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Isolation of singlet carbene derived 2-phospha-1,3-butadienes 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 $[(\text{IPr})\text{C}(\text{Ph})\text{P}(\text{cAAC}^{\text{Me}})]$ (**3a**) and $[(\text{IPr})\text{C}(\text{Ph})\text{P}(\text{cAAC}^{\text{Cy}})]$ (**3b**) (IPr = C((NDipp)CH)₂, Dipp = 2,6-*i*-Pr₂C₆H₃; 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 $[(\text{IPr})\text{C}(\text{Ph})\text{P}(\text{cAAC}^{\text{R}})]\text{GaCl}_4$ (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 $[(\text{IPr})\text{C}(\text{Ph})\text{P}(\text{cAAC}^{\text{R}})](\text{GaCl}_4)_2$ (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.

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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

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 divinylidiphosphenes **V**⁴⁴ and isolated the corresponding radical 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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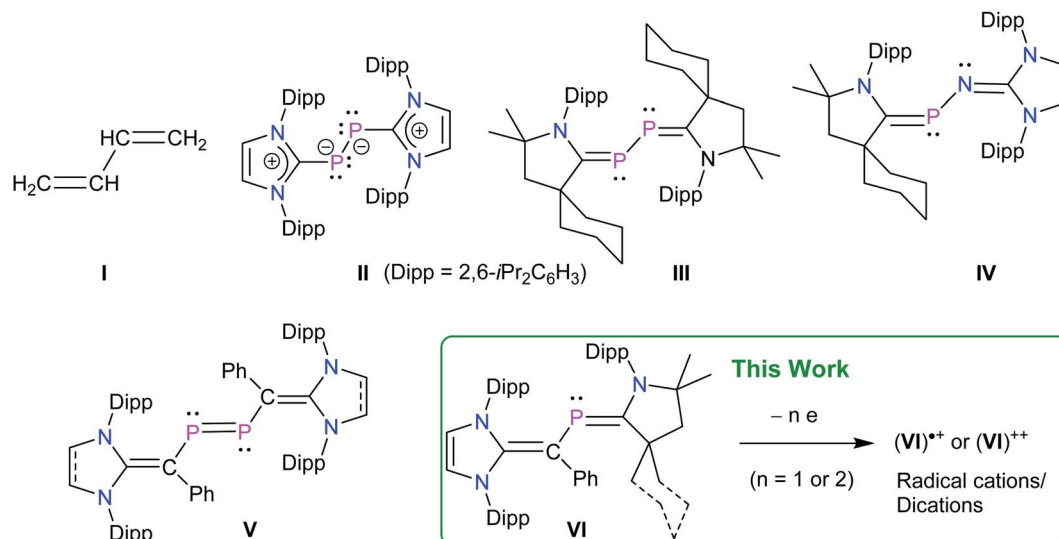


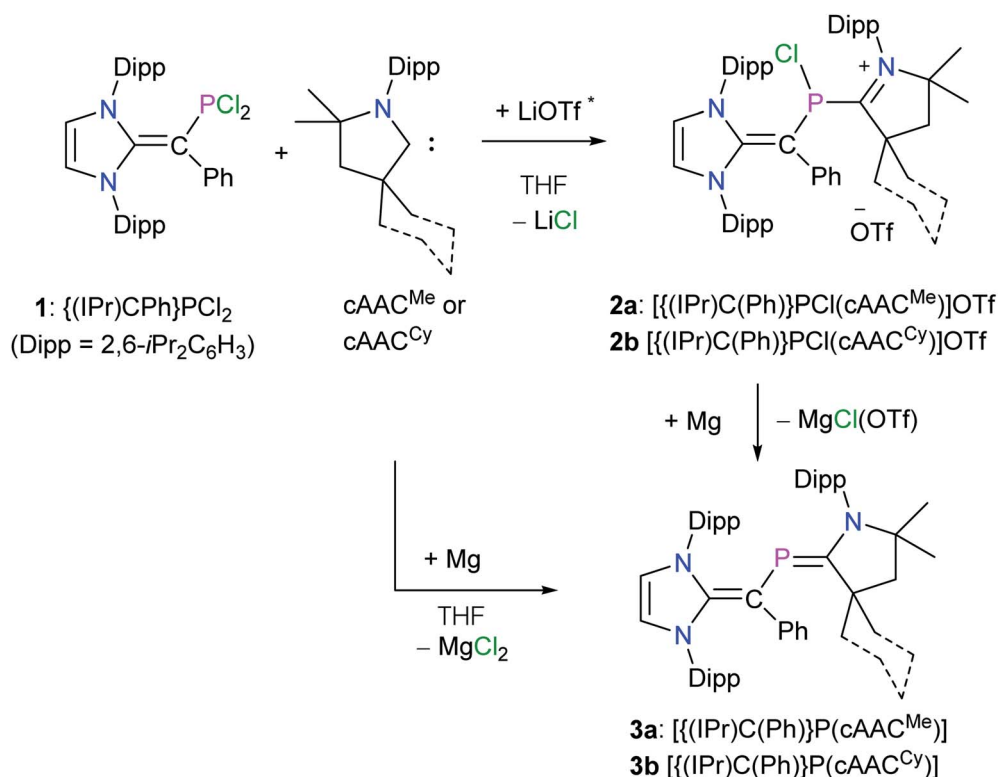
Fig. 1 1,3-Butadiene I. Selected examples of phosphorus containing derivatives II–IV and divinyl diphosphene V with singlet carbene frameworks.

Herein, we report the synthesis of 2-phospha-1,3-butadienes $[(\text{IPr})\text{C}(\text{Ph})\text{P}(\text{cAAC}^{\text{Me}})]$ (**3a**) and $[(\text{IPr})\text{C}(\text{Ph})\text{P}(\text{cAAC}^{\text{Cy}})]$ (**3b**) based on singlet carbene frameworks (IPr = $\text{C}\{(\text{NDipp})\text{CH}_2\}_2$, Dipp = 2,6-*i*Pr₂C₆H₃; cAAC^{Me} = $\text{C}\{(\text{NDipp})\text{CMe}_2\text{CH}_2\text{CMe}_2\}$; cAAC^{Cy} = $\text{C}\{(\text{NDipp})\text{CMe}_2\text{CH}_2\text{C}(\text{Cy})\}$, Cy = cyclohexyl) as crystalline solids. Sequential one-electron oxidation of **3a** and **3b** leads to the formation of corresponding radical cations $[(\text{IPr})\text{C}(\text{Ph})\text{P}(\text{cAAC}^{\text{Me}})](\text{GaCl}_4)$ (**4a**), $[(\text{IPr})\text{C}(\text{Ph})\text{P}(\text{cAAC}^{\text{Cy}})](\text{GaCl}_4)$

(**4b**) and dications $[(\text{IPr})\text{C}(\text{Ph})\text{P}(\text{cAAC}^{\text{Me}})](\text{GaCl}_4)_2$ (**5a**), $[(\text{IPr})\text{C}(\text{Ph})\text{P}(\text{cAAC}^{\text{Cy}})](\text{GaCl}_4)_2$ (**5b**) as crystalline solids.

Results and discussion

For the synthesis of desired 2-phospha-1,3-butadienes, N-heterocyclic vinyl (NHV)-substituted dichlorophosphine $[(\text{IPr})\text{C}(\text{Ph})\text{P}(\text{Cl})_2]$ (**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 $[\{(\text{IPr})\text{C}(\text{Ph})\}\text{P}(\text{Cl})(\text{cAAC}^{\text{R}})](\text{OTf})$ ($\text{R} = \text{Me}$ **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, Et_2O , 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 $^{13}\text{C}\{^1\text{H}\}$ 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 $^{31}\text{P}\{^1\text{H}\}$ 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 $^{31}\text{P}\{^1\text{H}\}$ 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 $\text{C}_{\text{NHV}}\text{-P}$ 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 $\text{P}=\text{C}$ double bonds in **III** (1.719(7) Å)¹³ and **IV** (1.719(2) Å).^{9c} The $\text{C1}=\text{C2}$, $\text{P1}=\text{C3}$, and P1-C2 bond lengths of **3a** and **3b** are in line with those of the literature known neutral 2-phospha-1,3-butadiene $(\text{Me}_3\text{SiO})t\text{BuC}=\text{P}(\text{SiMe}_3)=\text{C}(\text{OSiPr}_3)t\text{Bu}$ ($\text{C}=\text{C}$: 1.356(4), $\text{P}=\text{C}$: 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 $\text{C}_{\text{cAAC}}=\text{P}$ and $\text{C}_{\text{IPr}}=\text{C}_{\text{Ph}}$ bonds (Fig. 3). Remarkably, the HOMO energy of **3a** and **3b** (−4.95 eV) is quite high and comparable with those of related divinylidiphosphenes **V** (−4.71 to −5.25 eV),¹⁵ indicating the possibility of facile oxidation.

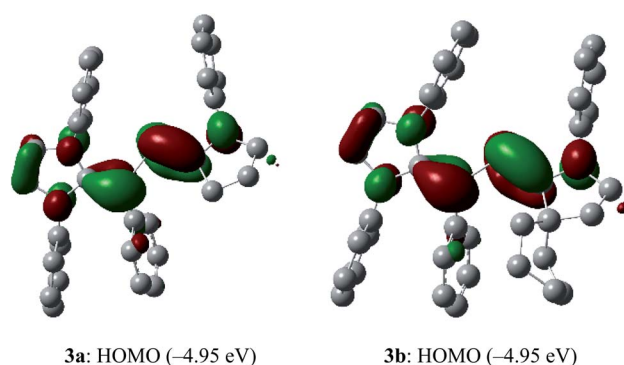


Fig. 3 HOMOs (highest occupied molecular orbitals, isovalue 0.04) of **3a** and **3b** calculated at M06-2X/def2-TZVPP//def2-SVP level of theory. Hydrogen atoms, methyl as well as iso-propyl groups were omitted for clarity.

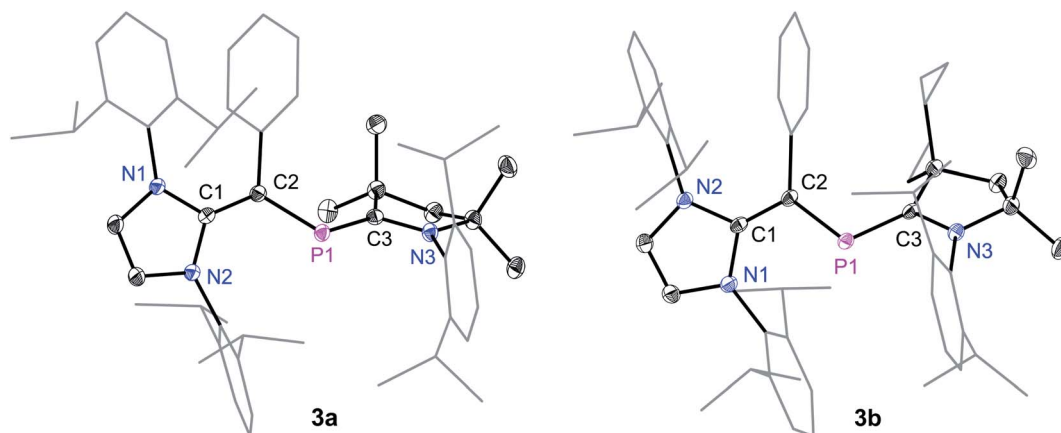
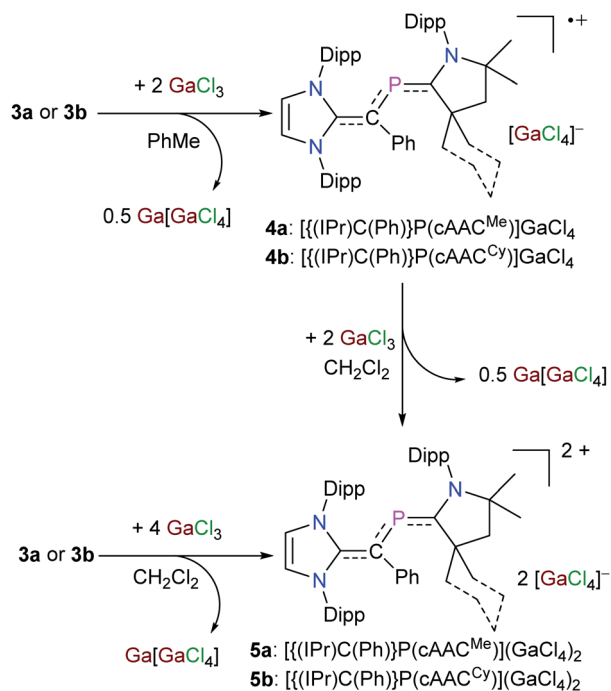


Fig. 2 Solid-state molecular structures of 2-phospha-1,3-butadienes **3a** and **3b**. Hydrogen atoms have been omitted for clarity. Selected bond lengths and bond angles are given in Table 1.

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



Scheme 2 Sequential one-electron oxidation of 2-phospha-1,3-butadienes **3a** and **3b** with $GaCl_3$ 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 $GaCl_3$ immediately led to the precipitation of a violet solid. After workup, the radical cation salts $[\{(IPr)C(Ph)P(cAAC^{Me})\}](GaCl_4)$ (**4a**) and $[\{(IPr)C(Ph)P(cAAC^{Cy})\}](GaCl_4)$ (**4b**) were isolated as violet crystals (Scheme 2). $GaCl_3$ acts as oxidizing agent and two molecules of $GaCl_3$ 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 one-electron oxidation of **4a** and **4b** with $GaCl_3$ (Scheme 2). Alternatively, **5a** and **5b** can also be prepared directly from **3a** and **3b** with four equivalent of $GaCl_3$, 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 ^{13}C $\{^1H\}$ NMR signals for the NHV and $cAAC^R$ units. The $^{31}P\{^1H\}$ 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 phosphalkenes (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

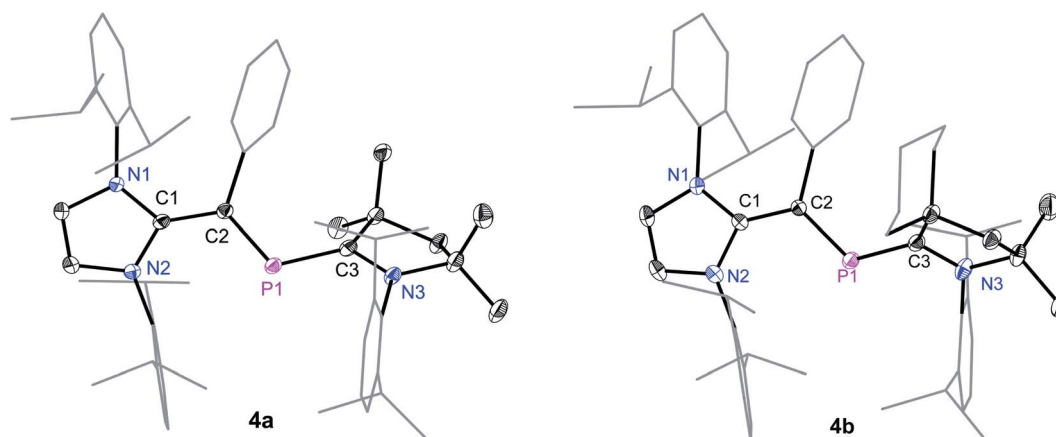


Fig. 4 Solid-state molecular structures of radical cation **4a** and **4b**. Hydrogen atoms, solvent molecules in **4b**, and the counter anions $GaCl_4^-$ have been omitted for clarity. Selected bond lengths and bond angles are given in Table 1.

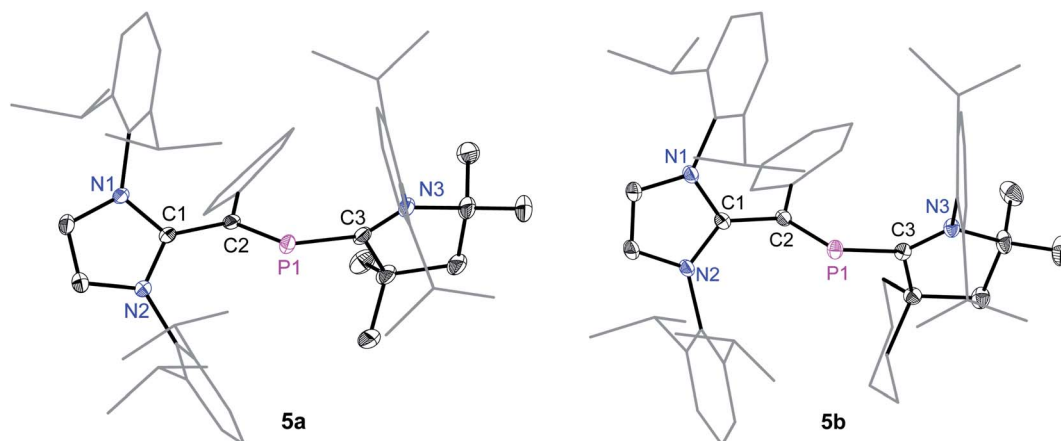


Fig. 5 Solid-state molecular structures of **5a** and **5b**. Hydrogen atoms, solvent molecules in **5b**, and the counter anions GaCl_4 have been omitted for clarity. Selected bond lengths and bond angles are given in Table 1.

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). 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 $\text{C}_{\text{sp}^2}\text{--C}_{\text{sp}^2}$ (*ca.* 1.47 Å) and $\text{P--C}_{\text{sp}^2}$ (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 phosphalkenes.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	1.386(1)	1.384(2)	1.432(2)	1.433(2)	1.479(3)	1.478(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 $\text{C}_{\text{NHV}}\text{--P}$ 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 $\text{P--C}_{\text{cAAC}}$ (**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 $\text{C}_{\text{IPr}}\text{=C}_{\text{vinyl}}$ 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 $\text{C}_{\text{IPr}}\text{=C}_{\text{vinyl}}$ and $\text{C}_{\text{cAAC}}\text{--N}$ 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 imidazole-ring nitrogen atoms (6% at each of N) of **4a** and **4b** is rather small compared to that at the pyrrolidine nitrogen atom (17%).

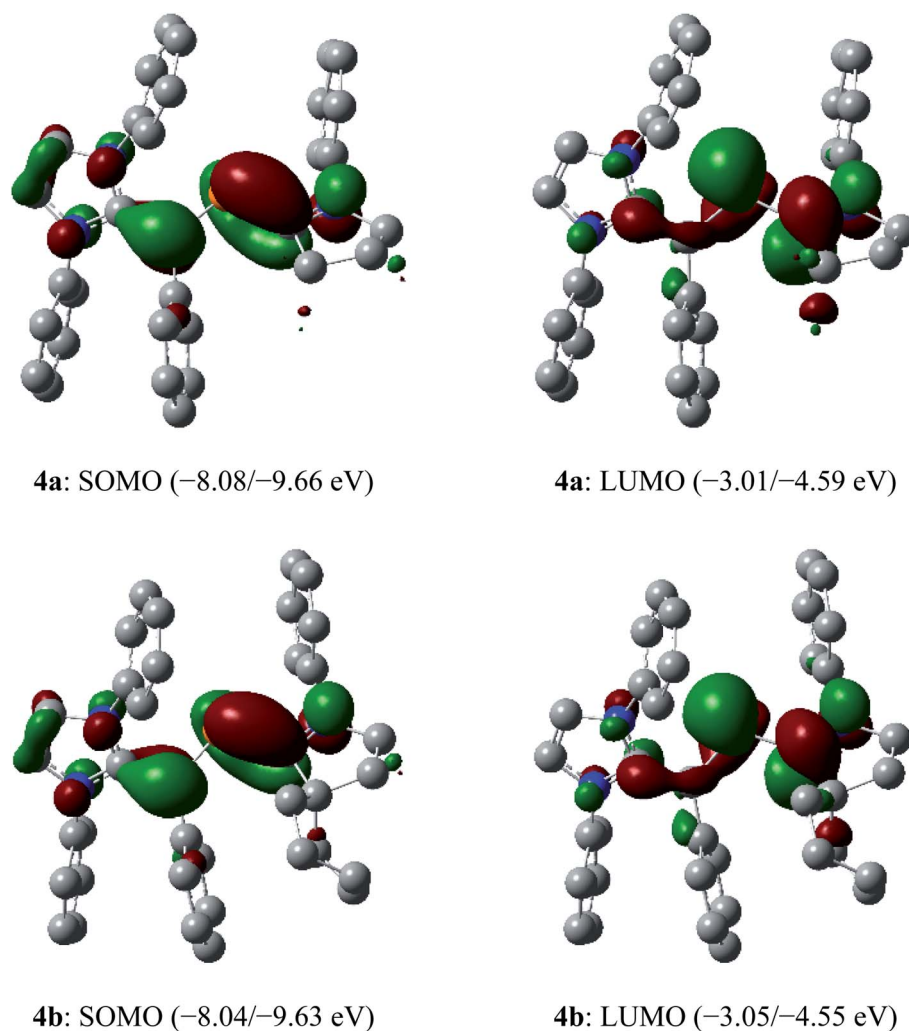


Fig. 6 Selected molecular orbitals (isovalue 0.04) of the radical cations 4a and 4b (α/β spin orbital energy) calculated at the M06-2X/def2-TZVPP//def2-SVP level of theory. Hydrogen atoms, methyl groups as well as iso-propyl groups were omitted for clarity.

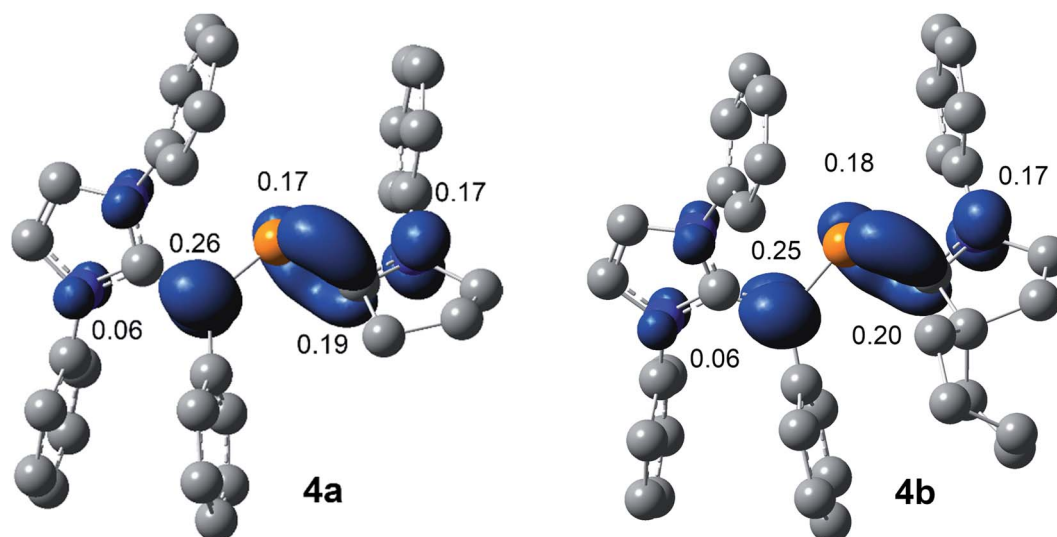


Fig. 7 Calculated Mulliken spin densities (isovalue 0.004 a.u.) of radical cations 4a and 4b at M06-2X/def2-TZVPP//def2-SVP level of theory.

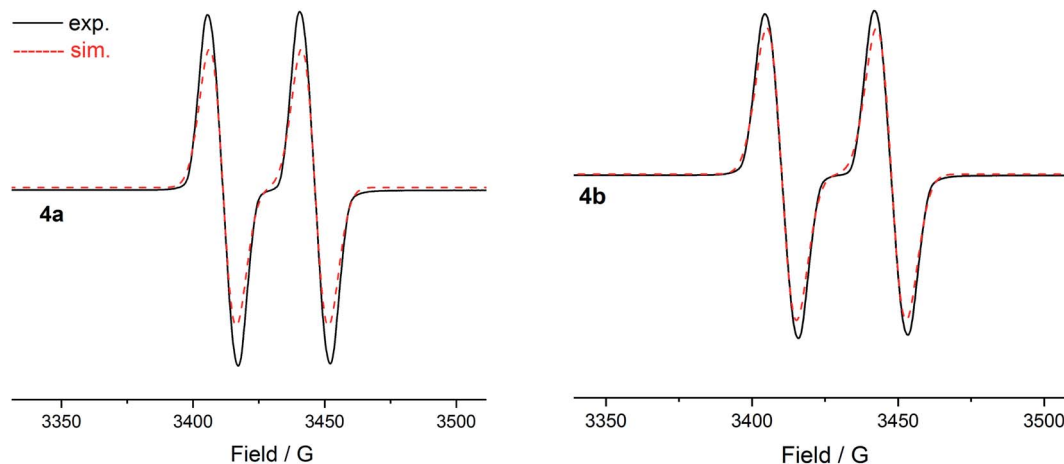


Fig. 8 X-band EPR spectra of radical cations **4a** and **4b** in THF at 298 K.

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 ($A_{\text{iso}}(^{31}\text{P}) = 35 \text{ G}$ **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**) $^{+\bullet}$ ($A_{\text{iso}}(^{31}\text{P}) = 44 \text{ G}$) 9b (**III**) $^{+\bullet}$ ($A_{\text{iso}}(^{31}\text{P}) = 42 \text{ G}$) 9b and (**IV**) $^{+\bullet}$ ($A_{\text{iso}}(^{31}\text{P}) = 44 \text{ G}$) 9c but that is larger than those of (**V**) $^{+\bullet}$ ($A_{\text{iso}}(^{31}\text{P}) = 12\text{--}20 \text{ G}$) featuring a longer π -conjugated system (Fig. 1). 15 This is, however, considerably smaller than that of the phosphinyl radical cation $[(\text{cAAC}^{\text{Cy}})\text{P}(\text{R})]^{+\bullet}$ ($A_{\text{iso}}(^{31}\text{P}) = 99 \text{ G}$) ($\text{R} = 2,2,6,6\text{-tetramethylpiperidino}$) 9a as well as those observed for phosphinyl radicals $\text{R}_2\text{P}^{\bullet}$ ($A_{\text{iso}}(^{31}\text{P}) = 92\text{--}96 \text{ G}$) ($\text{R} = \text{HC}(\text{SiMe}_3)_2$ or $\text{N}(\text{SiMe}_3)_2$) 8a,23 for which, particularly for the latter, the unpaired electron resides predominantly in a $3p(\text{P})$ valence orbital. The value of coupling constants is in good agreement with the computed values (Table S12 \dagger). These hfc 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 \dagger). The EPR spectra of **4a** (Fig. S29 \dagger) and **4b** (Fig. S30 \dagger) 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**: $A_z(^{31}\text{P}) = 149 \text{ MHz}$, $A_x(^{31}\text{P}) = -83 \text{ MHz}$, $A_y(^{31}\text{P}) = 39 \text{ MHz}$; **4b**: $A_z(^{31}\text{P}) = 179 \text{ MHz}$, $A_x(^{31}\text{P}) = -71 \text{ MHz}$, $A_y(^{31}\text{P}) = 49 \text{ MHz}$) 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

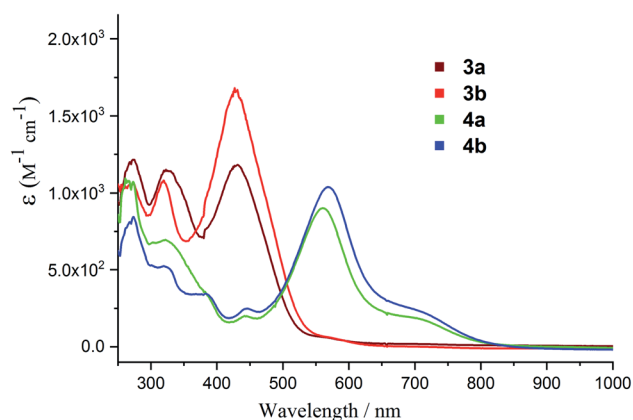


Fig. 9 UV-vis spectra of **3a** and **3b** and their radical cations **4a** and **4b** in THF.

calculations at TD-PCM(thf)/M06-2X/def2-SVP level of theory, comprise dominant contributions of the $\text{H}-1 \rightarrow \text{L}$, $\text{H} \rightarrow \text{L}+2$, and $\text{H} \rightarrow \text{L}$ transitions, respectively (Fig. S32 and S33, Tables S6 and S7 \dagger). 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 $\text{S} \rightarrow \text{L}$ and $\text{S}-1 \rightarrow \text{S}$ (Tables S8 and S9 \dagger).

In the dications **5a** and **5b**, the HOMO-2 is a π -type orbital with contributions from the aryl groups and $\text{C}_{\text{vinyl}}\text{-P}$ bond (Fig. 10). The LUMO of **5a** and **5b** is the π -orbital of the $\text{C}_{\text{IPr}}=\text{C}_{\text{vinyl}}$ and $\text{P}=\text{C}_{\text{CAAC}}$ 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).

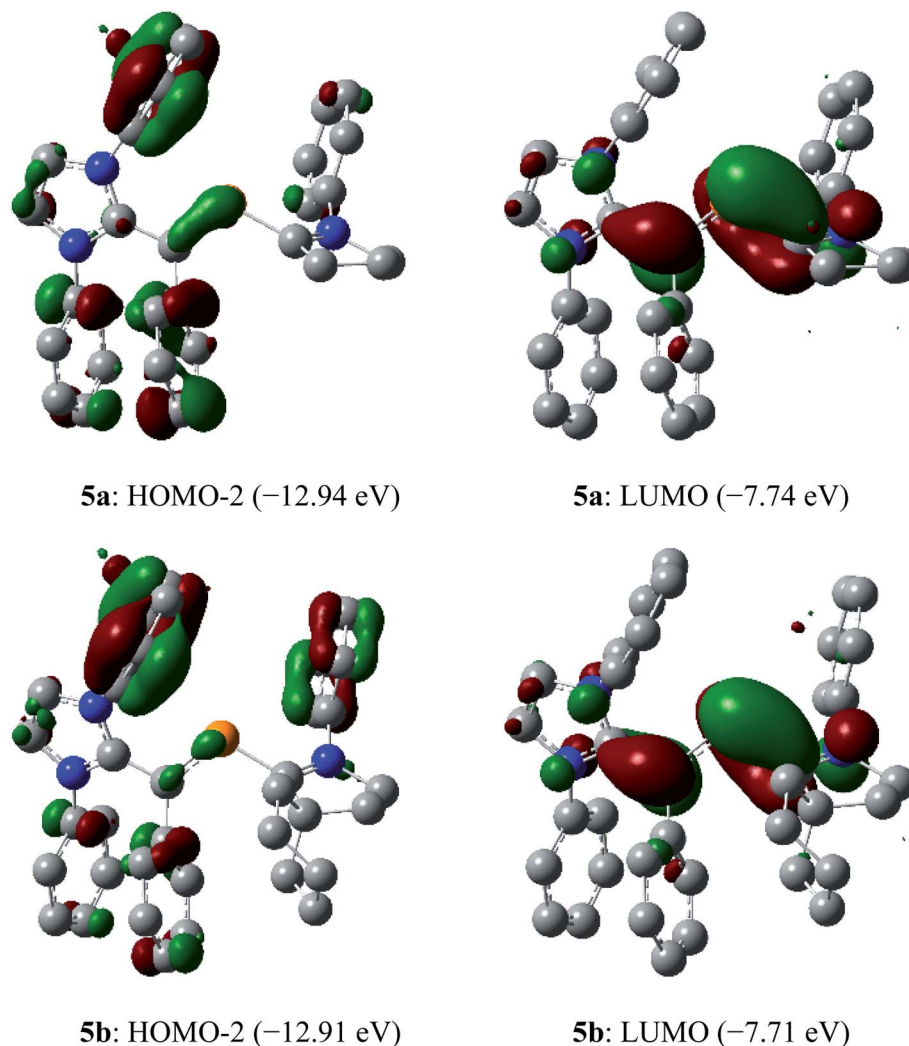


Fig. 10 Selected molecular orbitals (isovalue 0.04) of the dications **5a** and **5b** calculated at M06-2X/def2-TZVP//def2-SVP level of theory. Hydrogen atoms, methyl groups as well as iso-propyl groups were omitted for clarity.

Conclusions

In conclusion, we have isolated the crystalline 2-phospha-1,3-butadiene 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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