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One-Step Redox Route to N-Heterocyclic Phosphenium Ions

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One-step reactions of the appropriate *N*-alkyl-, *N*-cycloalkyl-, and *N*-aryl-substituted α-diimines with PI_3 afforded >80% yields of the triiodide salts of the following N-heterocyclic phosphenium ions, $[(R_1\overline{NC(R_2)C(R_2)NR_1)P}]^+$: **3** ($R_1$ = *t*-Bu; R_2 = H); **4** (R_1 = 2,6-*i*-$Pr_2C_6H_3$; R_2 = H), **5** (R_1 = Mes; R_2 = H), **6** (R_1 = 2,6-*i*-$Pr_2C_6H_3$; R_2 = H), and **7** (R_1 = cyclohexyl; R_2 = H). Treatment of **3** and **6** with $NaB(C_6H_5)_4$ resulted in virtually quantitative yields of the corresponding $[B(C_6H_5)_4]^-$ salts **8** and **9**, respectively. The X-ray crystal structures of **3** and **5**–**9** were determined.

Introduction

N-Heterocyclic phosphenium ions (**1**) have attracted recent attention because of their isovalent relationship to N-heterocyclic carbenes (NHCs) and their heavier group 14 analogues.[1] Interestingly, a structurally authenticated phosphenium ion of this type (**1**: $R_1 = R_4 = Cy$; R_2 = Cl; R_3 = H) was reported[2] prior to the first stable NHC.[3] This particular cation was isolated as the hexachloroantimonate salt by treatment of the precursor phosphorus chloride with $SbCl_5$, which, in turn, had been synthesized in 73% yield via the reaction of CyN=CHCH=NCy with PCl_3 in the presence of Et_3N.[4] Halide ion abstraction has also been effected by other Lewis acids such as $GaCl_3$.[5] These reactions result typically in >90% yields of the desired salts. However, as in the case of the earlier work,[2,4] the overall yields are more modest because one or two lower yield steps are required to convert the diimine into the phosphorus−halo phospholene precursor. A similar comment applies to the conversion of phosphorus−halo phospholenes into the corresponding N-heterocyclic phosphenium salts via metathetical reaction with, e.g., $AgPF_6$,[5] or by means of a Me_3SiCl elimination reaction with Me_3SiOTf.[6] The salt elimination reaction of the dilithio derivative LiN(*t*-Bu)C=CN(*t*-Bu)Li with PCl_3 has also been used to generate the corresponding phosphorus−chloro compound,[7] but once again the yield is relatively poor (55%). However, it has been found subsequently that overall yields of 70−80% can be realized if the dilithium salts are quenched by protonation with Et_3NHCl and the resulting α-aminoaldimines are treated with PCl_3 in the presence of Et_3N.[8] Conversion to the corresponding triflate salts can be achieved in >85% yields.[9] Nevertheless,

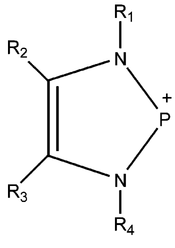

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Table 1. Crystallographic Data and Experimental Parameters for the X-ray Structure Analyses

	3·THF	**5**	**6**	**7**	**8**	**9**
formula	$C_{14}H_{28}I_3N_2OP$	$C_{20}H_{24}I_3N_2P$	$C_{26}H_{36}I_3N_2P$	$C_{14}H_{24}I_3N_2P$	$C_{34}H_{38}BN_2P$	$C_{50}H_{56}BN_2P$
fw	652.05	704.08	788.24	632.02	516.44	726.75
cryst syst	monoclinic	monoclinic	triclinic	triclinic	orthorhombic	monoclinic
space group	$P21/c$	$C2/c$	$P\bar{1}$	$P\bar{1}$	$Pbca$	$P2_1/c$
T (K)	153(2)	153(2)	153(2)	153(2)	153(2)	153(2)
λ (Å)	0.710 69	0.710 69	0.710 69	0.710 69	0.710 73	0.710 69
a (Å)	12.993(5)	21.647(4)	9.861(5)	13.817(5)	9.7482(19)	20.593(5)
b (Å)	15.126(5)	7.5469(15)	10.501(5)	17.943(5)	17.553(4)	17.637(5)
c (Å)	12.254(5)	16.488(3)	16.856(5)	18.382(5)	34.013(7)	23.597(5)
α (deg)	90	90	89.522(5)	82.750(5)	90	90
β (deg)	110.922(5)	112.69(3)	78.766(5)	68.210(5)	90	91.069(5)
γ (deg)	90	90	80.179(5)	70.130(5)	90	90
V (Å^3)	2249.5(15)	2485.1(10)	1686.4(13)	3980(2)	5820(2)	8569(4)
cryst size (mm^3)	0.20 × 0.18 × 0.16	0.13 × 0.11 × 0.11	0.05 × 0.03 × 0.02	0.18 × 0.15 × 0.15	0.18 × 0.18 × 0.10	0.15 × 0.14 × 0.12
d_{calcd} (g cm^{-3})	1.925	1.882	1.552	2.110	1.179	1.127
Z	4	4	2	8	8	8
μ (mm^{-1})	4.241	3.844	2.842	4.787	0.120	0.099
F(000)	1232	1328	760	2368	2208	3120
2θ range (deg)	2.15−27.50	2.68−27.45	1.97−27.50	2.95−27.50	2.40−27.47	1.52−27.49
no. of reflns colld	9040	4601	12191	28143	11712	33860
no. of ind reflns	5151 [R(int) = 0.0274]	2828 [R(int) = 0.0235]	7642 [R(int) = 0.0218]	18017 [R(int) = 0.0433]	6425 [R(int) = 0.0520]	19610 [R(int) = 0.0486]
no. of data/ restraints/ param	5151/0/200	2828/0/123	7642/0/297	18017/0/721	6425/7/350	19610/4/1005
GOF, F^2	1.078	1.065	1.107	1.103	1.023	1.014
R_1, wR_2 [$I > 2\sigma(I)$]	0.0341, 0.0738	0.0446, 0.1129	0.0450, 0.1163	0.0641, 0.1462	0.0672, 0.1755	0.0553, 0.1102
R_1, wR_2 (all data)	0.0635 0.0845	0.0609, 0.1244	0.0820, 0.1267	0.1169, 0.1651	0.1130, 0.2051	0.1124, 0.1314
peak/hole (e Å^{-3})	0.893/−0.871	1.831, −1.796	0.931, −1.082	1.817, −1.541	0.562, −0.528	0.327, −0.322

given the above brief summary, it is clear that a one-step, high-yield synthesis of N-heterocyclic phosphenium salts would be desirable.

Pioneering work by Schmidpeter et al.[10] established that the reduction of PCl_3 with $SnCl_2$ in the presence of chelating bis(phosphines) results in so-called triphosphenium ions (**2**) in which the central P atom possesses a formal 1+ oxidation state. While the mechanism of formation of **2** has not been established, it is reasonable to assume that the redox reaction $PCl_3 + SnCl_2 \rightarrow$ "PCl" + $SnCl_4$ is followed by chloride ion transfer to $SnCl_4$ from either free or chelated "PCl". Schmidpeter et al.[11] also demonstrated that acyclic analogues of **2** can be isolated when two monodentate tertiary phosphines are used in place of a chelating bis(phosphine). Interest in the general area of P^+ chemistry has been rekindled recently not only in terms of the variety of chelating phosphines that are capable of trapping this univalent cation[12] but also from the standpoint of new methods of generation. For example, Macdonald et al.[13] have shown that NHCs are capable of both reducing PCl_3 and trapping the resulting P^+ entity as cations of the type $[(NHC)-P-(NHC)]^+$. Moreover, this same group[14] established that chelating bis(phosphines) will cause disproportionation of PI_3, thus forming the iodide salt of **2** along with molecular iodine. Some of our own work in this area has focused on the use of the chelating 1,2-bis(arylimino)acenaphthene (aryl-BIAN) ligand class for entrapment of univalent group 15 cations. In contrast to previous work, it was shown that in the compounds [(dpp-BIAN)P][$SnCl_5$·THF] and [(dpp-BIAN)P][I_3] (dpp = 2,6-*i*-$Pr_2C_6H_3$; THF = tetrahydrofuran) the oxidation state of P is 3+ because of the transfer of two electrons from P into the low-lying lowest unoccupied molecular orbital (LUMO) of the BIAN ligand.[15] In turn, this result suggested a new one-step route to N-heterocyclic phosphenium salts, viz., the reaction of α-diimines with PI_3.[16] A potentially successful outcome for this redox route was indicated by our observation that "PCl" and "AsCl", generated by the Schmidpeter et al. route,[10] react with α-diimines to produce the $[SnCl_5·THF]^-$ salts of N-heterocyclic phosphenium and arsenium cations, respectively.[17] Moreover and retrospectively, it is possible that a redox reaction of this type is involved in the reaction of an N-heterocyclic germylene with PCl_3 and $AsCl_3$ to form the $[GeCl_5]^-$ salts of the corresponding phosphenium and arsenium cations.[7]

Experimental Section

General Procedures. All manipulations and reactions were performed under a dry, oxygen-free, catalyst-scrubbed Ar atmosphere using a combination of standard Schlenk techniques or in

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Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for the Phosphenium Ions

param	**3**	**5**	**6**	**7**	**8**	**9**
C(1)−C(2)	1.353(6)	1.342(9)	1.342(6)	1.344(17)	1.352(4)	1.355(3)
N(1)−C(1)	1.366(5)	1.371(6)	1.376(6)	1.388(15)	1.371(3)	1.387(3)
N(2)−C(2)	1.373(5)	1.371(6)	1.400(5)	1.370(15)	1.365(4)	1.370(4)
N(1)−P(1)	1.664(3)	1.665(3)	1.674(4)	1.673(10)	1.668(2)	1.686(2)
N(2)−P(1)	1.663(4)	1.665(3)	1.673(3)	1.679(10)	1.656(2)	1.664(3)
N(1)−P(1)−N(2)	90.14(17)	89.4(2)	89.75(17)	89.4(5)	90.09(11)	89.22(12)
N(1)−C(1)−C(2)	111.3(4)	111.4(2)	111.5(4)	112.7(11)	110.6(3)	111.5(3)
N(2)−C(2)−C(1)	111.7(4)	111.4(2)	111.5(4)	110.4(10)	112.3(3)	111.0(2)

an M-Braun or Vacuum Atmospheres drybox. All glassware was oven-dried and vacuum- and argon-flow-degassed before use. All solvents were distilled over sodium benzophenone ketyl, except dichloromethane, which was distilled over CaH_2 and degassed prior to use. The α-diimines RNC(H)C(H)NR [R = *t*-Bu,[18] Mes,[19] 2,6-*i*-$Pr_2C_6H_3$,[19] Cy,[20] and (*p*-tol)NC(Me)C(Me(*p*-tol))][21] were prepared according to the literature procedures. Phosphorus triiodide and Na-[$B(C_6H_5)_4$] were obtained from commercial sources and used without further purification.

Physical Measurements. Low-resolution chemical ionization (CI) mass spectral (MS) data were collected on a Finnigan MAT TSQ-700 mass spectrometer, and high-resolution CIMS spectra were recorded on a VG Analytical ZAB-VE sector instrument. All MS analyses were performed on samples that had been sealed in glass capillaries under an Ar atmosphere. Solution-phase NMR spectra were recorded at 298 K on a Varian Inova instrument (^{1}H NMR, 300.14 MHz; ^{13}C NMR, 75.48 MHz; ^{31}P NMR, 121.52 MHz) immediately following removal of the samples from a drybox. The ^{1}H and ^{13}C{^{1}H} chemical shift values are reported in parts per million (ppm) relative to $SiMe_4$ (δ 0.00), using residual solvent resonances as internal standards. The ^{31}P chemical shift values are reported relative to external 85% H_3PO_4.

X-ray Crystallography. Crystals of **3** and **5**−**9** were removed from Schlenk flasks under positive Ar pressure, placed on glass slides, covered with degassed hydrocarbon oil, and mounted on thin nylon loops. The X-ray diffraction data were collected at 153(2) K on a Nonius Kappa CCD area detector diffractometer equipped with an Oxford Cryostream low-temperature device and a graphite-monochromated Mo Kα radiation source (λ = 0.710 73 Å). Corrections were applied for Lorentz and polarization effects. All six structures were solved by direct methods and refined by full-matrix least-squares cycles on F^2.[22] All non-H atoms were refined with anisotropic thermal parameters, and H atoms were placed in fixed, calculated positions using a riding model (C−H 0.96 Å). Pertinent experimental data are listed in Table 1, and selected metrical parameters are compiled in Table 2.

Syntheses of 3−7. A solution of PI_3 in 30 mL of CH_2Cl_2 was added dropwise to a solution of the appropriate α-diimine ligand in 30 mL of CH_2Cl_2 over a period of 30 min. The reaction mixture was stirred for 12 h and then filtered through Celite. Removal of the volatiles under reduced pressure resulted in the formation of the powdered products, which were subsequently recrystallized from a 2:1 dichloromethane/hexane mixture at −40 °C under an Ar atmosphere.

3. The reaction of PI_3 (0.758 g, 1.48 mmol) with (*t*-Bu)NC(H)C(H)N(*t*-Bu) (0.310 g, 1.48 mmol) produced 0.9 g (84%) of dark-brown powder **3**. ^{1}H NMR (300.14 MHz, $CDCl_3$): δ 1.84 [s, 18 H, CH_3], 7.94 [s, 2 H, CH=CH]. ^{13}C{^{1}H} NMR (75.48 MHz, $CDCl_3$): δ 31.33 [d, $^3J(^{13}C-^{31}P) = 9.4$ Hz, CH−$_3$], 62.47 [*C*(CH_3)], 131.11 [C=C]. ^{31}P{^{1}H} NMR (121.52 MHz, $CDCl_3$): δ 204.3. LRMS (CI^+, *m/z*) (%): 323 (100%, *t*-Bu−$DABP^+$), 143 (38%, *t*-Bu−$DABP^+$−*t*-Bu). HRMS (CI^+, CH_4): calcd for $C_{10}H_{20}N_2P^+$, 199.1365; found, 199.1365.

4. The reaction of PI_3 (0.467 g, 1.13 mmol) with (*p*-tol)NC(Me)C(Me)N(*p*-tol) (0.300 g, 1.13 mmol) afforded 0.68 g (88%) of dark-brown powder **4**. ^{1}H NMR (300.14 MHz, $CDCl_3$): δ 2.37 [s, 6 H, CH_3], 2.49 [s, 6 H, CH_3], 7.43−7.58 [m, 4 H, H_{arom}]. ^{13}C{^{1}H} NMR (75.48 MHz, $CDCl_3$): δ 14.20, 21.66, 127.20 [$J(^{13}C-^{31}P) = 5.0$ Hz], 131.09, 131.47 [$J(^{13}C-^{31}P) = 12.2$ Hz], 140.99, 141.73. ^{31}P{^{1}H} NMR (121.52 MHz, $CDCl_3$): δ 227.1. LRMS (CI^+, *m/z*) (%): 323 (100%, *p*-tol−$DABP^+$). HRMS (CI^+, CH_4): calcd for $C_{18}H_{20}N_2P^+$, 295.1364; found, 295.1364.

5. The reaction of PI_3 (1.41 g, 3.42 mmol) with (Mes)NC(H)C(H)N(Mes) (1 g, 3.42 mmol) resulted in 2.1 g (87%) of brown powder **3**. ^{1}H NMR (300.14 MHz, $CDCl_3$): δ 2.25 [s, 12 H, CH_3], 2.41 [s, 6 H, CH_3], 7.17 [s, 4 H, H_{arom}−Mes], 7.94 [s, 2 H, CH=CH]. ^{13}C{^{1}H} NMR (75.48 MHz, $CDCl_3$): δ 18.64, 21,28 [CH_3], 130.60, 131.70 [$J(^{13}C-^{31}P) = 6.6$ Hz], 134.11 [$J(^{13}C-^{31}P) = 3.2$ Hz], 136.23 [$J(^{13}C-^{31}P) = 2.7$ Hz], 141.89 [C_{arom}]. ^{31}P{^{1}H} NMR (121.52 MHz, $CDCl_3$): δ 209.7. LRMS (CI^+, *m/z*) (%): 323 (100%, Mes−$DABP^+$). LRMS (CI^-, *m/z*) (%): 127 (100%, I^-). HRMS (CI^+, CH_4): calcd for $C_{20}H_{24}N_2P^+$, 323.1677; found, 323.1677.

6. The reaction of PI_3 (1.09 g, 2.66 mmol) with (2,6-*i*-$Pr_2C_6H_3$)-NC(H)C(H)(2,6-*i*-$Pr_2C_6H_3$) (1 g, 2.66 mmol) afforded 1.9 g (92%) of brown powder **6**. ^{1}H NMR (300.14 MHz, $CDCl_3$): δ 1.36 [d, $^3J(^1H-^1H) = 6.9$ Hz, 24 H, CH_3], 2.69 [m, 4 H, CH], 7.42−7.45 [m, 4 H, C($_{arom}$)−dpp], 7.63 [m, 2 H, C($_{arom}$)−dpp], 8.05 [s, 2 H, HC=CH]. ^{13}C{^{1}H} NMR (75.48 MHz, $CDCl_3$): δ 24.73, 25.72, 29.32 [*i*-Pr], 125.19, 130.48, 131.98, 136.26, 145.19 [C($_{arom}$)]. ^{31}P{^{1}H} NMR (121.52 MHz, $CDCl_3$): δ 207.4. LRMS (CI^+, *m/z*) (%): 407 (100%, dpp−$DABP^+$). LRMS (CI^-, *m/z*) (%): 127 (100%, I^-). HRMS (CI^+, CH_4): calcd for $C_{26}H_{36}N_2P^+$, 407.2616; found, 407.2617 (0.1 ppm).

7. The reaction of PI_3 (0.374 g, 0.91 mmol) with (Cy)NC(H)C(H)N(Cy) (0.2 g, 0.91 mmol) resulted in 0.46 g (81%) of brown powder **7**. ^{1}H NMR (300.14 MHz, $CDCl_3$): δ 1.39 [tt, 2 H, H_{Cy}], 1.60 [qt, 4 H, H_{Cy}], 1.81−2.05 [complex pattern, 10 H, H_{Cy}], 2.51 [mult, 4 H, H_{Cy}], 4.95 [m, 2 H, H_{Cy}], 7.97 [s, 2 H, CH=CH]. ^{13}C{^{1}H} NMR (75.48 MHz, $CDCl_3$): δ 24.74, 25.28 [$J(^{13}C-^{31}P) = 1.7$ Hz], 35.47 [$J(^{13}C-^{31}P) = 8.83$ Hz], 62.31 [$J(^{13}C-^{31}P) = 9.9$ Hz], 132.15 [$J(^{13}C-^{31}P) = 3.9$ Hz]. ^{31}P{^{1}H} NMR (121.52 MHz, $CDCl_3$): δ 209.9. LRMS (CI^+, *m/z*) (%): 251 (35%, Cy−$DABP^+$). HRMS (CI^+, CH_4): calcd for $C_{14}H_{24}N_2P^+$, 251.1677; found, 251.1676.

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Synthesis of 8 and 9. A mixture of the appropriate phospenium triiodide salt and $NaBPh_4$ in 50 mL of THF solution was stirred at room temperature for 12 h. All volatiles were removed under reduced pressure, and the resulting yellow residue was extracted with 30 mL of CH_2Cl_2 to give a clear light-yellow solution. Slow evaporation of the solvent under an Ar atmosphere resulted in the crystalline tetraphenylborate salts **8** and **9** in virtually quantitative yields.

8. The reaction of $NaBPh_4$ (0.342 g, 1.03 mmol) with **3** (0.2 g, 0.345 mmol) resulted in a virtually quantitative yield of colorless crystalline **8**. ^{1}H NMR (300.14 MHz, CD_2Cl_2): δ 1.61 [s, 18 H, CH_3], 6.87 [m, 4 H, BPh_4^-], 7.02 [m, 8 H, BPh_4^-], 7.94 [s, 2 H, CH=CH], 7.33 [m, 8 H, BPh_4^-]. $^{13}C\{^1H\}$ NMR (75.48 MHz, CD_2Cl_2): δ 31.42 [d, $^3J(^{13}C-^{31}P) = 9.3$ Hz), *C*H$-_3$], 63.15 [$^2J(^{13}C-^{31}P) = 7.7$ Hz, *C*(CH_3)], 122.12 [BPh_4^-], 125.95 [BPh_4^-], 132.79 [C=C], 136.22 [BPh_4^-], 164,19 [BPh_4^-]. $^{31}P\{^1H\}$ NMR (121.52 MHz, CD_2Cl_2): δ 202.5. LRMS (CI$^+$, *m/z*) (%): 199 (50%, *t*-Bu−DABP$^+$), 165 (100%, Ph_2B^+). HRMS (CI$^+$, CH_4): calcd for $C_{10}H_{20}N_2P^+$, 199.1365; found, 199.1365.

9. The reaction of $NaBPh_4$ (0.26 g, 0.762 mmol) with **6** (0.2 g, 0.254 mmol) resulted in a virtually quantitative yield of light-yellow crystals of **9**. ^{1}H NMR (300.14 MHz, $CDCl_3$): δ 1.19 [d, $^3J(^1H-^1H) = 6.9$ Hz, 12 H, CH_3], 1.32 [d, $^3J(^1H-^1H) = 6.9$ Hz, 12 H, CH_3], 2.22 [m, 4 H, CH], 6.10 [d, $^3J(^1H-^{31}P = 1.2$ Hz, 2 H, HC=CH], 6.74 [t, 4 H, $H_{arom}(BPh_4)$], 6.90 [t, 8 H, $H_{arom}(BPh_4)$], 7.38−7.43 [m, 14 H, $H_{arom}(BPh_4)$ and H_{arom}(dpp)]. $^{13}C\{^1H\}$ NMR (75.48 MHz, $CDCl_3$): δ 21.72, 24.23, 27.28 [*i*-Pr], 120.37, 123.09 [BPh_4^-], 124.02 [BPh_4^-], 130.42, 134.58 [BPh_4^-], 136.96, 137.67, 142.88, 162.3 $[BPh_4]^-$. $^{31}P\{^1H\}$ NMR (121.52 MHz, $CDCl_3$): δ 204.4 (br). LRMS (CI$^+$, *m/z*) (%): 484 (100%, dpp−DABP + Ph), 407 (61%, dpp−DABP). LRMS (CI$^-$, *m/z*) (%): 243 (30%, BPh_3). HRMS (CI$^+$, CH_4): calcd for $C_{26}H_{36}N_2P^+$, 407.2616; found, 407.2626.

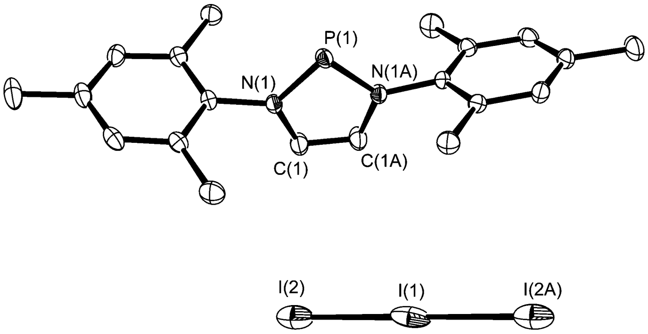


Figure 1. ORTEP diagram of **5** showing thermal ellipsoids at 30% probability with H atoms omitted for clarity.

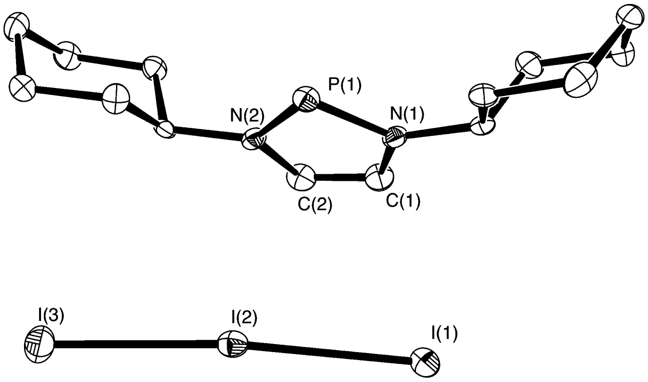


Figure 2. ORTEP diagram of **7** showing thermal ellipsoids at 30% probability with H atoms omitted for clarity.

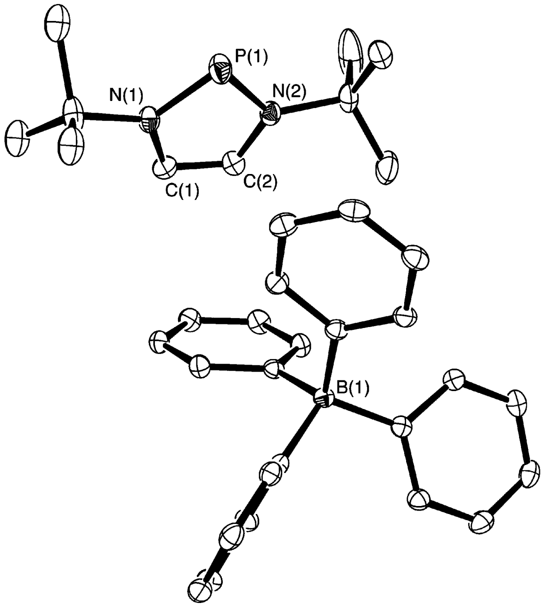
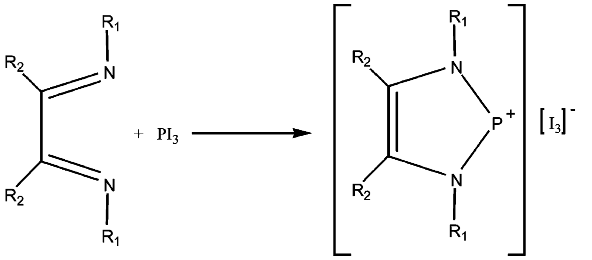


Figure 3. ORTEP diagram of **8** showing thermal ellipsoids at 30% probability with H atoms omitted for clarity.

Results and Discussion

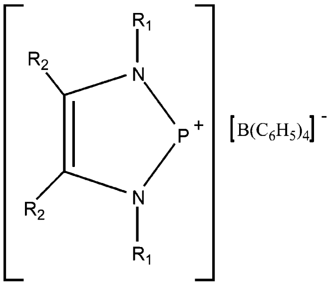


(1)

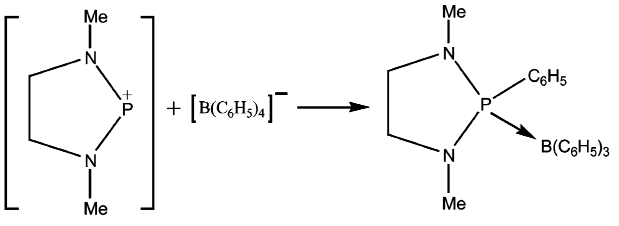
3: $R_1 = t$-Bu; R_2 = H
4: R_1 = p-tolyl; R_2 = Me
5: R_1 = Mes; R_2 = H
6: $R_1 = 2,6\text{-}i\text{-}Pr_2C_6H_3$; R_2 = H
7: R_1 = Cy; R_2 = H

As summarized in eq 1, the triiodide salts of *N*-alkyl and *N*-aryl-substituted N-heterocyclic phosphenium cations can be readily prepared in one step via the reaction of PI_3 with the appropriate diimine in CH_2Cl_2 solution. In each case, the yield of crude product is >80% and recrystallization results in 80−90% yields of red crystals of triiodide salts **3**−**7**. The phosphenium cations in **4**−**7** have not been reported previously. However, we note that the 4-chloro analogues of **5**[9] and **7**[2] have been prepared and structurally characterized, as has the 3,4-dimethyl analogue of **6**.[16] Compounds **3**−**7** were characterized by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy and high-resolution mass spectrometry (HRMS). The ^{31}P NMR chemical shifts for **3**−**7**, which fall in the range δ 200−230 ppm, are diagnostic of the presence of phosphenium cations[1] and thus supportive of the structural formula depicted in eq 1. Moreover, the CI mass spectra of **3**−**7** evidence a 100% abundance peak corresponding to the phosphenium ion in each case. Structural confirmation was provided by single-crystal X-ray diffraction studies of **3** and **5**−**7**. The metrical parameters for the phosphenium cations are very similar (Table 2); the structures of **5** and **7**, which are representative of the other cations, are shown in Figures 1 and 2, respectively. Akin to other phosphenium cation structures, the ring C−C bond distances, which range from 1.342(6) to 1.353(6) Å, are shorter than those of typical C−C single bond distances and the C−N bond distances, which range from 1.366(5) to 1.400(5) Å, correspond to a bond order of approximately 1. It is clear from the foregoing spectroscopic and structural data that P adopts the 3+ oxidation state in **3**−**7**. At this point, we have no mechanistic information regarding the diimine/PI_3 reactions. However, one scenario is that the interaction of the diimine with PI_3 results initially in the formation of I_2 and a donor−acceptor complex between the α-diimine and PI, from which I^- is abstracted by I_2. The process is completed by the subsequent or concomitant transfer of two electrons from the P^+ moiety into the LUMO of the α-diimine.

Further synthetic utility is conferred on this synthetic method by the observation that **3**−**7** undergo facile anion-exchange reactions with, e.g., $NaB(C_6H_5)_4$ to afford the corresponding tetraphenylborate salts in virtually quantitative yields. Two such salts have been structurally authenticated, namely, **8** and **9**. The structure of **8** is illustrated in Figure 3. The structures of tetraphenylborate salts of phosphenium ions are of particular interest because of the report by Burford et al.[23] that **10** undergoes phenyl back-transfer and $B(C_6H_5)_3$ coordination to form the covalent phosphine−borane complex **11** (eq 2). Because the acyclic phosphenium salt $[(i\text{-}Pr_2N)_2P][B(C_6H_5)_4]$ does not undergo such a transformation, these authors suggested that, in this case, the *N*-isopropyl groups provided a sufficient steric barrier to preclude this type of reaction. The structures of **8** and **9**, which feature bulky *t*-Bu and 2,6-$i\text{-}Pr_2C_6H_3$ groups, respectively, exhibit no close anion−cation contacts, thus supporting the view of Burford et al.[23] As expected, the metrical parameters for the phosphenium cations in **8** and **9** are identical within experimental error with those in the triiodide salts **3** and **6**, respectively.



8: R_1 = *t*-Bu; R_2 = H
9: R_1 = 2,6-$i\text{-}Pr_2C_6H_3$; R_2 = H



10 **11**

(2)

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Supporting Information Available: X-ray structural data for **3** and **5**−**9**. This material is available free of charge via the Internet at http://pubs.acs.org. The CCDC numbers for these compounds are 623579, 623578, 623576, 623,580, 623581, and 623577, respectively, and can be obtained free of charge upon request via www.ccdc.cam.ac.uk/data_request/cif from The Cambridge Crystallographic Data Centre (12 Union Road, Cmabridge CB2 1EZ, U.K., tel +44 1223 336408, fax +44 1223 336033).

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(23) Burford, N.; Losier, P.; Macdonald, C.; Kyrimis, V.; Bakshi, P. K.; Cameron, T. S. *Inorg. Chem.* **1994**, *33*, 1434.