Chem.* **2005**, *117*, 7402; *Angew. Chem. Int. Ed.* **2005**, *44*, 7236; c) V. Lavallo, J. Mafhouz, Y. Canac, B. Donnadieu, W. W. Schoeller, G. Bertrand, *J. Am. Chem. Soc.* **2004**, *126*, 8670; d) X. Cattoën, H. Gornitzka, D. Bourissou, G. Bertrand, *J. Am. Chem. Soc.* **2004**, *126*. 1342; e) S. Solé, H. Gornitzka, W. W. Schoeller, D. Bourissou, G. Bertrand, *Science* **2001**, *292*, 1901.

[5] a) R. Alder, in *Carbene Chemistry: From Fleeting Intermediates to Powerful Reagents* (Ed.: G. Bertrand), Marcel Dekker, New York, **2002**, pp. 153–171; b) M. K. Denk, A. Thadani, K. Hatano, A. J. Lough, *Angew. Chem.* **1997**, *109*, 2719; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2607; c) N. Kuhn, T. Kratz, *Synthesis* **1993**, 561.

[6] a) A. M. Magill, K. J. Cavell, B. F. Yates, *J. Am. Chem. Soc.* **2004**, *126*, 8717; b) M. T. Lee, C. H. Hu, *Organometallics* **2004**, *23*, 976; c) J. A. Cowan, J. A. C. Clyburne, M. G. Davidson, R. L. W. Harris, J. A. K. Howard, P. Küpper, M. A. Leech, S. P. Richards, *Angew. Chem.* **2002**, *114*, 1490; *Angew. Chem. Int. Ed.* **2002**, *41*, 1432; d) Y. J. Kim, A. Streitwieser, *J. Am. Chem. Soc.* **2002**, *124*, 5757; e) R. W. Alder, M. E. Blake, J. M. Oliva, *J. Phys. Chem. A* **1999**, *103*, 11200.

[7] X. Cattoen, S. Sole, C. Pradel, H. Gornitzka, K. Miqueu, D. Bourissou, G. Bertrand, *J. Org. Chem.* **2003**, *68*, 911.

[8] Y. Canac, S. Conejero, M. Soleilhavoup, B. Donnadieu, G. Bertrand, *J. Am. Chem. Soc.* **2006**, *128*, 459.

[9] H. J. Bestmann, A. J. Kos, K. Witsgall, P von R. Schleyer, *Chem. Ber.* **1986**, *119*, 1331.

[10] For reviews on phosphorus ylides, see: a) A. W. Johnson, *Ylides and Imines of Phosphorus*, Wiley, New York, **1993**, pp. 101–121; b) O. I. Kolodiazhnyi, *Phosphorus Ylides*, Wiley-VCH, Weinheim, **1999**.

[11] S. Conejero, Y. Canac. F. S. Tham, G. Bertrand, *Angew. Chem.* **2004**, *116*, 4181; *Angew. Chem. Int. Ed.* **2004**, *43*, 4089.

[12] a) R. W. Alder, M. E. Blake, S. Bufali, C. P. Butts, A. G. Orpen, J. Schütz, S. J. Williams, *J. Chem. Soc. Perkin Trans. 1* **2001**, 1586; b) R. W. Alder, P. R. Allen, M. Murray, A. G. Orpen, *Angew. Chem.* **1996**, *108*, 1211; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1121.

[13] R. Weiss, R. May, B. Pomrehn, *Angew. Chem.* **1996**, *108*, 1319; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1232.

[14] R. Weiss, N. J. Salomon, G. E. Miess, R. Roth, *Angew. Chem.* **1986**, *98*, 925; *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 917.

[15] F. Ramirez, C. P. Smith, J. F. Pilot, A. S. Gulati, *J. Org. Chem.* **1968**, *33*, 3787.

[16] Th. A. Van der Knaap, F. Bickelhaupt, *Tetrahedron* **1983**, *39*, 3189.
[17] W. W. Schoeller, E. J. Niecke, *J. Chem. Soc. Chem. Commun* **1982**, 569.
[18] a) V. D. Romanenko, T. V. Sarina, N. V. Kolotilo, L. N. Markovski, *Zh. Obshch. Khim.* **1985**, *55*, 1188; b) G. Becker, W. Uhl, H. J. Wessely, *Z. Anorg. Allg. Chem.* **1981**, *479*, 41; c) K. Issleib, E. Leissring, H. Meyer, *Tetrahedron Lett.* **1981**, *22*, 4475; d) K. Issleib, H. Schmidt, H. Meyer, *J. Organomet. Chem.* **1980**, *192*, 33; e) H. Oehme, E. Leissring, H. Meyer, *Tetrahedron Lett.* **1980**, *21*, 1975; f) H. Oehme, E. Leissring, H. Meyer, *Tetrahedron Lett.* **1980**, *21*, 1141.
[19] a) F. Castan, A. Baceiredo, J. Fischer, A. De Cian, G. Commenges, G. Bertrand, *J. Am. Chem. Soc.* **1991**, *113*, 8160; b) M. Soleilhavoup, Y. Canac, A. M. Polozov, A. Baceiredo, G. Bertrand, *J. Am. Chem. Soc.* **1994**, *116*, 6152.
[20] a) N. Merceron, K. Miqueu, A. Baceiredo, G. Bertrand, *J. Am. Chem. Soc.* **2002**, *124*, 6806; b) N. Merceron-Saffon, A. Baceiredo, H. Gornitzka, G. Bertrand, *Science* **2003**, *301*, 1223.
[21] M. Otto, S. Conejero, Y. Canac, V. D. Romanenko, V. Rudzevitch, G. Bertrand, *J. Am. Chem. Soc.* **2004**, *126*, 1016.
[22] K. Kobayashi, T. Uneda, M. Uchida, Y. Furuta, M. Tanmatsu, O. Morikawa, H. Konishi, *Chem. Lett.* **1998**, 87.
[23] M. K. Denk, A. Thadani, K. Hatano, A. Lough, *Angew. Chem.* **1997**, *109*, 2719; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2607.
[24] J. Navech, J. P. Majoral, A. Meriem, R. Kraemer, *Phosphorus Sulfur* **1983**, *18*, 27.
[25] B. L. Tumanskii, A. A. Khodak, S. P. Solodnikov, N. N. Budnov, V. A. Gilyarov, M. I. Kabachnik, *Izvest. Akad. Nauk. SSSR Ser. Khim.* **1981**, *5*, 1014.

Received: March 17, 2006

