Mechanism of the Exchange Reaction of Halodiazirines with Nucleophiles Revisited. Synthesis of Neutral, Mono- or Dicationic 4−16-Membered Phosphorus Heterocycles

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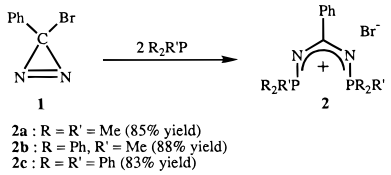
Abstract: Trimethyl-, diphenylmethyl-, triphenyl-, diphenylthienyl-, and bis(dimethylamino)(isopropylthio)phosphine react with bromophenyldiazirine (**1**) giving cationic *N*,*N*′-bis(phosphine) adducts **2a**−**c**, **7**, and **8** in 83−95% yields. Depending on the experimental conditions used, addition of 1,2-bis(diphenylphosphino)ethane to **1** leads to dicationic 14- and monocationic seven-membered heterocycles **3** (90% yield) and **4** (60% yield) or cationic *N*,*N*′-bis(diphosphine) adduct **5** (86% yield); similarly, when diphenyl(isopropylthio)phosphine is used, competitive reactions occur, leading to cationic five-membered heterocycle **9** (34% yield) and/or *N*,*N*′-Bis(diphosphine) adduct **10** (65% yield). 1,3-bis-(diphenylphosphino)propane also reacts with **1**, affording dicationic 16-membered heterocycle **6** (75% yield). Addition of bis(diisopropylamino)(trimethylstannyl)phosphine to **1** gives rise to a mixture of *N*-[(trimethylstannyl)imino]bis-(diisopropylamino)bromophosphorane (**11**) (32%), 2,2-bis(diisopropylamino)-4-phenyl-1,3,2λ^5-diazaphosphete (**12**) (26% yield), 1,3,5,2λ^5-triazaphosphinine **13** (3% yield), benzonitrile (35%), and bromotrimethylstannane (60%). The mechanisms involved in these reactions are studied.

Introduction

The mechanism of the exchange reaction of nucleophiles with halodiazirines has attracted considerable interest and has been a highly controversial topic in the last few years.[1] It was first suggested that the halodiazirine was in equilibrium with a diazirinium cation, which was captured by the nucleophile.[1b,2] On the basis of kinetic studies, labeling experiments, and the nature of the observed products, Creary[1a,3] and Dailey[4] independently concluded that the first step of the exchange reaction with nucleophiles such as MeO^-, F^-, and N_3^- proceeds in an S_N2' fashion. When the nucleophile was fluoride, a second S_N2' attack at carbon led to the C-fluoro-substituted diazirine, while with azide a nitrile was formed. Lastly, Creary[5a,b] and Moss[5c] showed that azide or acetate ions can also react with certain halodiazirines *via* an $S_{RN}1$ substitution mechanism, while with thiophenoxide a redox process can occur.[6]

On the other hand, diazirines are known to easily lose dinitrogen and therefore are powerful precursors for a variety of carbenes;[1b,7] however, these CN_2 rings[8] by themselves have never been used as building blocks.

Scheme 1



1 2

2a : R = R' = Me (85% yield)
2b : R = Ph, R' = Me (88% yield)
2c : R = R' = Ph (83% yield)

Here we report a detailed investigation[9] of the mechanism of the reaction of bromophenyldiazirine **1** with phosphines, and we demonstrate the enormous synthetic potentiality of this three-membered heterocycle.

Results

Bromophenyldiazirine (**1**)[2a] reacts, in dichloromethane solution, with 2 equiv of trimethyl-, diphenylmethyl-, and triphenylphosphine, affording the bisadducts **2** in near quantitative yields. According to ^{31}P NMR spectroscopy the reaction was complete within 5 min at −78 °C with trimethylphosphine, while with Ph_2MeP and Ph_3P, the reaction at room temperature reached completion after 10 and 18 h, respectively. The use of just 1 equiv of phosphine left 50% of the starting bromophenyldiazirine **1** unreacted. The ionic structure of bisadducts **2** was obvious from their poor solubility in nonpolar solvents and from the mass spectra. In the ^{13}C NMR spectra the *ipso* and imino carbon atoms of the benzamidine fragment appeared as triplets, indicating the presence of two magnetically equivalent phosphorus atoms (Scheme 1).

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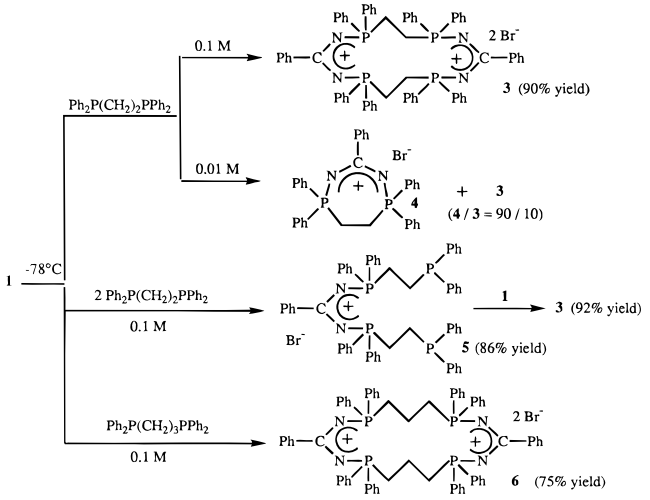
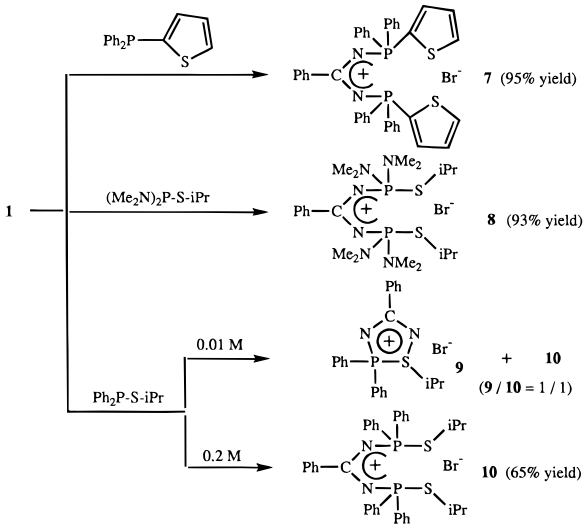
Scheme 2



Scheme 3



Since 2 equiv of phosphine were necessary, we then studied the reaction of **1** with diphosphines. Depending on the dilution, different products were obtained. Addition at −78 °C of a stoichiometric amount of 1,2-bis(diphenylphosphino)ethane to a 0.1 M dichloromethane solution of **1** cleanly led to dicationic 14-membered ring **3**, which was isolated in 90% yield (white solid, mp 278 °C). The dimeric and dicationic nature of **3** was proved by mass spectroscopy, and the high symmetry of the molecule was evident from the ^{31}P and ^{13}C NMR data [δ^{31}P +22.5 (s); δ^{13}C +180.2 (t, J(PC) = 3.6 Hz, C═N)].

When the reaction was performed under the same experimental conditions, but using a 0.01 M solution of **1**, a 90/10 mixture (according to ^{31}P NMR spectroscopy) of 7-membered ring **4** and macrocycle **3** was obtained. Cationic heterocycle **4** was isolated after purification by liquid chromatography in 60% yield as a white powder (mp 262 °C). The mass spectrum and elemental analysis of **4** indicate the addition of only one molecule of diphosphine. The presence of only one signal in the ^{31}P NMR spectrum (+20.8) and of a triplet for the amidine carbon at +169.7 (J(PC) = 5.3 Hz) in the ^{13}C NMR spectrum support the magnetic equivalence of the two phosphorus atoms as expected for seven-membered ring **4**.

When 2 equiv of bis(diphenylphosphino)ethane was added at −78 °C to a 0.1 M dichloromethane solution of bromophenyldiazirine (**1**), the formation of bisadduct **5** was observed. The reaction was complete after stirring one night at room temperature, and **5** was isolated as a white solid (mp 134 °C) in 86% yield. The mass spectrum indicates the presence of two bis(diphenylphosphino)ethane fragments for only one amidine. As expected, the ^{31}P NMR spectrum appears as an AX system [−12.6 and +23.5, J(PP) = 45.4 Hz], while in the ^{13}C NMR spectrum the amidine carbon appears as a triplet (+179.9, J(PC) = 6.5 Hz). Moreover, addition at room temperature of a stoichiometric amount of diazirine **1** to bisadduct **5** also led to macrocycle **3** in 92% yield (Scheme 2).

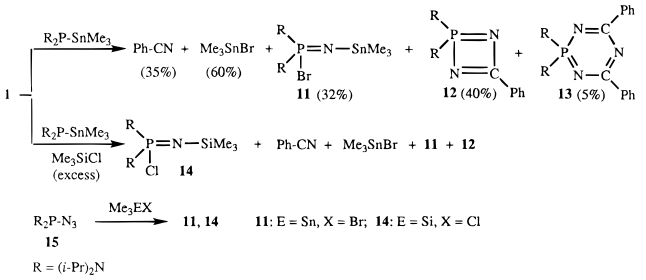
In order to demonstrate the generality of the method for the synthesis of dicationic macrocycles, a stoichiometric amount of 1,3-bis(diphenylphosphino)propane was added at low temperature to a 0.1 M solution of bromodiazirine **1**, and indeed, 16-membered heterocycle **6** was obtained and isolated after purification by liquid chromatography as a brown solid (mp 202 °C) in 75% yield (Scheme 2).

It was also of interest to investigate the reactivity of **1** toward reagents featuring two different nucleophilic centers. Whatever the experimental conditions, diphenylthienylphosphine and bis(dimethylamino)(isopropylthio)phosphine reacted with bromodiazirine **1**, leading to the cationic bisadducts **7** and **8**, in 95 and 93% yield, respectively. However, when the diphenylisopropylthiophosphine was used, once again, the outcome of the reaction was strongly dependent on the dilution. With a 0.01 M dichloromethane solution of **1** and diphenyl(isopropylthio)phosphine, a 50/50 mixture (according to ^{31}P NMR spectroscopy) of the cationic five-membered heterocycle **9** and the bisadduct **10** was obtained. Compound **9** was isolated as a white powder (mp 113 °C) in 34% yield, and its monoadduct structure easily proved by mass and ^{13}C NMR spectroscopies (+167.9, d, J(PC) = 10.3 Hz, NCN). Using a concentrated solution of **1** (0.2 M) and 1 equiv of thiophosphine, bisadduct **10** was obtained in 65% yield with no trace of **9** being observed (Scheme 3). The structure of **10** (with PF_6^- as counteranion) was clearly established by an X-ray diffraction study (see supporting information). As expected, the positive charge is delocalized on the PNCNP backbone, the phosphine being in a syn−anti arrangement with respect to the benzamidine fragment.

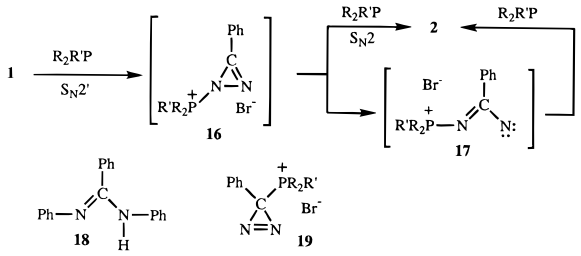
Lastly, the question arises as to what would be the outcome of the reaction using a phosphine bearing a leaving group, which could combine with the bromide anion and thus be eliminated. The phosphorus−tin bond is reactive, and bromotrimethylstannane easy to eliminate. Therefore, a stoichiometric amount of bis(diisopropylamino)(trimethylstannyl)phosphine was added at room temperature to a THF or dichloromethane solution of bromophenyldiazirine **1**. According to ^{31}P NMR spectroscopy and gas chromatographic analysis, the reaction mixture contained benzonitrile (35%), bromotrimethylstannane (60%), [(trimethylstannyl)imino]bis(diisopropylamino)bromophosphorane (**11**) (32%), 1,3,2λ^5-diazaphosphete **12** (40%), and 1,3,5,2λ^5triazaphosphinine **13** (5%). Benzonitrile, bromotrimethylstannane, and iminophosphorane **11** were characterized by comparison of their spectroscopic and physical data with authentic samples. Four-π-electron four-membered ring **12** and six-π-electron six-membered heterocycle **13** were isolated after careful fractional crystallization as white crystals in 26 and 3% yield, respectively (Scheme 4). Both heterocycles **12** and **13** have been fully characterized, and the X-ray crystal structures will be published elsewhere.

When the reaction of **1** with bis(diisopropylamino)(trimethylstannyl)phosphine was performed in the presence of a large excess of chlorotrimethylsilane, we observed (in addition to diazaphosphete **12**, benzonitrile, bromotrimethylstannane, and a very small amount of iminophosphorane **11**) the formation of [(trimethylsilyl)imino]bis(diisopropylamino)chloro-

Scheme 4



Scheme 5



phosphorane (**14**). Moreover, photolysis of bis(diisopropylamino)phosphine azide **15**[10] in the presence of bromotrimethylstannane and chlorotrimethylsilane, cleanly led to **11** and **14**, respectively (Scheme 4).

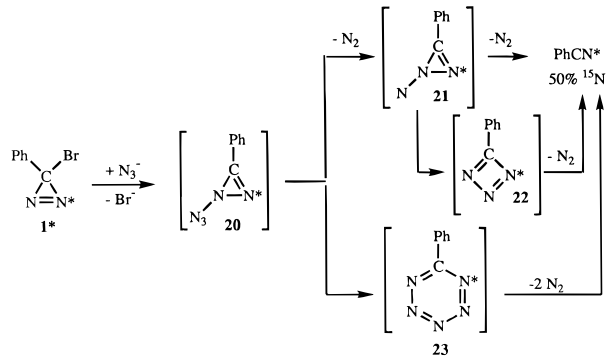
Discussion

The rate of the reaction of bromodiazirine **1** increases with the nucleophilicity of the phosphines, and the resulting products **2** featuring P−N bonds clearly demonstrate that the first step is an S_N2' reaction leading to 1*H*-diazirine **16**. These results are in perfect agreement with the findings of Creary and Dailey using other nucleophiles.[1a,3,4] Two mechanisms could rationalize the formation of the second P−N bond: either an S_N2 reaction of the phosphine with the second nitrogen atom of the 1*H*-diazirine **16** or the formation of an electrophilic imidoyl nitrene **17**, which would be trapped by phosphines (Scheme 5). Note that Padwa reported that phenyllithium reacts with phenylchlorodiazirine to give **18**, a product resulting from N−N bond cleavage[11] and that the trapping of imidoyl nitrenes by phosphines has been examplified.[12]

The results observed in the reaction of **1** with 1,2-bis(diphenylphosphino)ethane clearly indicate that the intermediate has a reasonable lifetime, allowing an intermolecular reaction (giving **3** or **5**) to compete with the formation of the seven-membered ring **4** (Scheme 2). Although, these results do not totally rule out the possible transient formation of an imidoyl nitrene of type **17**, it is quite unlikely that such an intermediate would afford the selectivity observed.

A similar conclusion can be drawn from the exclusive formation of the bisadduct **7** since nitrenes are known to be trapped by thiophene, although the difficulty of forming a seven-membered ring cannot be neglected. A strong argument against the transient formation of an imidoyl nitrene comes from comparing the outcome of the reaction of **1** with bis(dimethylamino)- and with diphenyl(isopropylthio)phosphine (Scheme 3). The formation of five-membered rings is usually facile, and the only difference between the two reactions is the higher nucleophilicity of the phosphorus atom in the bis(dimethylamino)phosphine compared to the diphenylphosphine derivative. Note that sulfides do not react with **1**.

Scheme 6



From these results, as a whole, it seems clear that only good nucleophiles can react with bromodiazirine **1** and that the first step of the reaction occurs through an S_N2' mechanism. When phosphines are used, the resulting 1*H*-diazirines **16** have a reasonable lifetime, probably due to the presence of the phosphonio group, which decreases the effect of the destabilizing anti-aromatic energy through negative hyperconjugation.[13] Then, either an intermolecular S_N2 reaction occurs with a second molecule of phosphine or, in the case where a phosphine substituent has a nucleophilic component, an intramolecular S_N2 reaction can compete. Note that the formation of *C*-phosphonio-3*H*-diazirine **19** (Scheme 5) is never observed, which is in marked contrast with the results observed by Creary and Dailey using small nucleophiles such as MeO^- or F^-.[1a,4b] A possible explanation is that the cationic nature of the phosphorus substituent of 1*H*-diazirines **16** strongly modifies the reactivity of the three-membered ring. Alternatively, one could imagine that the formation of the *C*-methoxy- or *C*-fluorodiazirine from the 1*H*-diazirines does not involve an S_N2' reaction, as previously postulated,[1a,4b] but a 1,3-sigmatropic reaction. Such a process would not occur in the case of 1*H*-diazirines **16** because of the poor migrating ability of phosphines.

These results and, particularly, the formation of seven- and five-membered heterocycles **4** and **9** allow us to postulate other mechanisms rationalizing the observations by Creary and Dailey in the reaction of ^{15}N-labeled bromodiazirine **1*** with azide anion.[1a,3,4a] On the basis of the presence of 50% of ^{15}N-labeled benzonitrile, they independently concluded that an S_N2' attack of azide upon the nitrogen atom led to *N*-azido-1*H*-diazirine **20**, which rapidly eliminates N_2 to give a transient 1,1-diazene **21** and then benzonitrile. Other possiblities are the following: starting from *N*-azidodiazirine **20**, an intramolecular attack of the terminal nitrogen of the azido group at the second nitrogen of the diazirine could give pentaazabenzene **23**,[14] or alternatively the diazene **21** could undergo a ring expansion reaction to triazacyclobutadiene **22**. Both compounds **22** and **23** would afford benzonitrile containing 50% ^{15}N on decomposition (Scheme 6). The latter possibility being rather fascinating, we tried to model it by attempting to prepare a *N*-phosphino-1*H*-diazirine **25** (Scheme 7) analogous with diazene **21**, the phosphorus atom of which possesses a lone pair of electrons and vacant orbitals playing the role of the nitrene (1,1-diazenes are nucleophilic nitrenes[15]).

We believe that the reaction of bis(diisopropylamino)(trimethylstannyl)phosphine with **1** gives the desired *N*-phos-

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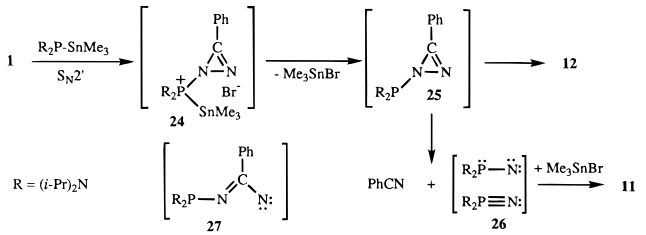
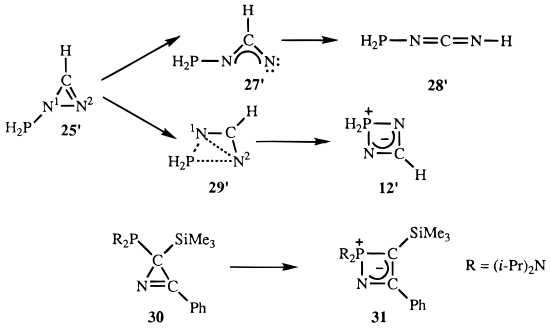
Scheme 7



Scheme 8



phino-1*H*-diazirine intermediate **25**, *via* the formation *N*-phosphoniodiazirine **24** with subsequent loss of trimethylbromostannane. A ring expansion then occurs, explaining the formation of the 1,3,2λ^5-diazaphosphete **12**, which can be considered as a stable analogue of triazacyclobutadiene **22** (Schemes 4 and 7).

The formation of benzonitrile and [(trimethylstannyl)imino]-bis(diisopropylamino)bromophosphorane (**11**) strongly suggest that *N*-phosphinodiazirine **25** can also be cleaved in a manner analogous to that for nitrenodiazirine **21**. Indeed, **11** probably results from the trapping of phosphinonitrene **26** ("analogue" of N_2) by bromotrimethylstannane. This hypothesis is confirmed by the formation of (i) [(trimethylsilyl)imino]bis(diisopropylamino)chlorophosphorane (**14**) in the reaction of **1** with the stannylphosphine in the presence of an excess of trimethylchlorosilane and (ii) **11** and **14** in the photolysis of phosphine azide **15** in the presence of trimethylbromostannane and trimethylchlorosilane, respectively (Schemes 2 and 4).[10]

In order to confirm the reaction mechanism, quantum chemical calculations[16] were performed on the parent 1,3,2λ^5-diazaphosphete **12′**, *N*-phosphino-1*H*-diazirine **25′**, and (*N*-phosphino)imidoylnitrene **27′**, as well as on the isomeric carbodiimide **28′** (Scheme 8). The calculations were carried out at RHF/6-31g** [A] and MP2(fc)/6-31g** [B] levels of optimization. Subsequently the energies were refined by MP4SDTQ(fc)[17] electron correlation and zero point energy corrections. At times the vibrational analyses of all stationary points on the electronic hypersurface (within the harmonic approximation) were performed at the same level as given by the energy optimization of structures (levels A and B) (Table 1). Of particular interest, the nitrene **27′** is an unstable species on the singlet hypersurface (at both levels of optimization) and rearranges without activation energy to the corresponding carbodiimide **28′**. On the other hand, the diazaphosphete **12′** is more stable than the 1*H*-diazirine **25′** by −23.7 kcal/mol (level B). The quantum chemical calculations indicate that the phosphino group is almost perpendicular relative to the ring plane and that there is a very long N−N distance for the strained three-membered ring **25′** (1.610 Å at the RHF level and 1.779 Å after reoptimization at the MP2 level) (Table 2). A similar elongation was experimentally observed for the C−N bond of the *C*-phosphino-2*H*-azirine **30** (1.629 Å), which also easily undergoes a ring expansion reaction affording the corresponding four-π-electron four-membered heterocycle **31**[18] (Scheme 8). The bond stretching is the consequence of the enormous ring strain in three-membered rings possessing an endocyclic π-bond.[19] The activation energy for the rearrangement of the 1*H*-diazirine **25′** into the diazaphosphete **12′** via the transition state **29′** was found to be 24.7 kcal mol^{-1} (level B). Interestingly, the transition state for this reaction refers to a PH_2^+ cation which interacts with an NCN^- allylic anion with concomitant three-center bonding between the phosphorus and the nitrogen atoms, as witnessed by a corresponding charge density analysis.

Table 1. Calculated Relative Energies (kcal mol^{-1}) for the Parent Diazaphosphete **12′**, 1*H*-Diazirine **25′**, Carbodiimide **28′**, and Transition State **29′**

	level A[a]	level B[b]
12′	−18.8	−23.7
25′	0	0
28′	−61.3	−56.6
29′	+19.0	+24.7

[a] MP4SDTQ(fc)/6-31g**//RHF/6-31g** plus zero point vibrational energy contribution at RHF level (unscaled). [b] MP4SDTQ(fc)/6-31g**//MP2(fc)/6-31g** plus zero point vibrational energy contribution at MP2 level (unscaled).

Table 2. Calculated Geometries for the Parent 1*H*-Diazirine **25′** and for Transition State **29′**, Bond Lengths (Å), and Bond Angles (deg)

	PN1	PN2	N1N2	N2C	CN1	<PNNC
25′ [a]	1.764		1.610	1.212	1.393	106.9
25′ [b]	1.782		1.779	1.266	1.399	106.2
29′ [a]	2.016	2.016	1.840	1.284	1.284	154.6
29′ [b]	1.999	1.999	1.873	1.316	1.316	157.5

[a] RHF/6-31g** optimization. [b] MP2/6-31g** optimization.

Table 3. Experimental Conditions for the Reaction of **1** with Phosphines

	1 (mmol)	R_3P (mmol)	CH_2Cl_2 (mL)	reaction time (h) (20 °C)	yield (%)
2a	2.18	Me_3P (4.36)	6	5 min (−78 °C)	85
2b	2.18	Ph_2MeP (4.36)	6	10	88
2c	2.18	Ph_3P (4.36)	6	18	83
3	2.49	$Ph_2P(CH_2)_2PPh_2$ (2.49)	25	18	90
4	2.49	$Ph_2P(CH_2)_2PPh_2$ (2.49)	250	18	60
5	5.02	$Ph_2P(CH_2)_2PPh_2$ (10.10)	50	36	86
6	2.49	$Ph_2P(CH_2)_3PPh_2$ (2.49)	25	18	75
7	2.18	(diphenyl)thienylphosphine (4.36)	21	36	95
8	1.05	$(Me_2N)_2P$-S-*i*Pr (2.16)	30	3	93
9	0.71	Ph_2P-S-*i*Pr (0.73)	70	24	34
10	0.71	Ph_2P-S-*i*Pr (0.73)	2.9	3	65

(16) All quantum chemical calculations were performed with the *Gaussian-92* set of programs: Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. *Gaussian-92*, Revision A; Gaussian, Inc.: Pittsburgh, PA, 1992. For the 6-31g** basis set see: Hariharan, P. C.; Pople, J. A. *Chem. Phys. Lett.* **1972**, *66*, 217. Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; Defrees, D. J.; Pople, J. A. *J. Chem. Phys.* **1982**, *77*, 3654.

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Conclusion

These results clearly confirm that, in the 3*H*-bromophenyldiazirine **1** exchange reactions with phosphines, the first step involves an S_N2' mechanism leading to transient *N*-phosphonio-1*H*-diazirines **16**. Then, inter- or/and intramolecular S_N2 reactions at the unsubstituted nitrogen of **16** occur, inducing N−N bond cleavage. The selectivity (intra- *versus* intermolecular reaction) observed, depending on the experimental conditions used, suggests that the antiaromatic three-membered heterocycles **16** have a reasonable lifetime. Since *C*-phosphonio-3*H*-diazirines **19** are not formed, it is quite likely that the second step of the substitution reaction of **1** by small nucleophiles (MeO^-, F^-) does not involve an S_N2' mechanism but a 1,3-sigmatropic reaction.

The experimental results and the ab initio calculations strongly suggest that *N*-phosphino-1*H*-diazirine **25** does not undergo a ring-opening reaction to the corresponding imidoyl nitrene **27**, which appears not even as a minimum on the singlet hypersurface. The antiaromatic 1*H*-diazirine **25** undergoes a concerted ring expansion reaction, leading to the four-π-electron four-membered heterocycle **12**.

Lastly, it appears that 3*H*-diazirines are powerful building blocks in heterocyclic chemistry; the high-yield synthesis of dicationic macrocycles is of special interest.

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, and ^{13}C NMR spectra were recorded on Bruker AC80, AC200, WM250, or AMX400 spectrometers. ^1H and ^{13}C chemical shifts are reported in parts per million relative to Me_4Si as external standard. ^{31}P downfield shifts are expressed with a positive sign, in parts per million, relative to external 85% H_3PO_4. Infrared spectra were recorded on a Perkin Elmer 1725 X. Mass spectra were obtained on a Ribermag R10 10E instrument. Conventional glassware was used.

General Procedure for the Reactions of 1 with Phosphines. To a dichloromethane solution of bromophenyldiazirine **1** was added at −78 °C the corresponding phosphine. The reaction was monitored by ^{31}P NMR spectroscopy. After evaporation of the solvent the products were purified as indicated below. Further details concerning the reaction conditions are summarized in Table 3.

Bisadduct 2a. The residue was washed several times with pentane to give 0.65 g (85% yield) of **2a** as a pale yellow powder: mp 170−171 °C; ^{31}P NMR $\{^1H\}$ ($CDCl_3$) +30.1; ^1H NMR ($CDCl_3$) 1.62 (d, J(PH) = 13.4 Hz, 18 H, CH_3), 7.08−7.18 (m, 5 H, H_{arom}); ^{13}C NMR ($CDCl_3$) 14.6 (d, J(PC) = 66.4 Hz, CH_3), 126.0 (s, C_p), 128.8 (s, C_o), 130.0 (s, C_m), 140.7 (t, J(PC) = 12.7 Hz, C_i), 178.1 (t, J(PC) = 7.2 Hz, NCN); mass spectrum (DCI/NH_3) *m/z* 269 (M^+ − Br). Anal. Calcd for $C_{13}H_{23}N_2P_2Br$: C, 44.71; H, 6.64; N, 8.02. Found: C, 43.97; H, 7.00; N, 7.65.

Bisadduct 2b. The residue was washed several times with pentane to give 1.1 g (88% yield) of **2b** as a pale yellow powder: mp 176−177 °C; ^{31}P NMR $\{^1H\}$ ($CDCl_3$) +20.1; ^1H NMR ($CDCl_3$) 2.20 (d, J(PH) = 13.0 Hz, 6 H, CH_3), 7.13−7.56 (m, 25 H, H_{arom}); ^{13}C NMR ($CDCl_3$) 13.4 (d, J(PC) = 66.1 Hz, CH_3), 124.9 (d, J(PC) = 80.0 Hz, C_i-P), 126.4 (s, C_m-Ph-C), 127.7 (s, C_oPh-C), 129.3 (d, J(PC) = 13.1 Hz, C_mPh-P), 130.0 (s, C_pPh-C), 131.0 (d, J(PC) = 10.4 Hz, C_oPh-P), 133.0 (s, C_pPh-P), 140.0 (t, J(PC) = 11.6 Hz, C_iPh-C), 179.4 (t, J(PC) = 6.1 Hz, NCN); mass spectrum (DCI/NH_3) *m/z* 517 (M^+ − Br). Anal. Calcd for $C_{33}H_{31}N_2P_2Br$: C, 66.33; H, 5.23; N, 4.88. Found: C, 65.21; H, 4.97; N, 5.14.

Bisadduct 2c. The residue was washed several times with pentane to give 1.31 g (83% yield) of **2c** as a pale yellow powder: mp 100−101 °C; ^{31}P NMR $\{^1H\}$ ($CDCl_3$) +16.6; ^{13}C NMR ($CDCl_3$) 124.8 (d, J(PC) = 101.5 Hz, C_i-P), 126.3 (s, C_mPh-C), 127.7 (s, C_oPh-C), 129.1 (d, J(PC) = 13.0 Hz, C_m-Ph-P), 129.5 (s, C_pPh-C), 132.3 (d, J(PC) = 10.5 Hz, C_oPh-P), 133.4 (s, C_pPh-P), 139.3 (t, J(PC) = 12.0 Hz, C_iPh-C), 178.6 (t, J(PC) = 6.2 Hz, NCN); mass spectrum *m/z* 641 (M^+ − Br). Anal. Calcd for $C_{43}H_{35}N_2P_2Br$: C, 71.57; H, 4.89; N, 3.88. Found: C, 71.01; H, 4.67; N, 3.70.

14-Membered Heterocycle 3. The residue was purified by flash chromatography on silica gel (MeOH) to give 1.33 g (90% yield) of **3** as a white powder: mp 277−278 °C; ^{31}P NMR $\{^1H\}$ ($CDCl_3$) +22.5; ^1H NMR ($CDCl_3$) 3.32 (s broad, 8 H, CH_2), 6.70−7.80 (m, 50 H, H_{arom}); ^{13}C NMR ($CDCl_3$) 19.0 (t, J(PC) = 29.8 Hz, CH_2), 123.5 (d, J(PC) = 99.6 Hz, C_i-P), 126.2 (s, C_mPh-C), 126.7 (s, C_oPh-C), 128.2 (s, C_pPh-C), 129.0 (d, J(PC) = 6.0 Hz, C_mPh-P), 131.3 (d, J(PC) = 4.5 Hz, C_oPh-P), 132.9 (s, C_pPh-P), 138.4 (t, J(PC) = 6.6 Hz, C_iPh-C), 180.2 (t, J(PC) = 3.6 Hz, NCN); mass spectrum (FAB) *m/z* 1111 (M^+ − Br), 515 (M^{2+} − 2Br). Anal. Calcd for $C_{66}H_{58}N_4P_4Br_2$: C, 66.56; H, 4.91; N, 4.70. Found: C, 66.08; H, 4.76; N, 4.55.

Seven-Membered Ring 4. The residue was purified by flash chromatography on silica gel (92:8 $CHCl_3$−MeOH) to give 0.44 g (60% yield) of **4** as a white powder: mp 261−262 °C; ^{31}P NMR $\{^1H\}$ ($CDCl_3$) +20.8; ^1H NMR ($CDCl_3$) 3.63 (d, J(PH) = 14 Hz, 4 H, CH_2), 7.25−8.57 (m, 25 H, H_{arom}); ^{13}C NMR ($CDCl_3$) 22.0 (dd, J(PC) = 4.5 and 45.7 Hz, CH_2), 125.0 (d, J(PC) = 111.5 Hz, C_i-P), 128.3 (s, C_mPh-C), 129.6 (d, J(PC) = 12.9 Hz, C_mPh-P), 129.9 (s, C_oPh-C), 131.1 (d, J(PC) = 11.2 Hz, C_oPh-P), 132.6 (s, C_pPh-C), 133.4 (s, C_pPh-P), 138.4 (t, J(PC) = 19.8 Hz, C_iPh-C), 169.7 (t, J(PC) = 5.3 Hz, NCN); mass spectrum (DCI/NH_3) *m/z* 515 (M^+ − Br). Anal. Calcd for $C_{33}H_{29}N_2P_2Br$: C, 66.56; H, 4.91; N, 4.70. Found: C, 66.38; H, 4.81; N, 4.52.

Bisadduct 5. The residue was washed several times with ether−THF (8:2) to give 4.33 g (86% yield) of **5** as a white powder: mp 133−134 °C; ^{31}P NMR $\{^1H\}$ ($CDCl_3$) −12.6 (d, J(PP) = 45.4 Hz, P-C), +23.5 (d, J(PP) = 45.4 Hz, P-N); ^1H NMR ($CDCl_3$) 1.81 (m, 4 H, CH_2), 2.36 (m, 4 H, CH_2), 6.86−7.65 (m, 45 H, H_{arom}); ^{13}C NMR ($CDCl_3$) 19.2 (dd, J(PC) = 28.8 and 5.0 Hz, CH_2), 23.1 (dd, J(PC) = 63.0 and 19.5 Hz, CH_2), 124.2 (d, J(PC) = 97.2 Hz, C_iP-N), 125.8 (s, C_mPh-C), 128.7 (d, J(PC) = 6.3 Hz, C_oPh-PN), 129.2 (s, C_oPh-C), 129.3 (d, J(PC) = 5.8 Hz, C_mPhP-C), 129.6 (s, C_pPhP-C), 130.1 (s, C_pPh-C), 131.2 (d, J(PC) = 9.6 Hz, C_mPhP-N), 132.3 (d, J(PC) = 18.9 Hz, C_oPhP-C), 133.7 (s, C_pPhP-N), 135.9 (d, J(PC) = 13.2 Hz, C_iPhP-C), 139.9 (t, J(PC) = 11.6 Hz, C_iPh-C), 179.9 (t, J(PC) = 6.5 Hz, NCN); mass spectrum (DCI/NH_3) *m/z* 913 (M^+ − Br). Anal. Calcd for $C_{59}H_{53}N_2P_4Br$: C, 71.30 ; H, 5.37 ; N, 2.82. Found: C, 70.86; H, 5.12; N, 2.80.

16-Membered Heterocycle 6. The residue was purified by flash chromatography on silica gel (96:4 $CHCl_3$−MeOH) to give 1.14 g (75% yield) of **6** as a white powder: mp 201−202 °C; ^{31}P NMR $\{^1H\}$ ($CDCl_3$) +21.3; ^1H NMR ($CDCl_3$) 1.25 (m, 4 H, CCH_2C), 3.70 (m, 8 H, PCH_2), 6.50−8.50 (m, 50 H, H_{arom}); ^{13}C NMR ($CDCl_3$) 22.6−30.0 (m, $PCH_2CH_2CH_2$), 123.5 (s, C_m-Ph-C), 125.6 (d, J(PC) = 86.8 Hz, C_i-P), 126.2 (s, C_oPh-C), 128.5 (d, J(PC) = 4.8 Hz, C_mPh-P), 128.6 (s, C_pPh-C), 128.7 (d, J(PC) = 4.4 Hz, C_mPh-P), 130.3 (d, J(PC) = 6.1 Hz, C_o-Ph-P), 130.5 (d, J(PC) = 4.9 Hz, C_oPh-P), 132.5 (s, C_pPh-P), 137.4 (t, J(PC) = 12.8 Hz, C_iPh-C), 179.7 (br. t, NCN); mass spectrum (FAB) *m/z* 1139 (M^+ − Br), 529 (M^{2+} − 2Br). Anal.

Calcd for $C_{68}H_{62}N_4P_4Br_2$: C, 67.00; H, 5.13; N, 4.60. Found: C, 66.18; H, 4.97; N, 4.52.

Bisadduct 7. The residue was washed several times with pentane to give 1.52 g (95% yield) of **7** as a brown powder: mp 110−111 °C, ^{31}P NMR {^{1}H} ($CDCl_3$) +11.0; ^{1}H NMR ($CDCl_3$) 6.90−7.90 (m, 31 H); ^{13}C NMR ($CDCl_3$) 124.2 (d, *J*(PC) = 111.7 Hz, PCS), 124.8 (d, *J*(PC) = 72.5 Hz, C_i-P), 126.7 (d, *J*(PC) = 5.8 Hz, PCC*C*), 128.1 (s, C_mPh-C), 129.4 (d, *J*(PC) = 12.5 Hz, C_mPh-P), 130.0 (s, C_oPh-C), 132.2 (s, C_pPh-C), 132.3 (d, *J*(PC) = 11.6 Hz, C_oPh-P), 133.8 (s, C_pPh-P), 137.5 (d, *J*(PC) = 5.5 Hz, S*C*C), 139.4 (t, *J*(PC) = 9.9 Hz, C_iPh-C), 139.8 (d, *J*(PC) = 11.7 Hz, PC*C*), 178.3 (t, *J*(PC) = 6.5 Hz, NCN); mass spectrum *m/z* 653 (M^+ − Br). Anal. Calcd for $C_{39}H_{31}N_2P_2S_2Br$: C, 63.84; H, 4.26; N, 3.82. Found: C, 63.50; H, 4.36; N, 3.87.

Bisadduct 8. The residue was washed several times with pentane to give 0.58 g (93% yield) of **8** as a yellow oil: ^{31}P NMR {^{1}H} ($CDCl_3$) +42.4; ^{1}H NMR ($CDCl_3$) 1.37 (dd, *J*(HH) = 6.9 Hz, *J*(PH) = 0.6 Hz, 12 H, CH_3C), 2.64 (d, *J*(PH) = 10.3 Hz, 24 H, CH_3N), 3.31 (sept.d, *J*(HH) = 6.9 Hz, *J*(PH) = 12.8 Hz, 2 H, CHS), 7.33 (m, 5 H, H_{arom}); ^{13}C NMR ($CDCl_3$) 25.3 (d, *J*(PC) = 5.8 Hz, *C*H_3C), 36.9 (d, *J*(PC) = 3.9 Hz, CH_3N), 37.4 (d, *J*(PC) = 2.9 Hz, CHS), 126.0 (s, C_m), 128.1(s, C_o), 129.6 (s, C_p), 141.2 (t, *J*(PC) = 13.9 Hz, C_i), 173.3 (t, *J*(PC) = 4.0 Hz, NCN). Anal. Calcd for $C_{21}H_{43}N_6P_2S_2Br$: C, 43.07; H, 7.40; N, 14.35. Found: C, 42.77; H, 7.15; N, 14.09.

Five-Membered Ring 9. The residue was washed several times with ether to give 0.12 g (34% yield) of **9** as a white powder: mp 112−113 °C; ^{31}P NMR {^{1}H} ($CDCl_3$) +28.4; ^{1}H NMR ($CDCl_3$) 1.34 (d, *J*(HH) = 6.8 Hz, 6 H, CH_3C), 3.27 (sept.d, *J*(HH) = 6.8 Hz, *J*(PH) = 9.8 Hz, 1 H, CHS), 7.11−8.55 (m, 15 H, H_{arom}); ^{13}C NMR ($CDCl_3$) 25.0 (d, *J*(PC) = 4.4 Hz, CH_3), 39.9 (d, *J*(PC) = 2.9 Hz, CHS), 125.5 (d, *J*(PC) = 112.1 Hz, C_i-P), 128.7 (s, C_mPh-C), 129.4 (d, *J*(PC) = 39.4 Hz, C_mPh-P), 130.0 (s, C_oPh-C), 131.2 (d, *J*(PC) = 10.3 Hz, C_oPh-P), 133.7 (s, C_pPh-C), 133.9 (d, *J*(PC) = 18.8 Hz, C_iPh-C), 134.4 (d, *J*(PC) = 3.7 Hz, C_pPh-P), 167.9 (d, *J*(PC) = 10.3 Hz, NCN). Anal. Calcd for $C_{22}H_{22}N_2PSBr$: C, 57.77; H, 4.85; N, 6.12. Found: C, 58.03; H, 5.08; N, 5.80.

Bis Adduct 10. An acetonitrile solution of **10** (Br^-) and a stoichiometric amount of KPF_6 was stirred for 24 h at room temperature. After filtration of KBr and evaporation of the solvent, **10** (PF_6^-) was recrystallized from a dichloromethane/ether solution as colorless crystals (0.33 g, 65% yield): mp 163−165 °C; ^{31}P NMR {^{1}H} ($CDCl_3$) +30.2; ^{1}H NMR ($CDCl_3$) 1.20 (d, *J*(HH) = 6.9 Hz, 12 H, CH_3), 3.00 (sept d, *J*(HH) = 6.9 Hz, *J*(PH) = 7.0 Hz, 2 H, SCH), 7.24−7.70 (m, 25 H); ^{13}C NMR ($CDCl_3$) 25.3 (d, *J*(PC) = 4.7 Hz, CH_3), 39.4 (d, *J*(PC) = 2.5 Hz, SCH), 127.2 (s, C_mPh-C), 127.3 (d, *J*(PC) = 107.6 Hz, C_i-P), 128.2 (s, C_oPh-C), 129.5 (d, *J*(PC) = 39.4 Hz, C_m-Ph-P), 130.6 (s, C_pPh-C), 131.7 (d, *J*(PC) = 10.8 Hz, C_oPh-P), 133.8 (d, *J*(PC) = 2.6 Hz, C_pPh-P), 139.5 (t, *J*(PC) = 13.2 Hz, C_iPh-C), 179.0 (t, *J*(PC) = 10.3 Hz, NCN). Anal. Calcd for $C_{37}H_{39}F_6N_2P_3S_2$: C, 56.77; H, 5.02; N, 3.58. Found: C, 56.85; H, 5.10; N, 3.50.

Reaction of Bromophenyldiazirine 1 with Bis(diisopropylamino)(trimethylstannyl)phosphine. To a dichloromethane solution (5 mL) of bis(diisopropylamino)(trimethylstannyl)-phosphine[20] (7.00 g, 17.7 mmol) was added at room temperature a dichloromethane solution (20 mL) of bromophenyldiazirine **1** (3.43 g, 17.4 mmol). The solution was stirred for 20 h at room temperature and analyzed. Benzonitrile and bromotrimethylstannane were characterized by gas chromatography and **11** by ^{31}P NMR spectroscopy. The solvent was removed under vacuum, and the oily residue was extracted with pentane (20 mL) leading to a mixture of **11**, **12**, and **13**. Addition of an ether/pentane solution precipitates **12** and **13**. Careful recrystallization at −20 °C from ether allowed first isolation of **13**, then of **12**.

Diazaphosphete 12: colorless crystals (1.6 g, 26% yield); mp 136−138 °C; ^{31}P NMR {^{1}H} ($CDCl_3$) +54.2; ^{1}H NMR ($CDCl_3$) 1.29 (d, *J*(HH) = 6.8 Hz, 24 H, CH_3), 3.70 (sept d, *J*(HH) = 6.8 Hz, *J*(PH) = 18.3 Hz, 4 H, CH), 7.77 (m, 5 H, H_{arom}); ^{13}C NMR ($CDCl_3$) 22.1 (s, CH_3), 47.2 (d, *J*(PC) = 4.3 Hz, CH), 126.6 (s, C_m), 128.2 (s, C_o), 130.8 (s, C_p), 136.1 (d, *J*(PC) = 22.4 Hz, C_i), 194.7 (d, *J*(PC) = 48.4 Hz, NCN). Anal. Calcd for $C_{19}H_{33}N_4P$: C, 65.49; H, 9.54; N, 16.08. Found: C, 65.69; H, 9.64; N, 16.34.

Triazaphosphinine 13: colorless crystals (3% yield); mp 213 °C; ^{31}P NMR {^{1}H} ($CDCl_3$) +35.6; ^{1}H NMR ($CDCl_3$) 1.19 (d, *J*(HH) = 6.8 Hz, 24 H, CH_3), 3.68 (m, 4 H, CH), 7.00- 8.70 (m, 10 H, H_{arom}); ^{13}C NMR ($CDCl_3$) 22.4 (d, *J*(PC) = 1.9 Hz, CH_3), 46.0 (d, *J*(PC) = 5.0 Hz, CH), 127.1 (s, C_m), 127.9 (d, *J*(PC) = 2.4 Hz, C_o), 130.0 (s, C_p), 139.7 (d, *J*(PC) = 16.9 Hz, C_i), 171.1 (d, *J*(PC) = 3.8 Hz, NCN). Anal. Calcd for $C_{26}H_{38}N_5P$: C, 75.14; H, 9.22; N, 16.85. Found: C, 75.39; H, 9.34; N, 16.80.

Photolysis of Phosphine Azide 15 with Bromotrimethylstannane. A toluene solution (10 mL) of **15** (0.56 g, 2.05 mmol) and bromotrimethylstannane (0.5 g, 2.05 mmol) was irradiated at 254 nm for 24 h at room temperature. After evaporation of the solvent and several washings with pentane, bromo(stannylimino)phosphorane **11** was obtained as a pale yellow oil: (0.60 g, 60% yield); ^{31}P NMR {^{1}H} ($CDCl_3$) −11.8; ^{1}H NMR ($CDCl_3$) 0.41 (s, *J*(^{119}SnH) = 57.6 Hz, *J*(^{117}SnH) = 55.0 Hz, 9 H, CH_3Sn), 1.24 (d, *J*(HH) = 6.8 Hz, 12 H, CH_3-CH), 1.31 (d, *J*(HH) = 6.8 Hz, 12 H, CH_3CH), 3.59 (sept d, *J*(HH) = 6.8 Hz, *J*(PH) = 21.0 Hz, 4 H, CH); ^{13}C NMR ($CDCl_3$) −3.8 (d, *J*(PC) = 4.3 Hz, *J*(^{119}SnC) = 394.8 Hz, CH_3-Sn), 22.6 (d, *J*(PC) = 2.1 Hz, *C*H_3CH), 23.1 (d, *J*(PC) = 3.0 Hz, *C*H_3CH), 48.6 (d, *J*(PC) = 4.3 Hz, CH).

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Supporting Information Available: ORTEP drawing and tables of crystal and intensity collection data, positional and thermal parameters, interatomic distances and angles, and least-squares planes equations for compound **10** (10 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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