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ARTICLE

A phosphenium cation supported by a seven-membered thiophene based ring system

Jacquelyn T. Price, Nathan D. Jones, and Paul J. Ragogna

Abstract: A novel diamine ligand containing a simple thiophene ring in the backbone has been synthesized. Substitution at the nitrogen atoms with either 2,4,6-trimethylphenyl (Mes) or 2,6-diisopropylphenyl (Dipp) was varied via a condensation reaction between the corresponding aniline and 3,4-diformylthiophene, giving two different ligand derivatives. In onwards chemistry that targeted the cyclic diaminochlorophosphines, the substitution at phosphorus was dependent on the ligand used. For example, when a stoichiometric reaction between PCl_3 and thiophene-3,4 diyldimethaneamine (R = Mes) was carried out, the synthesis of a bis-substituted diphosphino- product was isolated. If the R = Dipp ligand derivative was employed, both a 2:1 and 1:1 stoichiometric reaction between PCl_3 and the diamine was observed. Nevertheless, the cyclic diaminochlorophosphine (i.e., 1:1 stoichiometry) for R = Dipp was isolated in high yields and the synthesis of the corresponding phosphenium cation was achieved and structurally characterized.

Key words: thiophene, phosphenium, diaminochlorophosphine, diamine.

Résumé : On a synthétisé un nouveau ligand diamine dont le squelette contient un noyau thiophène simple. On a procédé à la substitution d'un groupe 2,4,6-triméthylphényle (Mes) ou d'un groupe 2,6-diisopropylphényle (Dipp) sur les atomes d'azote par une réaction de condensation entre l'aniline correspondante et le 3,4-diformylthiophène pour obtenir deux dérivés différents du ligand. Lors de réactions chimiques ultérieures ayant pour cible les diaminochlorophosphines cycliques, la substitution sur le phosphore dépendait du ligand utilisé. Par exemple, une réaction stœchiométrique entre PCl3 et la thiophène-3, 4 diyldiméthanamine (R = Mes) a donné la synthèse d'un produit diphosphiné bisubstitué. Lorsqu'on a employé le dérivé R = Dipp du ligand, on a observé une réaction de stœchiométrie 2:1 ainsi qu'une réaction de stœchiométrie 1:1 entre PCl3 et la diamine. Néanmoins, on a isolé avec un haut rendement la diaminochlorophosphine cyclique (c. à d. stœchiométrie 1:1) obtenue pour R = Dipp, et on a synthétisé le cation phosphénium correspondant et caractérisé sa structure. [Traduit par la Rédaction]

Mots-clés : thiophène, phosphénium, diaminochlorophosphine, diamine.

Introduction

The utility of the *N*-heterocyclic carbenes (NHCs) has given rise to a wide range of chemistries, from functional and structurally diverse metal coordination complexes to enhancing catalytic properties within transition metal catalysis, and in some cases defining new directions in materials chemistry.[1–5] The NHCs share many similarities with their heavier group 15 analogue the *N*-heterocyclic phosphenium cations (NHPs), as they are isovalent and isolobal to each other; however, NHPs are the electronic inverse of the NHCs.[6,7] The phosphorus atom in an NHP is dicoordinate and cationic, formally possesses a lone pair of electrons and an empty π orbital, and the central phosphorus is formally in the +3 oxidation state. The cationic charge at the phosphorus center is normally stabilized by two flanking amino substituents, and it is these combined components that dominate the chemistry of the NHPs. The cations are weak σ donors and strong π acceptors, thus enabling NHPs to be good Lewis acidic ligands for electron-rich transition metals.[8–10]

The NHP framework typically consists of four-, five-, or six-membered rings with phosphorus being the lone reactive site. The main focus in this field has been to harness the chemistry of the P^+ centre; however, a shifting philosophy within main group chemistry as a whole (which includes phosphenium chemistry) has moved from studying purely the fundamental structure, bonding, and reactivity of these species to their potential for applications in broader arenas. Examples have surfaced within the past few years in utilizing main group elements in the construction of OLEDs and within catalysis/small molecule activation by taking advantage of the unique properties that these main group centres posses.[11–15] Efforts in these fields by ourselves and other research groups have centred on designing new ligand sets containing thiophene, a ubiquitous building block in the area of redox active and fluorescent materials.[16,17] Ultimately such architectures target the photoluminescent and polymerizable properties of thiophene, yet look to tune the photophysics of the overall construct by varying the main group element centre. Our group has recently designed a diamine, which contains a fused conjugated bithiophene backbone and has demonstrated its ability to stabilize pnictenium cations (Pn = P, As, and Sb) and NHCs (Fig. 1, compound **i**).[18,19] Cowely et al. have developed a novel redox active diimine with pendent thiophene rings in the 2 and 3 position and have used this ligand to coordinate a phosphenium cation with a triiodide counter ion.[20] Furthermore, Cowley and Bielawski have used that same diimine to synthesize polymers containing NHCs orthogonal to the polymer backbone (Fig. 1, compound **ii**).[21,22] Although there are many different ligands able to support main group elements, there is a void in those that can combine the unique reactivity of the members of the p-block with the desired photophysical and polymerizable properties that are required for the design of new materials. A need exists to develop

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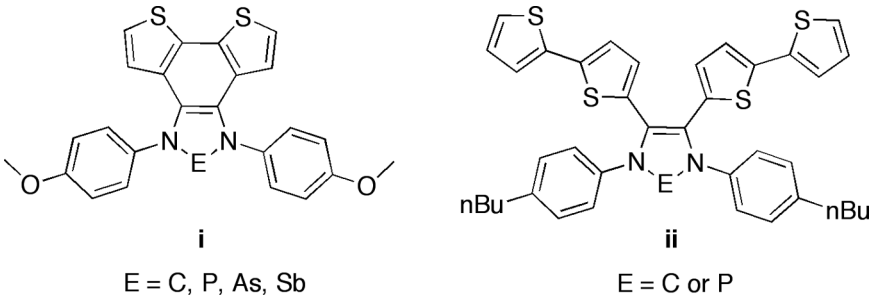
Fig. 1. Previously synthesized thiophene ligands coordinated to main group elements (**i** and **ii**).



ligands that can meet these requirements while continuing to push main group chemistry into the applied research fields. In this context, we have synthesized two new chelating diimino- (**2**^{Mes} and **2**^{Dipp}) and diamino- (**3**^{Mes} and **3**^{Dipp}) ligands with a thiophene unit in the backbone, where **3**^{Dipp} is able to support a phosphenium cation (**7**). This is the first synthesis and complete characterization of a seven-membered phosphenium cation and aids in identifying new opportunities in the unique structure, bonding, and reactivity of phosphorus.

Results and discussion

Synthesis

The thiophene substituted aryldiimines (**2**^{Mes} and **2**^{Dipp}) were synthesized via a condensation reaction between 3,4-diformylthiophene (**1**) and the appropriate arylamine in EtOH. The reaction mixtures were stirred overnight at room temperature and the yellow precipitates were isolated by filtration and washed with cold EtOH (Scheme 1). Upon examination of the ^{1}H NMR spectrum of the redissolved powders, the proton signal from the aldehyde (δ_H = 10.30) was no longer present and a resonance consistent with an imine appears (δ_H = 8.70). Compounds **2**^{Mes} and **2**^{Dipp} were isolated in 76% and 80% yields, respectively. Single crystals of **2**^{Mes} suitable for X-ray diffraction studies were grown from a concentrated solution of CH_2Cl_2 confirming the targeted connectivity (see Fig. 3).

Compounds **2**^{Mes} and **2**^{Dipp} were then reduced to the diamines **3**^{Mes} and **3**^{Dipp} using 3 stoichiometric equivalents of $LiAlH_4$ in Et_2O (Scheme 2).[23] The reaction mixture was stirred overnight at room temperature and then quenched with a 10% $KOH_{(aq)}$ solution. The filtrate was collected and concentrated under reduced pressure yielding a white solid. The bulk powders were redissolved in $CDCl_3$ and the corresponding ^{1}H NMR spectrum revealed that the aldimine proton was no longer present and a new singlet (δ_H = 4.0) appeared, indicative of the methylene protons adjacent to the thiophene ring. X-ray quality single crystals of **3**^{Dipp} were grown from a concentrated solution of CH_2Cl_2 confirming the synthesis of **3**^{Dipp}. The **3**^{Mes} and **3**^{Dipp} derivatives were isolated in 85% and 80% yields, respectively (Scheme 2).

The chlorophosphine **4** was synthesized using a 3:1:1 stoichiometric reaction between *N*-methylmorpholine, PCl_3, and **3**^{Mes} in tetrahydrofuran (THF), which resulted in an immediate formation of a white precipitate. Reaction progress was monitored by obtaining ^{31}P{^{1}H} NMR spectra of aliquots of the reaction mixture that indicated that the reaction was complete after 15 h, marked by the disappearance of PCl_3 (δ_P = 220) and the appearance of a new single resonance at δ_P = 153. In the proton ^{1}H NMR spectrum, the methylene protons in the 3 and 4 positions of the thiophene ring appear as a doublet because of coupling to phosphorus ($J1_H$–31_P = 2.8 Hz) and the methyl protons on the aryl rings were no longer identical, as distinct signals were observed. Subsequent halide abstraction using trimethylsilyl trifluoromethanesulfonate (Me_3SiOTf) surprisingly resulted in no shift of the phosphorus signal in the ^{31}P{^{1}H} NMR spectrum. X-ray quality crystals of **4** were grown from a concentrated CH_2Cl_2 solution of **4** layered with CH_3CN, and subsequent diffraction experiments revealed that the 1:2 stoichiometric reaction of diamine:phosphine occurred and explained the apparent lack of reactivity upon the addition of the halide-abstracting agent (Scheme 3).

Utilizing the ligand **3**^{Dipp} yielded differing results from those of **3**^{Mes}, where a 3:1:1 stoichiometric amount of *N*-methylmorpholine, PCl_3, and **3**^{Dipp} was stirred for 3 h at –78 °C and then warmed to room temperature and stirring was continued for 48 h. The reaction progress was monitored by ^{31}P{^{1}H} NMR spectroscopy, where two separate singlets emerged as the reaction proceeded (δ_p = 152 and δ_p = 155). The signal slightly upfield (δ_p = 152) was tentatively assigned to the 1:1 stoichiometric reaction of PCl_3 with the diamine (**3**^{Dipp}), ultimately yielding the cyclic diaminochlorophosphine (**5**) in 80%. The more downfield signal (δ_p = 155) was assigned to the 2:1 reaction between PCl_3 and the diamine, giving the bis(amino)dichlorophosphine (**6**), which was later confirmed by single crystal X-ray diffraction experiments. Compounds **5** and **6** had similar solubilities and the separation of compound **5** from **6** proved to be very difficult. However, changing the solvent to toluene and slowing the addition of a 0.043 mol L^{-1} toluene solution of PCl_3 (1 mL h^{-1} over 10 h), the selective synthesis of the cyclic diaminochlorophosphine (**5**) was achieved in a 90% isolated yield. Subsequent dehalogenation of **5** proceeded when an excess of Me_3SiOTf was added. An aliquot from the reaction solution was examined by ^{31}P{^{1}H} NMR spectroscopy where the original phosphorus signal (δ_p = 152) was no longer present, and a new peak appeared farther downfield (δ_p = 257), which was tentatively assigned to the phosphenium cation (**7**). The reaction mixture was then concentrated and washed with Et_2O leaving behind a white powder. A sample of the bulk powder was redissolved and examined by multinuclear NMR spectroscopy. The ^{31}P{^{1}H} spectrum revealed a single peak (δ_p = 257) consistent with the in situ formation of the phosphenium cation (Scheme 3).

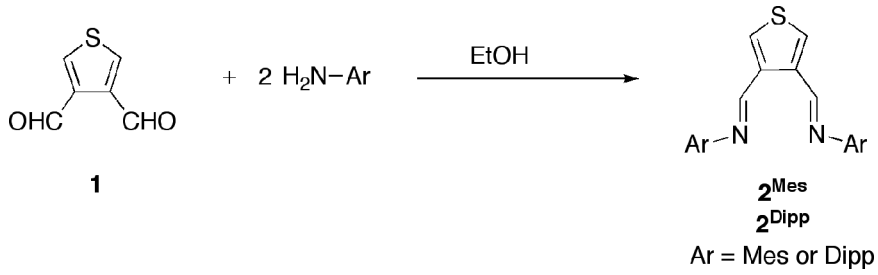
Photophysical properties

The UV-visible absorption spectra of compounds **2–7** are shown in Fig. 2, with the λ_{max} and the extinction coefficients listed in Table 1. Compounds **2–7** were all white to light yellow in colour and had λ_{max} values in the range of 220–240 nm, attributed to both π–π^* and n–π^* transitions. There was little variation in the UV-visible absorption spectra between the different compounds and the photophysical properties were dominated by the thiophene functionality in the backbone with no considerable influence from the phosphorus atom.

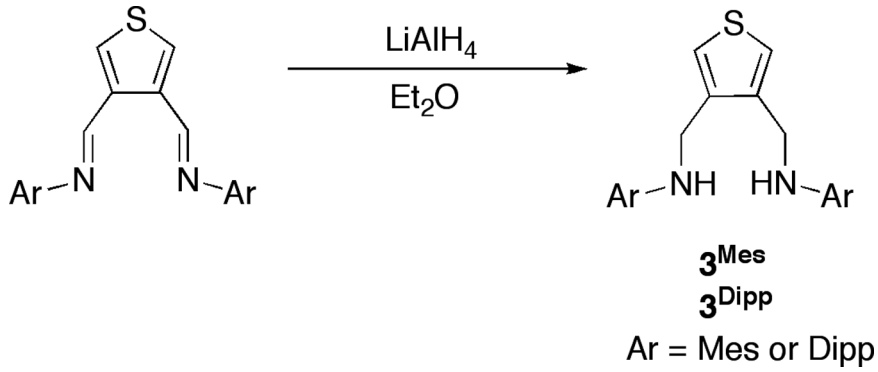
X-ray crystallography

Single crystals of compounds **2**^{Mes}, **3**^{Dipp}, **4**, **6**, and **7** were grown either by vapour diffusion using various solvent combinations or from concentrated solutions of CH_2Cl_2 layered with either CH_3CN or hexanes. Their solid-state structures were determined by single crystal X-ray diffraction and the relevant crystallographic data, metrical parameters, and structures are detailed in Table 2, Table 3 and Fig. 3, respectively.

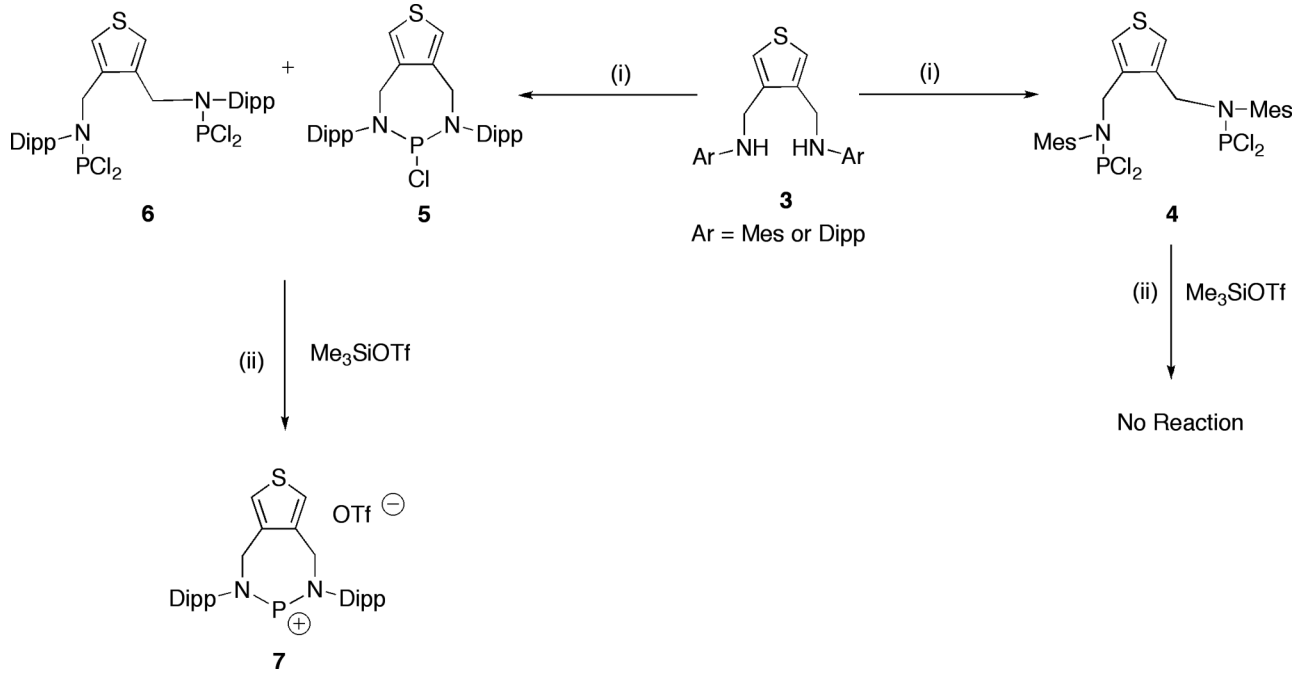
Scheme 1. Synthesis of 2^{Mes} and 2^{Dipp} diimines.



Scheme 2. Synthesis of compound 3^{Mes} and 3^{Dipp} diamines.



Scheme 3. Synthesis of compounds, 3, **4**, **5**, **6**, and **7**. (*i*) *N*-methylmorpholine, PCl_3, –78 °C, room temperature; (*ii*) TMSOTf, CH_2Cl_2, room temperature.



Examination of the solid-state structure of 2^{Mes} reveals that the $C_{\beta-N}$ bond is consistent with a double bond (1.270(4) Å average)[24] corresponding to the diimine, and upon reduction of 2^{Dipp} to 3^{Dipp}, the $C_{\beta-N}$ bond is reduced to a single bond with a length of 1.464(3) Å average.[25] A comparison of the metrical parameters for compounds 4 and **6** reveals that the P–Cl bond lengths range from 2.0725(13) to 2.1047(14) Å, which are similar to other aminodichlorophosphines, but much shorter compared with previously synthesized cyclic diaminochlorophosphines, where the P–Cl bonds can range from 2.2 to 2.7 Å.[26] These short P–Cl bonds explain the lack of reactivity with halide-abstracting agents observed in both compounds **4** and **6**, as they are more tightly bound to phosphorus.[27]

The solid-state structure of compound **7** shows a well-separated cation–anion pair with the distance between the oxygen and phosphorus being 3.8 Å, well outside the sum of the van der Waals radii for P–O ($\sum_{vdW}$ = 3.3 Å). The P–N bond is on average 1.625(1) Å, which is slightly shorter than compounds **4** and **6**, but still consistent with other related NHPs.[19,23] The bond angle between the N(1)–P(1)–N(2) is 111.28(8)° and is much larger than those reported

Fig. 2. UV-visible spectrum of compounds **2–7** in a 5×10^{-5} mol L^{-1} CH_2Cl_2 solution.

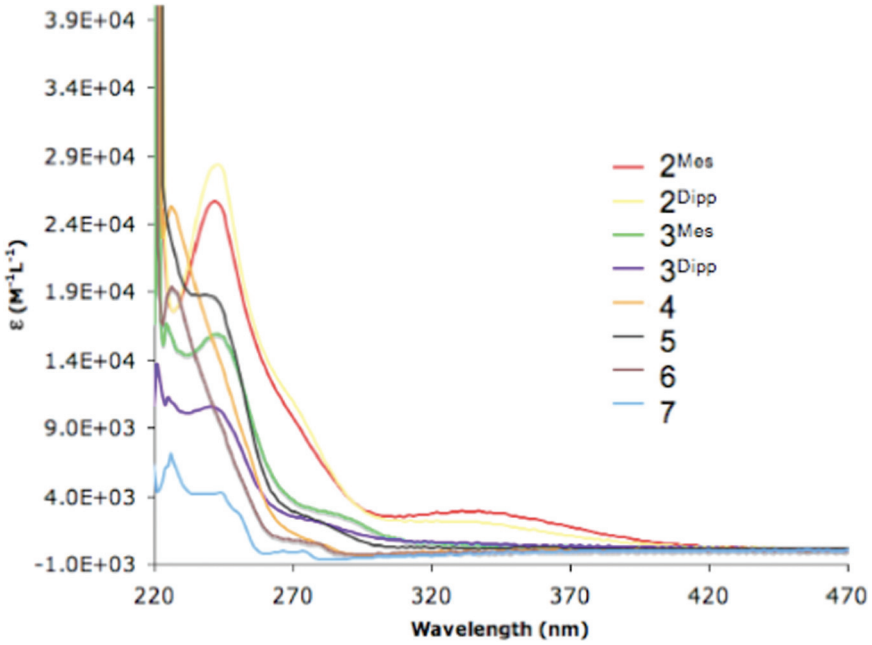


Table 1. UV-visible absorption and extinction coefficients of compounds **2–7**.

Compound	λ (nm) (ε (M^{-1} cm^{-1}))
2^{Mes}	240 nm (2.5×10^4)
	332 nm (2.8×10^3)
2^{Dipp}	242 nm (2.8×10^4)
	333 nm (2.1×10^3)
3^{Mes}	223 nm (1.6×10^4)
	242 nm (1.6×10^4)
	289 nm (2.4×10^3)
3^{Dipp}	241 nm (1.0×10^4)
	281 nm (2×10^3)
4	226 nm (2.5×10^4)
5	240 nm (1.8×10^4)
	270 nm (7.9×10^2)
6	226 nm (1.9×10^4)
7	226 nm (7.1×10^3)
	241 nm (4.1×10^3)

for five-membered[23] and six-membered NHPs,[28] which are approximately 90° and 105°. In the solid state, the thiophene ring sits at a 110.80(5)° angle from the C_2N_2P ring in an open book conformation.

Conclusions

A new class of thiophene-substituted diimine (**2^{Mes}** and **2^{Dipp}**) and diamine (**3^{Mes}** and **3^{Dipp}**) ligands has been synthesized and their reactivity with PCl_3 was explored. Due the inherent flexibility of the seven-membered ring system, there were difficulties controlling the degree of substitution at phosphorus. When Ar = Mes, a 1:2 stoichiometry of diamine:phosphine was observed (i.e., compound **4**); however, when Ar = Dipp, both the 1:1 (**5**) and 1:2 (**6**) products were isolated. When the solvent was changed from THF to toluene and the rate of addition of PCl_3 to **2^{Dipp}** was decreased, the cyclic diaminochlorophosphine (**5**) was successfully isolated. Compound **5** can be converted to NHP using the halide abstraction/metathesis reagent Me_3SiOTf, where the isolation and solid-state structure of a seven-membered NHP (**7**) was achieved. The thiophene ring in the backbone dominated the photophysical properties of these compounds and there was very little variation in the UV-visible spectrum.

General experimental

All manipulations were performed under N_2 atmosphere using standard Schlenk or glovebox techniques unless otherwise stated. Reagents where obtained from Sigma-Alrich and Alfa Aesar. $CDCl_3$ was dried over calcium hydride, distilled prior to use, and stored in the glovebox over 4 Å molecular sieves. All solvents were dried using an MBraun controlled-atmosphere solvent purification system and stored in Straus flasks under a N_2 atmosphere or over 4 Å molecular sieves with the exception of CH_3CN, which was stored over 3 Å molecular sieves in the glovebox. All NMR spectra were recorded on a Varian INOVA 400 MHz spectrometer (^1H = 399.76,[13] C = 100.52 MHz, ^{19}F = 376.15 MHz, ^{31}P = 161.85 MHz). All $^{31}P\{^1H\}$ NMR spectra were recorded relative to an external standard (85% H_3PO_4, δ = 0.00) at room temperature unless otherwise stated). UV-visible absorption spectra were recorded over a range of 220–600 nm using a Varian Cary 300 spectrometer in CH_2Cl_2. X-ray diffraction data were collected on a Nonius Kappa CCD or a Bruker ApexII CCD area detector using graphite monochromatic Mo–K_α radiation (λ = 0.71073 Å). Single crystals were selected under Paratone-N, mounted on nylon loops, and immediately placed in a cold stream of N2. Structures were solved by direct methods and refined using full matrix least squares on F^2. Hydrogen atom positions were calculated. FT–IR spectra were collected on samples as a KBr pellet using a Bruker Tensor 27 spectrometer with a resolution of 4 cm^{-1}. FT–Raman spectra were collected in flame-sealed capillary tubes on a Bruker RFS 100/s spectrometer with a resolution of 4 cm^{-1}. Decomposition/melting points were recorded in flame-sealed capillary tubes using a Gallenkamp Variable Heater. High resolution mass spectrometry (HRMS) data were collected using a Finnigan MAT 8200 instrument.

Synthesis

General synthesis for compounds 2^{Mes} and 2^{Dipp}

To a 20 mL EtOH solution of 3,4-diformylthiophene (1.00 g, 7.24 mmol), 2,6-diisopropylaniline (2.65 g, 14.28 mmol) or 2,3,6-trimethylaniline (1.93 g, 14.28 mmol) was added. The solution turned dark orange and a yellow solid precipitated from the reac-

Table 2. Crystal data for compounds 2^{Mes}, 3^{Dipp}, **4**, **6**, and **7**.

	2^{Mes}	3^{Dipp}	**4**	**6**	**7**
Empirical formula	$C_{24}H_{26}N_2S_1$	$C_{30}H_{42}N_2S_1$	$C_{24}H_{28}N_2S_1Cl_4P_2$	$C_{30}H_{40}N_2S_1Cl_4P_2$	$C_{31}H_{40}N_2S_2F_3O_3P_1$
FW (g mol^{-1})	374.53	462.72	580.28	664.44	640.74
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	$P2_1/c$	$C2/c$	$P\Sigma1$	$P\Sigma1$	$P\Sigma1$
a (Å)	8.116 (1)	26.186 (1)	9.547 (1)	9.983 (2)	10.227 (3)
b (Å)	15.946 (3)	13.392	10.435 (2)	13.907 (3)	10.949 (4)
c (Å)	16.190 (3)	16.408	14.707 (3)	25.630 (5)	15.625 (5)
α (°)	90	90	84.69 (3)	75.91 (3)	75.021 (9)
β (°)	91.76 (3)	106.997 (5)	80.09 (3)	84.28 (3)	75.056 (9)
δ (°)	90	90	75.51 (3)	83.86 (3)	85.202 (9)
V (Å^3)	2094.2 (7)	5502.7 (6)	1395.6 (5)	3421.3 (12)	1632.8 (9)
D_c (g cm^{-3})	1.188	1.117	1.381	1.290	1.303
$R_1[I > 2\int I]^a$	0.0631	0.0469	0.049	0.0546	0.0419
$wR_2(F^2)^a$	0.2237	0.1458	0.1631	0.1473	0.0908
GOF(S)	1.069	0.868	1.060	0.974	1.023
Scan range	2.60–25.48	2.60–25.48	1.00–27.28	1.00–27.48	2.64–26.35
Completeness	0.993	0.993	0.982	0.994	0.999

$^aR_1(F[I > 2(I)]) = \sum\| |F_o| - |F_c| \|/\sum |F_o|$; $wR_2(F^2$ [all data]) = $[w(F_o^2 - F_c^2)^2]^{1/2}$; S(all data) = $[w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ (n = no. of data; p = no. of parameters varied; $w = 1/[\int^2 (F_o^2) + (aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$ and a and b are constants suggested by the refinement.

Table 3. Selected average bond lengths (Å) and angles (°).

	2^{Mes}	3^{Dipp}	**4**	**6**	**7**
N–C_β	1.270 (4)	1.464 (3)	1.487 (3)	1.491 (7)	1.511 (3)
P–Cl			2.095 (2)	2.090 (3)	
N–P			1.646 (4)	1.648 (5)	1.625 (1)
N–P–Cl			103.07 (18)	103.1 (2)	
N–P–N					111.28 (8)

tion mixture. The reaction was stirred overnight at room temperature and the yellow powder was isolated by filtration. The product was washed with 5 × 5 mL of cold EtOH.

Compound 2^{Dipp}

Yield: 76% (2.51 g, 5.46 mmol); mp 192–194 °C. FT–IR (ranked intensity (cm^{-1})): 758 (7), 796 (11), 822 (3), 851 (3), 876 (12), 933 (16), 1166 (5), 1323 (9), 1384 (10), 1435 (4), 1470 (15), 1513 (8), 1634 (1), 2962 (2), 3074 (14). FT–Raman (ranked intensity (cm^{-1})): 169 (13), 273 (2), 528 (6), 799 (3), 857 (11), 957 (1), 1042 (12), 1110 (8), 1159 (4), 1247 (14), 2861 (9), 2905 (7), 2937 (5), 2961 (15), 3089 (10). ^{1}H NMR ($CDCl_3$ δ (ppm)): 8.72 (s, 2H), 8.04 (s, 2H, thienyl), 7.08 (m, 6H, phenyl), 2.94 (sept., 4H, $^3J_{HH}$ = 6.8 Hz), 1.10 (d, 24H, $^3J_{HH}$ = 6.8 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$ δ (ppm)): 157.8, 149.5, 138.8, 137.9, 131.7, 124.6, 123.4, 28.4, 23.9. HRMS $C_{30}H_{28}N_2S$ calcd. (found): 458.2756 (458.2764). λ_{max} = 240 nm (2.5 × 10^4 M^{-1} cm^{-1}), 273 (sh) nm (8.7 × 10^3 M^{-1} cm^{-1}), 332 (sh) nm (2.8 × 10^{-3} M^{-1} cm^{-1}).

Compound 2^{Mes}

Yield: 80% (2.13 g, 5.60 mmol); mp 139–141 °C. FT–IR (ranked intensity (cm^{-1})): 733 (13), 819 (2), 859 (8), 878 (12), 1138 (9), 1174 (5), 1212 (6), 1448 (15), 1476 (3), 1513 (10), 1629 (1), 2859 (4), 2916 (11), 3078 (7), 3100 (14). FT–Raman (ranked intensity (cm^{-1})): 124 (4), 573 (6), 1139 (7), 1174 (5), 1213 (15), 1297 (10), 1354 (8), 1379 (14), 1405 (11), 1449 (12), 1513 (3), 1604 (2), 1628 (2), 2918 (9), 3078 (13). ^{1}H NMR ($CDCl_3$ δ (ppm)): 8.73 (s, 2H), 8.00 (s, 2H, thienly), 6.86 (s, 4H, aryl), 2.26 (s, 6H, methyl), 2.12 (s, 12H, methyl). ^{13}C{^{1}H} NMR ($CDCl_3$ (ppm)): δ 158.0, 148.6, 138.5, 132.9, 130.6, 128.6, 126.9, 20.7, 18.3. HRMS $C_{24}H_{26}N_2S$ calcd. (found): 374.1817 (374.1824). λ_{max} = 242 nm (2.8 × 10^4 M^{-1} cm^{-1}), 269 (sh) nm (1.1 × 10^4 M^{-1} cm^{-1}), 333 (sh) nm (1.1 × 10^{-3} M^{-1} cm^{-1}).

General synthesis for compounds 3^{Mes} and 3^{Dipp}

Solid $LiAlH_4$ (0.248 g, 6.55 mmol) was added portion-wise to a 50 mL Et_2O solution of diimine (2.18 mmol). The suspension was stirred overnight at room temperature. Excess $LiAlH_4$ was quenched with 10 mL of a 10% $KOH_{(aq)}$ solution. The salts were removed by filtration and the colourless filtrate was dried over $MgSO_4$ and concentrated under reduced pressure to obtain the diamine.

Compound 3^{Mes}

Yield: 0.85% (0.86 g, 1.85 mmol); mp 104–105 °C. FT–IR (ranked intensity (cm^{-1})): 569 (8), 698 (13) 756 (15), 804 (2), 856 (7), 1025 (14), 1065 (5), 1154 (9), 1226 (3), 1300 (10), 1329 (12), 1480 (1), 2910 (4), 3108 (11), 3348. (6) FT–Raman (ranked intensity (cm^{-1})): 139 (15), 492 (12), 576 (1), 841 (14), 957 (9), 1066 (11), 1155 (13), 1228 (8), 1301 (3), 1379 (5), 1446 (7), 1608 (4), 2912 (2), 30109 (10). ^{1}H NMR ($CDCl_3$ δ (ppm)): 7.23 (s, 2H, thienyl), 7.83 (s, 4H, aryl), 4.03 (s, 4H, alkyl), 2.24 (s, 6H, methyl), 2.22 ppm (s, 12H, methyl). ^{13}C{^{1}H} NMR ($CDCl_3$ δ (ppm)): 143.1, 139.9, 131.7, 130.2, 129.4, 123.4, 46.7, 20.5, 18.2. HRMS $C_{24}H_{28}N_2S$ calcd. (found): 378.2130 (378.2139); λ_{max} = 223 nm (1.6 × 10^4 M^{-1} cm^{-1}) 242 nm (1.6 × 10^4 M^{-1} cm^{-1}), 289 (sh) nm (2.4 × 10^{-3} M^{-1} cm^{-1}).

Compound 3^{Dipp}

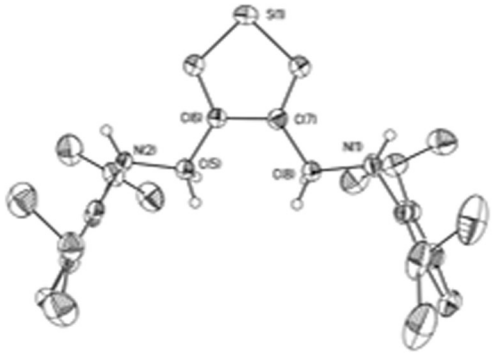
Yield: 80% (0.81 g, 1.75 mmol); mp 109–110 °C. FT–IR (ranked intensity (cm^{-1})): 527 (9), 573 (11), 732 (1), 803 (5), 856 (8), 932 (7), 1055 (4), 1114 (13), 1195 (6), 1258 (14), 1302 (10), 1382 (12), 1459 (3), 2961 (2), 3090 (15). FT–Raman (ranked intensity (cm^{-1})): 150 (4), 170 (5), 222 (10), 273 (14), 677 (9), 857 (13), 889 (8), 1043 (12), 1248 (11), 1448 (6), 1590 (7), 2908 (2), 2936 (1), 2960 (3). ^{1}H NMR ($CDCl_3$ δ (ppm)): 7.34 (s, 2H, thienyl), 7.10 (m, 6H, aryl), 4.03 (s, 4H, alkyl), 3.26 (sept., 4H, $^3J_{HH}$ = 6.8 Hz), 1.23 (d, 24H, $^3J_{HH}$ = 6.8 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$ δ (ppm)): 143.1, 139.8, 124.4, 123.8, 123.2, 50.3, 28.0, 24.5. HRMS $C_{30}H_{32}N_2S$ calcd. (found): 462.3069 (462.3065). λ_{max} = 241 nm (1.0 × 10^4 M^{-1} cm^{-1}), 281 (2.0 × 10^3 M^{-1} cm^{-1}).

Compound **4**

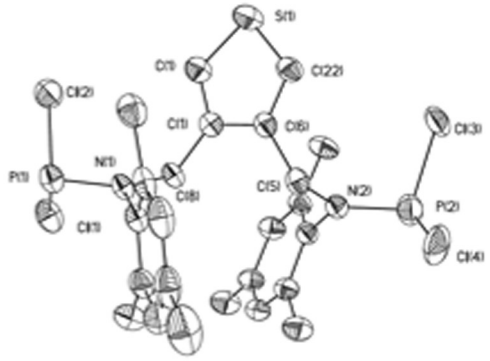
A 20 mL THF solution of PCl_3 (0.11 mL, 1.33 mmol) was cooled to –78 °C. A 10 mL THF solution of 3^{Mes} (0.50 g, 1.33 mmol) was then added dropwise via cannula and a white precipitate formed immediately. The reaction mixture was stirred at –78 °C for 2 h, then warmed to room temperature, and then stirred for 15 h. The white precipitate was removed by centrifuge and the resulting colourless solution was concentrated. Acetonitrile (5 mL) was then added to the residue resulting in the formation of a white precipitate. The CH_3CN was decanted and the product dried under vacuum. Yield: 34% (0.23 g, 0.45 mmol); mp 125–128 °C. FT–IR (ranked intensity (cm^{-1})): 434 (10), 481 (5), 508 (12), 525 (4), 568 (2), 683 (8), 808 (3), 855 (11), 883 (6), 1061 (1), 1120 (13), 1207 (7), 1346 (15), 1474 (9), 2917 (14). FT–Raman (ranked intensity (cm^{-1})): 191 (5), 240 (1), 418 (12), 456 (3), 513 (2), 560 (15), 574 (6), 633 (9), 859 (14), 1178 (11), 1307 (4), 1379 (10), 1606 (8), 2917 (7), 3112 (3). ^{1}H NMR ($CDCl_3$ δ (ppm)):

Fig. 3. Solid state structures of compounds $\mathbf{2}^{\mathbf{Mes}}$, $\mathbf{3}^{\mathbf{Dipp}}$, **4**, **5**, **6**, and **7**. Thermal ellipsoids are drawn to 50% probability and hydrogen atoms have been omitted for clarity with the exception of $\mathbf{3}^{\mathbf{Dipp}}$. For compound **7**, the triflate anion has been omitted for clarity and a side on view of the molecule is shown in **7b** in which the Dipp groups have been omitted.

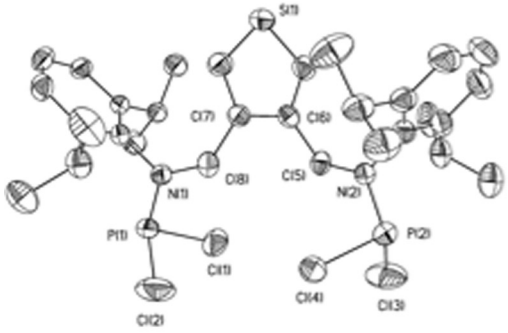
$\mathbf{2}^{\mathbf{Mes}}$



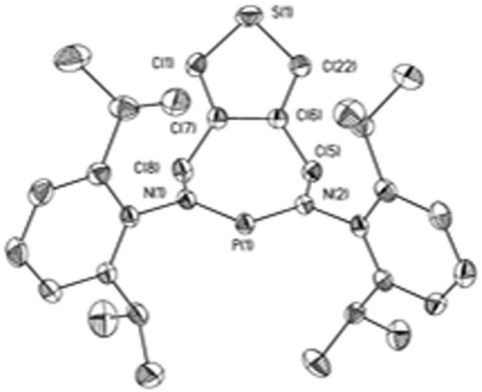
$\mathbf{3}^{\mathbf{Dipp}}$



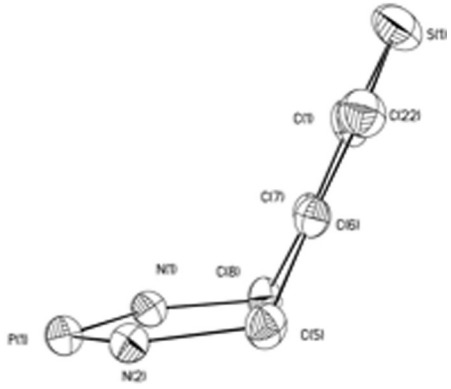
4



6



7



7b

6.99 (s, 2H, thienyl), 6.83 (s, 4H, aryl), 4.04 (d, 4H, $^2J_{HP}$ = 2.8 Hz alkyl), 2.27 (s, 3 H, methyl), 2.26 (s, 3H, methyl), 1.87 (s, 6H, methyl), 1.86 (s, 6H, methyl). $^{13}C\{^1H\}$ NMR ($CDCl_3$ δ (ppm)): 138.8, 138.7, 138.6, 136.0, 135.5, 129.8, 128.7, 127.5, 44.4 (d, $^1J_{CP}$ = 28 Hz), 20.9, 18.6. $^{31}P\{^1H\}$ NMR ($CDCl_3$ δ (ppm)): 153.8. λ_{max} = 224 nm (2.5 × 10^4 M^{-1} cm^{-1}). Elemental analysis (%) calcd. for $C_{24}H_{28}N_2S_1Cl_4P_2$: C 49.67, H 4.86, N 4.83, S 5.53; found: C 50.11, H 5.12, N 4.84, S 5.72.

Compound 5

A 10 mL toluene solution of **3^{Dipp}** (0.20 g, 0.43 mmol) was cooled to –78 °C in a dry ice – acetone bath. To this, a 10 mL toluene solution of PCl_3 (34 μL, 0.43 mmol) was added via a syringe pump at a rate of 1 mL h^{-1}. The reaction mixture was then warmed to room temperature and stirred for 24 h. Upon completion, the reaction was concentrated under reduced pressure and then taken up in 10 mL of Et_2O. The Et_2O solution was then centrifuged to remove the ammonium salt and was then concentrated yielding the desired product. Yield: 90% (0.20 g, 0.38 mmol); mp 98–100 °C. FT–IR (ranked intensity (cm^{-1})): 526 (5), 573 (8), 731 (10), 802 (2), 932 (13), 1055 (4), 1113 (14), 1194 (7), 1258 (6), 1302 (15), 1382 (11), 1459 (3), 1587 (9), 2961 (1), 3090 (12). (12) FT-Raman (ranked intensity (cm^{-1})): 149 (4), 169 (9), 274 (15), 676 (8), 857 (10), 889 (5), 1042 (7), 1110 (11), 1247 (6), 1446 (2), 1589 (3), 2862 (13), 2906 (14), 2961 (1), 3089. ^1H NMR ($CDCl_3$ δ (ppm)): 7.33 (s, 2H, thienyl), 7.11 (m, 6H, aryl), 4.04 (d, 4H, $^1J_{HP}$ = 7.37 Hz, alkyl), 3.26 (sept. 4H, $^3J_{HH}$ = 6.8 Hz), 1.14 (d, 24H, $^3J_{HH}$ = 6.8 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$ δ (ppm)): 142.9, 142.8, 124.1, 123.5, 122.9, 50.0, 27.8, 24.2. $^{31}P\{^1H\}$ NMR ($CDCl_3$ δ (ppm)): 152.2. λ_{max} = 240 nm (1.8 × 10^4 M^{-1} cm^{-1}), 280 (sh) nm (2.1 × 10^3 M^{-1} cm^{-1}).

Compound 6

A 10 mL Et_2O solution of **3^{Dipp}** (0.20 g, 0.43 mmol) was cooled to –78 °C. To this, a 10 mL Et_2O solution of PCl_3 was added dropwise via cannula. A white precipitate formed immediately and the reaction mixture was stirred at –78 °C for 2 h. The reaction was then warmed to room temperature and left to stir for an additional 24 h. Upon completion, the solvent was removed in vacuo leaving an orange residue, which was then taken up in CH_3CN. The orange solution was then concentrated again under reduced pressure yielding a yellow solid. The yellow solid was washed with 3 × 5 mL of CH_3CN yielding the product as a white solid. Yield 42% (0.12 g, 0.18 mmol); mp 157–159 °C. FT–IR (ranked intensity (cm^{-1})): 454 (10), 515 (7), 637 (2), 692 (15), 751 (14), 810 (5), 857 (9), 895 (13), 1028 (3), 1113 (11), 1169 (8), 1256 (1), 1467 (6), 1587 (12), 2970 (4). ^1H NMR ($CDCl_3$ δ (ppm)): 7.21 (m, 2H, aryl), 7.03 (d, 4H, $^3J_{HH}$ = 7.6 Hz, aryl), 6.30 (s, 2H, thienyl), 4.61 (d, 4H, $^2J_{HP}$ = 2.4 Hz, alkyl), 2.79 (sept. 4H, $^3J_{HH}$ = 6.8 Hz), 1.02 (d, 12H, $^3J_{HH}$ = 6.8 Hz), 0.90 (d, 12H, $^3J_{HH}$ = 6.8 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$ δ (ppm)): 149.9, 135.4, 134.1, 129.4, 126.7, 124.3, 46.3 ($^1J_{C\text{-}P}$ = 28.4 Hz), 28.8, 26.7, 22.6. $^{31}P\{^1H\}$ NMR ($CDCl_3$ δ (ppm)): 154.9. λ_{max} = 226 nm (1.9 × 10^4 M^{-1} cm^{-1}), 270 (sh) nm (7.9 × 10^2 M^{-1} cm^{-1}). HRMS $C_{30}H_{40}SN_2Cl_4P_2$ calcd. (found): 662.1142 (662.1135).

Compound 7

To a 5 mL CH_2Cl_2 of **5** (0.200 g, 0.38 mmol), neat $(CH_3)_3SiOTf$ (0.20 mL, 0.1.14 mmol) was added. The reaction mixture stirred was at room temperature for 2 h until all of the chlorophosphine was converted to the phosphenium cation. Upon completion, the reaction mixture was concentrated under reduced pressure yielding a white solid. The product was then washed with 3 × 5 mL of Et_2O and dried under vacuum. Yield: 32% (0.08 g, 0.12 mmol); mp. FT–IR (ranked intensity (cm^{-1})): 454 (10), 515 (7), 637 (2), 692 (15), 751 (14), 810 (5), 857 (9), 895 (13), 1028 (3), 1113 (11), 1169 (8), 1256 (1), 1467 (6), 1587 (12), 2970 (4). FT–Raman (ranked intensity (cm^{-1})): 201 (10), 308 (8), 693 (1), 720 (11), 882 (7), 1027 (3), 1043 (6), 1116 (2), 1239 (5), 1586 (4), 2870 (9), 2980 (12). ^1H NMR ($CDCl_3$ δ (ppm)): 7.36 (t, 2H, $^1J_{HH}$ = 8 Hz, aryl), 7.27 (s, 2H, thienyl), 7.19 (d, 4H, $^1J_{HH}$ = 8 Hz, aryl), 5.48 (br. s, 4H, alkyl), 3.18 (br. sept., 4H), 1.28 (d, 12H, $^3J_{HH}$ = 6.8 Hz), 1.07 (d, 12H, $^3J_{HH}$ = 6.8 Hz). $^{13}C\{^1H\}$ ($CDCl_3$ δ (ppm)): 147.4, 134.9, 134.7, 134.2, 131.4, 126.7, 125.4, 58.8, 28.7, 25.1, 24.2. $^{31}P\{^1H\}$ ($CDCl_3$ δ (ppm)): 257.1. λ_{max} = 224 nm (7.1 × 10^3 M^{-1} cm^{-1}), 241 nm (4.1 × 10^3 M^{-1} cm^{-1}). Elemental analysis (%) calcd. for $C_{31}H_{40}F_3O_3N_2S_2P_1$: C 57.88, H 6.51, N 4.38, S 10.07; found: C 58.11, H 6.29, N 4.37, S 10.01.

Supplementary material

Supplementary data are available with the article through the journal Web site at http://nrcresearchpress.com/doi/suppl/10.1139/cjc-2013-0015. CCDC 929309-929313 contain the crystallograhic data in CIF format for this article. These data can be obtained, free of charge, via http://www.ccdc.cam.ac.uk/products/csd/request (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1E2, UK; fax: +44 1223 33603; e-mail: deposit@ccdc.cam.ac.uk).

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