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A Convenient Method for the Preparation of N-Heterocyclic Bromophosphines: Excellent Precursors to the Corresponding N-Heterocyclic Phosphenium Salts

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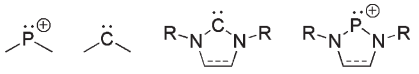
An in situ redox method is employed to prepare N-heterocyclic bromophosphines in good yield and purity. Such bromophosphines may be treated with a variety of bromide-abstracting reagents to produce the corresponding N-heterocyclic phosphenium salts in excellent yield.

Salts containing phosphenium cations have played an important role in the history and development of modern main-group chemistry. In the most general definition, a phosphenium cation (**1**) is a cation that contains a dicoordinate phosphorus center bearing a total of six valence electrons and is the isovalent analogue of a carbene (**2**).[1,2] While numerous types of phosphenium cations have been prepared and studied, the most important class of phosphenium compounds is the relatively stable species in which the dicoordinate phosphorus center is supported by two adjacent amido substituents. Although such compounds are analogous to the now-ubiquitous N-heterocyclic carbenes (NHCs, **3**)[3,4] and may be labeled N-heterocyclic phosphenium cations (NHPs, **4**), it is worth noting that well-characterized NHPs were reported more than 35 years ago[5,6] and thus predate the first report of a stable NHC considerably. In fact, the structural characterization of a salt containing a 1,3,2-diazaphospholenium cation, an unsaturated NHP directly analogous to the most common type of "Arduengo" NHC,[7] was reported as early as 1990.[8]



1 2 3 4

The rich and diverse chemistry of NHPs has been studied extensively.[1,2] Some recent highlights are depicted in Scheme 1 and include reversible cycloaddition chemistry,[9] azide chemistry for the preparation of phosphazenes,[10] hydride chemistry including small-molecule activation,[11,12] and the use of NHP fragments as components of highly polarized diphosphines that exhibit exceptional reactivity.[13−16] Perhaps more importantly, given the importance of NHCs as ligands for transition-metal complexes,[17] interest in NHPs as analogues of NHC ligands has been great and is growing significantly.[18]

Computational work demonstrates that, in spite of their isovalent "carbon copy"[21] relationship, NHPs are considerably electrophilic, whereas NHCs are typically considered as strongly nucleophilic in nature.[22] In this light, NHP ligands may be used to engender altered and perhaps improved reactivity on the resultant organometallic complexes and are being used to develop new types of catalysts for organic transformations.[18,23−28]

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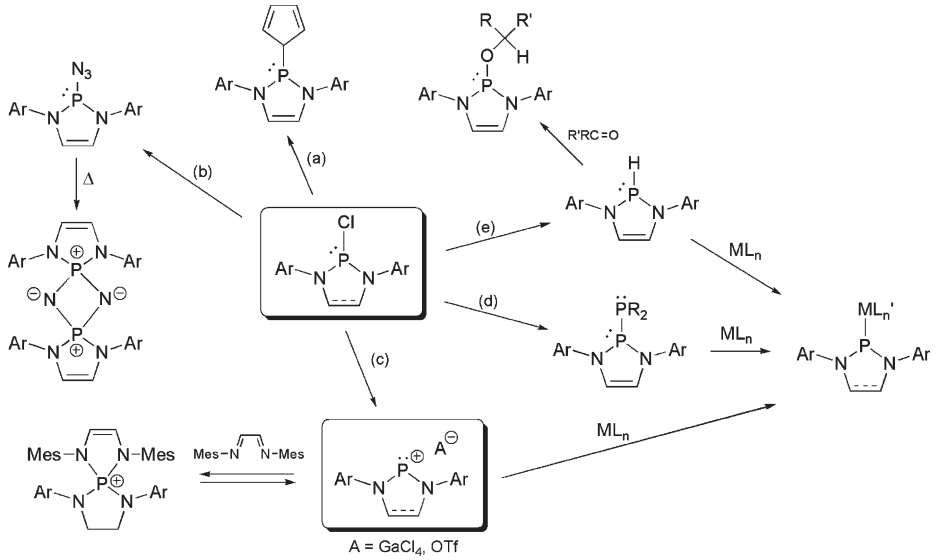
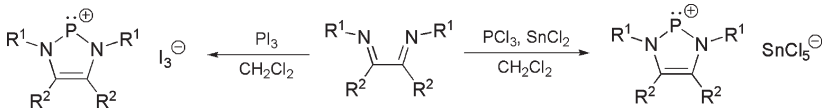
Scheme 1. Examples of Some of the Reactivity Reported Recently for N-Heterocyclic Chlorophosphines and the Corresponding N-Heterocyclic Phosphenium Salts[a]



[a] Reagents: (a) NaCp, −NaCl;[19] (b) NaN_3, LiCl, −NaCl;[10] (c) $GaCl_3$,[20] Me_3SiOTf, $-Me_3SiCl$ or AgOTf, −AgCl;[9] (d) $LiPR_2$, −LiCl;[13] (e) $LiAlH_4$, −LiCl.[11]

Scheme 2. Quantitative Redox Cycloaddition Routes to N-Heterocyclic Phosphenium Salts



Phosphenium salts have typically been prepared from a P-chlorinated precursor, either by chloride anion abstraction or by metathesis.[1,2] Given their long history and potential utility, it is surprising that convenient and high-yielding synthetic approaches to the P-chlorinated precursors to unsaturated NHPs (2-chloro-1,3,2-diazaphospholenes, NHP-Cl) remained absent until relatively recently. While logical approaches to such compounds, such as the treatment of salts of unsaturated α-diamide dianions with PCl_3, had been reported, the yields of the reactions were invariably low and unwanted byproducts were generally observed. Metathesis reactions of 1,3,2-diazasiloles and PCl_3 were employed as an alternative route; however, the yields of the reactions remained low.[4,29] More recently, Gudat and co-workers reported a multistep, one-pot route to the desired N-heterocyclic chlorophosphines that generates the products in good to excellent yield.[12,30]

As part of our continuing investigation of compounds containing phosphorus and other main-group elements in unusually low oxidation states,[31] we have developed new methods for the convenient generation of phosphorus(+1) centers.[32] Recently, the research group of Cowley and our group showed that the use of P^I synthons in the presence of α-diimines yields phosphenium cations as either chlorostannate or triiodide salts, as illustrated in Scheme 2.[33−37] Although these methods are simple and quantitative, the nature of the counteranions may diminish the utility of the resultant salts. In this note, we demonstrate that our newest method for the generation of P^I bromide salts[38] can be employed for the clean, convenient, and high-yield one-step synthesis of N-heterocyclic bromophosphines, which are excellent precursors for a wide variety of NHP salts by bromide anion abstraction or metathesis. This method thus combines the simplicity of a one-step redox synthetic approach with the utility of halide substitution and should provide a very useful route to phosphenium reagents and ligands.

Experimental Section

General Procedures. All manipulations were carried out using standard inert-atmosphere techniques. Phosphorus(III) bromide and phosphorus(III) chloride were purchased from Strem Chemicals Inc., and all other chemicals and reagents

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were purchased from Aldrich. Phosphorus(III) bromide and phosphorus(III) chloride were distilled before use, and all other reagents were used without further purification. All solvents were dried using a series of Grubbs-type columns[39] and were degassed prior to use. CD_2Cl_2, and $CDCl_3$ were dried over calcium hydride. The compounds 1,4-bis(2,4,6-trimethylphenyl)-2,3-dimethyl-1,4-diazabutadiene (^{Mes}DAB), 1,4-bis(2,6-diisopropylphenyl)-2,3-dimethyl-1,4-diazabutadiene (^{Dipp}DAB), 1,2-bis(2,4,6-trimethylphenylimino)acenaphthene (^{Mes}BIAN), and 1,2-bis(2,6-diisopropylphenylimino)acenaphthene (^{Dipp}BIAN) were synthesized according to literature procedures.[40]

NMR spectra were recorded at room temperature in $CDCl_3$ solutions on a Bruker Advance 300 MHz spectrometer. Chemical shifts are reported in ppm, relative to external standards ($SiMe_4$ for ^1H and ^{13}C, 85% H_3PO_4 for ^{31}P, $BF_3\cdot OEt_2$ for ^{11}B, $CFCl_3$ for ^{19}F, $AlCl_3$ in water for ^{27}Al). Coupling constant magnitudes, $|J|$, are given in Hz. The high-resolution mass spectra (HRMS) were obtained using electrospray ionization of acetonitrile solutions of species either by The McMaster Regional Centre for Mass Spectrometry, Hamilton, Canada, or in house; calculated and reported mass to charge ratios are reported for the most intense signal of the isotopic pattern. Melting points were obtained on samples sealed in glass capillaries under dry nitrogen using an Electrothermal melting point apparatus. Elemental analysis was performed by Atlantic Microlabs, Norcross, GA.

Specific Procedures. General Synthetic Route to Diaminobromophosphines 5−8. A solution of the given α-diimine (0.74 mmol) in CH_2Cl_2 (ca. 20 mL) was added to a solution of PBr_3 (0.74 mmol) and cyclohexene (2.22 mmol) in CH_2Cl_2 (ca. 20 mL). Upon addition, each solution undergoes a color change specific to the diimine employed and the resulting reaction mixture was stirred for 36 h. The volatile components were removed under reduced pressure to afford very dark colored foamlike solids which were covered with pentane and sonicated for 1 h. The remaining solids were filtered and washed with pentane, and then any remaining volatile components were removed under reduced pressure to afford solid powders of the diaminobromophosphines **5−8**. The reactions are almost quantitative, as assessed by ^{31}P NMR spectroscopy, but the purification procedure reduces the isolated yield; the specific observations and characterization data for the materials are detailed below. Microanalytical data and ^1H NMR spectroscopy indicate that varying amounts of CH_2Cl_2 coprecipitate with the diaminobromophosphines prepared as described. If desired, ^1H NMR experiments indicate that the dichloromethane solvent may be removed completely by dissolving the solid in toluene (ca. 15 mL) and distilling the solution to approximately half its original volume.

2-Bromo-1,3-dimesityl-1,3,2-diazaphospholene ((^{Mes}DAB)P-Br, 5). Reagents: PBr_3 (200 mg, 0.74 mmol); cyclohexene (180 mg, 2.22 mmol); ^{Mes}DAB (236 mg, 0.74 mmol). Reaction mixture color changes: initially bright red and gradually became dark green. Product: brown solid powder characterized as $\mathbf{5}\cdot{}^3/_4CH_2Cl_2$. Yield: 85% (310 mg, 0.63 mmol). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 188.8. ^1H NMR ($CDCl_3$): δ 7.03 (s, 4 H, *m*-H_{Mes}), 5.30 (s, 0.8 H, CH_2Cl_2), 2.27 (s, 6 H, CH_3), 2.11 (s, 12 H, *o*-CH_3), 2.06 (s, 6 H, *p*-CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 142.4 (N−C), 141.0 (*i*-C_{Mes}), 136.2 (*o*-C_{Mes}), 131.1 (*m*-C_{Mes}), 129.7 (*p*-C_{Mes}), 21.1 (CH_3) 19.2 (*o*-CH_3), 12.8 (*p*-CH_3). HRMS: calcd for $C_{22}H_{28}N_2P^+$ 351.1990, found 351.2005 (+4.2 ppm). Anal. Calcd for $C_{22}H_{28}N_2PBr\cdot{}^3/_4CH_2Cl_2$: C, 55.19; H, 6.01; N, 5.66. Found: C, 55.08; H, 6.63; N, 5.51.

2-Bromo-1,3-bis(2,6-diisopropylphenyl)-1,3,2-diazaphospholene ((^{Dipp}DAB)P-Br, 6). Reagents: PBr_3 (200 mg, 0.74 mmol); cyclohexene (180 mg, 2.22 mmol); ^{Dipp}DAB (300 mg, 0.74 mmol). Reaction mixture color changes: initially bright red and gradually became dark purple. Product: light green solid powder characterized as $\mathbf{6}\cdot{}^1/_2CH_2Cl_2$. Yield: 86% (356 mg, 0.64 mmol). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 191.7. ^1H NMR ($CDCl_3$): δ 7.42 (t, $^3J_{HH}$ = 7.8, *p*-C_{Dipp}), 7.25 (d, $^3J_{HH}$ = 7.8, *m*-C_{Dipp}), 5.29 (s, 0.4 H, CH_2Cl_2), 2.66 (m, ^{i}Pr−H, 4H), 2.13 (s, 6H, CH_3), 1.15 (m, 24H, ^{i}Pr-CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 146.8 (N−C), 131.1 (*o*-C_{Dipp}), 125.1 (*m*-C_{Dipp}), 124.2 (*p*-C_{Dipp}), 29.2 (^{i}Pr CH), 28.8 (^{i}Pr CH_3), 26.1 (^{i}Pr CH_3), 24.0 (CH_3), 23.7 (^{i}Pr CH). HRMS: calcd for $C_{28}H_{40}N_2P^+$ 435.2929, found 435.2928 (−0.3 ppm). Anal. Calcd for $C_{28}H_{40}N_2PBr\cdot{}^1/_2CH_2Cl_2$: C, 61.35; H, 7.41; N, 5.02. Found: C, 61.67; H, 7.69; N, 5.02.

(^{Mes}BIAN)P-Br (7). Reagents: PBr_3 (200 mg, 0.74 mmol); cyclohexene (180 mg, 2.22 mmol); ^{Mes}BIAN (207 mg, 0.74 mmol). Reaction mixture color changes: gradually darkens from orange to dark red. Product: purple solid powder characterized as $\mathbf{7}\cdot 1.5CH_2Cl_2$. Yield: 71% (334 mg, 0.53 mmol). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 202.0. ^1H NMR ($CDCl_3$): δ 7.67 (d, $^3J_{HH}$ = 8.4, 2H), 7.33 (t, $^3J_{HH}$ = 8.1, 2H), 7.09 (s, 4H), 6.82 (d, $^3J_{HH}$ = 6.9, 2H), 5.30 (s, 1.3 H, CH_2Cl_2), 2.52 (s, 12H, *o*-CH_3), 2.41 (s, 6H, *p*-CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 139.6 (N−C), 136.5, 130.7, 130.4, 128.1, 127.9, 127.2, 120.9, 119.9, 21.6 (*p*-CH_3), 19.8 (*o*-CH_3). HRMS: calcd for $C_{30}H_{28}N_2P^+$ 447.1990, found 447.2003 (+2.9 ppm). Anal. Calcd for $C_{30}H_{28}N_2PBr\cdot 1.5CH_2Cl_2$: C, 57.78; H, 4.77; N, 4.28. Found: C, 57.84; H, 5.15; N, 4.06.

Crystals of **7** suitable for analysis by single-crystal X-ray diffraction experiments were obtained by the slow evaporation of a solution of the compound in acetonitrile.

(^{Dipp}BIAN)P-Br (8). Reagents: PBr_3 (200 mg, 0.74 mmol); cyclohexene (180 mg, 2.22 mmol); ^{Dipp}BIAN (373 mg, 0.74 mmol). Reaction mixture color changes: gradually changes from orange to dark red. Product: light brown solid **8**. Yield: 83% (375 mg, 0.61 mmol). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 202.1. ^1H NMR ($CDCl_3$): δ 7.88 (d, $^3J_{HH}$ = 6.0, 2H), 7.56 (m, 2H), 7.3−7.1 (m, 6H), 6.64 (d, $^3J_{HH}$ = 6.3, 2H), 3.03 (m, 4H), 1.24 (d, $^3J_{HH}$ = 6.3, 12H), 0.97 (d, $^3J_{HH}$ = 6.7, 12H). ^{13}C NMR ($CDCl_3$): δ 161.0, 147.9, 135.6, 129.0, 128.0, 127.3, 125.1, 123.5, 120.8, 29.0, 28.7, 25.6, 25.0, 23.4, 23.2. HRMS: calcd for $C_{36}H_{40}N_2P^+$ 531.2929, found 531.2946 (+3.2 ppm). Anal. Calcd for $C_{36}H_{40}N_2PBr$: C, 70.70; H, 6.59; N, 4.58. Found: C, 70.95; H, 7.32; N, 4.85.

Synthesis of [(^{Mes}DAB)P][PF_6] (9[PF_6]). To a flask containing KPF_6 (115 mg, 0.50 mmol) was added a solution of ^{Mes}DABP-Br (215 mg, 0.50 mmol) in CH_3CN (40 mL). The reaction mixture was stirred overnight before the resulting KBr was removed by filtration. The volatile components were removed from the filtrate under reduced pressure to give a crude product, which was washed in pentane and sonicated for 1 h. The product was extracted with acetonitrile, and removal of the volatile components provided the dark red solid [(^{Mes}DAB)P][PF_6]. Yield: 85% (210 mg, 0.423 mmol). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −143.9 (sept, $^1J_{P-F}$ = 712), 199.8. ^1H NMR ($CDCl_3$): δ 7.14 (s, 4 H, *m*-H_{Mes}), 2.40 (s, 6H, CH_3), 2.24 (s, 6H, *p*-CH_3), 2.11 (s, 12H, *o*-CH_3). ^{13}C NMR ($CDCl_3$): δ 144.93 (s, N−C), 142.14 (s, *i*-C_{Mes}), 134.96 (s, *o*-C_{Mes}), 130.84 (s, *m*-C_{Mes}), 129.78 (s, *p*-C_{mes}), 21.64 (s, CH_3), 18.10 (s, *o*-CH_3), 13.01 (s, *p*-CH_3). $^{19}F\{^1H\}$ NMR ($CDCl_3$): δ −72.26 (d, $^1J_{P-F}$ = 712). HRMS: calcd for $C_{22}H_{28}N_2P^+$ 351.1990, found 351.1984 (−1.7 ppm); calcd for PF_6^- 144.9642, found 144.9780 (+95 ppm).

Synthesis of [(^{Mes}DAB)P][$B(C_6F_5)_4$] (9[$B(C_6F_5)_4$]). To a flask containing $LiB(C_6F_5)_4\cdot OEt_2$ (380 mg, 0.50 mmol) was added a solution of [(^{Mes}DAB)P][Br] (215 mg, 0.50 mmol) in CH_3CN (40 mL). The reaction mixture was stirred overnight before filtration to remove LiBr. The filtrate was concentrated under reduced pressure to give a crude product, which was washed in pentane and sonicated for 1 h. Any remaining volatile components were removed under reduced pressure to afford the light brown solid [(^{Mes}DAB)P][$B(C_6F_5)_4$]. Yield: 92% (476 mg, 0.463 mmol). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 200.8. ^1H NMR ($CDCl_3$): δ 7.18 (s, 4 H, *m*-H_{Mes}), 2.42 (s, 6 H, CH_3),

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Table 1. Summary of X-ray Crystallographic Data for (^{Mes}BIAN)P−Br (7) and [(^{Mes}DAB)P][I_3] (9[I_3])

	(^{Mes}BIAN)P−Br	[(^{Mes}DAB)P][I_3]
empirical formula	$C_{30}H_{28}BrN_2P$	$C_{22}H_{28}I_3N_2P$
formula wt	527.42	732.13
temp (K)	174(2)	174(2)
wavelength (Å)	0.710 73	
habit, color	prism, red	plate, orange
cryst syst	monoclinic	orthorhombic
space group	$P2_1/c$	$P2_12_12_1$
unit cell dimens		
a (Å)	11.4785(12)	14.0085(14)
b (Å)	17.6796(18)	15.5780(16)
c (Å)	37.784(4)	24.014(2)
α (deg)	90	90
β (deg)	93.030(2)	90
γ (deg)	90	90
V (Å^3)	7657.1(14)	5240.5(9)
Z	12	8
calcd density (g cm^{-3})	1.373	1.856
abs coeff (mm^{-1})	1.694	3.650
F(000)	3264	2784
θ range for data collection (deg)	1.08−27.50	1.56−27.50
limiting indices	$-14 \le h \le 14$, $-22 \le k \le 22$, $-49 \le l \le 47$	$-18 \le h \le 18$, $-19 \le k \le 20$, $-30 \le l \le 31$
no. of rflns collected	84 740	59 223
no. of indep rflns	17 321	11 915
R_{int}	0.3695	0.0550
abs cor	SADABS	
refinement method	full-matrix least squares on F^2	
no. of data/restraints/params	17 321/0/919	11 915/0/506
goodness of fit on F^2	0.975	1.029
final R indices[a] ($I > 2\sigma(I)$)	R1 = 0.1038, wR2 = 0.1603	R1 = 0.0464, wR2 = 0.0900
R indices (all data)	R1 = 0.3088, wR2 = 0.2386	R1 = 0.0772, wR2 = 0.1068
largest diff map peak and hole (e Å^{-3})	1.544 and −0.511	1.950 and −0.534

[a] $R1(F) = \sum(|F_o| - |F_c|)/\sum|F_o|\}$ for reflections with $F_o > 4(\sigma(F_o))$. $wR2(F^2) = \{\sum w(|F_o|^2 - |F_c|^2)^2/\sum w(|F_o|^2)^2\}^{1/2}$, where w is the weight given each reflection.

2.18 (s, 6 H, *p*-CH_3), 2.06 (s, 12 H, *o*-CH_3). ^{13}C NMR ($CDCl_3$): δ 148.2 (d(m), J_{C-F} = 234, C_6F_5 *m*-C), 143.4 (N−C), 142.6 (*i*-C_{Mes}), 133.7 (*o*-C_{Mes}), 130.7 (*m*-C_{Mes}), 21.1 (CH_3), 17.3 (*o*-CH_3), 12.2 (*p*-CH_3). ^{11}B{^{1}H} NMR ($CDCl_3$): δ −12.27. ^{19}F{^{1}H} NMR ($CDCl_3$): δ −166.22 (t, 8F, $^3J_{F-F}$ = 17.8, *m*-F), −162.42 (t, 4F, $^3J_{F-F}$ = 20.9, *o*-F), −132 (d, 8F, $^3J_{F-F}$ = 24.0, *o*-F). HRMS: calcd for $C_{22}H_{28}N_2P^+$ 351.1990, found 351.1987 (−0.9 ppm); calcd for $BC_{24}F_{20}^-$ 679.0358, found 678.9781 (−1.1 ppm).

Synthesis of [(^{Mes}DAB)P][OTf] (9[OTf]). To a flask containing trimethylsilyltrifluoromethanesulfonate (TMS-OTf; 111 mg, 0.50 mmol) was added a solution of [(^{Mes}DAB)P][Br] (215 mg, 0.50 mmol) in CH_2Cl_2 (40 mL). The reaction mixture was stirred overnight. The volatile components were removed under reduced pressure to give a crude product, which was washed in pentane and sonicated for 1 h. The product was extracted with acetonitrile, and removal of the volatile components provided the dark brown solid [(^{Mes}DAB)P][OTf]. Yield: 90% (224 mg, 0.448 mmol). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 199.6. ^{1}H NMR ($CDCl_3$): δ 7.14 (s, 4 H, *m*-H_{Mes}), 2.40 (s, 6 H, CH_3), 2.28 (s, 12 H, *o*-CH_3), 2.12 (s, 6 H, *p*-CH_3). ^{13}C NMR ($CDCl_3$): δ 144.90 (s, N−C), 142.15 (s, *i*-C_{Mes}), 134.89 (s, *o*-C_{Mes}), 130.84 (s, *m*-C_{Mes}), 129.78 (s, *p*-C_{Mes}), 21.62 (s, CH_3), 18.17 (s, *o*-CH_3), 13.23 (s, *p*-CH_3). ^{19}F{^{1}H} NMR ($CDCl_3$): δ −78.62. HRMS: calcd for $C_{22}H_{28}N_2P^+$ 351.1990, found 351.1996 (+1.7 ppm); calcd for $SO_3CF_3^-$ 148.9520, found 148.9662 (+96 ppm).

Synthesis of [(^{Mes}DAB)P][$AlBr_4$] (9[$AlBr_4$]). To a flask containing $AlBr_3$ (95 mg, 0.357 mmol) was added a solution of [(^{Mes}DAB)P][Br] (154 mg, 0.357 mmol) in toluene (40 mL). The volatile components were removed from the filtrate under reduced pressure to give a crude product, which was washed in pentane and sonicated for 1 h. The product was extracted with acetonitrile, and removal of the volatile components provided the dark purple solid [(^{Mes}DAB)P][$AlBr_4$]. Crude yield: 72% (180 mg, 0.258 mmol). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 197.89. ^{1}H NMR ($CDCl_3$): δ 7.16 (s, 4 H, *m*-H_{Mes}), 2.41 (s, 6 H, CH_3), 2.28 (s, 6H, *p*-CH_3), 2.12 (s, 12H, *o*-CH_3). ^{13}C NMR ($CDCl_3$): δ 143.8 (N−C), 142.0 (*i*-C_{Mes}), 134.2 (s, *o*-C_{Mes}), 130.6 (s, *m*-C_{Mes}), 129.1 (s, *p*-C_{Mes}), 21.2 (s, CH_3), 18.1 (s, *o*-CH_3), 13.3 (s, *p*-CH_3). ^{27}Al{^{1}H} NMR ($CDCl_3$): δ 80.4. HRMS: calcd for $C_{22}H_{28}N_2P^+$ 351.1990, found 351.2005 (+4.2 ppm); calcd for $AlBr_4^-$ 342.6549, found 342.6568 (+5.5 ppm).

Synthesis of [(^{Mes}DAB)P]"[$SnCl_5$]" (9"[$SnCl_5$]"). A solution of PCl_3 (100 mg, 0.74 mmol) and ^{Mes}DAB (237 mg, 0.74 mmol) in dichloromethane (40 mL) was added to a flask containing $SnCl_2$ (139 mg, 0.74 mmol). Upon addition the solution turned from green to dark red. The resulting reaction mixture was stirred overnight before the volatiles were removed under reduced pressure to produce the dark red solid [(^{Mes}DAB)P][$SnCl_5$]. Crude yield: 78% (375 mg, 0.58 mmol). Anal. Calcd for $C_{22}H_{28}N_2PSnCl_5$: C, 40.81; H, 4.36; N, 4.33. Found: C, 41.60; H, 4.57; N, 4.21. ^{31}P{^{1}H} NMR ($CDCl_3$): δ 199.9, 198.1 (please see the Results and Discussion); HRMS: calcd for $C_{22}H_{28}N_2P^+$ 351.1990, found 351.1989 (−0.3 ppm); calcd for $SnCl_3^-$ 224.8088, found 224.7971 (−52.0 ppm); calcd for $SnCl_5^-$ 294.7465, found 294.7616 (+51.2 ppm).

Synthesis of [(^{Mes}DAB)P][I_3] (9[I_3]). To a flask containing PI_3 (200 mg, 0.485 mmol) was added a solution of ^{Mes}DAB (155 mg, 0.485 mmol) in toluene (40 mL). Upon addition the solution turned from red to dark red. The resulting reaction mixture was stirred overnight before the volatiles were removed under reduced pressure to produce the dark red solid [(^{Mes}DAB)P][I_3]. Recrystallization by slow evaporation in acetonitrile yielded red crystals suitable for analysis by single-crystal X-ray diffraction. Crude yield: 76% (270 mg, 0.369 mmol). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 201.78. ^{1}H NMR ($CDCl_3$): δ 7.18 (s, 4 H, *m*-H_{Mes}), 2.43 (s, 6H, CH_3), 2.31 (s, 6H, *p*-CH_3), 2.18 (s, 12H, *o*-CH_3). ^{13}C NMR ($CDCl_3$): δ 142.80 (s, N−C), 141.99 (s, *i*-C_{Mes}), 134.33 (s, *o*-C_{Mes}), 130.81 (s, *m*-C_{Mes}), 129.40 (s, *p*-C_{Mes}), 21.49 (s, CH_3), 18.71 (s, *o*-CH_3), 13.62 (s, *p*-CH_3). HRMS: calcd for $C_{22}H_{28}N_2P^+$ 351.1990, found 351.1973 (−4.9 ppm); calcd for I_3^- 380.7134, found 380.7133 (−0.3 ppm). Anal. Calcd for

$C_{22}H_{28}N_2PI_3$: C, 36.09; H, 3.85; N, 3.83. Found: C, 38.32; H, 4.12; N, 3.91.

X-ray Crystallography. Each crystal was covered in Nujol and placed rapidly into a cold N_2 stream of the Kryo-Flex low-temperature device. The data were collected using the SMART[41] software package on a Bruker APEX CCD diffractometer employing a graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å) source. Hemispheres of data were collected using counting times of 10−30 s per frame at −100 °C. The details of crystal data, data collection, and structure refinement are given in Table 1. Data reductions were performed using the SAINT[42] software package, and the data were corrected for absorption using SADABS.[43] The structures were solved by direct methods using SIR97[44] and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-H atoms using SHELXL-97[45] and the WinGX[46] software package, and thermal ellipsoid plots were produced using SHELXTL.[45]

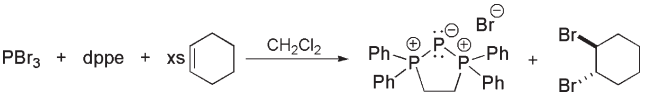
Results and Discussion

Recently, we reported that the reaction of PBr_3 with chelating diphosphines such as 1,2-bis(diphenylphosphino)-ethane (dppe) produces the corresponding P^I bromide salt in quantitative yield with the concomitant elimination of 1,2-dibromocyclohexane, as illustrated in Scheme 3.[38] The cyclohexene behaves as a sequestering agent for the 1 equiv of Br_2 that is formally eliminated in the redox process, and the volatility of both cyclohexene and 1,2-dibromocyclohexane greatly simplifies the purification and isolation of the salts prepared using this approach.

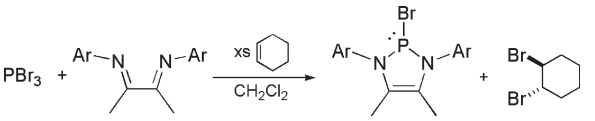
In light of the successful redox cycloaddition syntheses of NHP salts using the P^I synthons described above, we reasoned that a similar approach might be suitable for the preparation of N-heterocyclic bromophosphines. Thus, the treatment of a solution containing an α-diimine of the general type 1,4-bis(aryl)-2,3-dimethyl-1,4-diazabutadiene with a solution containing 1 equiv of PBr_3 in the presence of excess cyclohexene results in the formation of the corresponding N-heterocyclic bromophosphines, as illustrated in Scheme 4. Test reactions confirmed that the starting diimines do not undergo cycloaddition reactions, or exhibit any other observable reactivity, with cyclohexene. The resultant materials were completely characterized by multinuclear NMR spectroscopy, mass spectrometry, and elemental analysis and confirm the formation of the anticipated cyclic diaminobromo-phosphines (^{Mes}DAB)P-Br **5** and (^{Dip}DAB)P-Br **6**. It should be noted that, in the absence of cyclohexene, the reaction of PBr_3 and the α-diimines is considerably slower and generates several P-containing products, including modest amounts of the diaminobromophosphines.

The formation of the cyclic diaminobromophosphines is consistent with the formal generation of the synthon "P^I−Br", with the concomitant elimination of 1,2-dibromocyclohexane (identified by multinuclear NMR spectroscopy), which undergoes a formal 4 + 2 electron cycloaddition with the α-diimine. This cycloaddition process results in the formal transfer of two electrons from the putative P^I center to the diimine and thus produces the observed P^{III} center ligated by the corresponding unsaturated diamido dianion. It should be emphasized that mechanistic investigations on related phosphorus(+1) systems with nonreducible ligands such as diphosphines indicate that such reactions most likely occur in a stepwise manner and the redox process occurs after the phosphorus atom is chelated by the ligand;[47] it is probable that the reactions described above occur in a similar manner.

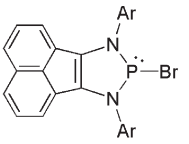
Scheme 3. Quantitative Synthetic Approach to a Chelated P^I Bromide Salt[38]



Scheme 4. Redox Cycloaddition Preparation of N-Heterocyclic Bromophosphines using Aryl-DAB ligands: 5 (Ar = Mes) and 6 (Ar = Dipp)



As Cowley and co-workers had demonstrated that related redox cycloaddition reactions occur with the extended aromatic α-diimines of the BIAN family,[33,48] we also investigated the reactivity of the "P^I−Br" synthon with two aryl-BIAN ligands; they both produce the desired bromophosphines **7** and **8** in quantitative yield according to ^{31}P NMR spectroscopy. All of the other spectroscopic and spectrometric methods were consistent with the proposed formulations and warrant no additional comment. In the case of the mesitylene-substituted BIAN ligand, we were able to obtain a solid from the recrystallization of **7** in acetonitrile that was suitable for examination by single-crystal X-ray diffraction studies. Although the data from even the best of the crystals that we examined was of low quality, the solution and refinement of the structure confirms the identity and connectivity of the compound.



Ar = Mes (**7**) or Dipp (**8**)

The bromophosphine **7** crystallizes in the space group $P2_1/c$ with three crystallographically independent molecules present in the asymmetric unit, as illustrated in Figure 1. The three independent molecules adopt very similar structures and, in each case, exhibit metrical parameters (Table 2) that are consistent with the BIAN ligand having been reduced during the progress of the reaction. For example, the endocyclic C−N bonds range from 1.380(10) to 1.402(10) Å, in comparison to the distance of 1.2662(16) Å reported for the

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(42) *SAINTPlus*; Bruker AXS, Madison, WI, 2001.
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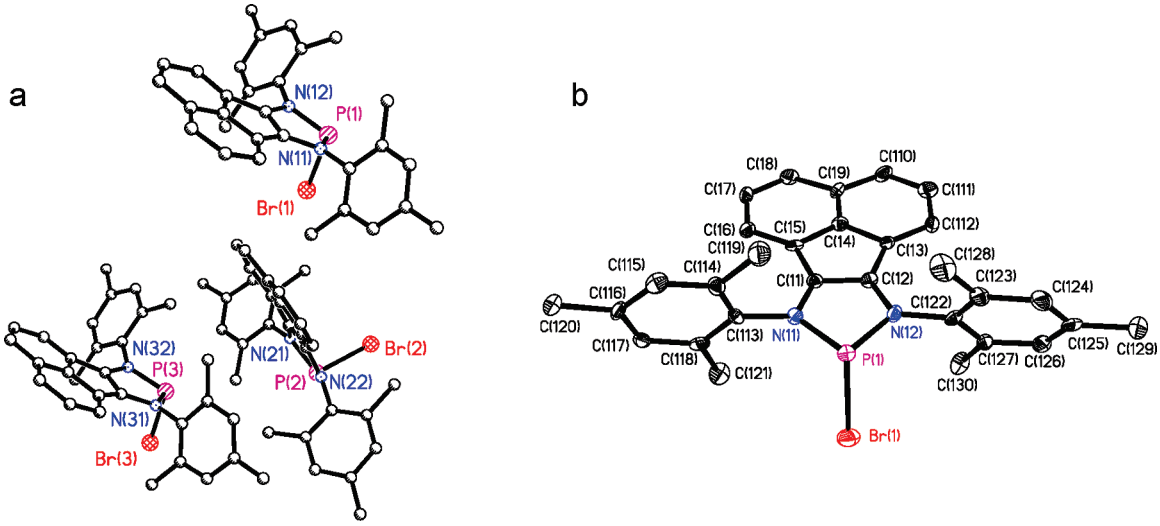


Figure 1. Asymmetric unit for **7** showing (a) the three crystallographically independent molecules and (b) a thermal ellipsoid plot (30% probability surface) illustrating the numbering scheme employed for each molecule. In each instance, hydrogen atoms are omitted for clarity.

Table 2. Selected Metrical Parameters for Bromophosphine 7 and NHP Salt 9[I_3][a]

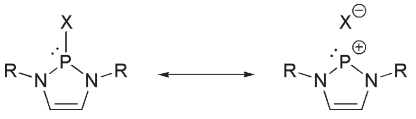
	7			9[I_3]	
param	molecule 1	molecule 2	molecule 3	molecule 1	molecule 2
			Distances		
P(x)−Br(x)	2.432(3)	2.452(3)	2.506(3)		
P(x)−N(x1)	1.673(7)	1.685(7)	1.680(7)	1.665(5)	1.658(5)
P(x)−N(x2)	1.675(7)	1.692(7)	1.696(7)	1.667(6)	1.680(6)
C(x1)−N(x1)	1.399(10)	1.380(10)	1.387(9)	1.376(8)	1.380(8)
C(x2)−N(x2)	1.402(10)	1.389(10)	1.398(10)	1.371(8)	1.370(8)
C(x1)−C(x2)	1.350(11)	1.362(10)	1.348(11)	1.356(8)	1.359(9)
I(x1)−I(x2)				2.9814(9)	2.8821(8)
I(x2)−I(x3)				2.8632(9)	2.9762(8)
			Angles		
N(x1)−P(x)−N(x2)	91.2(3)	91.2(3)	91.7(3)	88.5(3)	89.0(3)
$\sum\angle$@P	298.4(5)	295.7(5)	296.8(5)		
I(x1)−I(x2)−I(x3)				177.22(2)	179.10(2)

[a] Distances are reported in angstroms and angles in degrees.

free ligand,[49] and the endocyclic C−C distances for the five-membered ring range from 1.348(11) to 1.362(10) Å, in comparison to the distance of 1.528(2) Å in the uncomplexed ligand. Furthermore, the C−N and C−C bond distances in **7** are also only marginally different from those observed in the related cations in the salts [(^{Dipp}BIAN)P][A] (A = $SnCl_5$·THF, I_3),[33] which have C−N distances ranging from 1.351(5) to 1.366(5) Å and C−C distances of 1.395(5) and 1.380(8) Å; the P−N distances of 1.673(7)−1.696(7) Å in **7** are also consistent with the P−N distances in the cations of 1.694(4)−1.700(4) Å.

There are surprisingly few compounds that contain the N_2P^{III}−Br moiety reported in the Cambridge Structural Database (CSD)[50] for comparison, and the P−Br distances in **7** (2.432(3)−2.506(3) Å) are very long in relation to the P−Br distances in those diamidobromophosphines (range: 2.282(1)−2.324(1) Å).[51,52] The long bonds in the bromophosphine are consistent with the long phosphorus−element bonds observed for NHP-H, NHP-Cl, and other compounds containing the unsaturated NHP core. The unusual length of these bonds has been explained as arising from the hyperconjugation of the π system on the NHP core with the antibonding σ^* orbital of the phosphorus−element bond, which increases the relative weight of the "no-bond" canonical structure in the putative "bond−no-bond" resonance

Scheme 5. "Bond−No-Bond" Resonance Postulated for Some Substituted NHP Derivatives (X = H, Cl, Br, PR_2, etc.)



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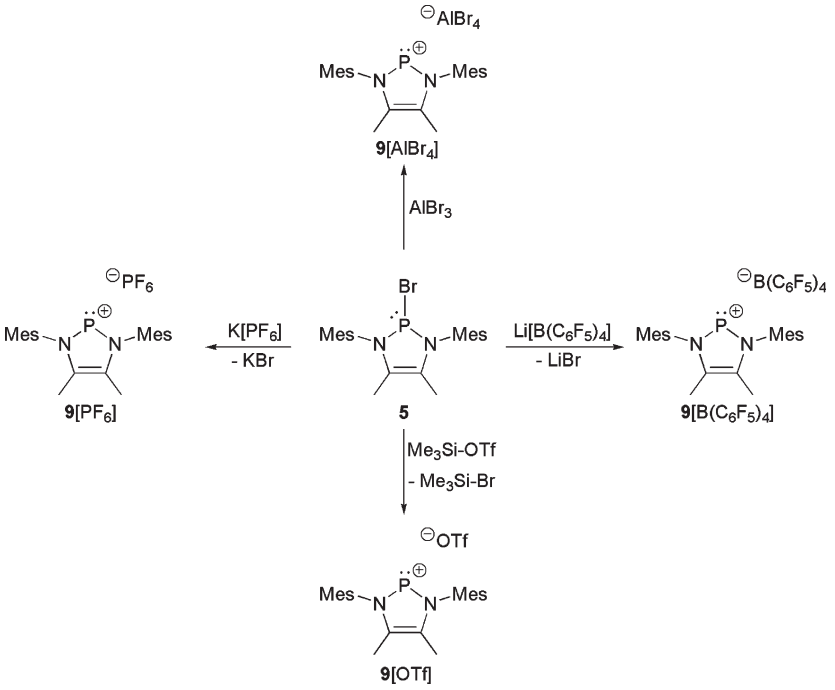
Scheme 6. Bromide Abstraction Reactions of 5 That Produce NHP Salts of 9



scheme illustrated in Scheme 5.[4,53] In spite of the poor quality of the data, it is perhaps also worth noting that the specific P−Br distances in the three independent molecules of **7** in the crystal structure appear to correlate qualitatively to the number of close contacts (within $\sum r_{vdw}$) to the phosphorus and bromine atoms in the given molecule: there are three close contacts to the molecule with the longest bond, two for the molecule with the intermediate distance, and one for the molecule with the shortest bond.

To confirm the applicability of the N-heterocyclic bromophosphines obtained using the method outlined above for the preparation of NHP salts, we examined the reaction of **5** with a selection of common anion metathesis or halide abstraction agents. As illustrated in Scheme 6, the treatment of a solution of **5** in either methylene chloride or acetonitrile with a solution containing an equimolar quantity of $AlBr_3$ results in the rapid and quantitative formation of the NHP salt [(^{Mes}DAB)P][$AlBr_4$] (**9**[$AlBr_4$]), as indicated by multinuclear NMR experiments. Similarly, anion metathesis reactions between **5** and K[PF_6] or Li[$B(C_6F_5)_4$ result in the complete loss of the ^{31}P NMR resonance at δ 189 ppm for **5** and the observation of a new signal at δ 200 ppm for the uncoordinated phosphenium cation **9**. Finally, the treatment of **5** with Me_3Si-OTf in dichloromethane produced **9**[OTf], as indicated by the ^{31}P resonance at δ 200 ppm.

We have been unable as of yet to obtain crystalline samples of the NHP salts of **9** derived from the brominated precursor **5** and, although the spectroscopic investigations confirm the formation of the desired products, we desired structural authentication of the cation. In an attempt to obtain such information, we employed the direct NHP redox syntheses reported previously. Thus, the diimine ^{Mes}DAB was treated with PCl_3 and $SnCl_2$ in CH_2Cl_2 in an attempt to produce **9**[$SnCl_5$]. While the microanalytical data are consistent with the proposed formula for **9**[$SnCl_5$], we were surprised to observe two distinct singlet signals in the solution ^{31}P NMR spectrum at 200 and 198 ppm. Each of these signals is consistent with the cation **9**, and we hypothesized that the close interaction of two different anions with the cation may explain the observation of two signals.[20] In fact, negative ion mode ESI mass spectra of solutions of "**9**[$SnCl_5$]" contain signal manifolds that confirm the presence of both [$SnCl_3^-$] and [$SnCl_5^-$] anions and are consistent with our supposition. The reason for the unexpected, but reproducible, behavior remains unclear; however, it is tangential to the work presented herein and was not pursued further. Thus, in order to obtain crystalline material containing **9** suitable for single-crystal X-ray diffraction experiments, we employed the other redox approach involving the disproportionation of phosphorus triiodide in the presence of the diimine. Gratifyingly, the corresponding phosphenium triiodide salt **9**[I_3] is obtained quantitatively by the treatment of ^{Mes}DAB with PI_3 in dichloromethane and concentration of a solution of the salt in acetonitrile did indeed produce crystals suitable for X-ray crystallography.

The salt **9**[I_3] crystallizes in the space group $P2_12_12_1$ with two pairs of crystallographically independent cations and anion in the asymmetric unit, as illustrated in Figure 2. As one would anticipate, the metrical parameters (also in Table 2) in the cation are completely consistent with those reported for related unsaturated NHP cations and do not mandate extensive commentary. For example, the P−N distances, which range from 1.655(5) to 1.680(6) Å, are indistinguishable from the P−N distance of 1.665(3) Å reported for the related triiodide salt in which the carbon atoms in the five-membered ring are substituted with hydrogen rather than with methyl groups.[54] The metrical parameters of the triiodide anions are likewise completely typical and are consistent with those anticipated for salts in which there is not extensive interaction between the cations and the anions.

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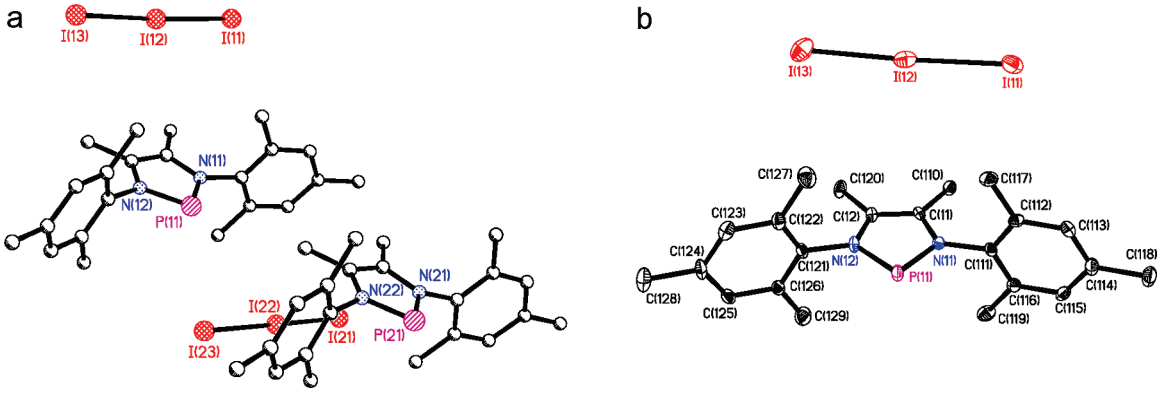

Figure 2. Depiction of the asymmetric unit for [^{Mes}NHP][I_3] showing (a) the two crystallographically independent ion pairs and (b) a thermal ellipsoid plot (30% probability surface) illustrating the numbering scheme employed for each molecule. In each instance, hydrogen atoms are omitted for clarity.

While the details of the metrical parameters of the salt **9**[I_3] are relatively unimportant, the structure clearly contains the cation postulated to exist in the products of the halide-abstraction reactions described above. Importantly, all of the spectroscopic data for the cation in **9**[I_3] are identical with those observed for the salts generated from the bromophosphine reagent **5** obtained using our new PBr_3/cyclohexene synthetic approach. Thus, the crystallographic results confirm the spectroscopic identification and illustrate the viability of our new synthetic approach.

The investigations outlined above indicate clearly that the redox-cycloaddion methodology may be employed for the convenient synthesis of unsaturated diaminobromophosphine precursors to N-heterocyclic phosphenium cations. Given that salt metathesis, which is often the most important and sometimes only synthetic approach to many inorganic or organometallic compounds, does not work well for the preparation of unsaturated NHP precursors, the mild and simple redox approach described above appears to provide an effective alternative route to this increasingly important class of reagent.

Conclusions

The treatment of α-diimines with PBr_3 in the presence of excess cyclohexene produces the corresponding cyclic diaminobromophosphines in good yield. In each instance, the results are consistent with product being derived from the formal 4 + 2 cycloaddition and electron transfer between the α-diimine with a putative "P^I−Br" fragment. For one of the α-diimines, the resultant diaminobromophosphine was shown to be a useful reagent for the generation of the corresponding N-heterocyclic phosphenium salts by several common methods of anion abstraction. More generally, this reaction adds to the growing number of syntheses involving the cycloaddition reactions of halogenated low-oxidation-state precursors and synthons from throughout the p block[55−60] with suitable chelating ligands; such reactions provide synthetic alternatives to metathesis chemistry for the preparation of inorganic heterocyclic ligands.

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Supporting Information Available: CIF files giving crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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