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Direct functionalization of white phosphorus with anionic dicarbenes and mesoionic carbenes: facile access to 1,2,3-triphosphol-2-ides†

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A series of unique C_2P_3 -ring compounds $[(ADC^{Ar})P_3]$ $(ADC^{Ar} = ArC\{(DippN)C\}_2; Dipp = 2,6-iPr_2C_6H_3; Ar = Ph 4a, 3-MeC_6H_4 4b, 4-MeC_6H_4 4c, and 4-Me_2NC_6H_4 4d)$ are readily accessible in an almost quantitative yield by the direct functionalization of white phosphorus (P_4) with appropriate anionic dicarbenes $[Li(ADC^{Ar})]$. The formation of 1,2,3-triphosphol-2-ides (4a-4d) suggests unprecedented [3+1] fragmentation of P_4 into P_3^+ and P^- . The P_3^+ cation is trapped by the $(ADC^{Ar})^-$ to give 4, while the putative P^- anion reacts with additional P_4 to yield the Li_3P_7 species, a useful reagent in the synthesis of organophosphorus compounds. Remarkably, the P_4 fragmentation is also viable with the related mesoionic carbenes $(iMICs^{Ar})$ $(iMIC^{Ar} = ArC\{(DippN)_2CCH\}$, i stands for imidazole-based) giving rise to 4. DFT calculations reveal that both the C_3N_2 and C_2P_3 -rings of 4 are 6π -electron aromatic systems. The natural bonding orbital (NBO) analyses indicate that compounds 4 are mesoionic species featuring a negatively polarized C_2P_3 -ring. The HOMO-3 of 4 is mainly the lone-pair at the central phosphorus atom that undergoes σ -bond formation with a variety of metal-electrophiles to yield complexes $[\{(ADC^{Ar})P_3\}M(CO)_n]$ (M = Fe, n = 4, Ar = Ph 5a or $4-Me-C_6H_4 5b$; M = Mo, n = 5, Ar = Ph 6; M = W, n = 5. $Ar = 4-Me_2NC_6H_4 7$).

Introduction

The direct conversion of white phosphorus (P_4) into useful organophosphorus compounds (OPCs) is of significant interest because this excludes the involvement of corrosive Cl_2 gas that is required to convert P_4 into PCl_3 , a common starting material for OPCs, and thus minimizes the waste and energy consumption. The activation and subsequent functionalization of P_4 has therefore become a topical objective. Both transition metal as well as main-group element compounds have been shown to activate or functionalize P_4 . In particular, compounds featuring a low-valent main-group element have made significant advances over the past years.

Among nonmetals, the use of singlet carbenes⁷ has given new impetus to the field of P₄ activation as it leads to the direct C-P bond formation (Fig. 1).⁸ Several stable carbenes (L1-L7) undergo reactions with P₄ and the fate of P₄ fragmentation to

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give P_n (n=1, 2, 4, 8 or 12) containing products **II-IX** depends on the relative σ -donor/ π -acceptor (ambiphilic) property as well as the steric demand of carbenes. Weakly π -accepting NHCs such as IPr (IPr = C{(DippN)CH}₂) do not react with P_4 , however, related derivatives containing the $[P_2]$ or $[P_3^-]$ moiety are accessible by alternative methods. Sterically demanding 1,3-bis(tBu)imidazol-2-ylidene (IBu t) activates P_4 in combination with B(C_6F_5)3 to give **X**. This frustrated Lewis pair (FLP) type reactivity led to the transformation of the classical NHC (IBu t) into the mesoionic carbene (iMIC) L8 based on an 1,3-imidazole framework.

iMICs are very potent σ-donor ligands with almost negligible π -acceptor properties.¹¹ Nonetheless, no reaction of an iMIC alone with P_4 has been described so far. This is most likely due to their limited synthetic accessibility.^{11α} We recently reported¹² C5-protonated iMICs^{Ar} (**XI**) as well as C4/C5-ditopic anionic dicarbenes [Li(ADC^{Ar})] **XII** (Fig. 1) by the deprotonation of C2-arylated 1,3-imidazolium salts.¹³ The dicarbenes **XII** feature two adjacent C4/C5-nucleophilic sites, and thus are well endowed to affect unique dual P_4 functionalization.^{5i,14} Herein, we showcase the direct functionalization of P_4 *via* unprecedented [3 + 1] fragmentation with [Li(ADC^{Ar}] and iMICs^{Ar} to give the 1,2,3-triphosphol-2-ide derivatives [(ADC^{Ar}) P_3] (ADC^{Ar} = ArC {NDipp)C}₂; Dipp = 2,6-iPr₂C₆H₃; Ar = C₆H₅ 4a, 3-MeC₆H₄ 4b, 4-MeC₆H₄ 4c, and 4-Me₂NC₆H₄ 4d) (Scheme 1).

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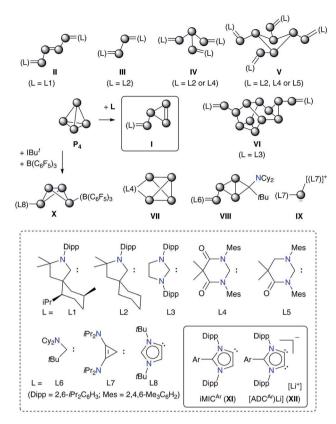


Fig. 1 Singlet carbene-mediated P_4 activation and fragmentation to II–X and a plausible intermediate I. Mesoionic carbenes (iMICs^{Ar}, XI) and anionic dicarbenes (XII) ([Li⁺] = solvated lithium ion) investigated in the current study.

$$\begin{array}{c} 3 \ [Li]^{+} \\ \hline Ar \\ \hline Ar \\ \hline Dipp \\ \hline Ar \\ \hline Oipp \\ O$$

Scheme 1 Synthesis of 1,2,3-triphosphol-2-ide derivatives 4a-4d by the direct fragmentation of white phosphorus with [Li(ADC^{Ar})] (2a-2d). Reaction of iMICs^{Ar} 3a and 3c with P_4 to form 4a and 4c.

Results and discussion

Treatment of [Li(ADC^{Ar})] (2a-2d),¹² which are readily accessible by the double deprotonation of C2-arylated 1,3-imidazolium salts 1a-1d with n-BuLi, with P_4 at room temperature afforded

the 1,2,3-triphosphol-2-ides **4a–4d** as crystalline solids in almost quantitative yields (Scheme 1). Compounds **4a–4d** are indefinitely stable (as solids as well as in solutions) under an inert gas atmosphere. The formation of **4a–4d** indicates formal [3+1] fragmentation of P_4 into P_3 and P_3 . The cationic P_3 species is captured by the ADCs to give **4a–4d**, whereas the P_3 nucleophile reacts with additional P_4 to eventually form the phosphide $(P_7)^{3-1}$ anion, a very common species in metal mediated fragmentation of P_4 . Indeed, P_4 is Indeed, P_4 is reaction with (IPr)HCl to give (IPr)PH, reported previously using P_3 .

Interestingly, treatment of iMICs^{Ar} **3a** and **3c** with P₄ also afforded, *albeit* in a lower yield, the corresponding products **4a** and **4c**, respectively. ¹H NMR analyses of the crude reaction product indicate the presence of a 1:1 mixture of **4a**: **1a** and **4c**: **1c**, suggesting the reprotonation of iMICs^{Ar} **3a** and **3b** to 1,3-imidazolium salts **1a** and **1c**. Pure **4a** and **4c** can be extracted from the mixture using toluene.

The 1 H NMR spectra of **4a–4d** are very symmetric and show two doublets and one septet for the isopropyl groups along with the signals due to the aryl protons. The 13 C $\{^1$ H $\}$ NMR resonances for **4a–4d** are fully consistent with their 1 H NMR spectra. The 13 C $\{^1$ H $\}$ NMR spectrum of **4a–4d** each exhibits a doublet at 167 ppm ($J_{P-C} \approx 84$ Hz) for the backbone carbon atoms due to coupling with the 31 P nucleus. The 31 P $\{^1$ H $\}$ NMR spectrum of **4a–4d** each shows a doublet at \sim 73 ppm and a triplet at 325 \pm 6 ppm in 2 : 1 ratio ($J_{P-P} \approx 500$ Hz), indicating the presence of an AB₂ type system with unsaturated P–P bonds. 18

Solid-state molecular structures¹⁹ of **4a** (Fig. 2), **4b** (Fig. S47†), and **4c** (Fig. S48†) reveal the presence of a C_2P_3 -ring that is coplanar with the imidazole C_3N_2 -ring plane. The metrical parameters of **4a–4c** are comparable (Table S1†) and hence, for brevity, only **4a** is discussed here. The P1–P2 bond length of **4a** (2.103(1) Å) is intermediate of the sum of covalent

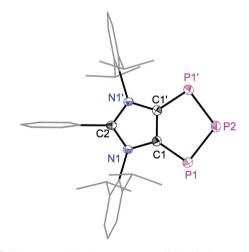


Fig. 2 Solid-state molecular structure of 4a. Hydrogen atoms are omitted for clarity. Symmetry code: 1-X, +Y, 3/2-Z. Selected experimental and calculated [M06-2X/def2SVP] bond lengths (Å) and angles (°): C1-C1′ 1.395(5) [1.402], N1-C1 1.404(3) [1.399], P1-C1 1.757(3) [1.764], P1-P2 2.103(1) [2.112], C1-P1-P2 94.9(1) [94.8], and P1-P2-P1′ 104.0(1) [104.1].

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Scheme 2 (a) Calculated Wiberg Bond Indices (WBIs) and (b) NPA atomic charges of 1,2,3-triphosphol-1,2-ides 4. (c) Schematic representation of 4 with atom numberings.

radii for P=P double (2.04 Å) and P-P single (2.22 Å) bond lengths, 20 indicating a partial π -bond character. Similarly, the C1-P1 (1.757(3) Å) bond length of 4a is shorter compared to a classical C-P single bond length (1.85 Å) but compares well with C=P bond lengths (ca. 1.75 Å) of inversely polarized phosphaalkenes. 17 The C1-C1′ (1.395(5) Å) and C2-N1 (1.404(3) Å) bond lengths of 4a are elongated in comparison with those of 1a (1.350(2) and 1.344(2) Å, respectively). 13 The C1-C1′, C1/C2-P1 and P1-P2 bond lengths of 4a-4c are comparable with the corresponding bond lengths of triphospholide anions $[P_3C_2R_2]^-$ (R = H, C-P 1.726(2) and 1.781(3), and P-P 2.081(1) and 2.094(1) Å; R = Ph, C-P 1.760(2) and 1.762(2), and P-P 2.091(2), 2.098(2) Å). 21 Thus, 4a-4d may be considered as the neutral analogues of the triphospholide anions.

To gain further insight into the electronic structures of 4a-4d, we performed DFT calculations at the M06-2X/def2-TZVPP// M06-2X/def2-SVP level of theory. The computed NPA charges (Table S7 \dagger) at the P2 (-0.10e) and the C1/C2 (-0.24e) atoms are negative, whereas both the P1 atoms bear a positive charge (0.12e) (Scheme 2). The Wiberg Bond Indices (WBIs) of 1.40 (P-P), 1.18 (C-P), and 1.31 (C-C) indicate a partial double bond character. The WBI for the C1-C2 bond of 4a (1.31) is significantly smaller compared to that of the imidazolium salt 1a (WBI = 1.64). The WBIs for the C3-N1/2 bonds in 1 (1.28) and 4 (1.26) are, however, almost equal. Thus, compounds 4 may be described as mesoionic species with 6π-electron C₂P₃ and C₃N₂ aromatic systems (Scheme 2c). The nitrogen atoms contribute 4π -electrons to the C₃N₃-ring, whereas the P₃ unit shares 4π electrons with the C_2P_3 -ring. The 2π -electrons of the C1=C2 bond are pooled by both the ring systems. Indeed, calculated nucleus-independent chemical shift (NICS)22 values for 4a-4d (Table 1) suggest the aromaticity of the C₃N₂- and C₂P₃-rings. For comparison, we also calculated the NICS values for C₆H₆ and cyclobutadiene (CBD) molecules.

The anisotropy of current-induced density (AICD) has been used to study the aromatic behavior of several molecules.²³ The AICD plots of **4a** (Fig. 3) and **4b–4d** (Fig. S62†) clearly show

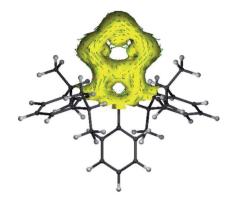


Fig. 3 AICD plot (based on M06-2X/def2-TZVPP//def2-SVP calculations) of the $C_3N_2P_3$ core of compound 4a. The isovalue was arbitrarily chosen to be 0.03, the magnetic field is orthogonal to the C_2P_3 -plane and points towards the viewer, and thus clockwise ring currents represent aromatic systems, whereas counter-clockwise ring currents are indicative of antiaromatic systems. AICD plots of the complete molecules 4a–4d are given in the ESI.†

significant delocalization of the π -electrons of both the C_3N_2 and the C_2P_3 heterocycles, forming one coherent π -system.

The HOMO of compounds 4a (Fig. 4) and 4b-4c (Fig. S58–S60†) corresponds to the π -orbitals of the C–P bonds with a small contribution from the lone pairs at the nitrogen atoms. The HOMO–1 corresponds mainly to the π -orbitals of the P_3 and the P_3 and the P_4 moieties of the P_4 ring. Like in alkali metal 1,2,3-triphospholides, P_4 the analyses of frontier molecular orbitals, HOMO and HOMO–1 in particular, of P_4 reveal the mixing of phosphorus orbitals with lone-pair character amongst the P_4 manifold frontier orbitals. The HOMO–3 and HOMO–2 are the lone pairs on the central and neighbouring P_4 atoms, respectively. The LUMO of P_4 corresponds to the P_4 orbital of the aryl group on the P_4 carbon atom along with a p-orbital at the central phosphorus atom. The LUMO+2 corresponds mainly to the P_4 -orbitals of the

The intriguing electronic structures of **4** prompted us to investigate their ligand properties as they may function as neutral two electron σ -donors (via phosphorus atoms) and/or 6π -electron η^5 -donors (C_2P_3 -ring) like triphospholide²¹ and cyclopentadienyl anions. Treatment of **4a**, **4b**, and **4c** with $Fe_2(CO)_9$ or $M(CO)_5(THF)$ (M=Mo or W) led to the formation of related complexes **5a**, **5b**, **6**, and **7** (Scheme 3). In all complexes, the central phosphorus atom functions as a two-electron σ -donor ligand to bind to the $M(CO)_n$ moiety. This is consistent with the NBO analysis, which suggests higher charge accumulation at the central phosphorus atom with respect to that of the

Table 1 Calculated NICS values for the C_3N_2/C_2P_3 units of 4a-4d at the M06-2X/def2TZVPP//M06-2X/def2SVP level of theory

C_3N_2/C_2P_3	4 a	4b	4c	4d	5a	C_6H_6/CBD^a
NICS(0) NICS(1) NICS(2)	-7.08/-10.19 $-5.94/-10.18$ $-2.43/-5.51$	-7.29/-10.31 $-6.11/-10.28$ $-2.53/-5.21$	-7.29/-10.31 $-6.11/-10.23$ $-2.53/-5.53$	-6.77/-10.37 $-5.64/-10.21$ $-2.36/-5.52$	-7.57/-9.95 $-6.29/-9.58$ $-2.52/-5.12$	-7.53/33.21 $-10.19/21.09$ $-5.22/4.98$

^a CBD (cyclobutadiene).

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LUMO+2 (-0.08 eV) LUMO (-1.25 eV)

Fig. 4 Selected MOs of 4a calculated at the M06-2X/def2-TZVPP// def2-SVP level of theory with an isovalue of 0.04. Hydrogen atoms were omitted for clarity.

HOMO (-6.08 eV)

HOMO-3 (-7.50 eV)

neighbouring phosphorus atoms. The $^{31}P\{^{1}H\}$ NMR spectrum of **5a**, **5b**, **6**, and 7 each exhibits one doublet (**5a**: 145; **5b**: 145; **6**: 160; 7: 157 ppm) and one triplet (**5a**: 316; **5b**: 315; **6**: 299; 7: 250 ppm), which have been upfield shifted with respect to that of **4a** (173, 332 ppm), **4b** (173, 331 ppm), and **4d** (173, 319 ppm). In the $^{31}P\{^{1}H\}$ NMR spectrum of 7, the triplet at 250 ppm is accompanied by the ^{183}W satellites ($J_{P-W}=202$ Hz).

The iron atom in **5a** (Fig. 5) and **5b** (Fig. S49†) each features a trigonal-bipyramidal geometry. Three equatorial positions are occupied by CO ligands, whereas one CO and one **4a** or **4b** are present at the axial positions. The P–Fe bond length of **5a** (2.240(1) Å) compares well with that of triphosphaindane-derived P_3Fe_3 iron-carbonyl clusters (av. 2.244 Å).²⁴ Interestingly, the metrical parameters of the C_3N_2 - and C_2P_3 -rings of **5a** and **5b** are very similar to those of the precursors **4a** and **4b**, respectively. This indicates that the aromatic π -systems remain virtually intact upon complexation of **4a** and **4b** with the Fe(CO)₄ fragment. As expected, the molecular structures of **6** (Fig. S50†) and **7** (Fig. S51†) feature six-fold coordinated Mo and W atoms, respectively.

4a,4b or 4d
$$\begin{array}{c}
Fe_2(CO)_9 \\
\text{or M(CO)}_5(THF) \\
-Fe(CO)_5 \text{ or THF} \\
(M = Mo \text{ or W})
\end{array}$$

$$\begin{array}{c}
Dipp \\
Ar \longrightarrow P - M(CO)_n \\
Dipp \\
(n = 4 \text{ or 5})$$

5a: M = Fe, Ar = Ph; **5b**: M = Fe, Ar = 3-MeC_6H_4 **6**: M = Mo, Ar = Ph; **7**: M = W, Ar = $4\text{-Me}_2NC_6H_4$

Scheme 3 Synthesis of complexes $[{(ADC^{Ar})P_3}M(CO)_n]$ 5a, 5b, 6, and 7

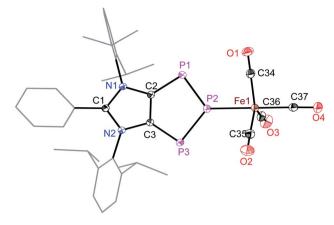


Fig. 5 Solid-state molecular structure of 5a. Hydrogen atoms and one solvent toluene molecule are omitted for clarity. Selected bond lengths (Å) and angles (°): C2–C3 1.394(2), C2–N1 1.399(1), C3–N2 1.403(1), C2–P1 1.756(1), C3–P3 1.764(1), P1–P2 2.081(1), P2–P3 2.089(1), P2–Fe1 2.240(1), Fe1–C34 1.791(1), Fe1–C35 1.797(2), Fe1–C36 1.810(1), Fe1–C37 1.783(1), P1–P2–P3 109.1(2), and P2–Fe1–C37 178.5(1).

DFT calculations suggest that the HOMO of **5a** (Fig. 6) is mainly located at the iron atom and has some contribution from the π -orbitals of the C–C and one P–P bond. The LUMO is comparable to that of **4a** but is lower in energy by -0.26 eV, indicating metal-to-ligand π -back bonding. The aromaticity of the C_2P_3 moiety in **5a** remains almost unchanged as indicated by NICS(0) = -9.95, NICS(1) = -9.58, and NICS(2) = -5.12 values. The aromaticity of **5a** is also corroborated by the AICD plot (Fig. S62†).

Experimental

All syntheses and manipulations were carried out under an inert gas atmosphere (Ar or N₂) using standard Schlenk techniques or a glove box (MBraun LABMasterPro). Solvents were dried over appropriate drying agents, distilled, and stored over a 3 Å molecular sieve prior to use. Deuterated solvents were dried over appropriate drying agents, distilled, and stored inside a glove box. NMR spectra were recorded on a Bruker Avance III 500 or a Bruker Avance III 500 HD spectrometer. Chemical shifts (in δ , ppm) are referenced to the solvent residual signals of CD₂Cl₂: ¹H 5.32; ¹³C 53.84 and C₆D₆: ¹H 7.16; ¹³C 128.62 ppm. ESI mass spectra were recorded using an Esquire 3000 ion trap mass spectrometer (Bruker Daltonik GmbH, Bremen, Germany) equipped with a nano-ESI source. Samples were dissolved in CH₂Cl₂ and introduced by static nano-ESI using in-house pulled glass emitters. Nitrogen served as a nebulizer gas as well as a dry gas and was generated by a Bruker nitrogen generator NGM 11. Helium served as a cooling gas for the ion trap. The mass axis was externally calibrated with ESI-L Tuning Mix (Agilent Technologies, Santa Clara, CA, USA) as the calibration standard. UV/ vis spectra were recorded on a ThermoFisher Evolution 300 spectrophotometer. Infrared spectra were recorded using a Bruker Alpha-T FTIR spectrometer equipped with a Bruker Platinum diamond ATR unit. Melting points were measured

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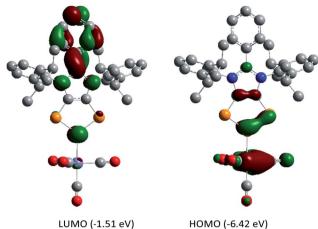


Fig. 6 Frontier molecular orbitals of 5a calculated at the M06-2X/ def2-TZVPP//def2-SVP level of theory. The isovalue was arbitrarily chosen to be 0.04. Hydrogen atoms were omitted for clarity.

with a Büchi B-545 melting point apparatus. (IPrAr)Br salts 1a-1d (Ar = Ph, 3-MeC_6H_4 , 4-MeC_6H_4 or $4\text{-Me}_2NC_6H_4$) were synthesized following the reported method. 13a n-BuLi (2.5 M solution in hexanes, Sigma-Aldrich) was used as received. White phosphorus was sublimed and stored inside a glovebox. Commercially available Fe₂(CO)₉ (Sigma-Aldrich), Mo(CO)₆ (Fluorochem), and W(CO)₆ (Sigma-Aldrich) were used as supplied.

Synthesis of compound (ADCPh)P3 (4a)

To a 15 mL THF suspension of 1a (0.88 g, 1.6 mmol), n-BuLi (2.5 M, 1.4 mL, 3.5 mmol) was added at -40 °C. The resulting reaction mixture was stirred at −20 °C for 1 h and then at room temperature (25 $^{\circ}$ C) for 15 minutes to obtain a clear light brown solution of 2a.12 To this solution, solid P₄ (0.4 g, 3.2 mmol) was added in one portion and then stirred overnight at rt. The resulting dark suspension was refluxed for 2 h and the red insoluble material (probably a mixture of Li₃P₇ and other polyphosphides) was removed by filtration. The volatiles from the filtrate were removed under vacuum to give a brown residue, which was extracted with dichloromethane, dried under vacuum, washed with toluene (2 × 10 mL), and re-dried to obtain compound 4a as a yellow solid. Yield: 96% (0.86 g). Single crystals suitable for X-ray diffraction analysis were grown by storing a saturated toluene solution of 4a at -24 °C for three days. Mp: 343 °C. Elem. anal. (%), calcd for C₃₃H₃₉N₂P₃ (556.6): C, 71.21; H, 7.06; N, 5.03; found: C, 71.02; H, 6.84; N, 4.87. ¹H NMR (500 MHz, CD_2Cl_2 , 298 K): $\delta = 7.59$ (t, J = 7.7 Hz, 2H, p- C_6H_3 , 7.38 (d, J = 7.8 Hz, 4H, m- C_6H_3), 7.34 (t, J = 6.6 Hz, 1H, p- C_6H_5), 7.23–7.18 (m, 4H, o-, m- C_6H_5), 2.62 (sept, J = 6.6 Hz, 4H, $CH(CH_3)_2$, 1.26 (d, J = 6.6 Hz, 12H, $CH(CH_3)_2$), and 1.03 (d, J =6.7 Hz, 12H, $CH(CH_3)_2$) ppm. ¹³C{¹H} NMR (126 MHz, CD_2Cl_2 , 298 K): $\delta = 167.6$ (d, $J_{P-C} = 84.4$ Hz, CP); 149.2 (NCN); 146.2, 133.5, 132.0, 131.8, 129.8, 129.1, 125.8, and 123.8 (C_6H_3 , C_6H_5); 29.7 ($CH(CH_3)_2$); 26.1 and 23.5 ($CH(CH_3)_2$) ppm. ³¹P{¹H} NMR (202 MHz, CD_2Cl_2 , 298 K): $\delta = 332.3$ (t, $J_{P-P} = 506$ Hz) and 173.7 $(d, J_{P-P} = 506 \text{ Hz}) \text{ ppm. MS (ESI, positive mode): } m/z = 557.3 \text{ [4a]}$ + H]⁺. UV-vis (λ /nm ε (M⁻¹ cm⁻¹)): 282 (22336), 346 (31017), and 361 (31397).

Compounds 4b-4d were prepared by employing a similar protocol to that described for 4a using the appropriate precursor 1b, 1c or 1d, n-BuLi, and P₄.

$(ADC^{3-Tol})P_3(4b)$

Yield: 98% (0.90 g). Mp: 338-341 °C. Elem. anal. (%), calcd for **4b**, C₃₄H₄₁N₂P₃, (570.6): C, 71.56; H, 7.24; N 4.91; found C, 70.64; H, 7.33; N 4.68. ¹H NMR (500 MHz, CD_2Cl_2 , 298 K): $\delta =$ 7.57 (t, J = 7.8 Hz, 2H, $p\text{-C}_6H_3$), 7.35 (d, J = 7.8 Hz, 4H, $m\text{-C}_6H_3$), 7.14 (d, J = 7.6 Hz, 1H, o-C₆ H_4), 7.08 (t, J = 7.8 Hz, 1H, m-C₆ H_4), 7.02 (s, 1H, o-C₆ H_4), 6.96 (d, J = 7.8 Hz, 1H, p-C₆ H_4), 2.60 (sept, J= 6.7 Hz, 4H, $CH(CH_3)_2$), 2.10 (s, 3H, CH_3), 1.24 (d, J = 6.7 Hz, 12H, $CH(CH_3)_2$), and 1.03 (d, J = 6.8 Hz, 12H, $CH(CH_3)_2$) ppm. ¹³C{¹H} NMR (126 MHz, CD₂Cl₂, 298 K): $\delta = 167.5$ (d, $J_{P-C} =$ 84.5 Hz, CP); 149.6 (NCN); 146.3, 139.3, and 133.6 (i-C₆H₄ and i-, $m-C_6H_3$; 132.7 ($o-C_6H_4$); 131.7 ($p-C_6H_3$); 130.5 ($o-C_6H_4$); 129.5 and 128.9 (m-C₆H₄); 126.9, 125.8, and 123.71 (m-C₆H₃); 29.7 $(C(CH_3)_2)$; 26.2 and 23.5 $(C(CH_3)_2)$; 21.2 (CH_3) ppm. ³¹P{¹H} NMR (202 MHz, CD_2Cl_2 , 298 K): $\delta = 331.1$ (t, $J_{P-P} = 506$ Hz) and 173.6 (d, $J_{P-P} = 506 \text{ Hz}$) ppm. MS (ESI, positive mode): m/z =571.3 $[4b + H]^+$. UV-vis ($\lambda/\text{nm } \varepsilon \text{ (M}^{-1} \text{ cm}^{-1})$): 280 (25637), 345 (36323), and 361 (36539).

$(ADC^{4-Tol})P_3$ (4c)

Yield: 93% (0.85 g). Single crystals suitable for X-ray diffraction were obtained by storing a saturated toluene solution of 4c for three days at -24 °C. Mp: 339–343 °C. Elem. anal. (%), calcd for C₃₄H₄₁N₂P₃ (570.6): C, 71.56; H, 7.24; N, 4.91; found C, 71.11; H, 7.06; N, 4.65. ¹H NMR (500 MHz, CD_2Cl_2 , 298 K): $\delta = 7.59$ (t, J =7.8 Hz, 2H, p-C₆ H_3), 7.38 (d, J = 7.8 Hz, 4H, m-C₆ H_3), 7.05 (d, J =8.4 Hz, 2H, C_6H_4), 7.02 (d, J = 8.3 Hz, 2H, C_6H_4), 2.61 (sept, J =6.8 Hz, 4H, $CH(CH_3)_2$), 2.23 (s, 3H, CH_3), 1.26 (d, J = 6.7 Hz, 12H, $CH(CH_3)_2$), and 1.03 (d, J = 6.9 Hz, 12H, $CH(CH_3)_2$) ppm. ¹³C $\{^{1}H\}$ NMR (126 MHz, CD₂Cl₂, 298 K): $\delta = 167.5$ (d, $J_{P-C} =$ 84.1 Hz, CP); 146.2 (NCN); 143.1, 133.7, 131.7, 129.8, 129.7, 125.8, and 120.9 (C_6H_3 and C_6H_4); 29.7 ($CH(CH_3)_2$); 26.1 and 23.5 $(CH(CH_3)_2)$; 21.7 (CH_3) ppm. ³¹P{¹H} NMR (202 MHz, CD_2Cl_2 , 298 K): $\delta = 329.9$ (t, $J_{P-P} = 506$ Hz) and 173.6 (d, $J_{P-P} =$ 506 Hz) ppm. MS (ESI, positive mode): $m/z = 571.3 [4c + H]^{+}$. UVvis $(\lambda/\text{nm } \varepsilon \text{ (M}^{-1} \text{ cm}^{-1}))$: 283 (23295), 336 (28771), 346 (29238), and 362 (29676).

$(ADC^{4-DMP})P_3$ (4d)

Yield: 94% (0.93 g). Mp: 270-273 °C (decomp.). Elem. anal. (%), calcd for C₃₅H₄₄N₃P₃ (599.3): C, 70.10; H, 7.40; N, 7.01; found: C, 69.66; H, 7.18; N 6.59. ¹H NMR (500 MHz, CD_2Cl_2 , 298 K): $\delta =$ 7.56 (t, J = 7.8 Hz, 2H, p-C₆ H_3), 7.35 (d, J = 7.8 Hz, 4H, m-C₆ H_3), 6.90 (d, J = 9.0 Hz, 2H, C_6H_4), 6.28 (d, J = 9.0 Hz, 2H, C_6H_4), 2.88 $(s, 6H, N(CH_3)_2), 2.67 (sept, J = 6.8 Hz, 4H, CH(CH_3)_2), 1.24 (d, J)$ = 6.7 Hz, 12H, $CH(CH_3)_2$), and 0.97 (d, J = 6.8 Hz, 12H, $CH(CH_3)_2$) ppm. ¹³C{¹H} NMR (126 MHz, CD_2Cl_2 , 298 K): $\delta =$ 167.0 (d, $J_{P-C} = 82.8$ Hz, CP); 151.9 (NCN); 146.2, 138.4, 134.6, 131.4, 130.8, 126.3, 125.8, and 111.1 (C_6H_3 and C_6H_4); 40.0 $(N(CH_3)_2)$; 29.6 $(CH(CH_3)_2)$; 25.7 and 23.5 $(CH(CH_3)_2)$ ppm. ³¹P **Edge Article**

{¹H} NMR (202 MHz, CD₂Cl₂, 298 K): δ = 319.5 (t, J_{P-P} = 504 Hz) and 173.3 (d, J_{P-P} = 504 Hz) ppm. MS (ESI, positive mode): m/z = 600.3 [4d + H]⁺. UV-vis (λ /nm (ε M⁻¹ cm⁻¹)): 285 (37768), 322 (46655), 343 (47543), 366 (48310), and 398 (45288).

Experimental identification of the insoluble material. A mixture of the insoluble material (20 mg, 80 μmol, calcd for Li₃P₇) and IPrHCl (80 mg, 188 μmol) was stirred in 3 mL of THF for three days at rt, resulting in a dark red suspension. A black solid was removed by filtration and the filtrate was dried in a vacuum, affording a dark red solid which was identified as IPr=PH¹⁷ by NMR spectroscopy. ¹H NMR (500 MHz, C₆D₆, 298 K): δ = 7.23 (t, J = 7.7 Hz, 2H, p-C₆H₃), 7.14 (d, J = 7.6 Hz, 4H, m-C₆H₃), 6.18 (s, 2H, NCH), 3.06 (sept, J = 6.7 Hz, 4H, CH(CH₃)₂), 1.92 (d, J_{PH} = 165.2 Hz, 1H, PH), 1.47 (d, J = 6.8 Hz, 12H, CH(CH₃)₂), and 1.15 (d, J = 6.9 Hz, 12H, CH(CH₃)₂) ppm. ³¹P NMR (C₆D₆, 298 K, 500 MHz): δ = -134.4 (d, J_{P-H} = 165.2 Hz) ppm. ³¹P{¹H} NMR (C₆D₆, 298 K, 500 MHz): δ = -134.4 ppm.

Alternative synthesis of 4a and 4c from iMICsAr 2a and 2c

To a 15 mL THF suspension of **1a** (0.98 g, 1.8 mmol), n-BuLi (2.5 M, 0.8 mL, 2.0 mmol) was added at -40 °C. The resulting brown solution was stirred at -20 °C for 45 min and then for 15 min at rt. Subsequently, P_4 (0.3 g, 2.4 mmol) was added in one portion and the resulting reaction mixture was stirred overnight at rt. The volatiles were removed under vacuum to obtain a dark residue, which was extracted with toluene (3 \times 10 mL). The filtrate was dried in a vacuum to obtain **4a**. Yield: 41% (0.4 g).

 $(ADC^{4-Tol})P_3$ (4c). Similarly, treatment of 3c with P_4 gave 4c. Yield: 36% (0.4 g).

Syntheses of complexes 5a, 5b, 6, and 7

 $[(ADC^{Ph})P_3]Fe(CO)_4$ (5a). To a mixture of 4a (651 mg, 1.2) mmol) and Fe₂(CO)₉ (510 mg, 1.4 mmol), 30 mL THF was added at rt. The brown colored solution changed to a dark red colored solution after 15 min, which was further stirred overnight. The volatiles were removed in a vacuum to afford a red solid, which was extracted with 30 mL toluene. The volume of the filtrate was reduced to 10 mL and stored at -30° for one week to obtained orange needles of 5a (696 mg, 80%), which were also suitable for X-ray diffraction. Mp: 167–172 °C (decomp.). Elem. anal. (%), calcd for C₃₇H₃₉FeN₂O₄P₃ (724.5): C, 61.34; H, 5.43; N, 3.87; found: C, 59.66; H, 5.24; N, 3.71. ¹H NMR (500 MHz, CD₂Cl₂, 298 K): $\delta = 7.60$ (t, J = 7.8 Hz, 2H, p-C₆ H_3), 7.38 (d, J = 7.8 Hz, 4H, m- C_6H_3), 7.34 (t, J = 7.5 Hz, 1H, p- C_6H_5), 7.22–7.15 (m, 4H, o-, m- C_6H_5 , 2.57 (sept, J = 6.7 Hz, 4H, $CH(CH_3)_2$), 1.27 (d, J = 6.7 Hz, 12H, $CH(CH_3)_2$), and 1.01 (d, J = 6.8 Hz, 12H, $CH(CH_3)_2$) ppm. ¹³C{¹H} NMR (126 MHz, CD₂Cl₂, 298 K): δ = 215.1 (CO); 161.7 (d, $J_{P-C} = 70.3 \text{ Hz}, CP$; 146.0 (NCN), 133.1, 132.2, 129.7, 129.5, 129.3, 128.7, 126.1, and 123.1 (C_6H_3 and C_6H_5); 29.8 ($CH(CH_3)_2$); 26.0 and 23.5 (CH(CH_3)₂) ppm. ³¹P{¹H} NMR (202 MHz, CD_2Cl_2 , 298 K): $\delta = 316.8$ (t, $J_{P-P} = 531$ Hz) and 145.4 (d, $J_{P-P} = 531$ Hz) ppm. MS (ESI, positive mode): $m/z = 725.1 [5a + H]^+$. UV-vis $(\lambda/\text{nm }\varepsilon (M^{-1} \text{ cm}^{-1}))$: 285 (33061), 328 (31345), and 428 (37184). IR (ATR, diamond): $\tilde{v}/\text{cm}^{-1} = 2041$, 1966, 1937, and 1919.

[(ADC^{3-Tol})P₃]Fe(CO)₄ (5b). Compound 5b was synthesized following a similar procedure to that described above for 5a using 4b (300 mg, 0.53 mmol) and Fe₂(CO)₉ (191 mg, 0.53 mmol) as an orange crystalline solid. Yield: 84% (333 mg). Crystals suitable for X-ray diffraction were obtained by storing a saturated toluene solution of 5b overnight at rt. Mp: 180-182 °C (decomp.) Elem. anal. (%), calcd for 5b, C₃₈H₄₁FeN₂O₄P₃ (738.5): C, 61.80; H, 7.56; N, 3.79; found C, 62.69; H, 5.95; N, 3.45. ¹H NMR (500 MHz, CD_2Cl_2 , 298 K): $\delta = 7.59$ (t, J = 7.8 Hz, 2H, p-C₆ H_3), 7.37 (d, J = 7.8 Hz, 4H, m-C₆ H_3), 7.15 (d, J = 7.4 Hz, 1H, o-C₆ H_4), 7.08 (t, J = 7.7 Hz, 1H, m-C₆ H_4), 7.00 (s, 1H, o-C₆ H_4), 6.94 (d, J = 7.7 Hz, 1H, $p\text{-C}_6H_4$), 2.56 (sept, J = 6.6 Hz, 4H, $CH(CH_3)_2$, 2.09 (s, 3H, CH_3), 1.27 (d, J = 6.6 Hz, 12H, $CH(CH_3)_2$), and 1.04 (d, J = 6.7 Hz, 12H, CH(C H_3)₂) ppm. ¹³C{¹H} NMR (126 MHz, CD_2Cl_2 , 298 K): $\delta = 215.1$ and 214.9 (CO); 161.6 (d, $J_{P-C} =$ 71 Hz, NCP); 147.6 (NCN); 146.1, 139.5, 133.1, 133.0, 132.1, 130.3, 129.9, 129.0, 126.8, 126.0, and 122.9 (C_6H_3 and C_6H_5); 29.8 (CH(CH₃)₂); 26.1 and 23.6 (CH(CH₃)₂); 21.2 (CH₃) ppm. 31 P $\{^{1}H\}$ NMR (202 MHz, $CD_{2}Cl_{2}$, 298 K): $\delta = 315.5$ (t, $J_{P-P} = 531$ Hz) and 145.4 (d, $J_{P-P} = 532 \text{ Hz}$) ppm. MS (ESI, positive mode): m/z =739.1 $[5b + H]^+$. UV-vis $(\lambda/\text{nm } \varepsilon \text{ (M}^{-1} \text{ cm}^{-1}))$: 282 (35189), 327 (29758), and 416 (37568). IR (ATR, diamond): $\tilde{v}/\text{cm}^{-1} = 2039$, 2007, 1962, and 1921.

 $[(ADC^{Ph})P_3]Mo(CO)_5$ (6). To a mixture of 4a (447 mg, 0.8) mmol) and Mo(CO)₆ (212 mg, 0.8 mmol), 20 mL THF was added at rt. The yellow suspension was stirred for three days at 60 °C. Filtration through a plug of Celite afforded an orange solution. The volatiles were removed under vacuum to obtain 6 as a yellow solid (523 mg, 81%). Crystals suitable for X-ray diffraction were obtained by a slow diffusion of n-hexane into a saturated toluene solution of 6. Elem. anal. (%), calcd for 6, C₃₈H₃₉MoN₂O₅P₃ (792.6): C, 57.58; H, 4.96; N, 3.53; found: C, 57.06; H, 4.73; N, 3.25. ¹H NMR (500 MHz, CD_2Cl_2 , 298 K): $\delta =$ 7.60 (t, J = 7.8 Hz, 2H, p-C₆ H_3), 7.38 (d, J = 7.8 Hz, 4H, m-C₆ H_3), 7.35 (t, J = 7.6 Hz, 1H, $p\text{-C}_6H_5$), 7.21 (t, J = 7.8 Hz, 2H, $m\text{-C}_6H_5$), 7.17 (d, J = 7.9 Hz, 2H, $o \cdot C_6 H_5$), 2.58 (sept, J = 6.7 Hz, 4H, $CH(CH_3)_2$, 1.27 (d, J = 6.7 Hz, 12H, $CH(CH_3)_2$), and 1.02 (d, J =6.8 Hz, 12H, $CH(CH_3)_2$). ¹³C{¹H} NMR (126 MHz, CD_2Cl_2 , 298 K): $\delta = 206.0$ and 201.8 (CO); 164.4 (d, $J_{P-C} = 73$ Hz, NCP); 146.1 (NCN); 133.2, 132.2, 132.1, 129.7, 129.2, and 126.1 (C₆H₃ and C_6H_5); 29.8 (CH(CH₃)₂); 26.0 and 23.6 (CH(CH₃)₂) ppm. ³¹P{¹H} NMR (202 MHz, CD₂Cl₂, 298 K): $\delta = 299.1$ (t, $J_{P-P} = 510$ Hz) and 160.2 (d, $J_{P-P} = 511 \text{ Hz}$) ppm. IR (ATR, diamond): $\tilde{v}/\text{cm}^{-1} =$ 2065, 2051, 1945, 1925, and 1911.

[(ADC^{4-DMP})P₃]W(CO)₅ (7). A 10 mL THF solution of W(CO)₆ (212 mg, 0.8 mmol) was irradiated under UV light for 3 h and then combined with a 6 mL THF solution of **4d** (447 mg, 0.8 mmol). The yellow solution was stirred overnight at rt. The volatiles were removed under vacuum to obtain 7 as a yellow solid (256 mg, 88%). Crystals suitable for X-ray diffraction were obtained by slow evaporation of a saturated toluene solution of 7 at rt. Elem. anal. (%), calcd for 7, C₄₀H₄₄N₃O₅P₃W (923.6): C, 52.02; H, 4.80; N, 4.55; found C, 51.40; H, 4.39; N, 4.10. ¹H NMR (500 MHz, CD₂Cl₂, 298 K): δ = 7.61 (t, J = 7.8 Hz, 2H, p-C₆H₃), 7.41 (d, J = 7.8 Hz, 4H, m-C₆H₃), 6.91 (d, J = 9.2 Hz, 2H, C₆H₄), 6.33 (d, J = 9.2 Hz, 2H, C₆H₄), 2.88 (s, 6H, N(CH₃)₂), 2.60 (sept, J

= 6.8 Hz, 4H, CH(CH₃)₂), 1.26 (d, J = 6.9 Hz, 12H, CH(CH₃)₂), and 1.00 (d, J = 6.8 Hz, 12H, CH(CH₃)₂) ppm. ¹³C{¹H} NMR (126 MHz, CD₂Cl₂, 298 K): δ = 197.3 and 192.0 (CO); 152.1 (NCP); 146.1 (NCN); 134.3, 131.8, 130.7, 129.9, 126.1, 111.2, and 108.7 (C₆H₃ and C₆H₅); 40.0 (N(CH₃)₂); 29.7 (CH(CH₃)₂); 25.6 and 23.6 (CH(CH₃)₂) ppm. ³¹P{¹H} NMR (202 MHz, CD₂Cl₂, 298 K): δ = 250.9 (t, J_{P-P} = 512 Hz, with ¹⁸³W satellites, J_{W-P} = 202 Hz) and

157.0 (d, $I_{P-P} = 505 \text{ Hz}$) ppm. MS (ESI): $m/z = 924.2 [7 + H]^+$. IR

(ATR, diamond): $\tilde{v}/\text{cm}^{-1} = 2063$, 1978, 1925, and 1907.

Conclusions

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In conclusion, the direct functionalization of white phosphorus (P₄) with anionic dicarbenes (ADCs) (2a-2d) as well as with mesoionic carbenes (iMICsAr) (3a and 3c) that leads to the formation of unique 1,2,3-triphosphol-2-ide derivatives 4a-4d as crystalline solids up to 98% yield has been reported. The isolation of C₂P₃-heterocycles **4a-4d** is unprecedented in the P₄ activation by singlet carbenes and main-group compounds. The formation of 4a-4d suggests unique [3 + 1] fragmentation of P₄ into P₃⁺ and P⁻. The former species combines with an ADC to give 4a-4d, whereas the latter reacts with additional P4 to form $(P_7)^{3-}$ that can be isolated as Li₃P₇. Electronic structures of 4a-4d have been analyzed by computational studies, which, along with the crystallographic data, show that both C₃N₂- and C₂P₃rings of 4a-4d are 6π -electron aromatic systems. Thus, 4a-4d can be considered as neutral analogues of cyclopentadienyl anions. The C₂P₃-ring of 4a-4d is negatively polarized towards the central phosphorus atom, and hence 4a-4d may also function as potent two-electron σ-donor ligands. This feature has been demonstrated with the isolation of transition metal complexes 5a, 5b, 6, and 7. Consequently, 4a-4d have interesting perspectives as ligands in main-group element as well as transition-metal chemistry and catalysis. Further investigations in this direction are currently underway in this laboratory.

Conflicts of interest

There are no conflicts to declare.

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