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Introduction

Organic π -conjugated molecules are currently of great academic and significant technological interest due to their intriguing optoelectronic properties.¹ In this context, π -conjugated systems featuring heavier main-group elements² and systems exhibiting a considerable open-shell (radical-type) character³ are particularly attractive as they display promising optical, electronic, and magnetic properties. Among heavier main-group elements, the choice to incorporate phosphorus into π -conjugated systems has been primarily driven by its semblance to the isoelectronic "CR" (R = H, alkyl or aryl group) unit, which is known as a diagonal relationship.⁴ Moreover, while the calculated P=C π -bond strength (43 kcal mol⁻¹) is lower than the C=C π -bond of ethene (65 kcal mol⁻¹)⁵ the conjugative properties of both P=C and C=C bonds are comparable.⁶

Among stable main-group radicals,⁷ various neutral,⁸ cationic,⁹ as well as anionic¹⁰ phosphorus radicals have been also isolated

Isolation of singlet carbene derived 2-phospha-1,3butadienes and their sequential one-electron oxidation to radical cations and dications[†]

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A synthetic strategy for the 2-phospha-1,3-butadiene derivatives [{(IPr)C(Ph)}P(cAAC^{Me})] (**3a**) and [{(IPr)C(Ph)}P(cAAC^{Cy})] (**3b**) (IPr = C{(NDipp)CH}₂, Dipp = 2,6-iPr₂C₆H₃; cAAC^{Me} = C{(NDipp)CMe₂CH₂CMe₂}; cAAC^{Cy} = C{(NDipp)CMe₂CH₂C(Cy)}, Cy = cyclohexyl) containing a C=C-P=C framework has been established. Compounds **3a** and **3b** have a remarkably small HOMO–LUMO energy gap (**3a**: 5.09; **3b**: 5.05 eV) with a very high-lying HOMO (-4.95 eV for each). Consequently, **3a** and **3b** readily undergo one-electron oxidation with the mild oxidizing agent GaCl₃ to afford radical cations [{(IPr)C(Ph)}P(cAAC^R)]GaCl₄ (R = Me **4a**, Cy **4b**) as crystalline solids. The main UV-vis absorption band for **4a** and **4b** is red-shifted with respect to that of **3a** and **3b**, which is associated with the SOMO related transitions. The EPR spectra of compounds **4a** and **4b** each exhibit a doublet due to coupling of the unpaired electron with the ³¹P nucleus. Further one-electron removal from the radical cations **4a** and **4b** is also feasible with GaCl₃, affording the dications [{(IPr) C(Ph)}P(cAAC^R)](GaCl₄)₂ (R = Me **5a**, Cy **5b**) as yellow crystals. The molecular structures of compounds **3-5** have been determined by X-ray diffraction and analyzed by DFT calculations.

and structurally characterized, however, phosphorus radicals based on a π -conjugated framework remain scarce. 1,3-Butadiene I is the simplest molecule with conjugated π -bonds (Fig. 1) that has also been an important structural motif in phosphorus chemistry.11 Indeed, unsubstituted as well as alkyl substituted phosphorus containing 1,3-butadiene derivatives were already reported by Appel,^{11b} Regitz,^{11f} and Denis,^{11g} however, these compounds are unlikely to afford stable radical compounds on oxidation or reduction. In 2008, Robinson et al. reported a diphosphorus compound II containing a weak π -acceptor N-heterocyclic carbene (NHC).12 Structural and theoretical data suggest that II should be better described as a base-stabilized diphosphinidene with C(NHC)-P and P-P single bonds. Compound III, reported by Bertrand's group in 2010, features a strong π -acceptor cyclic alkyl amino carbene (cAAC^R) and exhibits short C-P bond lengths, thus it may be regarded as a genuine 2,3-diphospha-1,3-butadiene.13 The same group also reported the 2-phospha-3-azabutadiene IV by an elegant choice of imine and cAAC precursors.9c Remarkably, these electron-rich species readily undergo one-electron oxidation to afford the corresponding radical cations (II)⁺⁺, (III)⁺⁺, and (IV)⁺⁺.^{9b,9c} We recently reported NHC-derived divinyldiphosphenes V14 and isolated the corresponding radicals cations $(V)^{+}$ by one-electron oxidation of V.15 These and other early results16 prompted us to reason that stable 2-phospha-1,3-butadienes VI as well as the corresponding radical cations $(VI)^{++}$ and dications $(VI)^{++}$ should be synthetically accessible by a rational choice of substrates and reaction conditions.



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Fig. 1 1,3-Butadiene I. Selected examples of phosphorus containing derivatives II-IV and divinyldiphosphene V with singlet carbene frameworks.

Herein, we report the synthesis of 2-phospha-1,3-butadienes $[{(IPr)C(Ph)}P(cAAC^{Me})]$ (3a) and $[{(IPr)C(Ph)}P(cAAC^{Cy})]$ (3b) based on singlet carbene frameworks ($IPr = C{(NDipp)CH}_2$, Dipp = 2,6-iPr₂C₆H₃; cAAC^{Me} = C{(NDipp)CMe₂CH₂CMe₂}; cAAC^{Cy} = C{(NDipp)CMe₂CH₂C(Cy)}, Cy = cyclohexyl) as crystalline solids. Sequential one-electron oxidation of 3a and 3b leads to the formation of corresponding radical cations [{(IPr) C(Ph)}P(cAAC^{Me})](GaCl₄) (4a), [{(IPr)C(Ph)}P(cAAC^{Cy})](GaCl₄)

(4b) and dications [{(IPr)C(Ph)}P(cAAC^{Me})](GaCl₄)₂ (5a), [{(IPr) C(Ph)}P(cAAC^{Cy})] (GaCl₄)₂ (5b) as crystalline solids.

Results and discussion

For the synthesis of desired 2-phospha-1,3-butadienes, N-heterocyclic vinyl (NHV)-substituted dichlorophosphine {(IPr) C(Ph)}PCl₂ (1)¹⁴ and strong π -acceptor cAAC^R (ref. 17) were chosen as the appropriate precursors (Scheme 1).¹⁸ Treatment of



Scheme 1 Synthesis of 2-phospha-1,3-butadiene derivatives 3a and 3b. * cAACs were prepared by the deprotonation of their triflate salts with LDA and the side-product LiOTf was not separated.

a colorless THF solution of **1** with one equivalent of cAAC^{Me} or cAAC^{Cy} immediately resulted in the formation of dark blue solutions (Scheme 1). After workup, the ionic compounds [{(IPr)C(Ph)}P(Cl)(cAAC^R)](OTf) (R = Me 2a, Cy 2b) were isolated as violet crystalline solids. Compounds 2a and 2b are highly air sensitive solids and have been characterized by elemental analysis and NMR spectroscopy. The solid state molecular structure of a typical compound 2a (Fig. S31†) was determined by X-ray diffraction. Reduction of 2a and 2b with magnesium turnings afforded the target compound 3a and 3b, respectively, as orange solids. Interestingly, 3a and 3b are also accessible in a one-pot reaction of 1 and cAAC^R with magnesium. Both 3a and 3b are soluble in common organic solvents (*n*-hexane, Et₂O, benzene, toluene, THF) and are stable under an inert gas atmosphere.

The ¹H NMR spectra of compounds **2a** and **2b** as well as **3a** and **3b** show expected resonances for the NHV and cAAC^R moieties. The ¹³C{¹H} NMR spectrum of **2a** and **2b** as well as **3a** and **3b** each is consistent with the ¹H NMR resonances and exhibits expected doublets for the phosphorus bound carbon atoms (see the ESI†). The ³¹P{¹H} NMR spectrum of **2a** (+100.9 ppm) and **2b** (+102.9 ppm) each shows a singlet, which is high-field shifted with respect to that of the **1** (+167 ppm). This is most likely due to the coordination of electron-rich cAAC^R to the phosphorus atoms in **2a** and **2b**. The ³¹P{¹H} NMR signal for **3a** (+102.5 ppm) and **3b** (+108.6 ppm), respectively, appears at a higher field compared to that of **IV** (+134.0 ppm),^{9c} which is expected because of the electronegativity difference between carbon and nitrogen.

The solid-state molecular structures of **3a** and **3b** (Fig. 2) adopt a *trans*-bent geometry along the $C_{\rm NHV}$ -P bond with the C2-P1 bond length of 1.818(1) and 1.820(1) Å, respectively. The C2-P1 bond length is larger compared to that in **1** (1.728(2) Å)¹⁴ and **2a** (1.751(2) Å), but it is comparable with those of the diphosphenes **V** (1.785 to 1.797 Å).¹⁵ The P1-C3

(3a: 1.735(1); 3b 1.735(1) Å) and C1–C2 (3a: 1.386(1); 3b: 1.384(2) Å) bonds are shorter compared to the same bonds in 2a (1.860(2) and 1.437(2) Å, respectively). The P1–C3 bond lengths of 3a and 3b are nonetheless in line with those of the P=C double bonds in III (1.719(7) Å)¹³ and IV (1.719(2) Å).^{9c} The C1=C2, P1=C3, and P1–C2 bond lengths of 3a and 3b are in line with those of the literature known neutral 2-phospha-1,3-butadiene (Me₃SiO)*t*BuC=P-C(SiMe₃)=C(OSiiPr₃)*t*Bu (C=C: 1.356(4), P=C: 1.702(3), P–C: 1.846(3) Å).¹⁹

To shed light on the electronic structure of **3a** and **3b**, we performed DFT calculations at the M06-2X/def2-TZVPP//def2-SVP level of theory. The HOMO of **3a** and **3b** is a π -type orbital mainly located at the C_{cAAC}=P and C_{IPr}=C_{Ph} bonds (Fig. 3). Remarkably, the HOMO energy of **3a** and **3b** (-4.95 eV) is quite high and comparable with those of related divinyldiphosphenes **V** (-4.71 to -5.25 eV),¹⁵ indicating the possibility of facile oxidation.



Fig. 3 HOMOs (highest occupied molecular orbitals, isovalue 0.04) of 3a and 3b calculated at M06-2X/def2-TZVPP//def2-SVP level of theory. Hydrogen atoms, methyl as well as iso-propyl groups were omitted for clarity.



Fig. 2 Solid-state molecular structures of 2-phospha-1,3-butadienes **3a** and **3b**. Hydrogen atoms have been omitted for clarity. Selected bond lengths and bond angles are given in Table 1.

These preliminarily theoretical findings encouraged us to analyze the redox properties of **3a** and **3b** by electrochemical studies to gain an initial insight into the viability and stability of derived radicals. The cyclic voltammograms (CVs) of **3a** (Fig. S19†) and **3b** (Fig. S20†) show two main redox events in the -2.0 to 1.5 V region. The first reversible wave at $E_{1/2} = -1.06$ V

Dipp Dipp + 2 GaCl₃ 3a or 3b [GaCl₄]⁻ PhMe Dipp 0.5 Ga[GaCl₄] 4a: [{(IPr)C(Ph)}P(cAAC^{Me})]GaCl₄ 4b: [{(IPr)C(Ph)}P(cAAC^{Cy})]GaCl₄ + 2 GaCl₃ CH₂Cl₂ 0.5 Ga[GaCl₄] 2 + Dipp Dipp + 4 GaCl₃ 3a or 3b CH₂Cl₂ 2 [GaCl₄]⁻ Dipp 5a: [{(IPr)C(Ph)}P(cAAC^{Me})](GaCl₄)₂ Ga[GaCl₄] 5b: [{(IPr)C(Ph)}P(cAAC^{Cy})](GaCl₄)₂

Scheme 2 Sequential one-electron oxidation of 2-phospha-1,3-butadienes 3a and 3b with GaCl₃ to the corresponding radical cations 4a and 4b and dications 5a and 5b.

for 3a and -1.08 V for 3b may be assigned to the corresponding radical cation, whereas the second quasi-reversible wave at $E_{1/2} = -0.28$ V for 3a and -0.24 V for 3b may correspond to the dicationic species. Indeed, treatment of an orange toluene solution of 3a or 3b with GaCl₃ immediately led to the precipitation of a violet solid. After workup, the radical cation salts [{(IPr)C(Ph)}P(cAAC^{Me})](GaCl₄) (4a) and [{(IPr)C(Ph)} $P(cAAC^{Cy})](GaCl_4)$ (4b) were isolated as violet crystals (Scheme 2). GaCl₃ acts as oxidizing agent and two molecules of GaCl3 are required for one-electron oxidation.15 Consistent with the CVs (Fig. S19 and S20[†]), the dication salts $[{(IPr)C(Ph)}P(cAAC^{Me})](GaCl_4)_2$ (5a) and $[{(IPr)C(Ph)}]$ $P(cAAC^{Cy})](GaCl_4)_2$ (5b) are selectively accessible on oneelectron oxidation of 4a and 4b with GaCl₃ (Scheme 2). Alternatively, 5a and 5b can also be prepared directly from 3a and 3b with four equivalent of GaCl₃, respectively (Scheme 2). Compounds 4a, 4b and 5a, 5b are stable both in solutions as well as in the solid-state under an inert gas atmosphere, but decompose rapidly when exposed to air. The radicals 4a and 4b are NMR silent, while dicationic salts 5a and **5b** are diamagnetic and exhibit well resolved ¹H and ¹³C ${^{1}H}$ NMR signals for the NHV and cAAC^R units. The ${^{31}P}{^{1}H}$ NMR signal for the dication salts 5a (+244 ppm) and 5b (+236 ppm) is downfield-shifted with respect to that of the 2-phospha-1,3-butadienes 3a (+102 ppm) and 3b (+108 ppm) but it is in the range expected for phosphaalkenes (200-300 ppm).20

Suitable single crystals for X-ray diffraction were obtained by a slow diffusion of *n*-hexane into a saturated THF or CH_2Cl_2 solution of each of radical cations **4a** and **4b** and dicationic salts **5a** and **5b**. The solid-state molecular structure of **4a** and **4b** (Fig. 4) as well as **5a** and **5b** (Fig. 5) each adopts a *trans*-bent geometry along the P-C_{NHV} bond and reveals an interesting bond length alteration trend with



Fig. 4 Solid-state molecular structures of radical cation 4a and 4b. Hydrogen atoms, solvent molecules in 4b, and the counter anions GaCl₄ have been omitted for clarity. Selected bond lengths and bond angles are given in Table 1.



Fig. 5 Solid-state molecular structures of 5a and 5b. Hydrogen atoms, solvent molecules in 5b, and the counter anions GaCl₄ have been omitted for clarity. Selected bond lengths and bond angles are given in Table 1.

respect to the precursors 3a and 3b (Table 1). The C2-P1 bond length of 4a (1.758(2) Å) and 4b (1.761(2) Å) is smaller compared to that of the respective 2-phospha-1,3-butadienes 3a (1.818(1) Å) and 3b (1.820(1) Å) but longer with respect to that of the dications **5a** (1.692(3) Å) and **5b** (1.692(2) Å) Å. The P1-C3 bond, however, steadily stretches on going from neutral to radical cations and to dications: 3a: 1.735(1), 3b: 1.735(1); 4a: 1.785(2), 4b: 1.790(2); 5a: 1.865(2), 5b: 1.853(2) Å. A similar trend in the C1-C2 bond length stretching can also be seen in 3a: 1.386(1), 3b: 1.384(2); 4a: 1.432(2), 4b: 1.433(2); and 5a: 1.479(3), 5b: 1.478(2) Å. In conclusion, the formally C1=C2 and P1=C3 double bonds in 3a and 3b become comparable to C_{sp^2} - C_{sp^2} (ca. 1.47 Å) and P- C_{sp^2} (1.85 Å) single bond lengths²¹ in 5a and 5b, whereas the C2–P1 single bond in 3a and 3b adopts double bond lengths (1.60–1.70 Å) in 5a and 5b as expected for phosphaalkenes.²²

Table 1 Selected bond lengths (Å) and angles (°) of 2-phospha-1,3-butadienes (3a and 3b), radical cations (4a and 4b) and dication salts (5a and 5b)

	3a	3b	4a	4b	5a	5b
C1_C2	1 296(1)	1 204(2)	1 422(2)	1 422(2)	1 470(2)	1 479(2)
C1-C2	1.380(1)	1.384(2)	1.432(2)	1.433(2)	1.479(3)	1.470(2)
C2-P1	1.818(1)	1.820(1)	1.758(2)	1.761(2)	1.692(2)	1.692(2)
P1-C3	1.735(1)	1.735(1)	1.785(2)	1.790(2)	1.865(2)	1.853(2)
C1-N1	1.401(1)	1.403(1)	1.375(2)	1.375(2)	1.351(3)	1.344(2)
C1-N2	1.408(1)	1.412(1)	1.382(2)	1.385(2)	1.355(3)	1.356(2)
C3-N3	1.387(1)	1.388(1)	1.349(2)	1.349(2)	1.295(3)	1.295(3)
C1-C2-P1	117.7(1)	118.0(1)	117.3(1)	117.4(1)	114.9(1)	115.3(1)
C2-P1-C3	109.7(1)	110.9(1)	108.8(1)	110.3(1)	106.1(1)	105.2(1)
P1-C3-N3	117.6(1)	116.4(1)	116.0(1)	115.1(1)	118.1(2)	121.5(1)
N1-C1-N2	103.0(1)	103.3(1)	104.8(1)	104.9(1)	107.2(2)	107.3(2)

DFT calculated geometries of 3-5 are found to be fully in agreement with their solid-state molecular structures determined by X-ray diffraction (Table S5[†]). An increasing value of the WBIs (Wiberg Bond Indices) for the C_{NHV}-P bond of 3a (0.95), 3b (0.95), 4a (1.22), 4b (1.22), 5a (1.63), and 5b (1.63) is consistent with the experimental C2-P1 bond lengths (Table 1). Similarly, the WBIs for the P-C_{cAAC} (3a: 1.57, 3b: 1.56; 4a: 1.19, 4b: 1.18; 5a: 0.92, 5b: 0.91) as well as C-C_{Ph} (3a: 1.49, 3b: 1.49; 4a: 1.20, 4b: 1.20; 5a: 1.06, 5b: 1.06) bonds also exhibit the expected trend. The NPA (Natural Population Analysis) atomic partial charges (Table S5[†]) calculated using the NBO (Natural Bond Orbital) method indicate that the phosphorous atom in 3a (0.49e), 3b (0.49e), 4a (0.65e), 4b (0.65e), 5a (0.85e), and 5b (0.85e) carries a positive charge. The former IPr carbene carbon atom (C1) also bears a positive charge (3a 0.45e, 3b 0.44e, 4a 0.47e, 4b 0.47e, 5a 0.43e and 5b 0.43e), which is larger compared to that of the cAAC carbene carbon atom C3 (3a -0.08e, 3b -0.08e, 4a 0.04e, 4b 0.04e, 5a 0.23e and 5b 0.24e). This is most likely because of the greater π -acceptor property of cAACs compared to the IPr.

The SOMO (singly occupied molecular orbital) of 4a and **4b** (Fig. 6) is the π -orbitals of the C_{IPr}=C_{vinyl} and P=C_{cAAC} bonds with a small contribution from the nitrogen atoms of the pyrrolidine and imidazole ring, whereas the LUMO (lowest unoccupied molecular orbital) is the π^* -orbitals of the P atom along with the π^* -orbitals of $C_{IPr}=C_{vinvl}$ and C_{cAAC}-N bonds of NHV and cAAC, respectively. The localized Mulliken atomic spin density (Fig. 7) and the plot of the SOMO (Fig. 6) for 4a and 4b reveal that the unpaired electron is mainly delocalized over the CPCN moiety with an almost equal spin density distribution on the phosphorus (4a: 17%, 4b: 18%), carbene C_{cAAC} (4a: 19%, 4b: 20%), and vinylic C_{Ph} (4a: 26%, 4b: 25%) atoms. The spin-density at the imidazolering nitrogen atoms (6% at each of N) of 4a and 4b is rather small compared to that at the pyrrolidine nitrogen atom (17%).



4a: SOMO (-8.08/-9.66 eV)



4b: SOMO (-8.04/-9.63 eV)

4b: LUMO (-3.05/-4.55 eV)

Fig. 6 Selected molecular orbitals (isovalue 0.04) of the radical cations 4a and 4b (α / β spin orbital energy) calculated at the M06-2X/def2-TZVPP//def2-SVP level of theory. Hydrogen atoms, methyl groups as well as iso-propyl groups were omitted for clarity.



Fig. 7 Calculated Mulliken spin densities (isovalue 0.004 a.u.) of radical cations 4a and 4b at M06-2X/def2-TZVPP//def2-SVP level of theory.



The room temperature X-band EPR spectra of 4a (g = 2.0064) and 4b (g = 2.0064) in THF exhibit a doublet (Fig. 8) owing to the coupling of the unpaired electron with the phosphorous nucleus $(A_{iso})^{(31)}P = 35$ G 4a; 38 G 4b). The magnitude of the hyperfine coupling constant (hfc) of 4a and 4b is comparable to those observed for radical cations (II)⁺⁺ $(A_{iso}(^{31}P) = 44 \text{ G})^{9b}$ (III)⁺⁺ $(A_{iso}(^{31}P) = 42 \text{ G})^{9b}$ and (IV)⁺⁺ $(A_{iso}(^{31}P) = 44 \text{ G}),^{9c}$ but that is larger than those of $(V)^{+}$ $(A_{iso}(^{31}P) = 12-20 \text{ G})$ featuring a longer π -conjugated system (Fig. 1).15 This is, however, considerably smaller than that of the phosphinyl radical cation $[(cAAC^{Cy})P(R)]^{+}$ $(A_{iso})^{(31}P) =$ 99 G) (R = 2,2,6,6-tetramethylpiperidino)^{9a} as well as those observed for phosphinyl radicals R_2P' ($A_{iso}(^{31}P) = 92-96$ G) $(R = HC(SiMe_3)_2 \text{ or } N(SiMe_3)_2)$,^{8*a*,23} for which, particularly for the latter, the unpaired electron resides predominantly in a 3p(P) valence orbital. The value of coupling constants is in good agreement with the computed values (Table S12[†]). These hfcs corroborate with the delocalization of the spin-density along the CPCN moiety of 4a and 4b (Fig. 7). The measured EPR spectra of 4a and 4b were simulated by employing the g values, the hyperfine coupling for the phosphorus atom, and two linewidth parameters (Table S13[†]). The EPR spectra of 4a (Fig. S29[†]) and 4b (Fig. S30[†]) measured in a frozen THF solution at 80 K show an anisotropic pattern. The *g*-factors (4a: $g_{\parallel} = 2.0062$, $g_{\perp} = 2.0082$; 4b: $g_{\parallel} = 2.0069$, $g_{\perp} =$ 2.0079) and hfc tensors (4a: $A_z({}^{31}P) = 149$ MHz, $A_x({}^{31}P) =$ -83 MHz, $A_y(^{31}P) = 39$ MHz; **4b**: $A_z(^{31}P) = 179$ MHz, $A_x(^{31}P)$ = -71 MHz, $A_{\nu}(^{31}P) =$ 49 MHz) were determined. The analysis of hfc tensors reveals the major contribution of phosphorus 3p (4a: 11.8%; 4b: 12.8%) orbital to the SOMO, whereas the contribution of the 3s (4a: 0.45%; 4b: 0.46%) orbital is small.

The UV-vis spectra of both 2-phospha-1,3-butadienes **3a** (277, 331, 427 nm) and **3b** (271, 322, 430 nm) exhibit three main absorptions (Fig. 9) which, based on TD-DFT



Fig. 9 UV-vis spectra of 3a and 3b and their radical cations 4a and 4b in THF.

calculations at TD-PCM(thf)/M06-2X/def2-SVP level of theory, comprise dominant contributions of the H-1 \rightarrow L, H \rightarrow L+2, and H \rightarrow L transitions, respectively (Fig. S32 and S33, Tables S6 and S7†). The UV-vis spectra of the radical cations **4a** and **4b**, respectively show a broad absorption at 563 and 571 nm along with a shoulder at *ca.* 700 nm (Fig. 9) that corresponds to the SOMO-related transitions S \rightarrow L and S-1 \rightarrow S (Tables S8 and S9†).

In the dications **5a** and **5b**, the HOMO-2 is a π -type orbital with contributions from the aryl groups and C_{vinyl} -P bond (Fig. 10). The LUMO of **5a** and **5b** is the π -orbital of the C_{IPr} = C_{vinyl} and P= C_{cAAC} bonds with a small contribution from the nitrogen atoms of pyrrolidine and imidazole rings. Upon removal of one and two electrons from the π -type orbital of **3a** and **3b**, the HOMO of **3a** and **3b** (Fig. 3) becomes SOMO in the radical cations **4a** and **4b** (Fig. 6) and LUMO in the dications **5a** and **5b** (Fig. 10).



Fig. 10 Selected molecular orbitals (isovalue 0.04) of the dications 5a and 5b calculated at M06-2X/def2-TZVPP//def2-SVP level of theory. Hydrogen atoms, methyl groups as well as iso-propyl groups were omitted for clarity.

Conclusions

In conclusion, we have isolated the crystalline 2-phospha-1,3butadiene derivatives 3a and 3b by a rational choice of combining a weak π -acceptor (IPr) and a strong π -acceptor $(cAAC^{R})$ singlet carbene scaffolds. Sequential one-electron oxidation of 3a and 3b affords the radical cations 4a and 4b and the dications 5a and 5b. The isolation of 4a, 4b and 5a, 5b as crystalline solids is consistent with the redox properties of 3a and 3b analyzed by electrochemical studies. Molecular structures of all compounds in the solid-state were established by single crystal X-ray diffraction. Computational and EPR spectroscopic data indicate that the unpaired electron in 4a and 4b is delocalized over the CPCN π -conjugated framework. The study emphasizes the advantage of merging singlet carbenes with dissimilar donor-acceptor properties in accessing stable open-shell π -conjugated systems. As a variety of stable singlet carbenes with adaptable properties are readily accessible, it is very likely that many π -conjugated systems with other heavier

main-group elements, which are hitherto believed to be synthetically challenging targets, may be isolated.

Conflicts of interest

There are no conflicts to declare.

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