This paper is published as part of a *Dalton Transactions* theme issue on:

Main group chemistry: from molecules to materials

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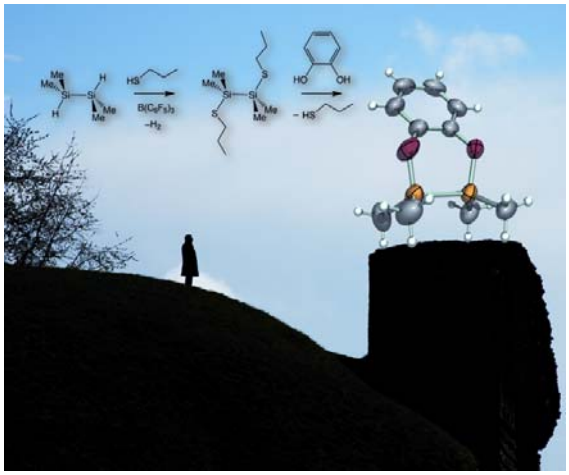
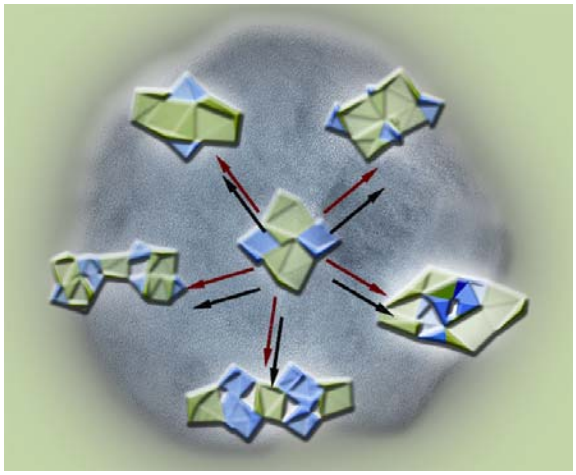
Published in issue 26, 2008 of *Dalton Transactions*





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N-Heterocyclic phosphenium cations: syntheses and cycloaddition reactions†

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Received 30th January 2008, Accepted 17th March 2008
First published as an Advance Article on the web 22nd April 2008
DOI: 10.1039/b801684d

A series of trifluoromethanesulfonate (OTf) salts of *N*-heterocyclic phospheniums (NHP) bearing phenyl (**1a**), *para*-methoxyphenyl (**1b**), 2,6-diisopropylphenyl (**1c**) and mesityl (**1d**) substituents is reported. The compounds **1b–d** are made by a modification to a literature procedure that improves the overall yields for **1c** and **1d** by 15 and 23%, respectively. Two unwanted side-products in the synthesis of **1d**, the diammonium salt, $[(2,6\text{-}i\text{Pr-}C_6H_3)N(H)_2CH_2CH_2N(H)_2(2,6\text{-}i\text{Pr-}C_6H_3)]Cl_2$ (**4**) and the bisphosphine $(2,6\text{-}i\text{Pr-}C_6H_3)N(PCl_2)CH_2CH_2N(PCl_2)(2,6\text{-}i\text{Pr-}C_6H_3)$ (**5**), are crystallographically characterized, as is the intermediate cyclic chlorophosphine, $C1PN(4\text{-}OMe\text{-}C_6H_4)CH_2CH_2N(4\text{-}OMe\text{-}C_6H_4)$ (**3b**). The phenyl-substituted NHP **1a** is fully characterized, including by X-ray crystallography, for the first time; this compound contains a short P–O contact of 2.1850(14) Å. Cycloaddition reactions of **1a–d** with 2,3-dimethyl-1,3-butadiene give the expected spirocyclic phospholeniums, 7,8-dimethyl-1,4-diaryl-1,4-diaza-5-phopshoniaspiro[4.4]non-7-ene, as their OTf salts (**6a–d**), while reactions with *N*,*N*′-dimesityl-1,4-diaza-1,3-butadiene give, except in the case of **1c**, which is too bulky to react, the aza analogues, 1,4-dimesityl-6,9-diaryl-1,4,6,9-tetraaza-5-phosphoniaspiro[4.4]non-2-ene (**7a**, **7b** and **7d**). The sterically congested **7d** is in thermal equilibrium with **1d** and free diazadiene, and undergoes a substitution reaction with 2,3-dimethyl-1,3-butadiene to give **6d**.

Introduction

N-Heterocyclic phosphenium cations (NHP, Chart 1) are the "carbon copies"[1] of the now ubiquitous Arduengo-type carbenes (NHC, Chart 1); both species may have saturated or unsaturated "backbones." Although the isolation of free NHP[2] preceded that of their carbon analogues,[3] they have garnered much less attention because the introduction of NHC as "phosphine replacement" ligands[4] precipitated nothing less than a paradigm shift in the field of homogeneous catalysis. Since their inception in the early 1990s, metal–NHC complexes have filled ever-expanding, and ever more successful, roles as catalysts primarily because their remarkable thermal, hydrolytic and oxidative stabilities give them significant advantages over their phosphine counterparts,[5] *e.g.*, in a variety of Pd-catalyzed C–C and C–N bond-forming reactions,[6] and in Ru-catalyzed olefin metatheses.[7]

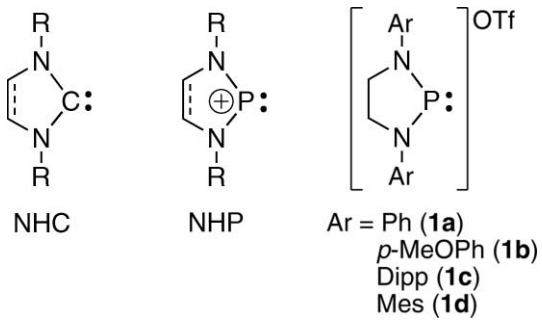

Chart 1 Comparison between *N*-heterocyclic carbenes (NHC) and -phospheniums (NHP), and compounds made in this study.

Reinvigorated research into NHP over the last several years has been spurred both by the similarities between NHP and NHC[8] and by the observation that although these species are isovalent, they are electronically inverse: NHC are strong σ-donors and weak π-acceptors, whereas NHP are weak σ-donors and good π-acceptors on account of the formal positive charge and isotropic s- (as opposed to sp^2-) character of the "lone pair" orbital.[9] Therefore, the two families should show reciprocal reactivity in transition metal chemistry.[10] With this in mind, new synthetic routes have been developed, *e.g.*, a one-step, redox route to unsaturated NHP,[11] and new types have emerged, *e.g.*, with diaminonaphthalene[10,12] and diaminocyclohexane[13–15] "backbones," together with a burgeoning metal chemistry[16,17] of Mo,[18] W,[16] Co,[19] Rh[10,20] and Pt.[21]

The present study focuses on fully saturated NHP, which are isovalent and isostructural to the imidazol-2-ylinylidenes.[22] Our interest in these molecules lies in their ability to act both as Lewis acids and Lewis bases.[23] In this paper, we report an improved general synthesis of the known saturated NHP with Ar = *p*-methoxyphenyl (**1b**), 2,6-diisopropylphenyl (**1c**) and mesityl (**1d**) as their trifluoromethanesulfonate (OTf) salts (Chart 1). In addition, we make and fully characterize, including by X-ray crystallography, the phenyl-substituted NHP (**1a**), which has hitherto remained poorly described in the literature. We probe the amphoteric character of these cations in cycloaddition reactions with 2,3-dimethyl-1,3-butadiene and *N*,*N*′-dimesityl-1,4-diaza-1,3-butadiene.

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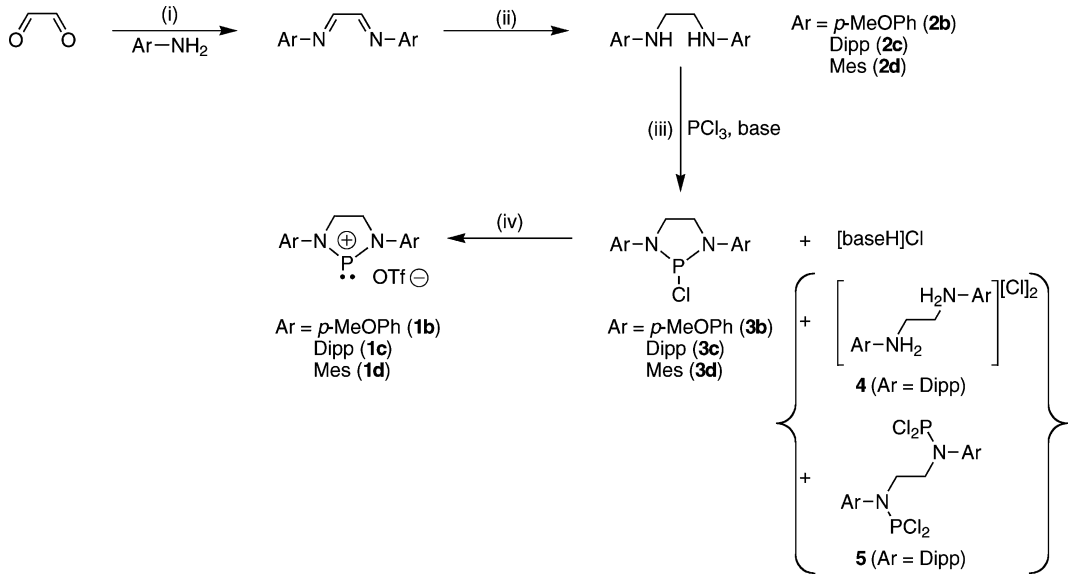
† CCDC reference numbers 676351–676354. For crystallographic data in CIF format see DOI: 10.1039/b801684d



Scheme 1 Synthesis of NHP **1a–d**. (i) EtOH, r.t. or reflux, 12–18 h, 70–85%. Method of Baker and coworkers: (ii) $NaBH_4$, EtOH, reflux, 77–87%; (iii) Et_3N, CH_2Cl_2, 0 °C–r.t., or 0 °C, 62–89%; (iv) AgOTf (in toluene) or $TlBAr_F$ (in CH_2Cl_2), 84–91%. Our method: (ii) $LiAlH_4$, Et_2O, 0 °C–r.t., 89–95%; (iii) NMM, THF, −78 °C–r.t., 18 h, 73–92%; (iv) Me_3SiOTf or AgOTf, toluene, 86–95%.

Results and discussion

Synthesis and structural analysis

The general synthetic approach to saturated NHP, developed by Baker and coworkers,[20] is shown in Scheme 1. The requisite aromatic groups are installed by condensation of the appropriate arylamine with glyoxal. The resulting diimine is then reduced to afford a symmetrical diamine that is subsequently treated with trichlorophosphine and base to give the cyclic chlorodiaminophosphine derivative. Finally, chloride abstraction gives the desired NHP. We have used the same basic approach, but have optimized the conditions for each step to circumvent several problems arising from the original synthesis. These were (i) the reduction of diimines by borohydride in our hands was unreliable and low-yielding; and (ii) the dehydrohalogenation step with Et_3N as base was complicated in several respects: by the formation of large quantities of diammonium salt side-products, by 1 : 2 reactions of diamine–phosphine (both shown in curly braces in Scheme 1), and by difficulty in removing stoichiometric $[Et_3NH]Cl$ from the reaction mixture. The overall reported yields starting from the diimines were modest to good: 43% (**1d**), 57% (**1c**) and 65% (**1b**).

Our initial modification to improve the synthesis was to switch from using $NaBH_4$ to $LiAlH_4$ as the reducing agent in the synthesis of the diamines. The reduction now proceeded smoothly and cleanly to give **2b–d** in very high yields (89–95%); **2a** was made differently (*vide infra*). We also conducted a survey of other bases to install the phosphine in the dehydrohalogenation step, and finally discovered that *N*-methylmorpholine (NMM) was ideal: excess could easily be pumped away, it minimized the formation of diammonium salt (*e.g.*, **4**) and 1 : 2 side-products (*e.g.*, **5**), and it was trivially separated from the reaction mixture by precipitation as the hydrochloride salt, which was less soluble than $[Et_3NH]Cl$. (*N*-methylmorpholine has been used previously by Renard and Kee in the synthesis of NHP containing diaminocyclohexane "backbones."[15]) When Et_3N was used as base, and in the case of Ar = Dipp, the side-products were recovered from the reaction mixture as X-ray quality crystals by slow evaporation of solvent. Thermal ellipsoid representations of the structures of **4** and **5** are shown in Fig. 1 and 2, respectively. Not only was the production of the bisphosphine **5** disadvantageous in that it reduced the overall yield, but also it was vexing because **5** had a $^{31}P\{^1H\}$ NMR spectrum that was almost identical to that of the desired chlorophosphine **3d** (δ_P 156.3 *vs.* 155.0, respectively, in $CDCl_3$ solution at r.t.), and it was difficult to remove from the reaction mixture due to its similar solubility. In the case of Ar = Dipp, we found that reversing the order of addition of reagents (*i.e.*,

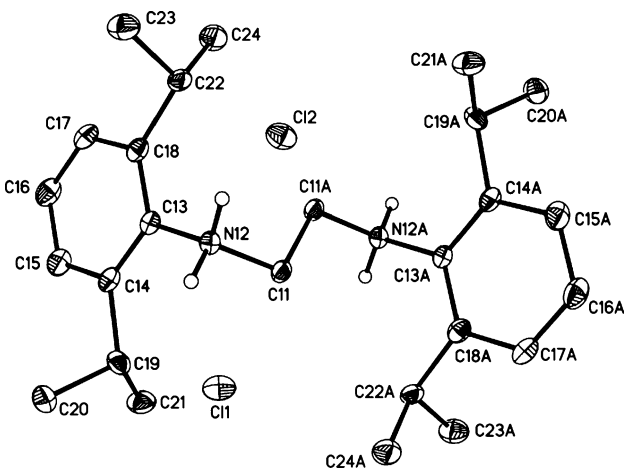


Fig. 1 ORTEP representation of the diammonium salt **4** (30% ellipsoids). Except for the N–H groups, H-atoms are omitted for clarity. Only one of the two crystallographically independent forms of the cation is shown, and the three cocrystallized $CHCl_3$ molecules have also been omitted. The hydrogen-bonded distances (Å) are: N12–Cl1 3.067, N12–Cl2 3.083 (sum of van der Waal's radii of N and Cl = 3.30 Å).

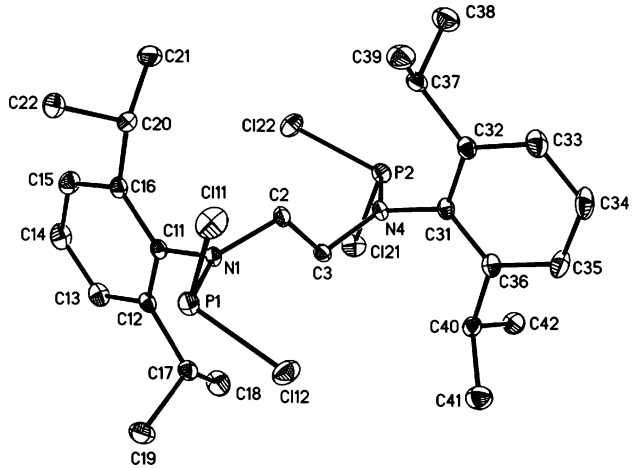


Fig. 2 ORTEP representation of the molecular structure of the bisphosphine **5** (30% ellipsoids). Selected bond distances (Å) and angles (°): P1–N1 1.6411(19), P1–Cl11 2.0970(9), P1–Cl12 2.0795(9), P2–N4 1.6417(19), P2–Cl22 2.0788(9), P2–Cl21 2.0988(9), N1–P1–Cl11 103.40(7), N1–P1–Cl12 101.23(7), Cl12–P1–Cl11 95.94(4), N4–P2–Cl21 103.16(7), N4–P2–Cl22 101.03(7), Cl21–P2–Cl22 95.81(4).

PCl_3 + NMM to diamine, instead of *vice versa* as for **3a**, **3b** and **3d**) dramatically suppressed formation of **5** during the synthesis of **3c**.

An ORTEP representation of the molecular structure of **3b** is shown in Fig. 3. Selected bond distances and angles appear in Table 1, together with those of **1b**, which was structurally characterized by Nozaki and coworkers;[24] **1b** has a weak P–O contact of 2.421 Å (sum of P + O van der Waal's radii = 3.32 Å). Comparison of the two species was instructive: replacement of chloride by triflate shortened the N–P bonds by approximately 0.03 Å from 1.6682(13) Å (av.) in **3b** to 1.631(2) Å (av.) in **1b**. This was consistent with an increase in N–P double bond character arising from enhanced N-to-P π-donation in **1b**. In addition, the N–P–X angle decreased dramatically from the nearly perfect tetrahedral 102.36(5)° (av.) in **3b** (X = Cl) to the almost square 93.94° (av.) in **1b** (X = O). The N–P–N angles showed less variation as they were constrained by the ethylene "backbone"

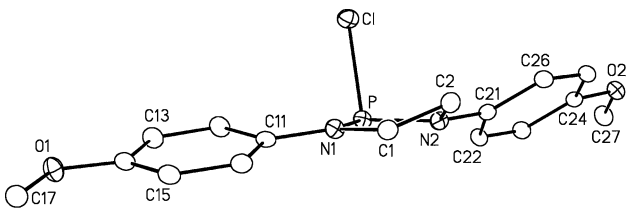


Fig. 3 ORTEP representation of the molecular structure of **3b** (20% ellipsoids). Selected bond distances and angles are collected in Table 1.

Table 1 Selected bond distances (Å) and angles (°) for **1a**, **1b** (determined by Nozaki and coworkers[24]) and **3b** with estimated standard deviations in parentheses where available

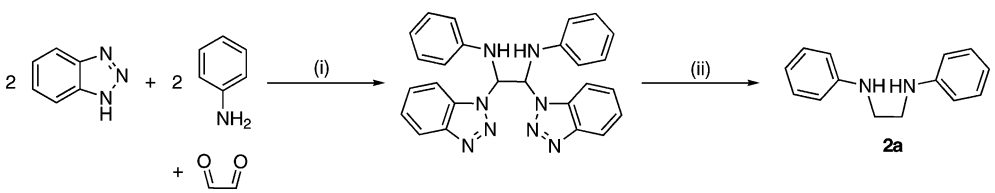
	1a (X = O)	**1b** (X = O)	**3b** (X = Cl)
P–X	2.1850(14)	2.4210(18)	2.1993(6)
P–N	1.6357(15)	1.628(2)	1.6684(13)
	1.6344(16)	1.634(2)	1.6678(13)
N–C	1.478(2)	1.479(3)	1.4735(18)
	1.485(2)	1.485(3)	1.4758(18)
C–C	1.525(3)	1.507(4)	1.518(2)
$N–C_{ex}$[a]	1.4233(17)	1.434(3)	1.413(19)
	1.4262(17)	1.426(3)	1.419(2)
N–P–N	93.58(8)	93.74(10)	91.49(6)
N–P–X	99.93(7)	93.48	103.09(5)
	99.50(7)	94.40	101.63(5)

[a] Exocyclic N–C bond length.

to approximately square values of 91.49(6)° in **3b** and 93.74(10)° in **1a**.

The NHP **1a–d** were produced by halide abstraction from the corresponding chlorophosphines **3a–d** using either Me_3SiOTf or AgOTf. Reactions of **3a–d** with $AgPF_6$ and $AgBF_4$ were complicated by B-to-P fluoride transfer and P–B bond formation, as evidenced by the appearance of both one- and two-bond P–F and one-bond P–B coupling in NMR spectra of the products.[25] The use of silver was additionally complicated in some cases by incorporation of the metal into the product; these results will be discussed in a forthcoming paper. Baker and coworkers used either AgOTf or $TlBAr_F$ for this abstraction (BAr_F = tetrakis(2,6-bis(trifluoromethyl)phenyl)borate).[20] We found that Me_3SiOTf worked well for dehalogenation of **3c** and **3d**, but was unreliable for the other chlorophosphines. Overall yields of NHP starting from the diimines using our modified route were: 63% (**1b**), 66% (**1d**) and 72% (**1c**). The new synthesis appeared to be particularly beneficial for the Dipp (**1c**) and Mes (**1d**) analogues, which saw 15 and 23% gains, respectively, over three steps compared to the original method. However, the *para*-methoxyphenyl-substituted NHP **1b** appeared not to benefit.

The phenyl-substituted NHP **1a** was produced starting with the alternate route shown in Scheme 2 because the diimine precursor could not be made by simple condensation of aniline and glyoxal. In this approach, the required diamine was produced in two steps using the method of Pohlke and coworkers:[26] reaction of glyoxal, aniline and benzotriazole gave an intermediate that was subsequently reduced with $NaBH_4$ to furnish **3a** in 53% overall yield. Subsequent dehydrohalogenation and halide abstraction steps were as shown in Scheme 1. However, the latter step could only be effected by AgOTf; inexplicably, the chloride could not be removed using Me_3SiOTf.



Scheme 2 Method for the synthesis of diamine **2a** for onward production of NHP **1a**. (i) EtOH, r.t., 18 h; (ii) (a) $NaBH_4$, THF, r.t., 18 h (b) H_2O.

The phenyl-substituted NHP **1a** has not been well characterized in the literature: to the best of our knowledge, it has been mentioned once and the only available datum is the $^{31}P\{^{1}H\}$ chemical shift of its $AlCl_4^-$ salt (δ_P 254).[27] Single crystals of **1a** suitable for X-ray diffraction deposited from CH_2Cl_2 solution by slow evaporation of solvent. An ORTEP representation of the molecular structure is shown in Fig. 4; selected bond distances and angles appear in Table 1. The metrical parameters of this compound were similar to those of other saturated NHP, but in this case, there was a P–O contact of 2.1850(14) Å. Other cases of close P–OTf contacts in phosphenium-like compounds have been observed by Niecke in Mes*N=P–OTf (1.923(3) Å) (Mes* = 2,4,6-tri-*t*-butylphenyl),[28] by Burford in dimers [Mes*N–P–OTf]$_2$ (1.781(6) Å) and [DippN–P–OTf]$_2$ (1.763(5), 1.784(6) Å)[29] and by Bertrand in $^{i}Pr_2NP(OTf)(2,6\text{-}(CF_3)_2C_6H_3)$ (1.882(2) Å), which as late as 2002 was the "first covalent (trifluoromethansulfonate)phosphane to be structurally characterized."[30] Although the P–O length in **1a** was longer than in the above examples, it was substantially shorter than those found in analogous saturated NHP compounds such as **1b** (2.4210(18) Å,[24] *vide infra*) and a diaminocyclohexane derivative by Kee (2.841(5) and 2.755(5) Å),[13] as well as two unsaturated NHP triflates reported by Gudat[8] that were clearly ionic in the solid state and had no cation–anion contacts closer than the sum of van der Waal's radii. Moreover, the $^{31}P\{^{1}H\}$ NMR chemical shift of **1a** (δ_P 172.9) was considerably upfield of that of its $AlCl_4^-$ analogue (δ_P 254), which was presumably ionic in solution, and those of the other NHP in this study (δ_P 196–203). It was also less dramatically downfield of its chloride precursor **3a** (δ_P 138.0; $\Delta\delta$ 34.9) than were the other NHP of their chlorides (δ_P 139–155; $\Delta\delta$ 45–58). Together with the solid-state data, these confirmed that **1a** possessed a considerably stronger P–O interaction than **1b–d**.

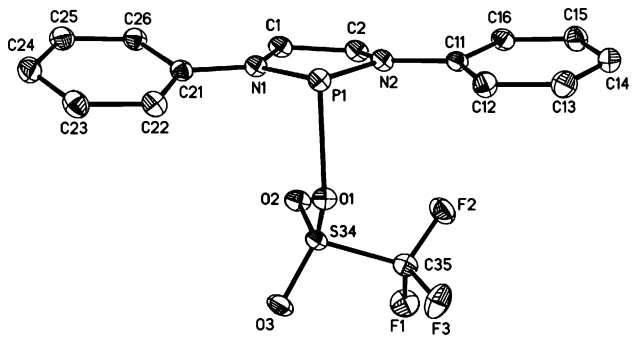


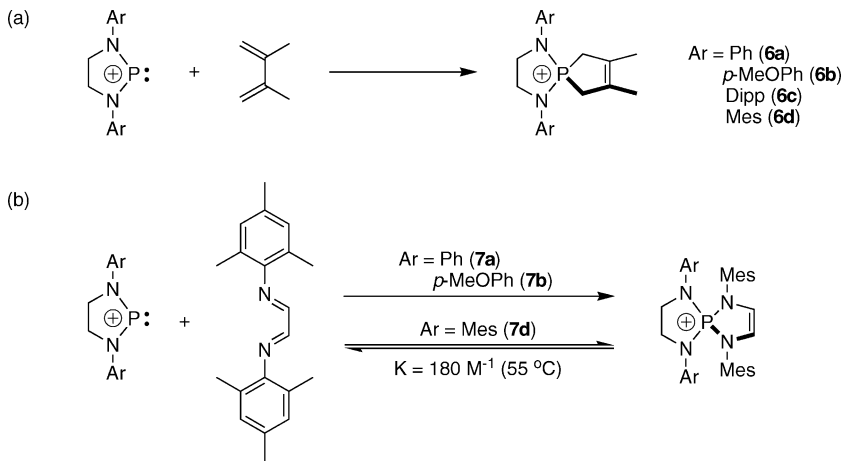
Fig. 4 ORTEP representation of the molecular structure of **1a** (30% ellipsoids). Selected bond distances and angles are collected in Table 1.

A comparison of the structural data for **1a** and **1b**[24] allowed determination of the response of the phosphenium centre to a distal electron-donating substituent. Related studies of the effects of even more distant and non-conjugated substituents in NHP have been carried out on the basis of NMR spectroscopy.[15] Our analysis could be made in isolation of steric effects because the *para*-methoxy substituents in **1b** were directed rigidly away from the phosphorus atom and did not crowd it in any way. The dramatic increase in P–O bond length (*ca.* 0.24 Å) in going from the methoxy-substituted NHP **1b** to **1a** made it clear that formal incorporation of electron-donating –OMe groups into **1b** significantly suppressed the electrophilicity of the phosphorus centre. Likewise, there was a significant increase in the N–P–O angle from nearly square in **1b** (av. 93.44°) to approximately tetrahedral in **1a** (av. 99.72°).

Cycloaddition reactions

A number of studies, *e.g.*, by the groups of Baxter and Cowley, have investigated the cycloaddition reaction between acyclic phosphoniums and 1,3-butadienes to give phospholenium cations,[31,32] and a report by Buono and coworkers demonstrated the formation of spirocyclic analogues starting from a chiral NHP.[14] Cowley has proposed that these reactions go *via* a [2 + 4] disrotatory cheletropic mechanism, and the energetics have been calculated using *ab initio* methods by Burford and coworkers.[33] We sought to confirm that the reaction could be extended to a variety of saturated NHP.

The cycloaddition reactions between 1,3-dimethyl-1,4-butadiene and **1a–d** cleanly generated spirocyclic phospholenium cations **6a–d** (Scheme 3(a)), although the reaction was very much slower for the Dipp analogue **1c** (24 h) than for the others (10 min), presumably for steric reasons. Redissolution of the isolated phosphonium spirocycles did not result in the regeneration of free NHP and diene, which indicated that the reactions were essentially irreversible in solution at r.t. Mass



Scheme 3 Reaction of NHP **1a–d** with (a) 2,3-dimethyl-1,3-butadiene, and (b) *N*,*N*′-dimesityl-1,4-diaza-1,3-butadiene. All cations have OTf anions.

Table 2 Comparison of $^{31}P\{^{1}H\}$ NMR data (ppm, $CDCl_3$ solution) for NHP **1a–d**, diazaphospholenium salts **6a–d**, and tetraazaphospholenium salts, **7a**, **7b** and **7d**

N–Ar group	**1**	**6**	**7**
Ph (**a**)	172.9	86.0	18.5
p-OMePh (**b**)	196.8[a]	84.0	17.9
Dipp (**c**)	199.4[a]	80.6	—
Mes (**d**)	203.1[a]	79.9	21.4

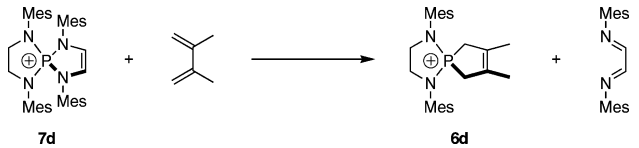
[a] As reported by Baker and coworkers.[20]

spectrometry revealed that **6d** released 1,3-dimethyl-1,4-butadiene on heating to 350 °C in the solid state.

The phospholenium cations were characterized by singlets in their $^{31}P\{^{1}H\}$ NMR spectra that were significantly upfield of those of the starting phospheniums (Table 2). Baxter's and Cowley's groups reported similar upfield shifts for their adducts.[31] Formation instead of both P–C *and* N–C bonds in putative Diels–Alder cycloaddition products was ruled out on the basis of ^{1}H NMR data, which clearly indicated that **6a–d** retained C_2 symmetry: the two olefinic methyl groups in all compounds were equivalent, as were the two P–CH_2 methylene groups. The latter displayed two-bond H-P coupling of 10–12 Hz, and there was clear one-bond C-P coupling of 65–68 Hz for these methylene carbon atoms in the $^{13}C\{^{1}H\}$ NMR spectra.

We also assayed **1a–d** in cycloaddition reactions with *N*,*N*′-dimesityl-1,4-diaza-1,3-butadiene to form tetraazaphospholenium cations. Closely related reactions of predominantly acyclic bis(amino)phospheniums have been carried out by Mazières *et al.*[34] In addition, work by the Lopez group demonstrated that di- and triazaphospholes underwent cycloadditions with 1,4-diaza-1,3-dienes to form analogous neutral spirophosphazenes, protonation of which gave cations that were similar to those we report here.[35,36] Some of Lopez's cycloadditions required added BF_3, which was necessary to suppress tetramerization of the azaphospholes and to increase the electrophilicity of the phosphorus atom.[36] In our case, addition of BF_3 was unnecessary; **1a** and **1b** reacted cleanly to give the spirocyclic compounds shown in Scheme 3(b). The very bulky Dipp analogue **1c** did not react, presumably because of steric congestion, and the Mes/Mes combination rendered **7d** in equilibrium with **1d** and free diazabutadiene (*vide infra*). Spectroscopic data are collected in Table 2. As was the case in the reaction of **1a–d** with butadiene, a dramatic upfield shift was associated with the transformation of the phosphorus centre from P(III) to P(V). Proton NMR data once again revealed that the C_2 symmetry was preserved in **7a** and **7b**: the olefinic C–H protons were equivalent and showed three-bond H–P coupling of *ca.* 23 Hz.

The ^{1}H NMR spectrum of isolated **7d** at r.t. showed only traces of free *N*,*N*′-dimesityl-1,4-diaza-1,3-butadiene, which indicated that at this temperature, the equilibrium heavily favoured the tetraazaphospholenium. The r.t. spectrum was substantially broad, but upon cooling to −15 °C, it sharpened sufficiently to submit to analysis. In the low temperature spectrum, six peaks were apparent for the mesityl methyl groups (four for the *ortho* and two for the *para* positions). These observations were consistent with steric congestion that restricted free rotation about the N–aryl bonds in **7d**, and hinted that it should be possible to exchange the diazabutadiene group. Indeed, when **7d** was exposed to 1 equiv. of 1,3-dimethyl-1,4-butadiene in $CDCl_3$ at 55 °C, it was consumed quantitatively within 90 min with concomitant formation of **6d** (Scheme 4; Fig. 5). When a solution containing **7d** was warmed to 55 °C in the absence of diene, NHP **1d** and free diazadiene were generated. The equilibrium constant at this temperature for the reaction in Scheme 3(b) was 180 M^{-1}.



Scheme 4 Substitution of *N*,*N*′-dimesityl-1,4-diaza-1,3-butadiene by 2,3-dimethyl-1,3-butadiene in **7d**.

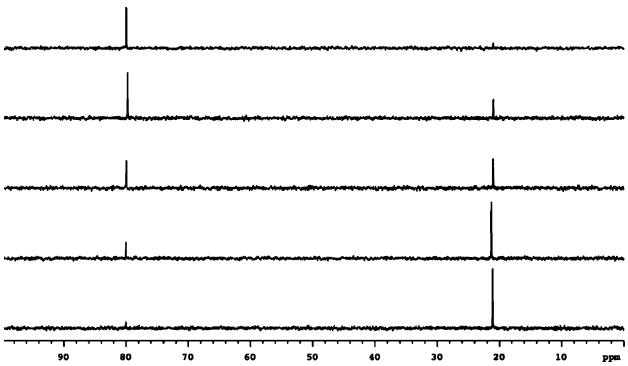


Fig. 5 $^{31}P\{^{1}H\}$ NMR spectra taken (from bottom) at 2, 10, 20 40 and 60 min during the reaction between **7d** and 1 equiv. 2,3-dimethyl-1,3-butadiene in $CDCl_3$ solution at 55 °C to give **6d**. The peak at δ_P 21.4 is due to **7d**, while that at δ_P 79.9 is due to **6d**.

Experimental

General considerations

Reagents were obtained from commercial sources and used as supplied, unless otherwise indicated. These were of American Chemical Society (ACS) grade or finer. Solvents were dried and deoxygenated either by N_2 purge followed by passage through alumina columns (Innovative Technology or MBraun solvent purification systems), or by distillation under N_2 from the appropriate drying agent. All reactions were carried out under N_2 atmosphere using standard Schlenk or glove box techniques unless stated otherwise. The *N*-aryl diimine precursors were prepared according to literature procedures.[20] The NHP **1b** was prepared as its trifluoromethanesulfonate salt by chloride removal from **3b** using AgOTf according to the method of Baker and coworkers.[20]

^{1}H, $^{13}C\{^{1}H\}$, $^{31}P\{^{1}H\}$, and $^{19}F\{^{1}H\}$ NMR data were recorded on 400 MHz Varian Mercury (400.085 MHz for for ^{1}H, 100.602 MHz for ^{13}C, 376.458 MHz for ^{19}F, 161.978 MHz for ^{31}P) or 400 MHz Varian Inova spectrometer (399.762 MHz for ^{1}H, 100.520 MHz for ^{13}C, 376.150 MHz for ^{19}F, 161.825 MHz for ^{31}P). Unless otherwise indicated, spectra were recorded at r.t. (room temperature) in $CDCl_3$ solution using residual solvent proton (relative to external $SiMe_4$, δ 0.00) or solvent carbon (relative to external $SiMe_4$, δ 0.00) as an internal reference. Phosphorus NMR spectra

acquired in both deuterated and non-deuterated solvent were run unlocked (referenced relative to external 85% aqueous H_3PO_4, δ 0.00). Downfield shifts were taken as positive. Data for ^1H NMR spectra are reported as follows: chemical shift (δ), multiplicity, integration, assignment and coupling constant(s). All coupling constants are reported in Hertz (Hz) and the spin multiplicities are indicated as follows: s (singlet), t (triplet), q (quartet), m (multiplet), p (pseudo) and br (broad). Low (LRMS) and high resolution mass spectrometry (HRMS) data were recorded by Mr Doug Hairsine (UWO) using a Micromass LCT and a Finnigan MAT 8200 instrument, respectively.

Syntheses

***N*,*N*′-Diphenylethane-1,2-diamine (2a).** The title compound was made according to the method of Pohlke *et al.*[26] However, few characterization data were given in this report. We, therefore, include them here. Yield: 53% over 2 steps. ^1H NMR: δ 3.38 (m, 4H, CH_2CH_2, 3.86 (br s, 2H, N*H*), 6.66 (d, 4H, Ar), 6.74 (t, 2H, Ar), 7.20 (t, 4H, Ar). $^{13}C\{^1H\}$ NMR: δ 43.5, 113.3, 118.1, 129.6, 148.3. M.p. 133–135 °C. HRMS for $C_{14}H_{16}N_2$ calcd (found) 212.1313 (212.1318).

General procedure for reduction of diarylimines to diarylamines. The syntheses of diarylamines were carried out according to a modification of the procedure originally reported by Baker and coworkers:[20] $LiAlH_4$ was used as the reducing agent instead of $NaBH_4$. In a typical synthesis, solid $LiAlH_4$ (1.30 g, 0.034 mol) was added portionwise to a cooled (0 °C) solution of diarylimine (0.014 mol) in dry Et_2O (300 mL). The solution changed from yellow to brown to colourless with a grey precipitate over 30 min. The ice bath was removed, and the suspension stirred for 24 h. The suspension was again cooled to 0 °C and excess $LiAlH_4$ was quenched by dropwise addition of a 1% KOH solution (6 mL). The mixture was stirred until all aluminium solids were white and no additional H_2(g) was evolved. The salts were removed by vacuum filtration and the filtrate was dried over $MgSO_4$ and concentrated *in vacuo* to obtain the diamine. Spectroscopic data were identical to those previously reported for these compounds, but yields were generally higher.[20]

N,N′-Bis-(4-methoxyphenyl)ethane-1,2-diamine (***2b***). Yield: 89%.

N,N′-Bis-(2,6-diisopropylphenyl)ethane-1,2-diamine (***2c***). Yield: 91%.

N,N′-Bis-(2,4,6-trimethylphenyl)ethane-1,2-diamine (***2d***). Yield: 95%.

General procedure for syntheses of chlorophosphines 3a–d. The reported synthesis by Baker and coworkers[20] was modified to use *N*-methylmorpholine (NMM) as a base instead of NEt_3. In a typical procedure, dry THF (25 mL) in a 50 mL Schlenk tube with was cooled to −78 °C, and NMM (0.310 mL, 0.003 mol) and PCl_3 (0.086 mL, 0.001 mol) were added. A solution of diamine (0.001 mol) in THF (15 mL) was then added dropwise *via* cannula to the cooled solution over 10 min to give a white suspension. (Note: for the 2,6-diisopropylphenyl compound **3c**, the PCl_3–NMM suspension was instead added dropwise *via* cannula to the cooled diamine solution over 60 min). The suspension was stirred at −78 °C for 1h. The cold bath was removed, the solution was allowed to warm to r.t. and stirred for 18 h prior to concentration *in vacuo*. The resulting pale yellow solid was brought into the glove box where a solution of 1 : 1 hexanes–THF (20 mL) was added. The solid was removed by centrifugation, and the liquid was concentrated *in vacuo*. The pale yellow residue was washed with hexanes–THF (2 × 20 mL) and dried under vacuum to give the title compound as a pale beige solid. Spectroscopic data were identical to those previously reported by Baker and coworkers,[20] unless otherwise noted.

2-Chloro-1,3-diphenyl[1,3,2]diazaphospholidine (***3a***). The only available datum for this known compound is its $^{31}P\{^1H\}$ NMR chemical shift, which was reported by Marre *et al.*[27,37] Yield: 73%. ^1H NMR: δ 4.19 (d, 4H, CH_2CH_2, $^3J_{PH} = 5.2$), 7.04 (d, 2H, Ar C*H*, $^3J_{HH} = 7.2$), 7.16 (m, 2H, Ar C*H*), 7.35 (t, 2H, Ar C*H*, $^3J_{HH} = 8.0$). $^{13}C\{^1H\}$ NMR: δ 47.9 (d, $^3J_{CP} = 10.0$), 117.1 (d, $^2J_{CP} = 14.6$), 122.3, 129.5, 142.3. $^{31}P\{^1H\}$ NMR: δ 138.0 (s). $^{19}F\{^1H\}$ NMR: δ −81.9 (s). LRMS for $C_{14}H_{14}N_2P^+$ *m/z* (ESI) 241.1 (M-Cl, 100%), 242.1 (8), 471.0 (8). Calcd for $C_{14}H_{14}N_2PCl$: C 60.8; H 5.1; N 10.1; found C 60.4; H 5.4; N 10.1%.

2-Chloro-1,3-bis-(4-methoxyphenyl)[1,3,2]diazaphospholidine (***3b***). Yield: 82%.

2-Chloro-1,3-bis-(2,6-diisopropylphenyl)[1,3,2]diazaphospholidine (***3c***). Yield: 92%.

2-Chloro-1,3-bis-(2,4,6-trimethylphenyl)[1,3,2]diazaphospholidine (***3d***). Yield: 73%.

[PN(C$_6$H$_5$)CH$_2$CH$_2$N(C$_6$H$_5$)]OTf (***1a***). The title compound was made from **3a** according to the method of Baker and coworkers.[20] Yield: 90%. ^1H NMR: δ 4.17 (d, 4H, CH_2CH_2, $^3J_{PH} = 5.2$), 7.04 (m, 2H, Ph), 7.34 (m, 4H, Ph), 7.22 (m, 4H, Ph). $^{13}C\{^1H\}$ NMR: δ 47.8 (d, $^2J_{CP} = 10.0$), 118.4 (d, $^2J_{CP} = 14.6$), 122.3, 129.5, 142.3. $^{31}P\{^1H\}$ NMR: δ 172.9 (s). $^{19}F\{^1H\}$ NMR: δ −77.5 (s). LRMS for $C_{14}H_{14}N_2P^+$ *m/z* (ESI) 241.0 (M^+, 100%), 242.1 (12), 287.0 (6). Calcd for $C_{15}H_{14}F_3N_2O_3PS$: C 46.2; H 3.6; N 7.2; found C 45.9; H 3.6; N 6.8%.

General procedure for synthesis of NHP trifluoromethanesulfonates using Me_3SiOTf. Trimethylsilyltriflate (Me_3SiOTf) (0.140 mL, 0.77 mmol) was added to a solution of chlorophosphine (0.77 mmol) in dry toluene (1 mL). The solution was stirred at r.t. for 1 h. The solution was then concentrated *in vacuo* to remove Me_3SiCl and give the product as a nearly colourless powder. Spectroscopic data were identical to those previously reported.[20]

*[PN(2,6-i*Pr*-C$_6$H$_3$)CH$_2$CH$_2$N(2,6-i*Pr*-C$_6$H$_3$)]OTf* (***1c***). Yield 86%.

[PN(2,4,6-Me$_3$C$_6$H$_2$)CH$_2$CH$_2$N(2,4,6-Me$_3$C$_6$H$_2$)]OTf (***1d***). Yield 95%.

General procedure for the synthesis of diazaphospholenium trifluoromethane sulfonate salts 6a–d. 2,3-Dimethyl-1,3-butadiene (0.25 mmol) was added dropwise to a solution containing the appropriate phosphenium triflate salt (**1a–d**, 0.23 mmol) dissolved in dry CH_2Cl_2 (5 mL). An orange–yellow solution formed that was stirred for 10 min at r.t. Solvent was removed *in vacuo* and the residue was washed with Et_2O (2 × 2 mL). In the case of **1c**, a longer reaction time of 24 h was required.

7,8-Dimethyl-1,4-diphenyl-1,4-diaza-5-phopshoniaspiro[4.4]non-7-ene trifluoromethanesulfonate salt (***6a***). Yield: 82%. ^1H NMR: δ 1.78 (s, 6H, CH_3), 3.14 (d, 4H, PCH_2, $^2J_{PH} = 12.4$), 4.19 (d, 4H, NCH_2, $^3J_{PH} = 7.2$), 7.13 (pt, 4H, Ar), 7.25 (s, 2H, Ar), 7.44 (pt, 4H, Ar). $^{13}C\{^1H\}$ NMR: δ 16.4 (d, $^2J_{PC} = 16.1$), 32.7 (d, $^1J_{PC} = 65.2$), 48.7 (d, $^3J_{PC} = 6.9$), 121.5 (d, $^3J_{PC} = 4.6$), 126.3,

128.6 (d, $^2J_{PC}$ = 13.8), 130.8, 137.8 (d, $^3J_{PC}$ = 7.6). $^{31}P\{^1H\}$ NMR: δ 86.0 (s). $^{19}F\{^1H\}$ NMR: δ −82.5 (s). LRMS for $C_{20}H_{24}N_2P^+$ *m/z* (ESI) 323.2 (M^+, 100%), 324.2 (30), 382.7 (48), 241.1 (28). Calcd for $C_{21}H_{24}F_3N_2O_3PS$: C 53.4; H 5.1; N 5.9; found C 53.0; H 4.9; N 5.8%.

*1,4-Bis(4-methoxyphenyl)-7,8-dimethyl-1,4-diaza-5-phopshoniaspiro[4.4]non-7-ene trifluoromethanesulfonate salt (**6b**).* Yield: 76%. ^1H NMR: δ 1.59 (d, 6H, CH_3, $^4J_{HH}$ = 1.2), 2.98 (dd, 4H, PCH_2, $^4J_{HH}$ = 1.2, $^2J_{PH}$ = 12.0), 3.80 (s, 6H, OCH_3), 4.04 (d, 4H, NCH_2, $^3J_{PH}$ = 7.6), 6.93 (m, 4H, Ar), 7.33 (m, 4H, Ar). $^{13}C\{^1H\}$ NMR: δ 16.2 (d, $^2J_{PC}$ = 15.3), 32.6 (d, $^1J_{PC}$ = 67.5), 51.0 (d, $^3J_{PC}$ = 9.2), 55.8, 115.9, 124.1, 126.9, 127.9 (d, $^2J_{PC}$ = 12.3), 129.5 (d, $^3J_{PC}$ = 6.1), 159.2. $^{31}P\{^1H\}$ NMR: δ 84.0 (s). $^{19}F\{^1H\}$ NMR: δ −82.4 (s). LRMS for $C_{22}H_{28}N_2P^+$ *m/z* (ESI) 383.1 (M^+, 100%), 384.1 (32), 465.2 (7).

*1,4-Bis(2,6-diisopropylphenyl)-7,8-dimethyl-1,4-diaza-5-phopshoniaspiro[4.4]non-7-ene trifluoromethanesulfonate salt (**6c**).* In this case, product **6c** could not be separated from starting phosphenium **1c**. Yield: 30% (by ^1H NMR spectroscopy). ^1H NMR: δ 1.29 (d, 3H, CHCH_3, $^3J_{HH}$ = 6.8), 1.31 (d, 3H, CH_3, $^3J_{HH}$ = 6.8), 1.50 (d, 6H, CH_3, $^4J_{HH}$ = 1.2), 2.77 (dd, 4H, PCH_2, $^4J_{HH}$ = 1.2, $^2J_{PH}$ = 10.8), 3.15 (spt, 4H, CHCH$_3$, $^3J_{HH}$ = 6.8), 3.93 (d, 4H, NCH_2, $^3J_{PH}$ = 7.2), 7.24 (m, 6H, Ar). $^{31}P\{^1H\}$ NMR: δ 80.6 (s). $^{19}F\{^1H\}$ NMR: δ −74.7 (s).

*1,4-Dimesityl-7,8-dimethyl-1,4-diaza-5-phopshoniaspiro[4.4]non-7-ene trifluoromethanesulfonate salt (**6d**).* Yield: 53%. ^1H NMR: δ 1.51 (d, 6H, CH_3, $^4J_{HH}$ = 0.8), 2.29 (s, 6H, *p*-ArCH_3), 2.38 (s, 12H, *o*-ArCH_3), 2.79 (dd, 4H, PCH_2, $^4J_{HH}$ = 0.8, $^2J_{PH}$ = 10.8), 3.96 (d, 4H, NCH_2, $^3J_{PH}$ = 6.8), 6.94 (s, 4H, Ar). $^{13}C\{^1H\}$ NMR: δ 16.0 (d, $^3J_{PC}$ = 13.8), 18.2, 18.9, 20.9, 30.9 (d, $^1J_{PC}$ = 68.3), 49.8 (d, $^2J_{PC}$ = 10.8), 127.0 (d, $^2J_{PC}$ = 11.6), 129.7, 130.0, 130.4, 136.7, 137.2, 137.7, 139.4. $^{31}P\{^1H\}$ NMR: δ 79.9 (s). $^{19}F\{^1H\}$ NMR: δ −78.3 (s). LRMS for $C_{26}H_{36}N_2P^+$ *m/z* (ESI) 407.1 (M^+, 100%), 408.2 (60). Calcd for $C_{27}H_{36}F_3N_2O_3PS$: C 58.3; H 6.5; N 5.0; found C 58.2; H 6.4; N 5.4%.

General procedure for the synthesis of tetraazaphospholenium trifluoromethane sulfonate salts 7a–d. To a solution of the appropriate phosphenium triflate salt (**1a–d**, 0.34 mmol) in dry CH_2Cl_2 (5 mL) was added dropwise a solution of *N*,*N*′-dimesityl-1,4-diaza-1,3-butadiene (0.41 mmol) in dry CH_2Cl_2 (5 mL). The resultant solution was stirred for 10 min at r.t. The reaction was monitored by $^{13}P\{^1H\}$ NMR spectroscopy in non-deuterated solvent. Solvent was removed *in vacuo* and the residue washed with Et_2O (2 × 2 mL).

*1,4-Dimesityl-6,9-diphenyl-1,4,6,9-tetraaza-5-phosphoniaspiro[4.4]non-2-ene trifluoromethanesulfonate salt (**7a**).* Yield: 98%. ^1H NMR: δ 1.82 (s, 12H, Me), 2.34 (s, 6H, Me), 4.03 (d, 4H, NCH_2 $^3J_{PH}$ = 9.2), 6.29 (d, 2H, NCH, $^3J_{PH}$ = 23.6), 6.65 (d, 4H, Ar, $^4J_{PH}$ = 8.0), 6.93 (s, 4H, Ar) 7.30 (m, 6H, Ar).$^{13}C\{^1H\}$ NMR: δ 19.7, 21.0, 48.0 (d, $^2J_{PC}$ = 15.1), 116.7 (d, $^2J_{PC}$ = 18.9), 123.6 (d, $^3J_{PC}$ = 4.5), 127.2, 130.2, 130.8 (d, $^3J_{PC}$ = 2.3), 131.3, 136.7 (d, $^3J_{PC}$ = 2.8), 136.9 (d, $^2J_{PC}$ = 6.2), 139.9 (d, $^3J_{PC}$ = 1.5). $^{31}P\{^1H\}$ NMR: δ 18.5 (s). $^{19}F\{^1H\}$ NMR: δ −78.7 (s). LRMS for $C_{34}H_{38}N_4P^+$ *m/z* (ESI) 533.1 (M^+, 100%), 534.2 (38), 323.1 (15). Calcd for $C_{35}H_{38}F_3N_4O_3PS$: C 61.5; H 5.6; N 8.2; found C 61.4; H 5.3; N 7.9%.

*1,4-Dimesityl-6,9-di(4-methoxyphenyl)-1,4,6,9-tetraaza-5-phosphoniaspiro[4.4]non-2-ene trifluoromethanesulfonate salt (**7b**).* Yield: 81%. ^1H NMR: δ 1.87 (s, 12H, Me), 2.36 (s, 6H, Me), 3.82 (s, 3H, OMe), 3.96 (d, 4H, NCH_2, $^3J_{PH}$ = 9.2), 6.26 (d, 2H, NCH, $^3J_{PH}$ = 23.1), 6.57 (d, 4H, Ar, $^3J_{HH}$ = 8.8), 6.85 (d, 4H, Ar, $^3J_{HH}$ = 8.8), 6.95 (s, 4H, Ar).$^{13}C\{^1H\}$ NMR: δ 19.8, 21.4, 48.1 (d, $^2J_{PC}$ = 15.2), 55.8, 115.3, 116.7 (d, $^2J_{PC}$ = 19.1), 124.8, 129.6, 130.9, 131.3, 136.8, 139.9, 158.4. $^{31}P\{^1H\}$ NMR: δ 17.9 (s). $^{19}F\{^1H\}$ NMR: δ −78.8 (s). LRMS for $C_{36}H_{42}N_4O_2P^+$ *m/z* (ESI) 593.2 (M^+, 100%), 594.3 (30). Calcd for $C_{37}H_{42}F_3N_4O_3PS$: C 59.8; H 5.7; N 7.5; found C 59.3; H 5.5; N 7.1%.

*1,4,6,9-Tetramesityl-1,4,6,9-tetraaza-5-phosphoniaspiro[4.4]non-2-ene trifluoromethanesulfonate salt (**7d**).* Yield: 85%. ^1H NMR (258 K): δ 1.44 (s, 6H, Me), 1.69 (s, 6H, Me), 2.19 (s, 6H, Me), 2.22 (s, 6H, Me), 2.37 (s, 6H, Me), 2.52 (s, 6H, Me), 3.52 (dd, 2H, NCH_2, $^3J_{PH}$ = 21.6, $^3J_{HH}$ = 6.2), 4.18 (d, 2H, NCH_2, $^3J_{HH}$ = 6.2), 5.96 (d, 2H, NCH, $^3J_{PH}$ = 22.8), 6.56 (s, 2H, Ar), 6.58 (s, 2H, Ar), 6.78 (s, 2H, Ar), 6.85 (s, 2H, Ar). $^{13}C\{^1H\}$ NMR (258 K): δ 18.5, 19.2, 19.5, 20.8, 22.3, 51.6 (d, $^2J_{PC}$ = 16.0), 118.7 (d, $^2J_{PC}$ = 18.4), 129.1, 130.0, 130.8, 133.6, 133.9, 135.5, 136.1, 137.1, 137.3, 138.3, 138.8. $^{31}P\{^1H\}$ NMR: δ 21.4 (s). $^{19}F\{^1H\}$ NMR: δ −81.9 (s). HRMS: $C_{40}H_{50}N_4P^+$ calcd (found) 617.3768 (617.3768). Calcd for $C_{41}H_{50}F_3N_4O_3PS$: C 64.2; H 6.6; N 7.3; found C 64.7; H 6.8; N 7.3%.

Crystallography†

Crystals of **3b** were grown from concentrated $CHCl_3$ solution as colourless plates. Data were collected at low temperature (−80 °C) at a wavelength of 0.71073 Å on a Bruker PLATFORM/SMART 1000 CCD area detector diffractometer. Unit cell parameters were calculated and refined from the full data sets using full-matrix least-squares on F^2. Programs for diffractometer operation, data collection, data reduction and absorption correction were those supplied by Bruker. The *SHELXL-97* suite of programs[38] was used to solve the structure by direct methods.

Crystals of **1a** and **4**·3 $CHCl_3$ were grown as pale yellow plates and colourless blocks, respectively, from concentrated $CHCl_3$ solution, while those of **5** were grown from concentrated CH_2Cl_2 solution as colourless plates. The crystals were cut and mounted on glass fibres. Data were collected at low temperature (−123 °C) at a wavelength of 0.71073 Å on a Nonius Kappa-CCD area detector diffractometer running COLLECT software (Nonius B.V., 1997–2002). Unit cell parameters were calculated and refined from the full data sets using full-matrix least-squares on F^2. Crystal cell refinement and data reduction were carried out using HKL2000 DENZO-SMN (Otwinowski & Minor, 1997), and absorption corrections were applied using HKL2000 DENZO-SMN (SCALEPACK). In all cases, the reflection data and systematic absences were consistent with the monoclinic space group #14. The SHELXTL/PC V6.14 for Windows NT (Sheldrick, G.M., 2001) suite of programs was used to solve the structures by direct methods. Subsequent difference Fourier syntheses allowed the remaining atoms to be located.

Data collection and refinement parameters for **1a**, **3b**, **4**·3$CHCl_3$, and **5** are collected in Table 3.

Conclusions

The use of $LiAlH_4$ instead of $NaBH_4$ in diimine reductions and NMM instead of Et_3N in dehydrohalogenation reactions

Table 3 Crystal data and structure refinement for **1a**, **3b**, **4**·3 $CHCl_3$ and **5**

	1a	**3b**	**4**·3 $CHCl_3$	**5**
Empirical formula	$C_{15}H_{14}F_3N_2O_3PS$	$C_{16}H_{18}ClN_2O_2P$	$C_{29}H_{45}Cl_{11}N_2$	$C_{26}H_{38}C_{l4}N_2P_2$
Formula weight/g mol^{-1}	390.31	336.74	811.62	582.32
Temperature/K	150(2)	193(2)	150(2)	150(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$ (#14)	$P2_1/n$ (#14)	$P2_1/n$ (#14)	$P2_1/c$ (#14)
a/Å	10.6619(3)	8.9575(6)	15.0405(6)	16.4412(5)
b/Å	19.3867(5)	6.3256(4)	12.2573(3)	9.6026(2)
c/Å	8.7282(3)	28.149(2)	21.8456(9)	19.6484(5)
β	112.851(2)	97.7496(10)	90.1020(10)	105.678(2)
Volume/$Å^3$	1662.52(9)	1580.39(18)	4027.4(3)	2986.64(13)
Z	4	4	4	4
Density (calcd)/g cm^{-3}	1.559	1.415	1.339	1.295
Abs. coefficient/mm^{-1}	0.340	0.351	0.781	0.522
$F(000)$	800	704	1680	1224
Crystal size/mm	0.50 × 0.25 × 0.06	0.31 × 0.27 × 0.18	0.50 × 0.40 × 0.33	0.60 × 0.35 × 0.28
Range for data collection/°	2.10 to 27.62	2.50 to 27.46	2.71 to 25.03	2.56 to 25.03
Index ranges	$-13 \le h \le 13$ -25 -11	$-11 \le h \le 11$ -8 -36	$-17 \le h \le 17$ -14 -26	$-19 \le h \le 19$ -11 -23
Reflections collected	16997	13207	13161	28460
Independent reflections (R_{int})	3830 [$R_{int} = 0.0264$]	3577 [$R_{int} = 0.0239$]	7018 [$R_{int} = 0.0397$]	5278 [$R_{int} = 0.0630$]
Maximum and minimum transmission	0.9790 and 0.8483	0.9395 and 0.8989	0.7855 and 0.6963	0.8699 and 0.7449
Data/restraints/parameters	3830/0/202	3577/0/199	7018/36/364	5278/0/283
Goodness-of-fit on F^2	1.046	1.053	1.027	1.050
Final R indices [$I > 2\sigma(I)$][a]	$R_1 = 0.0404$ $wR_2 = 0.1002$	$R_1 = 0.0357$ $wR_2 = 0.0867$	$R_1 = 0.0519$ $wR_2 = 0.1307$	$R_1 = 0.0383$ $wR_2 = 0.0908$
R indices (all data)[a]	$R_1 = 0.0527$ $wR_2 = 0.1081$	$R_1 = 0.0443$ $wR_2 = 0.0910$	$R_1 = 0.0825$ $wR_2 = 0.1466$	$R_1 = 0.0617$ $wR_2 = 0.0988$
Largest difference in peak and hole/e $Å^{-3}$	0.428 and −0.371	0.363 and −0.138	0.655 and −0.466	0.445 and −0.345

[a] $R1$ [$F_o^2 \ge 2\sigma(F_o^2)$] and wR_2 [$F_o^2 \ge -3\sigma(F_o^2)$] where $R_1 = \Sigma \| F_o | - | F_c \| / \Sigma | F_o |$ and $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^4)]^{1/2}$.

results in significantly improved overall yields in the syntheses of NHP cations bearing Mes and Dipp substituents. The use of NMM suppresses the formation of unwanted ammonium and bisphosphine side-products, which have been structurally characterized in this work. Substitution of chloride for triflate results in solid-state geometrical changes that reflect a phosphine-to-phosphenium transition in otherwise identical species (*e.g.*, in going from **3b** to **1b**). Likewise, introduction of electron-donating substituents to the *para* positions of the *N*-aryl substituents in otherwise identical "P–OTf" compounds results in structural perturbations that are consistent with reduced Lewis acidity at the phosphorus centre and a phosphine-to-phosphenium transition (*e.g.*, in going from **1a** to **1b**). The NHP cations react cleanly in cycloaddition reactions with 2,3-dimethyl-1,3-butadiene and *N*,*N*′-dimesityl-1,4-diaza-1,3-butadiene to generate spirocyclic di- (**6a–d**) and tetraaza (**7a**, **7b**, and **7d**) phospholenium species. Whereas the reactions between **1a–d** and diene are irreversible in solution at r.t., the sterically congested **7d** is in thermal equilibrium with **1d** and free diazadiene, and undergoes a substitution reaction with 2,3-dimethyl-1,3-butadiene to give **6d**.

Acknowledgements

We acknowledge financial support from the Natural Sciences and Engineering Research Council of Canada (NSERC) and a Petro-Canada Young Innovator's Award (to NDJ), and useful discussions with Dr Paul Ragogna.

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