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# Tetra-cationic imidazoliumyl-substituted phosphorus-sulfur heterocycles from a cationic organophosphorus sulfide $\dagger$ 

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#### Abstract

The reaction of imidazoliumyl-substituted $\mathrm{P}^{(\text {III })}$ cations of type $\left[\mathrm{L}^{(\mathrm{R}, \mathrm{Me})} \mathrm{PCl}_{2}\right]^{+}\left(3 \mathrm{a}, \mathrm{b}^{+} ; \mathrm{L}^{\mathrm{R}, \mathrm{Me}}=\right.$ imidazolium-2-yl a: $\mathrm{R}=\mathrm{Me}$; $\left.\mathrm{b}: \mathrm{R}=\mathrm{iPr}\right)$ with $\left(\mathrm{Me}_{3} \mathrm{Si}_{2} \mathrm{~S}\right.$ leads to the formation of tetra-cationic, eight-membered phosphorus sulfur heterocycles $\left[L^{(\mathrm{R}, \mathrm{Me})} \mathrm{PS}\right]_{4}{ }^{4+}\left(9 \mathrm{a}, \mathrm{b}^{4+}\right)$, which can be explained by the tetramerization of the intermediately formed cationic phosphorus monosulfide $\left[\mathrm{L}^{(\mathrm{R}, \mathrm{Me})} \mathrm{PS}\right]^{+}\left(8 \mathrm{a}, \mathrm{b}^{+}\right)$. The $\mathrm{P}_{4} \mathrm{~S}_{4}$ ring adopts a crown conformation as observed for cyclo- $\mathrm{S}_{8}$. The Lewis base DMAP (4-dimethylaminopyridine) initiates a deoligomerization- and dismutation reaction of $9 \mathrm{a}, \mathrm{b}^{4+}$ to give $\mathrm{P}^{(1)}$ centered cation $\left[\mathrm{L}^{(\mathrm{R}, \mathrm{Me})}{ }_{2} \mathrm{P}\right]^{+}$ (12a, $\mathrm{b}^{+}$) and phosphorus disulfide $\left[(D M A P)_{2} \mathrm{PS}_{2}\right]^{+}\left(14^{+}\right)$.


Organophosphorus-sulfur heterocycles with the general constitution $(\mathbf{R P S})_{n}(n=2-4)$ and phosphorus in the oxidation state + III remain scarce, since their main access is from the reaction of a dichlorophosphane $\mathrm{RPCl}_{2}(\mathrm{R}=\mathrm{Aryl})$ and a source of sulfide ( $\mathrm{S}^{2-} ;$ e.g. $\mathrm{M}_{2} \mathrm{~S}(\mathrm{M}=\mathrm{Li}$, $\mathrm{Na})$ or $\left.\left(\mathrm{Me}_{3} \mathrm{Si}\right)_{2} \mathrm{~S}\right) .{ }^{1}$ The formation of these compounds can formally be viewed as a combination of divalent RP: and S: units to give monomeric phosphorus mono-sulfides such as $\mathbf{1}$, which then can either yield oligomerization products (Fig. 1; path I) or ylidylphosphorus sulfide 2 a (path II). ${ }^{1} \mathbf{2 a}$ represents a rare example of a stable and structurally confirmed monomeric ylidylphosphorus monosulfide. Its stability is rationalized by a high contribution of the zwitterionic resonance formula $\mathbf{2 b}$ (path $\mathbf{I I}$ ). ${ }^{2}$ Aiming at the synthesis of new cationic phosphorus species, we are investigating reactions of imidazoliumyl-substituted P-centered cations such as $\left[\mathrm{L}^{(\mathrm{R}, \mathrm{R})} \mathrm{PCl}_{2}\right]^{+} 3^{+}$ $\left(\mathrm{L}^{\mathrm{R}, \mathrm{Me}}=\text { imidazolium-2-yl, } \mathrm{R}=\text { Aryl, Alkyl; } \mathrm{R}^{\prime}=\mathrm{H}, \mathrm{Me}, \mathrm{Cl}\right)^{3}$ towards substitution ${ }^{3,4}$ (e.g. $4^{+}, 5^{+}$), coordination, ${ }^{5}$ oxidation ${ }^{6}$ or reduction ${ }^{7}$

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Fig. 1 Formation of oligomeric phosphorus sulfides (RPS) $n_{n}(n=2-4$; $\mathrm{R}=$ Aryl, $\mathrm{R}^{\prime}=$ Alkyl; path I) and phosphorus monosulfide $\mathbf{2 a}, \mathbf{b}$ (path II).
(e.g. $\mathbf{6}^{+}, 7^{+}$) and successfully isolated a series of novel cationic derivatives with intriguing bonding motives (Fig. 2). In this contribution we present the results of the attempted preparation of the imidazoliumyl-substituted $\left[\mathrm{L}^{(\mathrm{R}, \mathrm{Me})} \mathrm{PS}\right]^{+}$cations 8a, $\mathbf{b}^{+}$(a: $\mathrm{R}=\mathrm{Me}$; b: $\mathrm{R}=\mathrm{iPr})$ from the reaction of $3 \mathbf{a}, \mathbf{b}^{+}$with $\left(\mathrm{Me}_{3} \mathrm{Si}\right)_{2} \mathrm{~S}$ and the respective oligomerization to tetra-cations $9 \mathbf{9 a}, \mathbf{b}^{4+}$ which can be isolated as triflate salts (Scheme 1). Compounds $\mathbf{3 a}, \mathbf{b}[\mathrm{OTf}]$ (ref. 3) were reacted with 1 eq. $\left(\mathrm{Me}_{3} \mathrm{Si}\right)_{2} \mathrm{~S}$ in fluorobenzene for 5 h at ambient temperature, accompanied by the formation of colorless precipitates. After workup, compounds $\mathbf{9 a}, \mathbf{b}[\mathrm{OTf}]_{4}$ were isolated in excellent yields ( $>90 \%$; Scheme 1). The ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectra of the dissolved compounds in $\mathrm{d}_{3}-\mathrm{MeCN}$ display one major resonance next to a


Fig. 2 Selected P -centered cations $\mathbf{3 - \mathbf { 7 } ^ { + }}$ featuring imidazoliumyl-substituents (Dipp = 2,6-diisopropylphenyl).


Scheme 1 Preparation of tetrameric imidazoliumyl-substituted phos-phorus-sulfur heterocycles $9 \mathbf{a}, \mathbf{b}[\mathrm{OTf}]_{4}$ from the intermediately formed cation $\mathbf{8 a}, \mathbf{b}^{+}(\mathrm{a}: \mathrm{R}=\mathrm{Me} ; \mathrm{b}: \mathrm{R}=\mathrm{iPr})$; (i) $+\left(\mathrm{Me}_{3} \mathrm{Si}\right)_{2} \mathrm{~S}, \mathrm{C}_{6} \mathrm{H}_{5} \mathrm{~F}, \mathrm{rt},-2 \mathrm{Me}_{3} \mathrm{SiCl}$.
minor singlet in the typical region of tri-coordinate phosphorus derivatives $\left(\mathbf{9 a}^{4+}: \delta(\mathrm{P})_{\text {major/minor }}=48.2 \mathrm{ppm} / 48.0 \mathrm{ppm} ; \mathbf{9 b}^{4+}\right.$ : $\left.\delta(\mathrm{P})_{\text {major/minor }}=50.5 \mathrm{ppm} / 50.3\right)$ indicating the oligomerization of the intermediately formed cationic phosphorus monosulfide $\mathbf{8 a}, \mathbf{b}^{+}$. However, no evidence for the formation of other ring sizes was found, showing a high selectivity of the oligomerization process. It can be assumed that, under these conditions, the formation of the $\mathrm{P}_{4} \mathrm{~S}_{4}$ ring is thermodynamically (considering ring strain and steric effects) favored. The variable-temperature (VT) ${ }^{31} \mathrm{P}$ NMR spectra for $\mathbf{9 b}[\mathrm{OTf}]_{4}$ are depicted in Fig. 3a, evidencing a dynamic behavior and the presence of two highly symmetric conformational isomers (crown $\left(C_{4 \mathrm{v}}\right)$ vs. boat-chair ( $C_{\mathrm{s}}$ ) conformer) of the $\mathrm{P}_{4} \mathrm{~S}_{4}$ ring in solution (Scheme 2). A significant broadening of the two resonances upon


Fig. 3 (a) $\mathrm{VT}{ }^{31} \mathrm{P}$ NMR spectra of $\mathbf{9 b}[\mathrm{OTf}]_{4}$ recorded in $\mathrm{CD}_{3} \mathrm{CN}$ (see ESI $\dagger$ ) * indicates minor amounts of the conformational isomer of $9 b^{+}$; (b) ${ }^{31} \mathrm{P}$ EXSY NMR spectrum of $\mathbf{9 b}[\mathrm{OTf}]_{4}$ recorded at 335 K with a mixing time of $t_{\mathrm{m}}=0.55 \mathrm{~s}$.


Scheme 2 Interconversion process of cations $\mathbf{9 a}, \mathbf{b}^{\mathbf{4 +}}$ from the conformational isomer with crown shape ( $C_{4 v}$ ) to the boat-chair $\left(C_{5}\right)$ conformer without considering the imidazoliumyl substituents.
cooling is observed. The VT ${ }^{1} \mathrm{H}$ NMR spectra also show additional dynamic behavior of the iPr-groups. We thus confirmed the existence of two conformational isomers independently by ${ }^{31} \mathrm{P}$ EXSY NMR experiments (Fig. 3b), although quantitative accuracy (to determine kinetic processes or exchange rates) was limited by the narrow temperature range in which useful spectra could be measured. The ${ }^{31}$ P EXSY NMR experiments suggest exchange of two conformers in which one of the sulfur-bridges reversibly changes its relative position, giving either the approximate $C_{4 \mathrm{v}}$ or $C_{\mathrm{s}}$ symmetric cations $\mathbf{9 a}, \mathbf{b}^{\mathbf{4 +}}$ (Scheme 2). The cross peaks in the 2D spectrum demonstrate the exchange between the two symmetric conformers in solution, consistent with the observation of singlet resonances as expected for an $A_{4}$ spin-system for both isomers.

Satisfactory crystal structure analyses could be performed confirming the formation of the suggested eight-membered organophosphorus-sulfur heterocycles (Fig. 4). In the case of compound $\mathbf{9 b}[\mathrm{OTf}]_{4}$ the refinement of the X-ray data confirmed the crown-shaped $\mathrm{P}_{4} \mathrm{~S}_{4}$ moiety, similarly to cation $\mathbf{9 a}^{4+}$, however, due to severe disorder caused by alternating ring orientation full refinement was only possible after treatment by an appropriate disordered model. ${ }^{8}$ The $\mathrm{P}^{\mathrm{III}}-\mathrm{S}$ bond lengths (av. $2.129 \AA$ ) in $9 \mathrm{a}^{4+}$ are in the typical range for $\mathrm{P}^{\mathrm{II}}-\mathrm{S}$ single bonds and compare well with those reported by Sheldrick et al. for the neutral derivative (MesPS) $4_{4}$ (av. 2.117 Å; Mes $=2,4,6$-trimethylphenyl). ${ }^{1 b}$ The pyramidalization of the P atoms, as well as the lengths of the C-P bonds (av. $1.817 \AA$ ), together with the internal angle $\mathrm{N} 1-\mathrm{C} 1-\mathrm{N} 2$ of the imidazoliumyl moieties ( $9 \mathrm{a}^{4+}$ : av. $106.9^{\circ}$ vs. $\sim 101^{\circ}$ in NHCs$)^{9}$ are in agreement with the ability of the imidazoliumyl fragment to (a) delocalize the positive charge, (b) reduce the nucleophilicity of a directly bonded $P$ atom and thus may account for the stability of these cations. ${ }^{5,10,11}$


Fig. 4 Molecular structure of tetracation $9 a^{4+}$ in $\mathbf{9 a}[O T f]_{4}$. All hydrogen atoms and triflate anions are omitted for clarity. Selected bond lengths in $\AA$ and angles in ${ }^{\circ}$ : P1-S1 2.1306(9), P1-S4 2.1364(9), P2-S1 2.1234(9), P1-C1 1.820(3), S1-P1-S4 101.99(4), S1-P1-C1 99.31(8), S4-P1-C1 101.26(9), N1-C1-N2 101.26(9).


Scheme 3 Deoligomerization of $9 \mathbf{b}[\mathrm{OTf}]_{4}$ with DMAP and proposed intermediates; (i) +4 DMAP, MeCN, rt.

To confirm that the formation of tetracations $\mathbf{9 a}, \mathbf{b}^{\mathbf{4 +}}$ proceeds via monomeric phosphorus mono-sulfides $\mathbf{8 a}, \mathbf{b}^{+}$, we reacted $\mathbf{9 a}, \mathbf{b}[\mathrm{OTf}]_{4}$ with DMAP in MeCN, since this Lewis base has been widely used to stabilize low-coordinate phosphorus species. ${ }^{12}$ The $\sigma$-donor strength of DMAP should be high enough to deoligomerize tetracations $\mathbf{9 a}, \mathbf{b}^{\mathbf{4 +}}$ to cations 10a, $\mathbf{b}^{+}$which represent DMAP adducts of the elusive cations $\mathbf{8 a}, \mathbf{b}^{+}$(Scheme 3). The reaction of 4 equivalents DMAP in MeCN proceeds comparably clean with $\mathbf{9 b}[\mathrm{OTf}]_{4}$ at ambient temperature giving pale-yellow solutions. The ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectra of the reaction mixture of $\mathbf{9 b}[\mathrm{OTf}]_{4}$ and DMAP after reaction times of 10 min to 7 d are depicted in Fig. 5. After 10 min a broad resonance at $\delta(\mathrm{P})=147.1 \mathrm{ppm}$ is observed which splits into 2 singlets at low temperature $(\delta(\mathrm{P})=140.3 \mathrm{ppm}$ and $\delta(\mathrm{P})=144.4 \mathrm{ppm} ; 253 \mathrm{~K})$. We believe that the splitting of the resonances results from two rotational isomers caused by a restricted rotation of the iPr groups at low temperature. ${ }^{8,13}$ From the distinctive chemical shift a dimeric derivative with tetra-coordinate phosphorus atoms


Fig. $5 \quad{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectra of the $1: 4$ reaction of $\mathbf{9 b}[\mathrm{OTf}]_{4}$ and DMAP in $\mathrm{CD}_{3} \mathrm{CN}$ showing the scrambling reaction to cations $\mathbf{1 1}^{+}, \mathbf{1 2} \mathbf{b}^{+}, \mathbf{1 4}^{+}$and adduct 13.
$\left(c f .\left[\left(\mathrm{Et}_{2} \mathrm{~N}\right)_{2} \mathrm{PS}_{2}\right]\left[\mathrm{AlCl}_{4}\right]_{2}: \delta(\mathrm{P})=21.0 \mathrm{ppm}\right)^{14}$ can be excluded and we thus propose the formation of DMAP adduct $\mathbf{1 0} \mathbf{b}^{+}$which is also supported by our NMR investigation. ${ }^{8}$ We were not able to isolate $\mathbf{1 0 b}[\mathrm{OTf}]$, however, we assume that cation $\mathbf{1 0 b}^{+}$readily dismutates to cations $\mathbf{1 1}^{+}(\delta(\mathrm{P})=215.8 \mathrm{ppm})$ and $\mathbf{1 2 \mathbf { b } ^ { + }}(\delta(\mathrm{P})=-126.1 \mathrm{ppm})$ via an intermolecular scrambling reaction, i.e. an intermolecular exchange of imidazolium-2-yl and sulfur substituents. Related exchange reactions were discussed for the DMAP induced disproportionation of $\mathrm{POCl}_{3}{ }^{15}$ and scrambling reactions of imidazoliumylsubstituted $\left[\mathrm{L}^{(\mathrm{Me}, \mathrm{Me})} \mathrm{PCl}_{2}\right]^{+}$cations. ${ }^{4} \mathrm{P}^{\mathrm{I}}$ centered cation $\mathbf{1 3} \mathbf{b}^{+}$ $(\delta(\mathrm{P})=-126.1 \mathrm{ppm})$ was recently reported by Macdonald et al. and unambiguously confirmed by its characteristic chemical shift (cf. lit: $\delta(\mathrm{P})=-124.2 \mathrm{ppm}, \mathrm{CD}_{2} \mathrm{Cl}_{2}$ ). ${ }^{16}$ Cations of type $12 \mathbf{a}^{+}$are also known and reported by Schmidpeter et al. as ylidylphosphorusdisulfide containing a tri-coordinate $\mathrm{R}-\mathrm{PS}_{2}$ moiety. For these types of compounds the chemical shift strongly depends on the nature of the supporting substituent R and is typically observed in the range of $\delta(\mathrm{P})=170-240 \mathrm{ppm}\left(c f . \mathrm{Ph}_{3} \mathrm{PCMe}^{-} \mathrm{PS}_{2}: \delta(\mathrm{P})_{\mathrm{PS}_{2}}=243.4 \mathrm{ppm}\right.$, $\left.\mathrm{d}_{8}-\mathrm{THF}\right) .{ }^{2}$ In an equilibrium reaction of cation $\mathbf{1 1}^{+}$with the triflate anion the formation of $\mathbf{1 3}$ is explained and supported by the pronounced upfield shifted triplet resonance due to the coupling to the ortho-protons of the DMAP ligand (eqn (1); $\delta(\mathrm{P})=72.5 \mathrm{ppm}$, triplet, ${ }^{3} J_{\mathrm{PH}}=9.0 \mathrm{~Hz} ; c f . \mathrm{PyPS}_{2} \mathrm{Br}: \delta(\mathrm{P})=65.5 \mathrm{ppm}, \mathrm{Py}=$ pyridine; $\left.\mathrm{d}_{3}-\mathrm{MeCN}\right) .{ }^{17}$ The formation of cation $\mathbf{1 4}^{+}$results either from the equilibrium reaction of $\mathbf{1 1}^{+}$(eqn (2)) or $\mathbf{1 3}$ (eqn (3)) with DMAP which is liberated during the dismutation of cation $\mathbf{1 0 b}^{+}$(Scheme 3). The ${ }^{31} \mathrm{P}$ NMR spectrum displays a quintet resonance which is indicative for the presence of two DMAP substituents consistent with the $C_{2 \mathrm{v}}$ symmetry of cation $14^{+}\left(\delta(\mathrm{P})=96.9 \mathrm{ppm} ; c f .\left[\mathrm{Py}_{2} \mathrm{PS}_{2}\right]^{+}\right.$: $\delta(\mathrm{P})=104.7 \mathrm{ppm}$, quintet, ${ }^{3} J_{\mathrm{PH}}=9.6 \mathrm{~Hz} ; \mathrm{Py}=$ pyridine; $\left.\mathrm{d}_{3}-\mathrm{MeCN}\right)$. Similar equilibria and cations have been observed by Meisel et al. who reported on the pyridine ( Py ) stabilized phosphorus disulfide $\left[\mathrm{Py}_{2} \mathrm{PS}_{2}\right]^{+}$cation. ${ }^{18}$ Two crystalline polymorphs of $\mathbf{1 4 [ \mathrm { OTf } ] \text { were }}$ obtained after layering the reaction mixtures with $\mathrm{Et}_{2} \mathrm{O}$ (Fig. 6). ${ }^{19}$ The obtained structural parameters compare well with those reported for the related pyridine cation $\left[\mathrm{Py}_{2} \mathrm{PS}_{2}\right]^{+}$by Meisel et al. ${ }^{18}$

$$
\begin{gather*}
11[\mathrm{OTf}] \rightleftharpoons 13  \tag{1}\\
11[\mathrm{OTf}]+\mathrm{DMAP}  \tag{2}\\
\rightleftharpoons 14[\mathrm{OTf}]  \tag{3}\\
13+\mathrm{DMAP} \rightleftharpoons 14[\mathrm{OTf}]
\end{gather*}
$$



Fig. 6 Molecular structure of $\mathbf{1 4}^{+}$in $\mathbf{1 4 [ O T f ] . ~ A l l ~ h y d r o g e n ~ a t o m s ~ a n d ~ t h e ~}$ triflate anion are omitted for clarity. Selected bond lengths in $\AA$ and angles in ${ }^{\circ}$ : P1-S1 1.9309(8), P1-S2 1.9321(8), P1-N1 1.782(2), P1-N2 1.798(2), S1-P1-S2 124.09(4), N1-P1-N2 96.77(8), S-P1-N av. 108.14.


Fig. 7 Gibbs free energy in kcal $\mathrm{mol}^{-1}$ of the observed and proposed phosphorus species.

In order to confirm our findings and support the suggested dismutation, quantum chemical calculations have been performed from the reaction of $\mathbf{9 a}^{\mathbf{4 +}}$ with 4 eq. DMAP to derive geometry and Gibbs free energy of the involved species as well as the suggested reaction intermediate $\mathbf{1 0 a}{ }^{+} .{ }^{20}$ The density functional theory (DFT) hybrid model B3LYP ${ }^{21}$ was used in combination with Grimme's atom-pairwise dispersion correction (D3). ${ }^{22}$ Fig. 7 illustrates the Gibbs free energy $\Delta G$ of educts $\left(\mathbf{9 a}{ }^{\mathbf{4 +}}\right.$, DMAP), products $\left(\mathbf{1 2 b}^{+}, \mathbf{1 4}^{+}\right)$and the proposed intermediate ( $\mathbf{1 0 a}^{+}$) calculated at the B3LYP-D3/def-SVP level of theory. The whole reaction pathway is thermodynamically favored $\left(\Delta G=-284.4 \mathrm{kcal} \mathrm{mol}{ }^{-1}\right)$. The proposed reaction intermediate $\mathbf{1 0 a}^{+}$is energetically less favorable by $22 \mathrm{kcal} \mathrm{mol}^{-1}$ compared to the final products, but $262 \mathrm{kcal} \mathrm{mol}^{-1}$ lower in energy than the educt molecules ( $\Delta G=-262.4 \mathrm{kcal} \mathrm{mol}^{-1}$ ). This observation is perfectly in line with the assumption of $\mathbf{1 0 a}{ }^{+}$being the main reaction intermediate.

In summary, we reported on the oligomerization reaction of cationic phosphorus monosulfides $\mathbf{8 a}, \mathbf{b}^{+}$which were formed in situ from the reaction of $\left[\mathrm{L}^{(\mathrm{R}, \mathrm{Me})} \mathrm{PCl}_{2}\right]^{+}$cations 3a, $\mathbf{b}^{+}\left(\mathrm{L}^{\mathrm{R}, \mathrm{Me}}=\right.$ imidazolium-2-yl a: $\mathrm{R}=\mathrm{Me} ; \mathrm{b}: \mathrm{R}=\mathrm{iPr})$ and $\left(\mathrm{Me}_{3} \mathrm{Si}\right)_{2} \mathrm{~S}$. The obtained tetra-cationic, eight-membered phosphorus-sulfur heterocycles $\left[\mathrm{L}^{(\mathrm{R}, \mathrm{Me})} \mathrm{PS}\right]_{4}{ }^{4+} \mathbf{9 a}, \mathbf{b}^{4+}$ primarily exist as crown conformers similar to cyclo- $\mathrm{S}_{8}$, however, the boat-chair $\left(C_{\mathrm{s}}\right)$ conformers of the $\mathrm{P}_{4} \mathrm{~S}_{4}$ rings also exist in solution according to 2D-EXSY ${ }^{31} \mathrm{P}$ NMR experiments. Cations $\mathbf{9 a}, \mathbf{b}^{\mathbf{4 +}}$ can be deoligomerized by DMAP to yield adducts 10a, $\mathbf{b}^{+}$of the elusive cations $\mathbf{8 a}, \mathbf{b}^{+}$. Subsequent dismutation of 10a, $\mathbf{b}^{+}$gives cations $\left[\mathrm{L}^{(\mathrm{R}, \mathrm{Me})}{ }_{2} \mathrm{P}\right]^{+}\left(\mathbf{1 2 a}, \mathbf{b}^{+}\right)$and $\left[(\mathrm{DMAP})_{2} \mathrm{PS}_{2}\right]^{+}\left(\mathbf{1 4}^{+}\right)$as final products. The suggested reaction pathway was supported by DFT calculations.

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    $\dagger$ Electronic supplementary information (ESI) available: For detailed experimental procedures and characterization details of new compounds, NMR spectra, crystallographic details and computational data. CCDC 1424341-1424343 and 1426199. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5cc08182c

