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Synthesis of Transient and Stable *C*-Amino Phosphorus Ylides and Their Fragmentation into Transient and Stable Carbenes

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Abstract: Only basic phosphines, such as tris(dimethylamino)phosphine, allow for the synthesis of a stable acyclic β-amino phosphonium salt **1c**, which upon deprotonation with butyllithium affords the corresponding stable *C*-amino phosphorus ylide **2c**. In contrast, cyclic β-amino phosphonium salts **5a** and **5b** are stable despite the presence of weakly basic triarylphosphine fragments. They are prepared by intramolecular insertion of the carbene center of (amino)(phosphonio)carbenes into the CH bond of a phosphorus substituent. Deprotonation of **5a** leads to the corresponding cyclic *C*-amino phosphorus ylide **6a**, which has been fully characterized including an X-ray diffraction study. Deprotonation of **5b** affords enamine **8**, probably via fragmentation of ylide **6b** into transient carbene **7b** and a subsequent 1,2-hydrogen shift. Transient cyclic *C*-amino phosphorus ylides **6c** and **6d** have been prepared by intramolecular addition of a carbanion generated by deprotonation of a phosphorus substituent. Three-membered heterocycle **6c** rearranges into alkene **9**, whereas the four-membered ring system undergoes a ring opening affording the stable carbene **7d**. The latter results pave the route for the synthesis of various mixed carbene−phosphine bidentate ligands.

Introduction

In the last 15 years, our understanding of carbene chemistry has advanced dramatically.[1] In particular, starting from the pioneering push−pull phosphinosilylcarbenes[2] and push−push N-heterocyclic carbenes (NHCs),[3] the availability of stable singlet carbenes[4] has allowed for spectacular achievements both in organic[5] and in organometallic[6] chemistries. Having said that, we note that the diversity of stable carbenes available is still rather limited. This is due to the fact that only a few types of carbenes are believed to be stable but also because most of them cannot be conveniently prepared.

The classical method for generating transient carbenes is the thermolysis or photolysis of diazo derivatives.[7] This route can be used for phosphinocarbenes,[4] but it involves the handling of rather toxic and explosive substances; moreover amino-, oxy-, and sulfenyl-substituted diazo derivatives are unknown.[8] Diazirines have often been used for the generation of transient carbenes[9] but not for stable carbenes, with the dramatic exception of the fluorophenoxycarbene generated inside a hemicarcerand.[10] Diazirines can be explosive and therefore cannot be prepared in large quantities. Enders reported that the thermolysis of a "methanol adduct" led to triazol-2-ylidenes.[11] This route is attractive but seems specific to N-heterocyclic carbenes (NHCs); moreover, the temperature required is too high for more thermally sensitive carbenes. Following the first report by Kuhn,[12] there are a few examples of NHCs prepared by treatment of a thione with potassium metal in refuxing toluene.[13] Attempts to extrapolate this method to non-NHCs failed,[14] and

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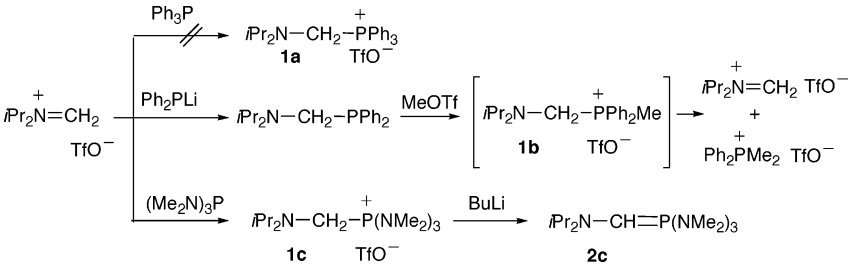
Scheme 1



the experimental conditions used are far too drastic to be of broad applicability. Thermolytic methods, starting from cyclopropanes[15] or Warkentin-type precursors,[16] have so far been unsuccessful for the synthesis of stable carbenes; the preparation of the starting material is also not straightforward. Deprotonation of the conjugate acid of carbenes is by far the most frequently used method, as long as at least one substituent is an amino group.[4] A major advantage here is that deprotonation is a rapid reaction, even at low temperatures. However, even *N*,*N*-dialkylimidazolium ions have pK_a values of around 24 in DMSO,[17] and on the basis of the calculated proton acidity, Alder estimated the pK_a values for acyclic diaminocarbenes to be from 2 to 6 pK_a units higher than those for imidazol-2-ylidenes.[18] Therefore, strong anionic bases are required, and side reactions occurred including nucleophilic addition to the starting salt[14] and deprotonation at other sites of the molecule.[19] Furthermore, another important issue has been raised by Alder in connection with the deprotonation method: When relatively small substituents are used, the carbene can attack its highly electrophilic precursor to generate an amidinium ion, which is then deprotonated to give the dimer.[20a] In other words, the formation of the dimer does not necessarily mean that the carbene is not stable and dimerizes.[20b,c]

This critical analysis of the existing methods for the preparation of carbenes clearly demonstrates the necessity of finding new synthetic strategies involving mild conditions and readily accessible and nonelectrophilic precursors. The simplest conceivable route would be the thermal dissociation of suitably substituted alkenes. However, despite early[21] and recent claims,[22] no examples of successful preparations of carbenes, which include diaminocarbenes, by this process are known.[23] Interestingly, according to calculations at the HF/3-21G* level, although the dissociation energy of *C*-alkyl phosphorus ylides, such as $H_3P{=}C(H)(CH_3)$, into phosphine and carbene is rather high (53.2 kcal/mol), that of the corresponding parent *C*-amino phosphorus ylide $H_3P{=}C(H)(NH_2)$ would be only 8.1 kcal/mol.[24] We were not able to find in the literature any examples of isolated *C*-amino phosphorus ylides.[25] The closest example was a *C*-amido phosphorus ylide reported by Paterson et al.[26] It is reasonable to believe that *C*-amino-substituted phosphorus ylides are destabilized by the two-center, four-electron system (lone pairs at carbon and nitrogen); the Paterson ylide is stable because of the conjugation of the N lone pair with the carbonyl group.

Here, we describe the synthesis of the first stable *C*-amino phosphorus ylides and the preparation of transient analogues, which undergo clean fragmentations into the corresponding phosphine, and transient or even stable carbenes. Evidence for the possible existence of an equilibrium between the ylide and its two fragments is presented.

Results and Discussion

The most general method for the preparation of phosphorus ylides is the deprotonation of the corresponding phosphonium salts, but to the best of our knowledge, no examples of β-amino-substituted phosphonium salts **1** are known. To reach such compounds, the obvious route is the addition of a phosphine to an aldiminium salt. However, no reaction occurred between the triphenylphosphine and the *N*,*N*-diisopropyliminium salt (Scheme 1). Because this result does not necessarily imply that the phosphonium salt **1a** is not stable, we tried to access the related compound **1b** by quaternarization of the phosphine resulting from the addition of lithium diphenylphosphide to the *N*,*N*-diisopropyliminium salt. Here also, the desired compound **1b** was not observed; instead, the starting iminium salt, along with the dimethyldiphenylphosphonium salt, was isolated in good yield. This result clearly implies that the β-amino-substituted phosphonium salt **1b** is unstable toward fragmentation. In marked contrast, tris(dimethylamino)phosphine cleanly reacts with the *N*,*N*-diisopropyliminium salt to give the stable adduct **1c**, which was isolated in 85% yield. Deprotonation with butyllithium cleanly afforded the desired *C*-amino phosphorus ylide **2c**, which was isolated as a light yellow oil in 85% yield and fully characterized by spectroscopy. All attempts to promote the fragmentation of this compound into the corresponding carbene and phosphine failed. Clearly, the tris(dimethylamino)-phosphine is much too basic and is therefore too strongly linked to the carbene fragment.

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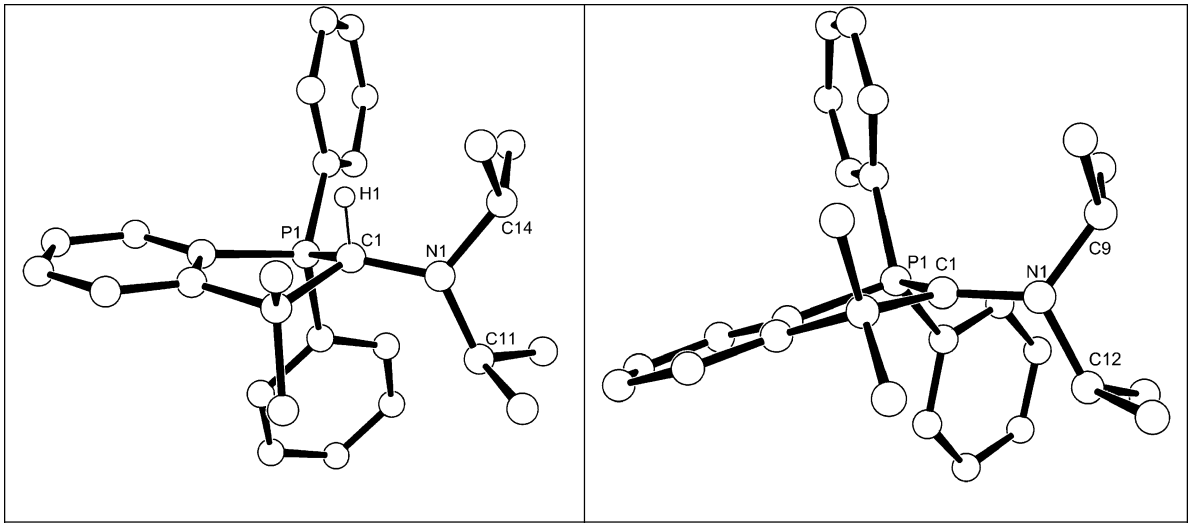
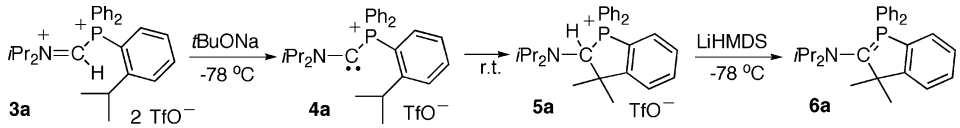


Figure 1. Thermal ellipsoid diagram (50% probability) of **5a** (left) and **6a** (right) (H atoms are omitted). Selected bond distances (Å) and angles (deg). **5a**: P1−C1 1.9010(13), C1−N1 1.4164(16), P1−C1−C2 102.83(8), P1−C1−N1 123.34(10), C2−C1−N1 119.21(11), C1−N1−C14 118.85(11), C1−N1−C11 123.02(11), C11−N1−C14 116.38(12). **6a:** P1−C1 1.695(2), C1−N1 1.422(3), P1−C1−C2 109.98(16), P1−C1−N1 128.69(18), C2−C1−N1 121.03(19), C1−N1−C9 122.7(2), C1−N1−C12 118.67(19), C9−N1−C12 115.8(2).

Scheme 2



From these results as a whole, it seems that, on one hand, *C*-amino phosphorus ylides bearing strongly basic nucleophilic phosphines, such as **2c**, are too stable to undergo fragmentation to the carbene and phosphine fragments and, on the other hand, phosphonium precursors featuring nonbasic phosphines such as **1a** or **1b** are not stable. Thus, we turned our attention to cyclic systems in the hope that entropic factors could help in stabilizing β-substituted phosphonium salts bearing a weakly basic phosphorus fragment. To reach our target molecules, we developed an original synthetic route. Recently, we have reported[27] that highly thermally stable phosphonio-substituted aldiminium salts **3** are readily prepared by addition of phosphines to Alder's dimer $[(R_2NCH)_2O^{2+}\ 2TfO^-]$.[28] Interestingly, dications **3** can be prepared not only with very basic phosphines, such as Cy_3P and $(Me_2N)_3P$, but also with weakly basic ones, such as triphenylphosphine. We envisaged that upon deprotonation the corresponding (amino)(phosphonio)carbene **4**[29] could undergo an intramolecular CH-insertion[30] reaction with a suitably designed phosphorus substitutent. To test this hypothesis, we prepared dication **3a**, and a subsequent deprotonation with sodium *tert*-butoxide cleanly led to the cyclic phosphonium salt **5a**, which was isolated in 82% yield as pale yellow crystals (Scheme 2, Figure 1). By monitoring the latter reaction by multinuclear NMR spectroscopy at −40 °C, we have been able to characterize the carbene **4a**. In marked contrast with the acyclic phosphonium salts **1a**,**b**, which feature an analogous phosphorus fragment, derivative **5a** appeared to be quite thermally stable (mp: 180−181 °C) and no evidence for the intramolecular dissociation into the phosphine and the iminium fragments was observed. A second deprotonation with LiHMDS afforded the corresponding ylide **6a**, which was fully characterized including a single-crystal X-ray diffraction study (Figure 1). The carbon−nitrogen bond distances for **5a** and **6a** are almost identical (1.42 Å), suggesting the absence of any interaction between the amino group and the ylidic carbon. In fact, the nitrogen and ylide lone pairs are perpendicular, to escape from a destabilizing four-electron interaction. Compared to the phosphorus−carbon bond distance in the phosphonium salt **5a** (1.90 Å), the P1−C1 in the ylide **6a** is very short (1.69 Å) and, in fact, is similar to those reported for nonstabilized ylides. Despite the presence of a weakly basic phosphine, no evidence for the dissociation of **6a** has been found, even upon irradiation at 250 nm or heating in refluxing toluene.

It is known that carbenes featuring a CH bond in a position α to the carbene center readily rearrange into alkenes via a 1,2-hydrogen shift.[31,32] This prompted us to attempt the preparation of phosphorus ylide **6b**, with a methylene group directly linked to the potential carbene center. A first deprotonation of dication **3b** cleanly afforded the desired cyclic phosphonium salt **5b**

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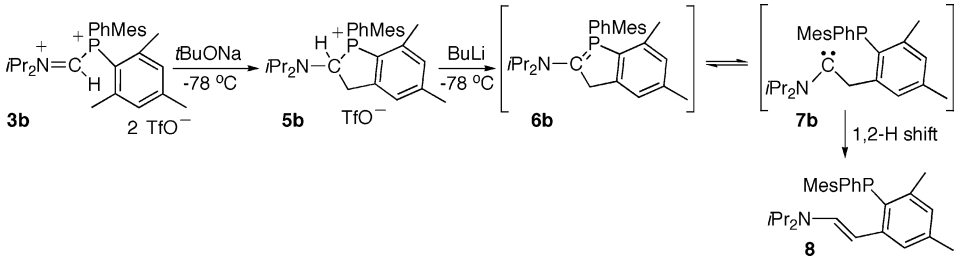
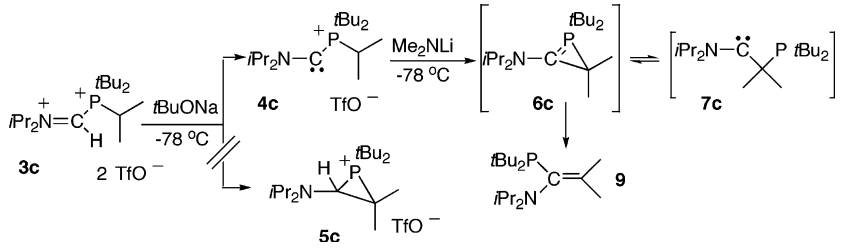
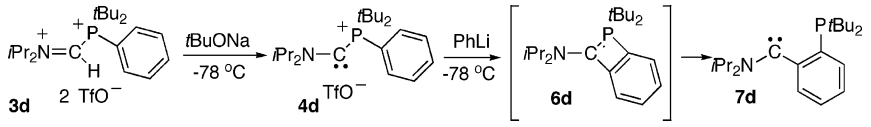
Scheme 3



Scheme 4



Scheme 5



(Scheme 3). Then, the second deprotonation did not lead to the cyclic ylide **6b** but to the alkene **8**, which was isolated in 68% yield. Clearly, alkene **8** results from the expected rearrangement of carbene **7b**. Because the substituent patterns for ylides **6a** and **6b** are very similar, these results as a whole suggest the existence of an equilibrium between phosphorus ylides and their two fragments.

More evidence for such an equilibrium was found when we attempted to prepare a stable (alkyl)(amino)carbene.[33] We thought that, because of the ring strain, a three-membered ring phosphorus ylide would easily undergo fragmentation and, provided that the carbene is linked to a tertiary carbon (no 1,2-H shift possible), the resulting carbene would be stable. We prepared dication **3c**, and our first surprise was the observation that upon deprotonation carbene **4c** was perfectly stable and did not undergo a CH insertion, which would have led to the desired phosphonium salt **5c**. However, taking advantage of the acidity of the proton in a position α to the phosphonium center, we reacted **4c** with a stoichiometric amount of sodium dimethylamide, and alkene **9** was obtained in 71% yield (Scheme 4). It is reasonable to postulate that the carbanion formed next to the phosphonium center added to the carbene to give the cyclic ylide **6c**. This ylide is certainly destabilized by the ring strain and can undergo a ring opening leading to carbene **7c**. The latter is very similar to the (diisopropylamino)(*tert*-butyl)-carbene,[33a] which is stable enough to be isolated. Therefore, the instability of **7c** can only be explained by the presence of an equilibrium with ylide **6c**, which can also undergo a cleavage of a PC single bond to give **9**. The other possibility, the 1,2-migration of the *t*-Bu_2P fragment in **7c**, is very unlikely.

Both three- and four-membered heterocycles have ring strain, but because of entropic factors, in contrast to three-membered rings, four-membered rings are not keen to undergo ring closure. Therefore, a phosphorus ylide when part of a four-membered ring should easily undergo an irreversible fragmentation. Using a reaction sequence similar to that described above [preparation of (amino)(phosphonio)carbene **4d**, followed by ortho-metalation of the phenyl with phenyllithium], we observed the quantitative formation of carbene **7d**, which was characterized in solution at room temperature by multinuclear NMR spectroscopy (Scheme 5).

Conclusion

β-Amino phosphonium salts can only be prepared using basic phosphines. The corresponding *C*-amino phosphorus ylides can be isolated and do not undergo fragmentation into phosphine and carbene. In contrast, cyclic β-amino phosphonium salts can be synthesized even with weakly basic phosphines such as triarylphosphines. Depending on the ring size and the nature of the substituent on the ylidic carbon, cyclic phosphorus ylides can either be stable or undergo fragmentation into the corresponding phosphine and transient or even stable carbene. Importantly, cyclic phosphorus ylides can be prepared by deprotonation of the β-amino phosphonium salts but also by intramolecular addition of a carbanion to the carbene center of an (amino)(phosphonio)carbene. The synthesis by the latter route of derivative **7d**, related to the well-known 1,2-bis(diphenylphosphino)benzene ligand, paves the way for the preparation of a variety of mixed carbene−phosphine bidentate ligands, and the scope of this approach is under active investigation.

Experimental Section

General. All manipulations were performed under an inert atmosphere of argon using standard Schlenk techniques. Dry, oxygen-free

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solvents were employed. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on Varian Inova 300, 500, and Brucker Avance 300 spectrometers.

Synthesis of Phosphonium Salt 1c. Hexamethylphosphorus triamide (3.25 g, 19.9 mmol) was added at −60 °C to a dichloromethane solution (15 mL) of diisopropyliminium salt (4.56 g, 17.3 mmol). The solution was warmed to 0 °C and stirred for 2 h. After evaporation of the solvent, the solid residue was washed with cold ethanol (15 mL) affording **1c** as white crystals (6.30 g, 85%): mp 137−138 °C; ^{31}P NMR ($CDCl_3$, 25 °C) +55.5; ^{1}H NMR ($CDCl_3$, 25 °C) 1.03 (d, J_{HH} = 6.6, 12H, CH_3), 2.79 (d, J_{PH} = 9.3, 18H, N(CH_3)$_2$), 3.04 (sept, J_{HH} = 6.6, 2H, CHCH$_3$), 3.41 (d, J_{PH} = 3.9, 2H, CH$_2$); ^{13}C NMR (CD_3CN, 25 °C) 20.8 (*C*H$_3$), 38.1 (N(*C*H$_3$)$_2$), 40.6 (d, J_{PC} = 83.4, *C*H$_2$), 49.9 (d, J_{PC} = 3.8, *C*H), 122.5 (q, J_{FC} = 321.6, *C*F$_3$). HRMS (FAB+) calcd for $C_{13}H_{34}N_4P$, 277.2521; found, 277.2524.

Synthesis of Phosphonium Ylide 2c. A THF solution (10 mL) of the phosphonium salt **1c** (1.82 g, 4.3 mmol) was cooled at −65 °C and 1 equiv of BuLi (2.5 M in pentane) was added. The solution was stirred at room temperature for 1 h, and after evaporation of the solvent, the residue was extracted with toluene (10 mL), affording **2c** as a yellow oil (1.0 g, 85%): ^{31}P NMR (C_6D_6, 25 °C) +58.6; ^{1}H NMR (C_6D_6, 25 °C) 1.18 (d, J_{HH} = 6.3, 12H, CHCH_3), 1.85 (d, J_{PH} = 60.9, 1H, CH═P), 2.54 (d, J_{PH} = 8.4, 18H, N(CH_3)$_2$), 3.12 (sept, J_{HH} = 6.3, 2H, CHCH$_3$); ^{13}C NMR (C_6D_6, 25 °C) 21.2 (CH*C*H$_3$), 33.5 (d, J_{PC} = 249.7, *C*H═P), 38.2 (N(*C*H$_3$)$_2$), 54.0 (d, J_{PC} = 7.1, *C*HCH$_3$); DCI-MS *m*/*z* 227 [carbene dimer + H$^+$]; EI-MS *m*/*z* 226 [carbene dimer$^+$].

Representative Procedure for the Preparation of Phosphonio-Substituted Aldiminium Salts 3. A CH_3CN solution (15 mL) of (2-^{i}Pr-phenyl)diphenylphosphine (0.98 g, 3.2 mmol) was added at −40 °C to a CH_3CN solution (15 mL) of Alder's dimer [(^{i}Pr$_2$NCH)$_2$O^{2+} 2TfO$^-$] (1.59 g, 2.9 mmol). The suspension was stirred for 4 h at room temperature. After evaporation of the solvent under vacuum, the solid residue was washed with THF (20 mL) affording **3a** as a white microcrystalline solid (1.91 g, 91%).

Phosphonio-Substituted Aldiminium Salts 3a: ^{31}P NMR (CD_3CN, 25 °C) +20.4; ^{1}H NMR (CD_3CN, 25 °C) 0.82 (d, J_{HH} = 6.3, 6H, CHCH_3), 1.04 (d, J_{HH} = 6.3, 6H, CHCH_3), 1.66 (d, J_{HH} = 6.6, 6H, CHCH_3), 2.61 (sept, J_{HH} = 6.3, 1H, CHCH$_3$), 4.32 (sept, J_{HH} = 6.3, 1H, CHCH$_3$), 4.77 (sept d, J_{HH} = 6.6, J_{HP} = 3.3, 1H, CHCH$_3$), 7.74−8.12 (m, 14H, CH_{ar}), 9.53 (d, J_{HP} = 24.6, 1H, CH); ^{13}C NMR (CD_3CN, 25 °C) 19.0 (CH*C*H$_3$), 23.3 (CH*C*H$_3$), 24.3 (CH*C*H$_3$), 36.3 (d, J_{CP} = 6.7, *C*HCH$_3$), 65.3 (d, J_{CP} = 4.5, *C*HCH$_3$), 69.9 (d, J_{CP} = 5.9, *C*HCH$_3$), 111.5 (d, J_{CP} = 90.1, C_{ar}), 114.3 (d, J_{CP} = 86.5, C_{ar}), 122.1 (q, J_{CF} = 321.6, *C*F$_3$SO$_3^-$), 130.0 (d, J_{CP} = 14.0, C_{ar}), 131.6 (d, J_{CP} = 12.1, C_{ar}), 132.7 (d, J_{CP} = 14.0, C_{ar}), 135.9 (d, J_{CP} = 15.7, C_{ar}), 136.1 (d, J_{CP} = 12.0, C_{ar}), 138.5 (C_{ar}), 139.5 (C_{ar}), 156.0 (d, J_{CP} = 12.1, C_{ar}), 171.1 (d, $^1J_{CP}$ = 62.9, *C*H).

Phosphonio-Substituted Aldiminium Salts 3b: (1.2 g, 50%); ^{31}P NMR (CD_3CN, 25 °C) +10.8; ^{1}H NMR (CD_3CN, 25 °C) 1.33 (d, J_{HH} = 6.3, 6H, CHCH_3), 1.67 (d, J_{HH} = 6.6, 6H, CHCH_3), 2.10 (s, 12H, CH_3), 2.41 (s, 6H, CH_3), 4.45 (sept, J_{HH} = 6.3, 1H, CHCH$_3$), 4.88 (sept d, J_{HH} = 6.6, J_{HP} = 3.6, 1H, CHCH$_3$), 7.31 (s, 2H, CH_{ar}), 7.33 (s, 2H, CH_{ar}), 7.74−8.06 (m, 5H, CH_{ar}), 9.50 (d, J_{HP} = 23.4, 1H, CH); ^{13}C NMR (CD_3CN, 25 °C) 19.9 (CH*C*H$_3$), 21.6 (CH*C*H$_3$), 23.8 (*C*H$_3$), 24.6 (*C*H$_3$), 65.5 (d, J_{CP} = 4.8, *C*HCH$_3$), 70.1 (d, J_{CP} = 3.6, *C*HCH$_3$), 111.6 (d, J_{CP} = 83.0, C_{ar}), 122.0 (q, J_{CF} = 321.6, *C*F$_3$SO$_3^-$), 133.2 (d, J_{CP} = 14.6, C_{ar}), 135.2 (d, J_{CP} = 12.4, C_{ar}), 138.4 (s, C_{ar}), 145.4 (d, J_{CP} = 10.3, C_{ar}), 149.8 (s, C_{ar}), 172.5 (d, J_{CP} = 62.3, *C*H).

Phosphonio-Substituted Aldiminium Salts 3c: (0.91 g, 79%); ^{31}P NMR (CD_3CN, 25 °C) +63.0; ^{1}H NMR (CD_3CN, 25 °C) 1.65−1.74 (m, 36H, CH_3), 3.95 (sept, J_{HH} = 7.0, 1H, CHCH$_3$), 4.68 (sept, J_{HH} = 6.3, 1H, CHCH$_3$), 5.00 (sept d, J_{HH} = 6.7, J_{HP} = 2.8, 1H, CHCH$_3$), 8.65 (d, J_{HP} = 18.4, 1H, CH); ^{13}C NMR (CD_3CN, −30 °C) 19.2 (CH*C*H$_3$), 20.6 (CH*C*H$_3$), 23.4 (CH*C*H$_3$), 27.5 (d, J_{CP} = 24.9, *C*H), 28.33 (C(*C*H$_3$)), 41.8 (d, J_{CP} = 20.7, *C*(CH$_3$)), 66.0 (*C*HCH$_3$), 67.6 (*C*HCH$_3$), 121.5 (q, J_{CF} = 321.6, *C*F$_3$SO$_3^-$), 167.8 (d, J_{CP} = 31.1, *C*H).

Phosphonio-Substituted Aldiminium Salts 3d: (3.3 g, 92%); ^{31}P NMR (CD_3CN, 25 °C) +49.7; ^{1}H NMR (CD_3CN, 25 °C) 1.53 (d, J_{HH} = 6.0, 6H, CHCH_3), 1.68 (d, J_{HP} = 18.3, 18H, C(CH_3)$_3$), 1.80 (d, J_{HH} = 6.9, 6H, CHCH_3), 4.35 (sept, J_{HH} = 6.0, 1H, CHCH$_3$), 5.00 (sept d, J_{HH} = 6.9, J_{HP} = 3.0, 1H, CHCH$_3$), 7.87−7.94 (m, 4H, C$_6H_5$), 8.02−8.09 (m, 1H, C$_6H_5$), 9.06 (d, J_{HP} = 21.0, 1H, CH); ^{13}C NMR (CD_3CN, −40 °C) 19.7 (CH*C*H$_3$), 23.2 (CH*C*H$_3$), 27.0 (C(*C*H$_3$)), 40.5 (d, J_{CP} = 24.9, *C*(CH$_3$)), 65.7 (*C*HCH$_3$), 68.4 (*C*HCH$_3$), 110.9 (d, J_{CP} = 66.4, C_{aro}), 121.0 (q, J_{CF} = 319.5, *C*F$_3$SO$_3^-$), 131.4 (d, J_{CP} = 12.5, C_{aro}), 134.4 (d, J_{CP} = 8.3, C_{aro}), 137.5 (s, C_{aro}), 167.6 (d, J_{CP} = 39.4, *C*H).

General Procedure for the Synthesis of (Amino)(phosphonio)-carbenes 4. A 1:1 mixture of *t*-BuONa and dication **3** (2.0 mmol) was cooled at −78 °C, and 15 mL of THF were added. In the case of **3c** and **3d**, the suspension was warmed to room temperature and stirred for 20 min. The solvent was removed under vacuum, and the residue was washed with Et_2O (5 mL). An orange solid, containing carbene **4c,d** and NaOTf, was obtained (quantitative reaction according to ^{31}P NMR spectroscopy) and used for the next reaction without further purification. In the case of **3a**, the suspension was warmed to −40 °C, and the (amino)(phosphonio)carbene **4a** was characterized in solution at −40 °C.

(Amino)(phosphonio)carbene 4a: ^{31}P NMR (THF-d_8, −40 °C) −9.6; ^{1}H NMR (THF-d_8, −40 °C) 0.92 (m, 6H, CHCH_3), 1.31 (m, 6H, CHCH_3), 1.40 (m, 6H, CHCH_3), 2.38 (m, 1H, CHCH$_3$), 4.14 (m, 1H, CHCH$_3$), 4.91 (m, 1H, CHCH$_3$), 7.17−7.88 (m, 14H, CH_{ar}); ^{13}C NMR (THF-d_8, −40 °C) 20.4 (CH*C*H$_3$), 23.1 (CH*C*H$_3$), 36.3 (s, *C*H), 59.3 (d, J_{CP} = 26.4, *C*HCH$_3$), 75.0 (d, J_{CP} = 31.1, *C*HCH$_3$), 121.4 (d, J_{CP} = 79.5, C_{ar}), 122.0 (q, J_{CF} = 321.2, *C*F$_3$SO$_3^-$), 123.4 (d, J_{CP} = 79.5, C_{ar}), 129.1 (d, J_{CP} = 10.4, C_{ar}), 129.9 (d, J_{CP} = 12.1, C_{ar}), 131.4 (d, J_{CP} = 10.4, C_{ar}), 135.1 (d, J_{CP} = 8.5, C_{ar}), 135.4 (s, C_{ar}), 135.9 (s, C_{ar}), 153.7 (d, J_{CP} = 10.3, C_{ar}), 292.0 (d, J_{CP} = 113.9, *C*).

(Amino)(phosphonio)carbene 4c: ^{31}P NMR (THF-d_8, 25 °C) +29.8; ^{1}H NMR (THF-d_8, 25 °C) 1.12−1.60 (m, 36H, CH_3), 3.30 (m, 1H, CHCH$_3$), 4.03 (m, 1H, CHCH$_3$), 4.85 (m, 1H, CHCH$_3$); ^{13}C NMR (THF-d_8, 25 °C) 20.9 (CH*C*H$_3$), 26.4 (CH*C*H$_3$), 29.1 (C(*C*H$_3$)), 31.4 (d, J_{CP} = 13.9, *C*H), 38.6 (d, J_{CP} = 49.2, *C*(CH$_3$)), 59.3 (*C*HCH$_3$), 74.6 (*C*HCH$_3$), 121.9 (q, J_{CF} = 320.4, *C*F$_3$SO$_3^-$), 307.5 (d, J_{CP} = 113.3, *C*).

(Amino)(phosphonio)carbene 4d: ^{31}P NMR (CD_3CN, 25 °C) +18.0; ^{1}H NMR (CD_3CN, 25 °C) 1.42 (d, $^3J_{HH}$ = 7.5, 12H, CHCH_3), 1.44 (d, $^3J_{HP}$ = 15.0, 18H, C(CH_3)$_3$), 3.88 (m, 1H, CHCH$_3$), 4.84 (m, 1H, CHCH$_3$), 7.61−7.63 (m, 4H, C$_6H_5$), 7.70−7.74 (m, 1H, C$_6H_5$); ^{13}C NMR (CD_3CN, 25 °C) 21.1 (CH*C*H$_3$), 25.2 (CH*C*H$_3$), 27.9 (d, J_{CP} = 5.0, C(*C*H$_3$)), 37.0 (d, J_{CP} = 50.3, *C*(CH$_3$)), 59.9 (*C*HCH$_3$), 74.5 (*C*HCH$_3$), 121.9 (d, J_{CP} = 28.4, C_{aro}), 122.0 (q, J_{CF} = 320.4, *C*F$_3$SO$_3^-$), 130.3 (d, J_{CP} = 8.3, C_{aro}), 134.3 (s, C_{aro}), 134.7 (d, J_{CP} = 5.0, C_{aro}), 309.4 (d, J_{CP} = 120.7, *C*).

Synthesis of Cyclic *C*-Amino Phosphonium Salt 5a. A 1:1 mixture of *t*-BuONa and dication **3a** (1.91 g, 2.7 mmol) was cooled to −78 °C, and 30 mL of THF was added. The suspension was warmed to room temperature and stirred for 12 h. After evaporation of the solvent, the residue was washed with Et_2O (30 mL). Recrystallization in THF/Et_2O at −20 °C afforded **5a** as pale yellow crystals (1.25 g, 82%): mp 180−181°C; ^{31}P NMR (CD_3CN, 25 °C) +12.2; ^{1}H NMR (CD_3CN, 25 °C) 0.96 (m, 12H, CHCH_3), 1.51 (s, 6H, CH_3), 3.22 (sept, J_{HH} = 6.9, 2H, CHCH$_3$), 5.04 (d, J_{HP} = 12.3, 1H, CH), 7.63−7.90 (m, 14H, CH_{ar}); ^{13}C NMR (CD_3CN, 25 °C) 24.0 (CH*C*H$_3$), 24.1 (CH*C*H$_3$), 29.0 (d, J_{CP} = 4.3, *C*H$_3$), 48.8 (*C*HCH$_3$), 51.4 (d, J_{CP} = 29.3, *C*), 81.7 (d, J_{CP} = 19.0, *C*H), 119.3 (d, J_{CP} = 83.4, C_{ar}), 122.2 (q, J_{CF} = 321.3, *C*F$_3$SO$_3^-$), 126.1 (d, J_{CP} = 8.8, C_{ar}), 130.7 (d, J_{CP} = 9.7, C_{ar}), 131.2 (d, J_{CP} = 12.5, C_{ar}), 133.1 (d, J_{CP} = 5.2, C_{ar}), 135.2 (d, J_{CP} = 8.9, C_{ar}), 135. 7 (d, J_{CP} = 2.8, C_{ar}), 137.2 (d, J_{CP} = 2.0, C_{ar}), 158.8 (d, J_{CP} = 17.2, C_{ar}). HRMS (FAB+) calcd for $C_{28}H_{35}NP$, 416.2507; found, 416.2499.

Synthesis of Cyclic *C*-Amino Phosphonium Salt 5b. A 1:1 mixture of *t*-BuONa and dication **3b** (0.85 g, 1.1 mmol) was cooled to −78 °C, and 15 mL of THF was added. The suspension was warmed to

room temperature and stirred for 12 h. After evaporation of the solvent and washing with Et_2O (30 mL), **5b** was obtained as a pale yellow powder (0.63 g, 93%): ^{31}P NMR (THF-d_8, 25 °C) +19.3; ^1H NMR (CD_3CN, 25 °C) 0.79 (d, J_{HH} = 6.3, 6H, CHCH_3), 1.15 (d, J_{HH} = 6.0, 6H, CHCH_3), 1.78 (s, 3H, CH_3), 2.10 (s, 6H, CH_3), 2.37 (s, 3H, CH_3), 2.38 (s, 3H, CH_3), 2.99 (m, 2H, CHCH$_3$), 3.74 (dd, J = 8.1 and 16.2, 1H, CH_2), 3.91 (dd, J = 10.2 and 16.2, 1H, CH_2), 5.54 (m, 1H, CH), 7.02−7.27 (m, 4H, CH_{ar}), 7.59−7.80 (m, 5H, CH_{ar}); ^{13}C NMR (CD_3CN, 25 °C) 21.4 (*C*H_3), 21.8 (*C*H_3), 22.4 (*C*H_3), 23.0 (*C*H_3), 38.8 (d, J_{CP} = 23.8, *C*H_2), 49.3 (*C*HCH$_3$), 66.8 (d, J_{CP} = 62.6, *C*H), 122.0 (q, J_{CF} = 321.6, *C*$F_3SO_3^-$), 122.4 (d, J_{CP} = 85.0, C_{ar}), 123.6 (d, J_{CP} = 75.6, C_{ar}), 126.5 (d, J_{CP} = 8.1, C_{ar}), 130.8 (d, J_{CP} = 12.1, C_{ar}), 133.1 (d, J_{CP} = 9.8, C_{ar}), 133.6 (d, J_{CP} = 11.2, C_{ar}), 134.8 (s, C_{ar}), 142.8 (d, J_{CP} = 6.7, C_{ar}), 146.5 (d, J_{CP} = 9.7, C_{ar}), 147.0 (s, C_{ar}), 148.1 (s, C_{ar}), 148.2 (d, J_{CP} = 19.6, C_{ar}); FAB-MS *m*/*z* 458 [M^+].

Synthesis of Cyclic *C*-Amino Phosphorus Ylide 6a. A 1:1 mixture of LiHMDS and phosphonium salt **5a** (0.41 g, 0.7 mmol) was cooled to −78 °C, and 15 mL of THF was added. The suspension was warmed to room temperature and stirred for 20 min. After evaporation of the solvent, the residue was extracted with hexane (20 mL). Recrystallization in hexane at −20 °C afforded **6a** as red crystals (0.28 g, 92%): mp 153−155 °C; ^{31}P NMR (C_6D_6, 25 °C) −10.4; ^1H NMR (C_6D_6, 25 °C) 0.93 (d, J_{HH} = 6.0, 12H, CHCH_3), 1.67 (s, 6H, CH_3), 3.17 (sept, J_{HH} = 6.0, 2H, CHCH$_3$), 6.72−7.24 and 7.55−7.61 (m, 14H, CH_{ar}); ^{13}C NMR (C_6D_6, 25 °C) 25.2 (CH*C*H$_3$), 33.2 (*C*H$_3$), 52.7 (d, J_{CP} = 58.6, *C*), 54.9 (*C*HCH$_3$), 62.3 (d, J_{CP} = 128.5, *C*), 124.4 (d, J_{CP} = 7.2, C_{ar}), 127.0 (d, J_{CP} = 10.0, C_{ar}), 128.4 (d, J_{CP} = 6.7, C_{ar}), 128.7 (d, J_{CP} = 10.7, C_{ar}), 129.6 (s, C_{ar}), 130.5 (s, C_{ar}), 133.3 (d, J_{CP} = 10.0, C_{ar}), 136.4 (d, J_{CP} = 68.6, C_{ar}), 159.2 (d, J_{CP} = 15.7, C_{ar}). HRMS (FAB+) calcd for $C_{28}H_{35}NP$, 416.2507; found, 416.2494.

Synthesis of Enamine 8. Butyllithium (435 μl, 1.05 mmol) was added at −78 °C to a THF solution (10 mL) of the phosphonium salt **5b** (0.63 g, 1.0 mmol). The suspension was stirred for 4 h at room temperature. After evaporation of the solvent, extraction with hexane (10 mL), and washing with an aqueous saturated solution of NH_4Cl, a yellow oil was obtained (0.31 g, 68%): ^{31}P NMR ($CDCl_3$, 25 °C) −29.4; ^1H NMR ($CDCl_3$, 25 °C) 1.27 (m, 12H, CHCH_3), 2.41 (s, 3H, CH_3), 2.45 (s, 6H, CH_3), 2.55 (s, 3H, CH_3), 2.57 (s, 3H, CH_3), 3.47 (m, 2H, CHCH$_3$), 5.63 (d, J_{HH} = 13.5, 1H, CH), 6.87 (d, J_{HH} = 13.5, 1H, CH), 6.94−7.65 (m, 9H, CH_{ar}); ^{13}C NMR ($CDCl_3$, 25 °C) 21.1 (*C*H$_3$), 21.4 (*C*H$_3$), 21.8 (*C*H$_3$), 21.9 (*C*H$_3$), 23.2 (*C*H$_3$), 23.4 (*C*H$_3$), 46.0 (*C*HCH$_3$), 97.3 (d, J_{CP} = 14.5, *C*H), 122.3 (s, *C*H), 125.9 (d, J_{CP} = 18.7, C_{ar}), 127.3 (s, C_{ar}), 127.4 (s, C_{ar}), 128.0 (d, J_{CP} = 6.3, C_{ar}), 129.9 (s, C_{ar}), 131.3 (d, J_{CP} = 18.6, C_{ar}), 133.6 (s, C_{ar}), 133.7 (s, C_{ar}), 137.9 (s, C_{ar}), 138.7 (d, J_{CP} = 12.4, C_{ar}), 142.9 (d, J_{CP} = 18.6, C_{ar}), 143.2 (d, J_{CP} = 20.0, C_{ar}), 145.6 (d, J_{CP} = 10.4, C_{ar}); EI-MS *m*/*z* 458 [M + H^+].

Synthesis of Enamine 9. A THF solution (5 mL) of the lithium dimethylamide (0.10 g, 2.0 mmol) was added at −78 °C to a THF solution (5 mL) of the carbene **4c** (2.0 mmol). The suspension was stirred for 2 h at room temperature. After evaporation of the solvent, extraction with ether (10 mL), and washing with CH_3CN (10 mL), **9** was obtained as a white solid (0.42 g, 71%): ^{31}P NMR (C_6D_6, 25 °C) +42.4; ^1H NMR (C_6D_6, 25 °C) 1.22 (d, $^3J_{HH}$ = 6.5, 6H, CHCH_3), 1.32 (d, J_{HP} = 11.5, 18H, C(CH_3)), 1.33 (d, J_{HH} = 6.5, 6H, CHCH_3), 1.79 (s, 3H, CH_3), 1.80 (s, 3H, CH_3), 3.57 (sept d, J_{HH} = 6.5, J_{HP} = 2.5, 2H, CHCH$_3$); ^{13}C NMR (C_6D_6, 25 °C) 24.2 (*C*H$_3$), 24.4 (*C*H$_3$), 24.9 (*C*H$_3$), 26.2 (*C*H$_3$), 32.9 (d, J_{CP} = 14.5, C(*C*H$_3$)), 34.4 (d, J_{CP} = 37.3, *C*(CH$_3$)), 52.3 (d, J_{CP} = 8.2, *C*HCH$_3$), 139.8 (*CC*P), 144.1 (d, J_{CP} = 39.5, *CC*P); DCI-MS *m*/*z* 300 [M + H^+].

Synthesis of (Amino)(aryl)carbene 7d. Phenyllithium (1.19 mL, 2.38 mmol) was added at −78 °C to a THF solution (20 mL) of the amino(phosphonio)carbene **4d** (2.16 mmol). The suspension was stirred for 30 min at room temperature. The ^{13}C, ^1H, and ^{31}P NMR spectra show the quantitative formation of the (amino)(aryl)carbene **7d**: ^{31}P NMR (THF-d_8, 25 °C) 20.48; ^1H NMR (THF-d_8, 25 °C) 1.06 (d, J_{HH} = 6.9, 6H, CHCH_3), 1.10 (d, J_{HH} = 6.0, 6H, CHCH_3), 1.16 (d, J_{HP} = 11.4, 18H, C(CH_3)$_3$), 4.16 (m, 2H, CHCH$_3$), 7.02−7.68 (m, 4H, CH_{ar}); ^{13}C NMR (THF-d_8, 25 °C) 20.0 (CH*C*H$_3$), 22.4 (CH*C*H$_3$), 32.1 (C(*C*H$_3$)$_3$), 34.9 (*C*(CH$_3$)$_3$), 51.4 (*C*HCH$_3$), 58.5 (*C*HCH$_3$), 113.9 (d, J_{CP} = 12.1, C_{ar}), 121.0 (s, C_{ar}), 123.4 (d, J_{CP} = 20.7, C_{ar}), 129.8 (s, C_{ar}), 135.7 (s, C_{ar}), 161.2 (d, J_{CP} = 34.6, C_{ar}), 314.9 (d, J_{CP} = 15.6, *C*).

Crystal Structure Determination of Compounds 5a and 6a. The Bruker X8-APEX[34a] X-ray diffraction instrument with Mo radiation was used for data collection of compounds **5a** and **6a**. All data frames were collected at low temperatures (T = 100 K for **5a** and T = 160 K for **6a**) using an ω ϕ-scan mode (−0.5° ω-scan width, hemisphere of reflections) and integrated using a Bruker SAINTPLUS software package.[34b] The intensity data were corrected for Lorentzian polarization. Absorption corrections were performed using the SADABS program included in the SAINTPLUS software package. The Bruker SHELXTL software package[34c] was used for direct methods of phase determination and structure refinement. Atomic coordinates and isotropic and anisotropic displacement parameters of all the non-hydrogen atoms of two compounds were refined by means of a full matrix least-squares procedure on F^2. All H-atoms were included in the refinement in calculated positions riding on the atoms to which they were attached. **5a** was found to be twinned by a nonmerohedral twin law. The Cell_Now program[34d] was used to determine a suitable cell and to perform the indexation of the crystal system. Twinabs software[34e] was used for scaling and absorption correction calculations.

Crystal and Structure Parameters of 5a: size = 0.26 × 0.21 × 0.21 mm^3; monoclinic; space group $P2(1)/c$; a = 10.9466(6) Å, b = 9.0296(5) Å, c = 29.4485(17) Å, α = 90°, β = 93.0750(10)°, γ = 90°; V = 2906.6(3) Å^3; ρ_{calcd} = 1.293 g/cm^3; $2\theta_{max}$ = 52.74°; Mo-radiation (λ = 0.71073 Å); low temperature = 100(2) K; reflections collected = 26 603; independent reflections = 11 878 (R_{int} = 0 0.0589, R_{sig} = 0.0449); 7019 (59.1%) reflections were greater than 2σ(I); index ranges −13 ≤ h ≤ 13, −11 ≤ k ≤ 11, 0 ≤ l ≤ 36; absorption coefficient μ = 0.216 mm^{-1}; max/min transmission = 0.9561 and 0.9460; 415 parameters were refined and converged at R1 = 0.0413, wR2 = 0.0960, with intensity I > 2σ(I); the final difference map was 0.327 and −0.315 e.Å^{-3}.

Crystal and Structure Parameters of 6a: size 0.35 × 0.31 × 0.10 mm^3; triclinic; space group $P\bar{1}$; a = 10.189(2) Å, b = 10.608(2) Å, c = 12.500(4) Å, α= 98.449(3)°, β= 95.173(3)°, γ = 116.258(2)°; V =1180.0(5) Å^3; ρ_{calcd} = 1.169 Mg/m^3; $2\theta_{max}$ = 46.52°; Mo-radiation (λ = 0.71073 Å); low temperature = 160(2)° K; total reflections collected =5947; independent reflections = 3255 (R_{int} = 0.0464, R_{sig} = 0.0887); 2907 (89.3%) reflections were greater than 2σ(I); index ranges −9 ≤ h ≤ 11, −11 ≤ k ≤ 11, −13 ≤ l ≤ 13; absorption coefficient μ = 0.131 mm^{-1}; max/min transmission = 0.9869 and 0.9557277 parameters were refined and converged at R1 = 0.0687, wR2 = 0.1897, with intensity I > 2σ(I); the final difference map was 0.533 and −0.403 e.Å^{-3}.

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Supporting Information Available: X-ray crystallographic data for **5a** and **6a** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(34) (a) *APEX 2*, version 1.0−22; Bruker AXS Inc.: Madison, WI, 2004. (b) *SAINT*, version V7.06A.; Bruker AXS Inc.: Madison, WI, 2003. (c) *SHELXTL*, version 6.14; Bruker AXS Inc.: Madison, WI, 2003. (d) *Cell_Now*; Bruker AXS Inc., Madison, WI, 2004. (e) *Twinabs Bruker Nonius Scaling and corrections for Twinned Crystals*, version 1.05; Bruker AXS Inc., Madison, WI.