Synthesis and Rearrangement of Intramolecularly Stabilized $1\sigma^2,3\sigma^2$-Diphosphaallylic Cations into Intramolecularly Stabilized $1\sigma^1,3\sigma^3$-Diphosphaallylic Cations

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Abstract: Two equivalents of boron trifluoride–diethyl ether complex or 1 equiv of trifluoromethanesulfonic acid reacts with *C*-[bis(diisopropylamino)phosphino]-*C*,*P*-bis(diisopropylamino)phosphaalkene **1**, cleaving one of the diisopropylamino substituents at the σ^3-phosphorus atom. This affords the corresponding $1\sigma^2,3\sigma^2$-diphosphaallylic cation **4**, which is isolated as the four-membered-heterocycle **3**. Addition of a catalytic amount of base to **3** leads to a $1\sigma^1,3\sigma^3$-diphosphaallylic cation **5**, which is isolated as the diphosphirenium salt **2**. Mesityllithium and the lithium salts of diisopropylamine or dicyclohexylamine react at the σ^2-phosphorus atom of the cationic heterocycles **2** and **3**, affording the corresponding phosphaalkenes **8**, **1**, and **6**, respectively. All the results demonstrate the high electrophilicity of low-coordinated diphosphaallylic cations, which are only isolable as intramolecular donor–acceptor complexes.

Introduction

Phosphonium[1] and phosphenium[2] salts are well-known compounds, and a few tricoordinate phosphorus cations, namely, methylenephosphenium salts, have been fully characterized.[3] To date, the *N*-tri-*tert*-butylphenyl iminophosphenium ion reported by Niecke et al.[4] is the only example of a monocoordinated phosphorus cation. Several diphosphaallylic cations have been reported;[5,6] they feature a dicoordinate and a tetracoordinate phosphorus atom. Here we report the generation of $1\sigma^2,3\sigma^2$-diphosphaallylic cations[6] stabilized by intramolecular donor–acceptor interactions and their rearrangement into the isomeric (intramolecularly stabilized) $1\sigma^1,3\sigma^3$-diphosphaallylic ions. The reactivity of both compounds with nucleophiles is presented.

Results

We have recently reported the synthesis of the first diphosphirenium salt **2**,[7] through the addition of 2 equiv of boron trifluoride–ethylamine complex to *C*-[bis(diisopropylamino)-phosphino]-*C*,*P*-bis(diisopropylamino)phosphaalkene **1**. Surprisingly, when the same reaction was performed with boron trifluoride–diethyl ether complex, a new compound, **3**, was obtained in near quantitative yield along with a corresponding amount of (diisopropylamino)difluoroborane (Scheme 1).

The ionic nature of **3** (mp 123–124 °C) was indicated by its very low solubility in nonpolar solvents and by an exchange reaction with potassium hexafluorophosphate. The quantitative formation of R_2N–BF_2, the mass spectral data, and elemental analysis demonstrated that one of the original four diisopropylamino groups had been removed. Among the possible structures for **3**, the symmetrical cation **4** could be ruled out since the ^{31}P NMR spectrum showed an AX system, indicating that the molecule possessed two different phosphorus atoms. The low-field ^{31}P NMR chemical shifts (P_A +211.6 and P_X +181.6) were in the range expected for low-coordinate phosphorus atoms.[8] The ^{13}C NMR resonance at 188.4 indicated an sp^2-hybridized carbon, and the values of the phosphorus–phosphorus (J_{PP} = 34.9 Hz) and phosphorus–carbon (J_{P_AC} = 66.8 Hz, J_{P_XC} = 19.7 Hz) coupling constants suggested a PCP sequence. All these results were in favor of the unsymmetrical cation **5**. However, in the ^{13}C NMR spectrum, there were six inequivalent isopropyl-CH resonances, suggesting diisopropylamino groups in three different environments, each exhibiting hindered rotation, which was hardly possible for **5**. Thus, a novel structure had to be invoked for **3**, the true assignment coming from high-level ab initio calculations performed by Ahlrichs and Treutler on the amino analogs (R = H).[9] They concluded that species **5** was not even a minimum on the total potential energy surface, while the symmetrical cation **4** was 34 kJ/mol higher in energy than the four-membered-heterocycle **3** (Scheme 1). It became apparent that the calculated structure **3** corresponded well with all the spectroscopic data.

The four-membered-ring salt **3** slowly rearranged in solution, even at low temperature (1 week at −20 °C), into the isomeric diphosphirenium salt **2**, precluding recrystallization of **3**. Moreover, the addition at room temperature of a stoichiometric amount of Et_3N, Me_3P, or Me_2S, spontaneously induced the rearrangement of **3** into **2**, with no visible intermediate detectable by ^{31}P NMR spectroscopy (Scheme 1).

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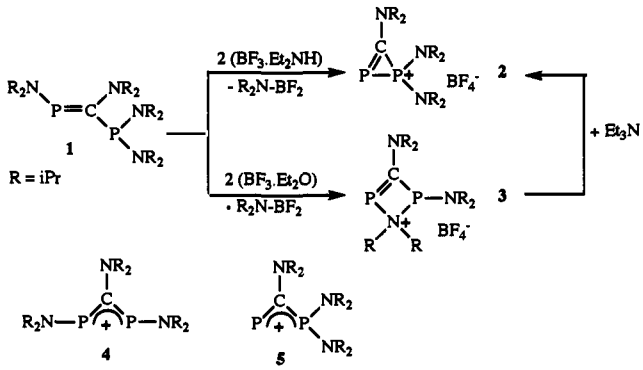
Scheme 1



Addition of lithium diisopropylamide to salts **2** or **3** cleanly reformed the phosphaalkene **1** in good yield. When lithium dicyclohexylamide was used, a 50/50 mixture of *P*-(dicyclohexylamino)phosphaalkene **6** and its isomeric *P*-(diisopropylamino)phosphaalkene **7** was isolated, after workup. However, when this reaction was monitored by ^{31}P NMR at low temperature (−78 °C), we first observed the formation of *P*-(dicyclohexylamino)phosphaalkene **6**, with phospaalkene **7** only appearing on warming to room temperature. Lastly, *P*-(mesityl)phosphaalkene **8** was isolated, in the reaction of **2** or **3** with mesityllithium (Scheme 2).

Treatment of this 50/50 mixture of phosphaalkenes **6**/**7** with 2 equiv of boron trifluoride–ether complex afforded a 12/12/76 mixture of four-membered-rings **3**, **9**, and **10**. According to ^{31}P NMR spectroscopy, the reaction only occurred at room temperature, no starting material was left, and no other products were formed. Addition of triethylamine to this mixture led to the formation of diphosphirenium salts **2** and **11** in a 14/86 ratio (Scheme 3).

Addition of trifluoromethanesulfonic acid to phosphaalkene **1** at −78 °C also cleanly led to the formation of salt **3** ($CF_3SO_3^-$ as counterion). However, monitoring this reaction by ^{31}P NMR spectroscopy allowed the characterization of the $1\sigma^2,3\sigma^4$-diphosphaallylic cation **12** (+220 (J_{PP} = 19.7 Hz), +20 (J_{PP} = 19.7 Hz, J_{PH} = 560 Hz)). Lastly, addition of trifluoromethanesulfonic acid to *P*-(dicyclohexylamino)phosphaalkene **6** at −78 °C gave rise to a mixture of the four-membered-ring salts **9** and **10** in a 15/85 ratio; addition of a stoichiometric amount of triethylamine quantitatively afforded the diphosphirenium salt **11** (Scheme 4).

Discussion

The different outcome of the reaction of phosphaalkene **1** with boron trifluoride–diethyl ether, instead of boron trifluoride–triethylamine complex, was easily explained since the addition of triethylamine to the four-membered-heterocycle **3** gave diphosphirenium **2** (Scheme 1). However, the mechanism of this rearrangement was not obvious especially since Ahlrichs[9] calculated **2** (R = H) to be 27 kJ/mol less stable than **3**. So the first question was to find the role played by the base (even a very weak one, such as THF) in the ring contraction reaction. The addition of lithium diisopropylamide to the four-membered-ring **3**, which reafforded the phosphaalkene **1**, clearly showed that a nucleophile could interact with the ring, but did not indicate on which of the phosphorus atoms. In contrast, the formation of *P*-(dicyclohexylamino)phosphaalkene **6** as the kinetic product and the isolation of *P*-mesitylphosphaalkene **8** in the reaction of **3** with lithium dicyclohexylamide and mesityllithium, respectively, demonstrated that the nucleophilic attack occurred at the σ^2-phosphorus atom. The equilibrium between phosphaalkenes **6** and **7** is not surprising since exchange reactions between aminophosphines are well-known,[10] the ratio obtained being dictated by the entropic factor (Scheme 2).

At that point, it was reasonable to postulate that a weak nucleophile could induce the ring opening of **3**, giving a transient donor–acceptor complex, **13**. This could be displaced by an intramolecular nucleophilic attack by the lone pair of the σ^3-phosphorus atom, giving rise to the diphosphirenium salt **2**; in other words the diphosphirenium salt **2** has to be regarded as an intramolecularly stabilized monocoordinated phosphorus cation (note that Niecke et al. have recently reported the synthesis and X-ray crystal structure of an intermolecularly stabilized methylenephosphenium cation, **14**[11]) (Scheme 5).

In the same vein, the four-membered-heterocycle **3** can be regarded either as a dicoordinate or monocoordinate phosphorus cation stabilized by a donor–acceptor interaction with the nitrogen lone pair of a diisopropylamino substituent (Scheme 6).

Thus, the next question was to elucidate from which phosphorus atom the diisopropylamino group was cleaved by boron trifluoride. The results observed for the reaction of BF_3·OEt_2 with the mixture of phosphaalkenes **6**/**7** (50/50) nicely argued for the cleavage of a diisopropylamino group from the σ^3-phosphorus atom, implying that the first intermediate was probably the $1\sigma^2,3\sigma^2$-diphosphaallylic cation **4**. Indeed, if an amino group bonded to the σ^2-phosphorus atom had been cleaved, we should have obtained 50% of the four-membered-heterocycle **3**, featuring only diisopropylamino groups; in contrast, we observed only 12% of **3** (Schemes 3 and 7).

The observed ratio (**3**/**9**/**10** 12/12/76) also indicated that a diisopropylamino group was preferentially cleaved, compared to a dicyclohexylamino group, and was also preferentially involved in the donor–acceptor interaction. Not surprisingly, addition of triethylamine to this four-membered-ring mixture led to the expected ratio of three-membered-rings **2** and **11** (14/86) (Scheme 3).

We found that in contrast with boron trifloride, trifluoromethanesulfonic acid reacts with phosphaalkene **1** at −78 °C, which allowed us to characterize the intermediate $1\sigma^2,3\sigma^4$-diphosphaallylic cation **12**, reinforcing our hypothesis (Scheme 4). This observation confirmed that the elimination of diisopropylamine led to the formation of the $1\sigma^2,3\sigma^2$-diphosphaallylic cation **4**. Since, trifluoromethanesulfonic acid reacts with phosphaalkenes at low temperature, it was possible to start from pure *P*-(dicyclohexylamino)phosphaalkene **6**, allowing us to observe the formation of the two four-membered-rings **9** and **10**, both of which possess a dicyclohexylamino group, in the expected 15/85 ratio, addition of triethylamine giving pure diphosphacyclopropenium salt **11** (Scheme 4).

Conclusion

Addition of BF_3·OEt_2, or trifluoromethanesulfonic acid, to *C*,*P*-diamino-*C*-(diaminophosphino)phosphaalkenes led to the $1\sigma^2,3\sigma^4$-diphosphaallylic cations A. After elimination of R_2NBF_2 (or R_2NH) from the σ^4-phosphorus atom, transient $1\sigma^2,3\sigma^2$-diphosphaallylic cations B were formed and isolated as intramolecular donor–acceptor complexes C. Addition of base to these four-membered heterocycles gave transient intermolecular donor–acceptor complexes of $1\sigma^1,3\sigma^3$-diphosphaallylic cations D, which are displaced toward diphosphacyclopropenium salts E; the latter compounds can be considered as intramolecularly stabilized $1\sigma^1,3\sigma^3$-diphosphaallylic cations F (Scheme 8).

These results clearly demonstrate the high electrophilicity of low-coordinated diphosphaallylic cations.

Experimental Section

All experiments were performed under an atmosphere of dry argon or nitrogen. Melting points were obtained on an Electrothermal capillary apparatus and were not corrected. ^1H, ^{31}P, ^{13}C, and ^{11}B NMR spectra were recorded on Bruker AC80, AC200, or WM250 spectrometers. ^1H and ^{13}C chemical shifts are reported in parts per million relative to Me_4Si

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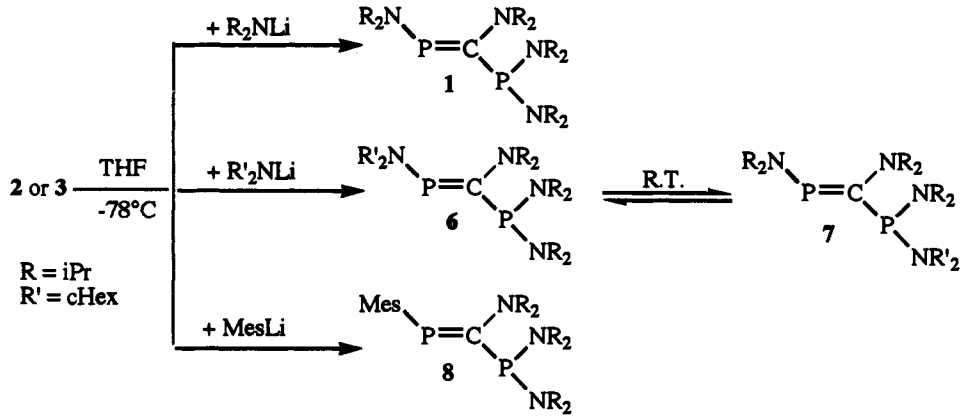
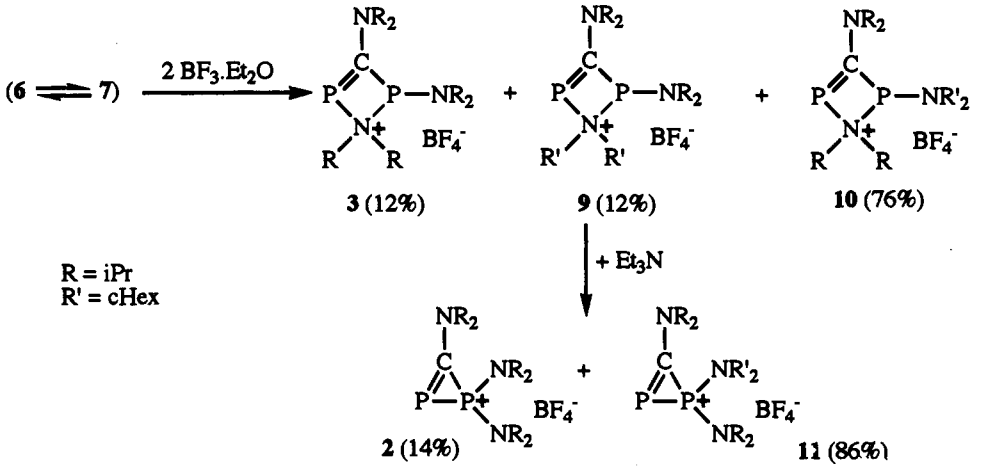
Scheme 2



Scheme 3



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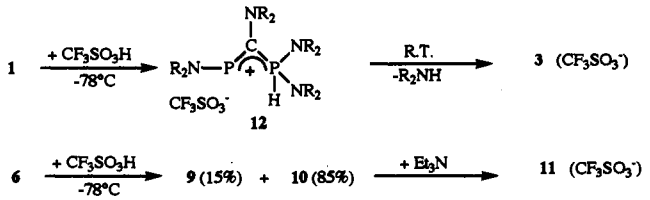
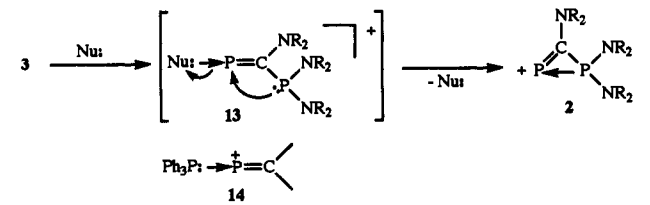
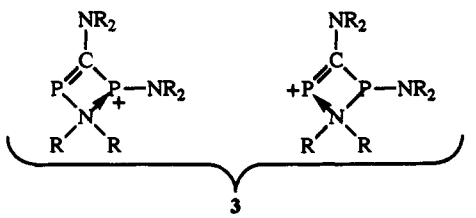


Scheme 5



Scheme 6

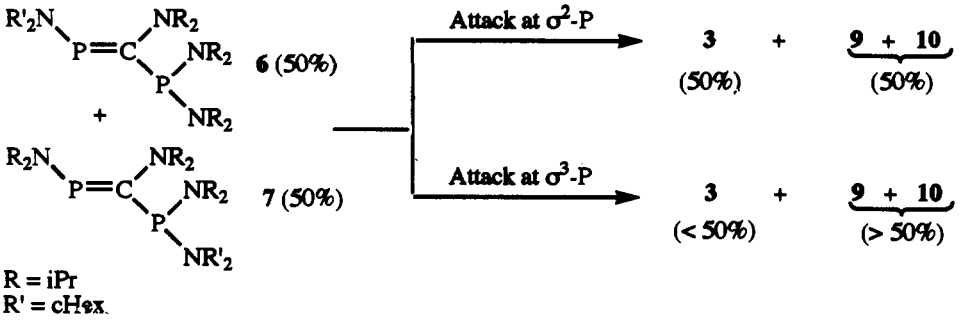


as external standard. ^{31}P and ^{11}B downfield shifts are expressed with a positive sign, in parts per million, relative to external 85% H_3PO_4 and $BF_3{\cdot}OEt_2$, respectively. Infrared spectra were recorded on a Perkin-Elmer lattice spectrometer (Mol 597). Mass spectra were obtained on a Ribermag R10 10E instrument. Conventional glassware was used.

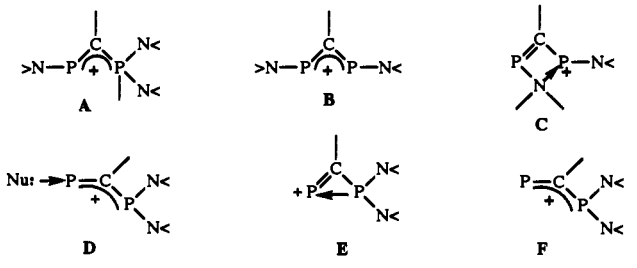
Synthesis of Cationic Four-Membered-Heterocycle 3. To a toluene solution (5 mL) of phosphaalkene **1** (0.47 g, 1 mmol) was added at room temperature 2 equiv of $BF_3{\cdot}OEt_2$ (0.28 g, 2 mmol). After stirring for 10 min at room temperature, the solvent was removed under vacuum, and the residue was washed several times with Et_2O. Compound **3** (BF_4^-) was obtained as a yellow powder (0.28 g, 60% yield): mp 123–124 °C; ^{31}P NMR{^1H} (CD_2Cl_2) +211.6 (d, J(PP) = 34.9 Hz, P_A), +181.6 (d, J(PP) = 34.9 Hz, P_X); ^{11}B NMR (CD_2Cl_2) +0.7; ^1H NMR (CD_2Cl_2) 1.23 (d, J(HH) = 6.5 Hz, 3 H, CH_3), 1.30 (m, 18 H, CH_3), 1.46 (d, J(HH) = 6.8 Hz, 6 H, CH_3), 1.53 (d, J(HH) = 6.8 Hz, 3 H, CH_3), 1.68 (d, J(HH) = 7.0 Hz, 3 H, CH_3), 1.77 (d, J(HH) = 6.4 Hz, 3 H, CH_3), 3.80 (m, 2 H, CH), 3.83 (m, 2 H, CH), 4.04 (sept d, J(HH) = 6.8 Hz, $J(P_XH)$ = 2.8 Hz, 1 H, CH), 4.30 (sept d, J(HH) = 6.5 Hz, $J(P_XH)$ = 3.5 Hz, 1 H, CH); ^{13}C NMR (CD_2Cl_2) 16.8 (d, $J(P_AC)$ = 18.6 Hz, CH_3), 16.9 (d, $J(P_AC)$ = 11.2 Hz, CH_3), 19.2 (s, CH_3), 20.7 (d, $J(P_AC)$ = 17.9 Hz, CH_3), 21.1 (dd, $J(P_AC)$ = 5.3 Hz, $J(P_XC)$ = 24.6 Hz, CH_3), 22.0 (s, CH_3), 22.4 (m, CH_3), 26.2 (d, $J(P_XC)$ = 14.2 Hz, CH_3), 26.4 (d, $J(P_XC)$ = 11.1 Hz, CH_3), 48.5 (d, $J(P_XC)$ = 30.5 Hz, CH), 49.8 (s, CH), 51.8 (dd, $J(P_AC)$ = 1.4 Hz, $J(P_XC)$ = 12.1 Hz, CH), 56.2 (dd, $J(P_AC)$ < 1 Hz, $J(P_XC)$ = 15.6 Hz, CH), 57.2 (dd, $J(P_AC)$ = 5.2 Hz, $J(P_XC)$ = 11.9 Hz, CH), 58.4 (dd, $J(P_AC)$ = 5.5 Hz, $J(P_XC)$ = 2.7 Hz, CH), 188.4 (dd, $J(P_AC)$ = 66.8 Hz, $J(P_XC)$ = 19.7 Hz, PCP); mass spectrum m/z 374 (M^+). Anal. Calcd for $C_{19}H_{42}BF_4N_3P_2$: C, 49.46; H, 9.18; N, 9.11. Found: C, 49.58; H, 9.10; N, 9.06.

Synthesis of Diphosphirenium Salts 2 from 3. To a THF solution (5 mL) of **3** (0.46 g, 1 mmol) was added at room temperature an excess of Et_3N, Me_2P, or Me_2S. According to the ^{31}P NMR spectroscopy, three-membered-ring **3** was instantaneously obtained in near quantitative yield. After removal of the solvent under vacuum, derivative **3** (BF_4^-) was purified by crystallization from a saturated THF solution as non-air-sensitive pale-yellow crystals (0.28 g, 60%): mp 118 °C; ^{31}P NMR (CD_2Cl_2) +58.53 (d-broad, J(PP) = 247.4 Hz, J(PH) < 3 Hz, P_A), -46.63 (dq, J(PP) = 247.4 Hz, J(PH) = 19.8 Hz, P_X); ^{11}B NMR (CD_2Cl_2) +0.7; ^1H NMR (CD_2Cl_2) 1.35 (d, J(HH) = 6.9 Hz, 12 H, PNCCH_3), 1.38 (d, J(HH) = 6.9 Hz, 12 H, PNCCH_3), 1.39 (d, J(HH) = 6.6 Hz, 6 H, CNCCH_3), 1.48 (d, J(HH) = 6.8 Hz, 6 H, CNCCH_3), 3.71 (sept d, J(HH) = 6.9 Hz, $J(P_XH)$ = 19.8 Hz, 4 H, PNCH), 3.89 (sept, J(HH) = 6.6 Hz, 1 H, CNCH), 4.18 (sept d, J(HH) = 6.8 Hz, $J(P_AH)$ = 2.4

Scheme 7



Scheme 8



Hz, 1 H, CNCH); ^{13}C NMR (CD_2Cl_2) 18.2 (d, $J(P_AC)$ = 6.4 Hz, CNCCH_3), 20.2 (s, CNCCH_3), 22.6 (d, $J(P_XC)$ = 2.6 Hz, PNCCH_3), 23.2 (d, $J(P_XC)$ = 3.4 Hz, CNCCH_3), 50.1 (d, $J(P_XC)$ = 4.0 Hz, PNC), 50.8 (dd, $J(P_AC)$ = 2.2 Hz, $J(P_XC)$ = 9.1 Hz, CNC), 66.4 (dd, $J(P_AC)$ = 4.4 Hz, $J(P_XC)$ = 7.8 Hz, CNC), 185.9 (d, $J(P_AC)$ = 81.2 Hz, PCP); mass spectrum m/z 374 (M^+); the results of the single-crystal X-ray diffraction study have already been reported.[7] Anal. Calcd for $C_{19}H_{42}BF_4N_3P_2$: C, 49.46; H, 9.18; N, 9.11. Found: C, 49.50; H, 9.16; N, 9.10.

***C*-[Bis(diisopropylamino)phosphino]-*C*,*P*-bis(diisopropylamino)phosphaalkene 1 from 2 or 3.** To a THF solution (5 mL) of **2** or **3** (0.46 g, 1 mmol) at −78 °C was added a stoichiometric amount of lithium diisopropylamide (0.107 g, 1 mmol). After the solution was warmed to room temperature, the solvent was removed under vacuum, and the residue was treated with pentane and filtered to eliminate the lithium salts. Evaporation of pentane led to compound **1** as a red oil[12] (0.43 g, 90% yield).

Synthesis of *C*-[Bis(diisopropylamino)phosphino]-*C*-(diisopropylamino)-*P*-(dicyclohexylamino)phosphaalkene 6 and *C*-[(Dicyclohexylamino)-(diisopropylamino)phosphino]-*C*,*P*-bis(diisopropylamino)phosphaalkene 7 from 2 or 3. To a THF solution (5 mL) of **2** or **3** (0.46 g, 1 mmol) at −78 °C was added a stoichiometric amount of lithium dicyclohexylamide (0.187 g, 1 mmol). Monitoring the reaction by low-temperature NMR allowed the characterization of **6**: ^{31}P NMR{^{1}H} ($CDCl_3$) +167.2 (d, J(PP) = 16.2 Hz, P_A), +50.4 (d, J(PP) = 16.2 Hz, P_X); ^{13}C NMR ($CDCl_3$) 23.0–26.8 (m, CH_3, NCCCH_2 and NCCCCH_2), 35.3 (d, $J(P_AC)$ = 6.3 Hz, P_ANCCH_2), 46.8 (dd, $J(P_AC)$ = 5.1 Hz, $J(P_XC)$ = 12.3 Hz, P_XNCHCH$_3$), 49.7 (d, $J(P_XC)$ = 13.9 Hz, CNCHCH$_3$), 56.8 (d, $J(P_AC)$ = 2.7 Hz, P_ANCHCH$_2$), 175.5 (dd, $J(P_AC)$ = 104.2 Hz, $J(P_XC)$ = 29.5 Hz, PCP). After warming the solution to room temperature, the solvent was removed under reduced pressure, and the residue was treated with pentane and filtered to eliminate the lithium salts. Evaporation of pentane led to a 50/50 mixture of phosphaalkenes **6** and **7** as a red oil (0.50 g, 90% total yield). The spectroscopic data for **7** were deduced from the spectra of the mixture: ^{31}P NMR{^{1}H} ($CDCl_3$) +161.1 (d, J(PP) = 15.6 Hz, P_A), +52.8 (d, J(PP) = 15.6 Hz, P_X); ^{13}C NMR ($CDCl_3$) 23.0–26.8 (m, CH_3, NCCCH_2 and NCCCCH_2), 34.3 and 34.5 (d, $J(P_XC)$ = 4.0 and 6.0 Hz, P_XNCCH_2), 46.7 (dd, $J(P_AC)$ = 5.9 Hz, $J(P_XC)$ = 12.0 Hz, P_XNCHCH$_3$), 47.4 (d, $J(P_AC)$ = 4.5 Hz, P_ANCHCH$_3$), 49.8 (d, $J(P_XC)$ = 14.8 Hz, CNCHCH$_3$), 57.1 (dd, $J(P_AC)$ = 5.1 Hz, $J(P_XC)$ = 10.5 Hz, P_XNCHCH$_2$), 177.5 (dd, $J(P_AC)$ = 106.2, $J(P_XC)$ = 47.2 Hz, PCP).

Synthesis of *C*-[Bis(diisopropylamino)phosphino]-*C*-(diisopropylamino)-*P*-(mesityl)phosphaalkene 8 from 2 or 3. To a THF solution (5 mL) of **2** or **3** (0.46 g, 1 mmol) at −78 °C was added a stoichiometric amount of mesityllithium (0.126 g, 1 mmol). After the solution was warmed to room temperature, the solvent was removed in vacuo, and the residue was treated with pentane and filtered to eliminate the lithium salts. Evaporation of pentane led to the isolation of compound **8** as a yellow oil (0.34 g, 70% yield): ^{31}P NMR{^{1}H} ($CDCl_3$) +94.2 (d, J(PP) = 44.5 Hz, P_A), +55.9 (d, J(PP) = 44.5 Hz, P_X); ^{1}H NMR ($CDCl_3$) 1.10 (d, J(HH) = 7.0 Hz, 12 H, CNCCH_3), 1.22 (d, J(HH) = 6.6 Hz, 24 H, PNCCH_3), 2.28 (s, 3 H, *p*-CH_3), 2.45 (s, 6 H, *o*-CH_3), 3.84 (sept dd, J(HH) = 6.6 Hz, $J(P_AH)$ = 1.65 Hz, $J(P_XH)$ = 13.2 Hz, 4 H, P_XNCH), 4.60 (sept d, J(HH) = $J(P_XH)$ = 7.0 Hz, 2 H, CNCH), 6.80 (s, 2 H, H_{aro}); ^{13}C NMR ($CDCl_3$) 20.9 (d, $J(P_AC)$ = 10.1 Hz, *o*-CH_3), 22.1 (s, *p*-CH_3), 22.8–24.1 (m, NCC), 47.3 (dd, $J(P_XC)$ = 13.1, $J(P_AC)$ = 4.8 Hz, P_XNC), 53.3 (d, $J(P_XC)$ = 20.5 Hz, CNCH), 127.2 (d, $J(P_AC)$ = 47.8 Hz, C_m), 136.1 (d, $J(P_AC)$ = 1.1 Hz, C_p), 140.6 (dd, $J(P_AC)$ = 7.9, $J(P_XC)$ = 1.5 Hz, C_o), 141.9 (d, $J(P_AC)$ = 68.3 Hz, C_i), 197.3 (dd, $J(P_AC)$ = 118.5, $J(P_XC)$ = 46.3 Hz, PCP). Anal. Calcd for $C_{28}H_{53}N_3P_2$: C, 68.12; H, 10.82; N, 8.51. Found: C, 68.60; H, 10.89; N, 8.40.

Synthesis of the Mixture of Four-Membered-Heterocycles 3, 9, and 10. To a THF solution (5 mL) of a 50/50 mixture of phosphaalkenes **6** and **7** (0.55 g, 1 mmol) was added at room temperature 2 equiv of BF_3·OEt_2 (0.28 g, 2 mmol). After stirring for 10 min at room temperature, the solvent was removed under vacuum, and the residue was washed several times with Et_2O. The 12/12/76 mixture (according to ^{31}P NMR) of compounds **3**, **9**, and **10** was obtained as a yellow powder (0.35 g). ^{31}P NMR{^{1}H} ($CDCl_3$) **3**, +211.6 and 181.7 (J_{PP} = 34.9 Hz); **9**, +220.0 and 190.1 (J_{PP} = 30.4 Hz); **10**, +212.8 and 186.2 (J_{PP} = 33.3 Hz). The complexity of the ^{1}H and ^{13}C NMR spectra precluded further assignment. However, compound **3** was identified in the mixture by ^{31}P NMR by adding a small amount of an authentic sample. The assignment of structure **9** versus **10** is based on the ^{31}P NMR chemical shifts.

Synthesis of Diphosphirenium Salt 11. To a dichloromethane solution (5 mL) of a 15/85 mixture of compounds **9** and **10** (prepared by addition at −78 °C of a stoichiometric amount of trifluoromethanesulfonic acid to a dichloromethane solution of phosphaalkene **6** (1 mmol)) was added an excess of Et_3N at room temperature. According to the ^{31}P NMR spectroscopy, three-membered-heterocycle **11** was obtained in near quantitative yield after stirring for 24 h at room temperature. After removal of the solvent under vacuum, derivative **11** ($CF_3SO_3^-$) was isolated by crystallization at −20 °C from a THF/ether solution as non-air-sensitive orange crystals (0.36 g, 70%): mp 117–119 °C; ^{31}P NMR ($CDCl_3$) +61.71 (d-broad, J(PP) = 246.7 Hz, J(PH) < 3 Hz, P_A), −44.92 (dq, J(PP) = 246.7 Hz, J(PH) = 19.7 Hz, P_X); ^{13}C NMR ($CDCl_3$) 17.9 (d, J(PC) = 5.7 Hz, CNCCH_3), 20.1 (d, J(PC) = 5.7 Hz, CNCCH_3), 22.4–23.0 (m, PNCCH_3), 24.6–26.2 (m, NCCC and NCCCC), 33.1 and 33.6 (d, J(PC) = 3.0 and 3.1 Hz, NCCH_2), 49.7 (d, J(PC) = 3.8 Hz, PNCHCH$_3$), 50.4 (dd, J(PC) = 2.4 Hz, J(PC) = 9.3 Hz, CNC), 59.1 (d, J(PC) = 3.3 Hz, NCHCH$_2$), 65.9 (dd, J(PC) = 4.2 Hz, J(PC) = 7.7 Hz, CNC), 184.9 (d, J(PC) = 80.9 Hz, PCP). Anal. Calcd for $C_{26}H_{50}F_3N_3O_3P_2S$: C, 51.72; H, 8.35; N, 6.96. Found: C, 51.60; H, 8.34; N, 7.00.

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