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 C2P3-ring compounds [(ADCAr)P3] (ADCAr = ArC{(DippN)C}2; Dipp = 2,6-iPr2C6H3; Ar = Ph 5a, 3-MeC6H4 5b, 4-MeC6H4 5c, and 4-Me2NC6H4 5d) are readily accessible in an almost quantitative yield by the direct functionalization of white phosphorus (P4) with appropriate anionic dicarbenes [Li(ADCAr)]. The formation of 1,2,3-triphosphol-2-ides (4a–4d) suggests unprecedented [3 + 1] fragmentation of P4 into P3+ and P2−. The P3+ cation is trapped by the (ADCAr)− to give 4, while the putative P− anion reacts with additional P4 to yield the Li3P7 species, a useful reagent in the synthesis of organophosphorus compounds. Remarkably, the P4 fragmentation is also viable with the related mesoionic carbenes (iMICAr) (iMICAr = ArC{(DippN)2CCH}, i stands for imidazole-based) giving rise to 4.

DFT calculations reveal that both the C3N2 and C2P3-rings of 4 are σ-electron aromatic systems. The natural bonding orbital (NBO) analyses indicate that compounds 4 are mesoionic species featuring a negatively polarized C2P3-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 [{(ADCAr)P3}M(CO)n] (M = Fe, n = 4, Ar = Ph 5a or 4-MeC6H4 5b; M = Mo, n = 5, Ar = Ph 6; M = W, n = 5, Ar = 4-Me2NC6H4 7).

give Pn (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 P4, however, related derivatives containing the [P3+] or [P4−] moiety are accessible by alternative methods. Sterically demanding 1,3-bis(2Bu)imidazol-2-ylidene (IBu) activates P4 in combination with B(C6F5)3 to give X. This frustrated Lewis pair (FLP) type reactivity led to the transformation of the classical NHC (IBu) 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. Nonetheless, no reaction of an iMIC alone with P4 has been described so far. This is most likely due to their limited synthetic accessibility. We recently reported C5-protonated iMICs (XI) as well as C4/C5-ditopic anionic dicarbenes [Li(ADCAr)] XII (Fig. 1) by the deprotonation of C2-arylated 1,3-imidazolium salts. The dicarbenes XII feature two adjacent C4/C5-nucleophilic sites, and thus are well endowed to affect unique dual P4 functionalization. Herein, we showcase the direct functionalization of P4 via unprecedented [3 + 1] fragmentation with [Li(ADCAr)] and iMICs (ADCAr to give the 1,2,3-triphosphol-2-ide derivatives [{ADCAr}P3] (ADCAr = ArC{(Dipp)C}2; Dipp = 2,6-iPr2C6H3; Ar = C6H4 4a, 3-MeC6H4 4b, 4-MeC6H4 4c, and 4-Me2NC6H4 4d) (Scheme 1).

Introduction

The direct conversion of white phosphorus (P4) into useful organophosphorus compounds (OPCs) is of significant interest because this excludes the involvement of corrosive Cl2 gas that is required to convert P2 into PCl3, a common starting material for OPCs, and thus minimizes the waste and energy consumption. The activation and subsequent functionalization of P4 has therefore become a topical objective. Both transition metal as well as main-group element compounds have been shown to activate or functionalize P4. In particular, compounds featuring a low-valent main-group element atom have made significant advances over the past years.

Among nonmetals, the use of singlet carbenes has given new impetus to the field of P4 activation as it leads to the direct C–P bond formation (Fig. 1). Several stable carbenes (L1–L7) undergo reactions with P4 and the fate of P4 fragmentation to give Pn (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 P4, however, related derivatives containing the [P3+] or [P4−] moiety are accessible by alternative methods. Sterically demanding 1,3-bis(2Bu)imidazol-2-ylidene (IBu) activates P4 in combination with B(C6F5)3 to give X. This frustrated Lewis pair (FLP) type reactivity led to the transformation of the classical NHC (IBu) into the mesoionic carbene (iMIC) L8 based on an 1,3-imidazole framework.

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and anionic dicarbenes (II) salts by the double deprotonation of C2-arylated 1,3-imidazolium salts by the double deprotonation of C2-arylated 1,3-imidazolium salts.

Results and discussion

Treatment of [Li(ADCAr)] (2a–2d), which are readily accessible by the double deprotonation of C2-arylated 1,3-imidazolium salts 1a–1d with n-BuLi, with P4 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 P4 into P3+ and P−. The cationic P3+ species is captured by the ADCs to give 4a–4d, whereas the P− nucleophile reacts with additional P4 to eventually form the phosphide (P2)3− anion, a very common species in metal mediated fragmentation of P4. Indeed, Li3P7 can be isolated as a red-brown solid,15,16 which was confirmed by its reaction with [IPr]HCl to give (IPr)PH, reported previously using Na3P7.17

Interestingly, treatment of iMICsAr 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 iMICsAr and 4d to 1,3-imidazolium salts 1a and 1c. Pure 4a and 4c can be extracted from the mixture using toluene.

The 1H 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. The13C{1H} NMR spectra of 4a–4d each shows a doublet at 73 ppm and a triplet at 325 ppm, respectively. Mesoionic carbenes (iMICsAr, 12) which are readily accessible and a plausible intermediate X with P4 to form 2a–2d, solvated lithium ion) investigated in the current study.

Fig. 1 Single carbene-mediated P4 activation and fragmentation to II–X and a plausible intermediate I. Mesoionic carbenes (iMICsAr, XI) and anionic dicarbenes (XII) ([Li+] = solvated lithium ion) investigated in the current study.

Scheme 1 Synthesis of 1,2,3-triphosphol-2-ide derivatives 4a–4d by the direct fragmentation of white phosphorus with [Li(ADCAr)] (2a–2d).

Reaction of iMICsAr 3a and 3c with P4 to form 4a and 4c.

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–C2 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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radii for P–P double (2.04 Å) and P–P single (2.22 Å) bond lengths, 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. 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). The C1–C1′, C1/C2–P1 and P1–P2 bond lengths of 4a–c are comparable with the corresponding bond lengths of triphospholide anions [P₃C₃R₃]⁻ (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). Thus, 4a–d 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†) 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 C₃P₃ and C₃N₂ aromatic systems (Scheme 2c). The nitrogen atoms contribute επ-electrons to the C₃N₂-ring, whereas the P₃ unit shares 4π-electrons with the C₃P₃-ring. The 2π-electrons of the C1–C2 bond are pooled by both the ring systems. Indeed, calculated nucleus-independent chemical shift (NICS) values for 4a–4d (Table 1) suggest the aromaticity of the C₃N₂ and C₃P₃-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.† The AICD plots of 4a (Fig. 3) and 4b–4d (Fig. S62†) clearly show significant delocalization of the π-electrons of both the C₃N₂ and the C₃P₃ 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 P₃ and the C₂ moieties of the C₃P₃-ring. Like in alkali metal 1,2,3-triphospholides, the analyses of frontier molecular orbitals, HOMO and HOMO–1 in particular, of 4a–4d reveal the mixing of phosphorus orbitals with lone-pair character amongst the π-manifold frontier orbitals. The HOMO–3 and HOMO–2 are the lone pairs on the central and neighbouring P atoms, respectively. The LUMO of 4a–4d corresponds to the π* orbital of the aryl group on the C3 carbon atom along with a p-orbital at the central phosphorus atom. The LUMO+2 corresponds mainly to the π*-orbitals of the C₃P₃ unit.

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 η3-donors (C₃P₃-ring) like triphospholide and cyclopentadienyl anions. Treatment of 4a, 4b, and 4c with Fe₂(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)₅ moiety. This is consistent with the NBO analysis, which suggests higher charge accumulation at the central phosphorus atom with respect to that of the

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**Table 1** Calculated NICS values for the C₃N₂/C₃P₃ units of 4a–4d at the M06-2X/def2TZVPP//M06-2X/def2SVP level of theory

|          | 4a        | 4b        | 4c        | 4d        | 5a        | C₆H₆/CBD
|----------|-----------|-----------|-----------|-----------|-----------|-----------
| NICS(0)  | −7.08/−10.19 | −7.29/−10.31 | −7.29/−10.31 | −6.77/−10.37 | −7.57/−9.95 | −7.53/33.21 |
| NICS(1)  | −5.94/−10.18 | −6.11/−10.28 | −6.11/−10.23 | −5.64/−10.21 | −6.29/−9.58 | −10.19/21.09 |
| NICS(2)  | −2.43/−5.51 | −2.53/−5.21 | −2.53/−5.53 | −2.36/−5.52 | −2.52/−5.12 | −5.22/4.98 |

* CBD (cyclobutadiene).
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 $^{18}$W satellites ($J_{W-W} = 202$ 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$_3$Fe$_2$ iron-carbonyl clusters (av. 2.244 Å).24 Interestingly, the metrical parameters of the C$_{3}$N$_{2}$- and C$_{3}$P$_{2}$-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. S31†) feature six-coordinated Mo and W atoms, respectively.

### Experimental

All syntheses and manipulations were carried out under an inert gas atmosphere (Ar or N$_2$) 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 HD spectrometer. Chemical shifts (in δ, ppm) are referenced to the solvent residual signals of CD$_2$Cl$_2$: $^1$H 5.32, $^{13}$C 53.84 and C$_{6}$D$_6$: $^1$H 7.16, $^{13}$C 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 CH$_3$CN 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...
C6NMR (500 MHz, CD2Cl2, 298 K): insoluble material (probably a mixture of Li₃P₇ and other polyphosphides) was removed by filtration. The resulting dark suspension was re-added in one portion and then stirred overnight at rt. The viscous toluene solution was extracted with dichloromethane, dried under vacuum, washed with toluene (2 × 3 mL), and then stored at −20 °C 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 C₅₈H₇₉N₅P₃: C, 71.21; H, 7.06; N, 5.03; found: C, 71.02; H, 6.84; N, 4.87.

1H NMR (500 MHz, CD2Cl2, 298 K): δ = 7.59 (t, J = 7.7 Hz, 2H, p-C6H5), 7.38 (d, J = 7.8 Hz, 4H, m-C6H4), 7.34 (t, J = 6.6 Hz, 1H, p-C6H4), 2.53–7.18 (m, 4H, o-C6H3), 2.62 (sept, J = 6.6 Hz, 4H, CH(CH3)2), 1.26 (d, J = 6.6 Hz, 12H, CH(CH3)2), and 1.03 (d, J = 6.7 Hz, 12H, CH(CH3)2) ppm. 13C{1H} NMR (126 MHz, CD2Cl2, 298 K): δ = 167.6 (d, J = 7.8 Hz, 2H, p-C6H5), 165.7 (d, J = 8.4 Hz, 2H, C6H5), 70.2 (d, J = 8.3 Hz, 2H, C6H5), 26.1 (sept, J = 6.8 Hz, 4H, CH(CH3)2), 2.23 (s, 3H, CH3), 1.26 (d, J = 6.7 Hz, 12H, CH(CH3)2), and 1.03 (d, J = 6.9 Hz, 12H, CH(CH3)2) ppm. 13C{1H} NMR (126 MHz, CD2Cl2, 298 K): δ = 167.5 (d, J = 8.3 Hz, 2H, p-C6H5), 165.2 (d, J = 8.7 Hz, 2H, C6H5), 70.1 (d, J = 8.6 Hz, 2H, C6H5), 26.0 (sept, J = 6.8 Hz, 4H, CH(CH3)2), 2.23 (s, 3H, CH3), 1.26 (d, J = 6.7 Hz, 12H, CH(CH3)2), and 1.03 (d, J = 6.9 Hz, 12H, CH(CH3)2) ppm. MS (ESI, positive mode): m/z = 571.3 [4a + H]+. UV-vis (λ/nm ε (M⁻¹·cm⁻¹)): 283 (23295), 336 (28771), 346 (29238), and 362 (29676).

Yield: 94% (0.93 g). Single crystals suitable for X-ray diffraction were obtained by storing a saturated toluene solution of 4d for three days at −24 °C. Mp: 339–343 °C. Elem. anal. (%), calcd for C₅₈H₇₉N₅P₃: C, 71.56; H, 7.24; N, 4.91; found: C, 71.11; H, 7.06; N, 4.65.

1H NMR (500 MHz, CD2Cl2, 298 K): δ = 7.56 (d, J = 7.8 Hz, 4H, m-C6H4), 7.46 (d, J = 8.3 Hz, 4H, m-C6H4), 7.05 (d, J = 8.4 Hz, 2H, C6H5), 7.02 (d, J = 8.3 Hz, 2H, C6H5), 2.61 (sept, J = 6.8 Hz, 4H, CH(CH3)2), 2.23 (s, 3H, CH3), 1.26 (d, J = 6.7 Hz, 12H, CH(CH3)2), and 1.03 (d, J = 6.9 Hz, 12H, CH(CH3)2) ppm. 13C{1H} NMR (126 MHz, CD2Cl2, 298 K): δ = 167.5 (d, J = 8.3 Hz, 2H, p-C6H5), 165.2 (d, J = 8.7 Hz, 2H, C6H5), 70.1 (d, J = 8.6 Hz, 2H, C6H5), 26.0 (sept, J = 6.8 Hz, 4H, CH(CH3)2), 2.23 (s, 3H, CH3), 1.26 (d, J = 6.7 Hz, 12H, CH(CH3)2), and 1.03 (d, J = 6.9 Hz, 12H, CH(CH3)2) ppm. MS (ESI, positive mode): m/z = 690.2 [4d + H]+. UV-vis (λ/nm ε (M⁻¹·cm⁻¹)): 283 (23295), 336 (28771), 346 (29238), and 362 (29676).
(3H) NMR (202 MHz, CD2Cl2, 298 K): δ = 319.5 (t, J= 504 Hz) and 173.3 (d, J= 504 Hz) ppm. MS (ESI, positive mode): m/z = 603.0 [M+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, calculated for Li2P) 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=PH2 by NMR spectroscopy. 1H NMR (500 MHz, CD2Cl2, 298 K): δ = 7.23 (t, J= 7.7 Hz, 2H, p-C6H5), 7.14 (d, J= 7.6 Hz, 4H, m-C6H4), 6.18 (s, 2H, NCH), 3.06 (sept, J = 6.7 Hz, 4H, CH(CH3)2), 1.92 (d, J = 165 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. 13P NMR (CD2Cl2, 298 K, 500 MHz): δ = -134.4 (d, J= -165 Hz) ppm. 13P(1H) NMR (CD2Cl2, 298 K, 500 MHz): δ = -134.4 ppm.

Alternative synthesis of 4a and 4c from iMCs-Ar 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, P4 (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 × 10 mL). The filtrate was dried in a vacuum to obtain 4a. Yield: 41% (0.4 g).

(ADC1-10+P)3P3(4c). Similarly, treatment of 3c with P4 gave 4c. Yield: 36% (0.4 g).

Syntheses of complexes 5a, 5b, 6, and 7
(ADC10+P)3Fe(CO)4 (5a). To a mixture of 4a (651 mg, 1.2 mmol) and Fe(CO)5 (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 °C for one week to obtain orange needles of 5a (696 mg, 80%), which were also suitable for X-ray diffraction. Mp: 167−172 °C (decomp.). Elem. anal. (%), calc for C37H25Fe3N3O12P3: C, 61.34; H, 4.53; N, 3.87; found: C, 59.66; H, 5.24; N, 3.71. 1H NMR (500 MHz, CD2Cl2, 298 K): δ = 7.60 (t, J = 7.8 Hz, 2H, p-C6H5), 7.38 (d, J = 7.8 Hz, 4H, m-C6H4), 7.34 (t, J = 7.5 Hz, 1H, o-C6H4), 7.22–7.15 (m, 4H, ortho), m-C6H4, 2.57 (sept, J = 6.7 Hz, 4H, CH(CH3)2), 1.27 (d, J = 6.7 Hz, 12H, CH(CH3)2), and 1.01 (d, J = 6.8 Hz, 12H, CH(CH3)2) ppm. 13C(1H) NMR (126 MHz, CD2Cl2, 298 K): δ = 215.1 (CO); 161.7 (d, J= 7.9 Hz, 2H, o-C6H4), 7.17 (d, J = 7.9 Hz, 2H, o-C6H4), 2.58 (sept, J = 6.7 Hz, 4H, CH(CH3)2), 1.27 (d, J = 6.7 Hz, 12H, CH(CH3)2), and 1.01 (d, J = 6.8 Hz, 12H, CH(CH3)2) ppm. 31P(1H) NMR (126 MHz, CD2Cl2, 298 K): δ = 206.0 and 201.8 (CO); 164.4 (d, J= -73 Hz, NCP); 146.1 (NCN); 133.2, 132.2, 132.1, 129.7, 129.2, and 126.1 (C6H4 and C6H4); 29.8 (CH(CH3)2); 26.0 and 23.6 (CH(CH3)2) ppm. 13C(1H) NMR (202 MHz, CD2Cl2, 298 K): δ = 299.1 (t, J= -510 Hz) and 160.2 (d, J= -511 Hz) ppm. IR (ATR, diamond): v/cm⁻¹ = 2065, 2051, 1945, 1925, and 1911.

(ADC10+P)3Mo(CO)6 (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 slow diffusion of n-hexane into a saturated toluene solution of 6. Elem. anal. (%), calc for C38H20Mo3N3O12P3 (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, CD2Cl2, 298 K): δ = 7.60 (t, J = 7.8 Hz, 2H, p-C6H5), 7.38 (d, J = 7.8 Hz, 4H, m-C6H4), 7.35 (t, J = 7.6 Hz, 1H, o-C6H4), 7.21 (t, J = 7.8 Hz, 2H, m-C6H4), 7.17 (d, J = 7.9 Hz, 2H, o-C6H4), 2.58 (sept, J = 6.7 Hz, 4H, CH(CH3)2), 1.27 (d, J = 6.7 Hz, 12H, CH(CH3)2), and 1.01 (d, J = 6.8 Hz, 12H, CH(CH3)2) ppm. 13C(1H) NMR (126 MHz, CD2Cl2, 298 K): δ = 206.0 and 201.8 (CO); 164.4 (d, J= -73 Hz, NCP); 146.1 (NCN); 133.2, 132.2, 132.1, 129.7, 129.2, and 126.1 (C6H4 and C6H4); 29.8 (CH(CH3)2); 26.0 and 23.6 (CH(CH3)2) ppm. 31P(1H) NMR (202 MHz, CD2Cl2, 298 K): δ = 299.1 (t, J= -510 Hz) and 160.2 (d, J= -511 Hz) ppm. IR (ATR, diamond): v/cm⁻¹ = 2065, 2051, 1945, 1925, and 1911.
= 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 (NCCN); 134.3, 131.8, 130.7, 129.9, 126.1, 111.2, and 108.7 (C6H4 and C5H3): 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, JP–P = 512 Hz, with 133W satellites, JW–P = 202 Hz) and 157.0 (d, JP–P = 505 Hz) ppm. MS (ESI): m/z = 924.2 [7 + H]+. IR (ATR, diamond): ν/cm−1 = 2063, 1978, 1925, and 1907.

Conclusions
In conclusion, the direct functionalization of white phosphorus (P4) with anionic dicarbenes (ADCs) (2a–2d) as well as mesoionic carbenes (iMICS4+) (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 (P3)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 C2P3-rings 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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