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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$_6$H$_4$ **4c**, and 4-Me$_2$NC$_6$H$_4$ **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$_6$H$_4$ **5b**; M = Mo, *n* = 5, Ar = Ph **6**; M = W, *n* = 5, Ar = 4-Me$_2$NC$_6$H$_4$ **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.[1] The activation and subsequent functionalization of P_4 has therefore become a topical objective.[2] Both transition metal[3] as well as main-group element[4] compounds have been shown to activate or functionalize P_4.[5] In particular, compounds featuring a low-valent main-group element have made significant advances over the past years.[6]

Among nonmetals, the use of singlet carbenes[7] has given new impetus to the field of P_4 activation as it leads to the direct C–P bond formation (Fig. 1).[8] Several stable carbenes (L1–L7) undergo reactions with P_4 and the fate of P_4 fragmentation to 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.[7] 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.[9] Sterically demanding 1,3-bis(*t*Bu)imidazol-2-ylidene (IBu^t) activates P_4 in combination with $B(C_6F_5)_3$ to give **X**.[6h] This frustrated Lewis pair (FLP) type reactivity[10] 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.[11a] We recently reported[12] 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-iPr$_2C_6H_3$; Ar = C$_6H_5$ **4a**, 3-MeC$_6$H$_4$ **4b**, 4-MeC$_6$H$_4$ **4c**, and 4-Me$_2$NC$_6$H$_4$ **4d**) (Scheme 1).

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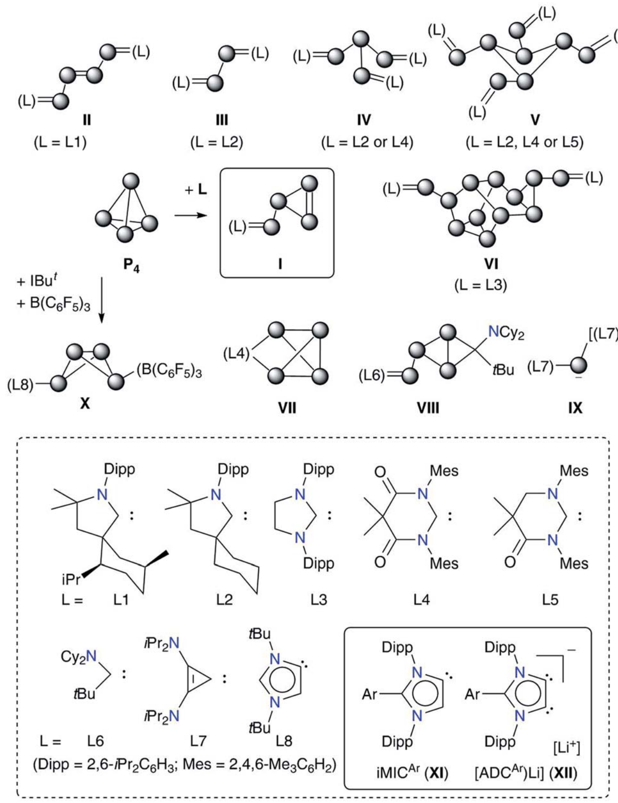
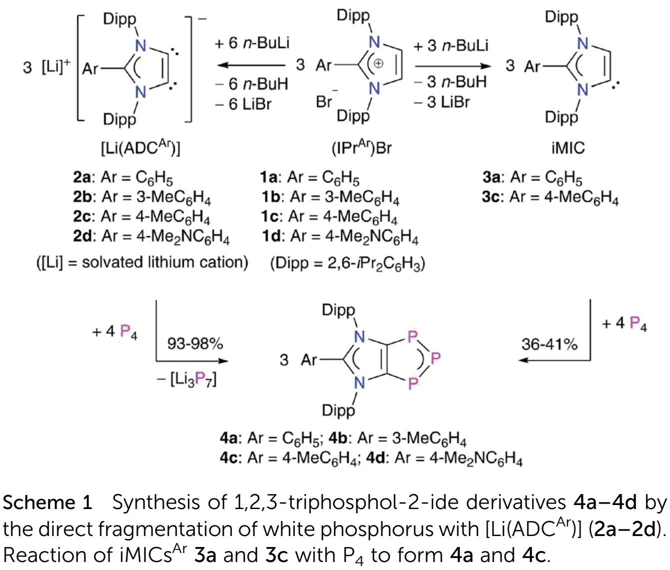


Fig. 1 Singlet carbene-mediated P_4 activation and fragmentation to II–X and a plausible intermediate I. Mesoionic carbenes (iMICs^{Ar}, XI) and anionic dicarbenes (XII) ([Li$^+$] = solvated lithium ion) investigated in the current study.



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^-. The cationic P_3^+ species is captured by the ADCs to give **4a–4d**, whereas the P^- nucleophile reacts with additional P_4 to eventually form the phosphide $(P_7)^{3-}$ anion, a very common species in metal mediated fragmentation of P_4.[15] Indeed, Li_3P_7 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 Na_3P_7.[17]

Interestingly, treatment of iMICs^{Ar} **3a** and **3c** with P_4 also afforded, *albeit* in a lower yield, the corresponding products **4a** and **4c**, respectively. ^{1}H 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 ~73 ppm and a triplet at 325 ± 6 ppm in 2 : 1 ratio ($J_{P-P} \approx 500$ Hz), indicating the presence of an AB_2 type system with unsaturated P–P bonds.[18]

Solid-state molecular structures[19] 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

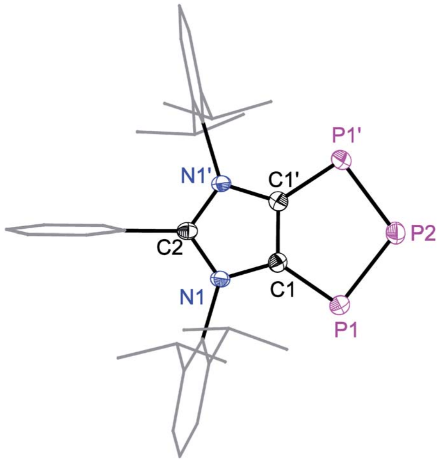
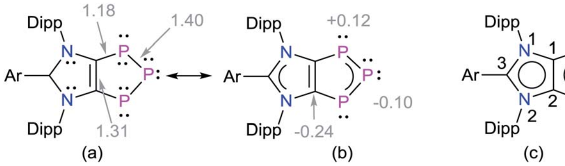


Fig. 2 Solid-state molecular structure of **4a**. Hydrogen atoms are omitted for clarity. Symmetry code: 1 − X, +Y, 3/2 − Z. Selected experimental and calculated [M06-2X/def2SVP] bond lengths (Å) and angles (°): C1–C1′ 1.395(5) [1.402], N1–C1 1.404(3) [1.399], P1–C1 1.757(3) [1.764], P1–P2 2.103(1) [2.112],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



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)[15] 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†) at the P2 (−0.10*e*) and the C1/C2 (−0.24*e*) atoms are negative, whereas both the P1 atoms bear a positive charge (0.12*e*) (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 C_2P_3 and C_3N_2 aromatic systems (Scheme 2c). The nitrogen atoms contribute 4π-electrons to the C_3N_3-ring, whereas the P_3 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 C_3N_2- and C_2P_3-rings. For comparison, we also calculated the NICS values for C_6H_6 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 significant delocalization of the π-electrons of both the C_3N_2 and the C_2P_3 heterocycles, forming one coherent π-system.

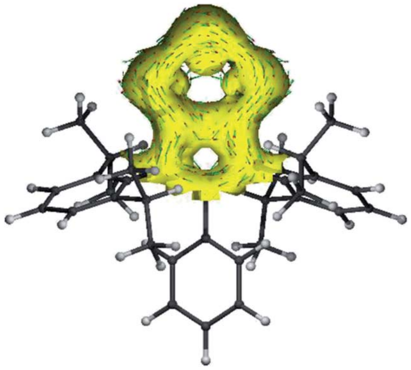


Fig. 3 AICD plot (based on M06-2X/def2-TZVPP//def2-SVP calculations) of the $C_3N_2P_3$ core of compound **4a**. The isovalue was arbitrarily chosen to be 0.03, the magnetic field is orthogonal to the C_2P_3-plane and points towards the viewer, and thus clockwise ring currents represent aromatic systems,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

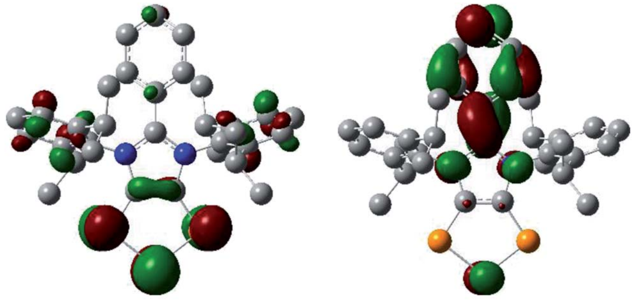
The HOMO of compounds **4a** (Fig. 4) and **4b–4c** (Fig. S58–S60†) corresponds to the π-orbitals of the C–P bonds with a small contribution from the lone pairs at the nitrogen atoms. The HOMO−1 corresponds mainly to the π-orbitals of the P_3 and the C_2 moieties of the C_2P_3-ring. Like in alkali metal 1,2,3-triphospholides,[21b] 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 C_2P_3 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 η⁵-donors (C_2P_3-ring) like triphospholide[21] 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

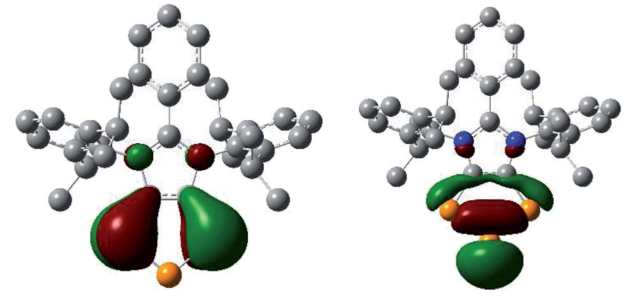
C_3N_2/C_2P_3	4a	4b	4c	4d	5a	C_6H_6/CBD[a]
NICS(0)	−7.08/−10.19	−7.29/−10.31	−7.29/−10.31	−6.77/−10.37	−7.57/−9.95	−7.53/33.21
NICS(1)	−5.94/−10.18	−6.11/−10.28	−6.11/−10.23	−5.64/−10.21	−6.29/−9.58	−10.19/21.09
NICS(2)	−2.43/−5.51	−2.53/−5.21	−2.53/−5.53	−2.36/−5.52	−2.52/−5.12	−5.22/4.98

[a] CBD (cyclobutadiene).



LUMO+2 (-0.08 eV)

LUMO (-1.25 eV)



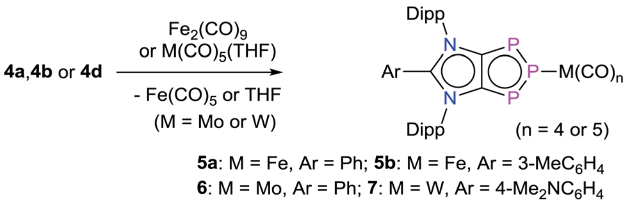
HOMO (-6.08 eV)

HOMO-3 (-7.50 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.

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 ($J_{P\text{–}W}$ = 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.



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

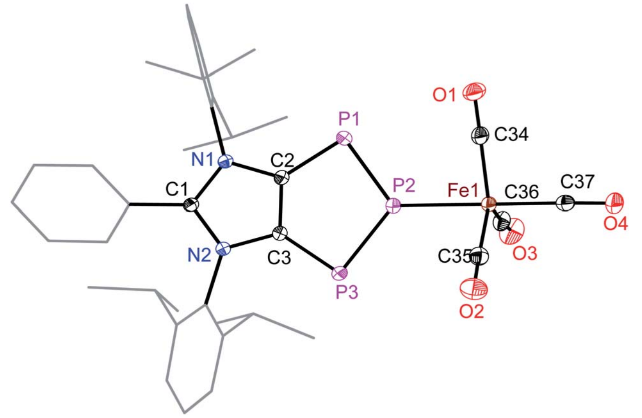


Fig. 5 Solid-state molecular structure of **5a**. Hydrogen atoms and one solvent toluene molecule are omitted for clarity. Selected bond lengths (Å) and angles (°): C2–C3 1.394(2), C2–N1 1.399(1), C3–N2 1.403(1), C2–P1 1.756(1), C3–P3 1.764(1), P1–P2 2.081(1), P2–P3 2.089(1), P2–Fe1 2.240(1), Fe1–C34 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 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 or a Bruker Avance III 500 HD spectrometer. Chemical shifts (in *δ*, ppm) are referenced to the solvent residual signals of CD_2Cl_2: ^{1}H 5.32; ^{13}C 53.84 and C_6D_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_2Cl_2 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

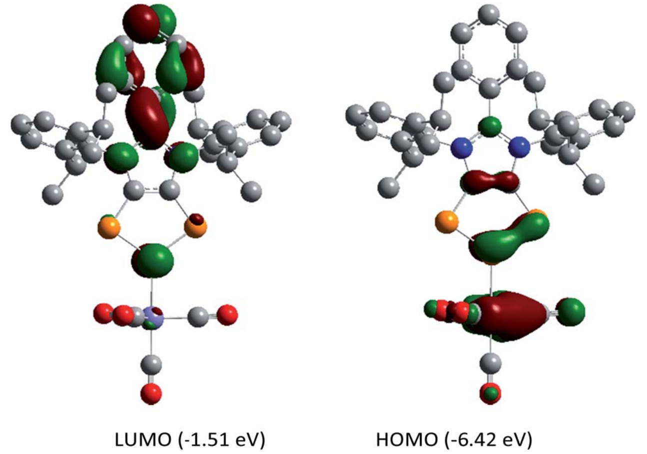


Fig. 6 Frontier molecular orbitals of **5a** calculated at the M06-2X/def2-TZVPP//def2-SVP level of theory. The isovalue was arbitrarily chosen to be 0.04. Hydrogen atoms were omitted for clarity.

with a Büchi B-545 melting point apparatus. $(\mathrm{IPr^{Ar}})$Br salts **1a–1d** (Ar = Ph, 3-MeC$_6$H$_4$, 4-MeC$_6$H$_4$ or 4-Me$_2$NC$_6$H$_4$) 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 Fe$_2$(CO)$_9$ (Sigma-Aldrich), Mo(CO)$_6$ (Fluorochem), and W(CO)$_6$ (Sigma-Aldrich) were used as supplied.

Synthesis of compound $(\mathrm{ADC^{Ph}})\mathrm{P_3}$ (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 °C) for 15 minutes to obtain a clear light brown solution of **2a**.[12] To this solution, solid P$_4$ (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 Li$_3$P$_7$ 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 C$_{33}$H$_{39}$N$_2$P$_3$ (556.6): C, 71.21; H, 7.06; N, 5.03; found: C, 71.02; H, 6.84; N, 4.87. ^{1}H NMR (500 MHz, CD$_2$Cl$_2$, 298 K): δ = 7.59 (t, J = 7.7 Hz, 2H, *p*-C$_6$*H*$_3$), 7.38 (d, J = 7.8 Hz, 4H, *m*-C$_6$*H*$_3$), 7.34 (t, J = 6.6 Hz, 1H, *p*-C$_6$*H*$_5$), 7.23–7.18 (m, 4H, *o*-, *m*-C$_6$*H*$_5$), 2.62 (sept, J = 6.6 Hz, 4H, C*H*(CH$_3$)$_2$), 1.26 (d, J = 6.6 Hz, 12H, CH(C*H*$_3$)$_2$), and 1.03 (d, J = 6.7 Hz, 12H, CH(C*H*$_3$)$_2$) ppm. ^{13}C{^{1}H} NMR (126 MHz, CD$_2$Cl$_2$, 298 K): δ = 167.6 (d, $J_{\mathrm{P–C}}$ = 84.4 Hz, *C*P); 149.2 (N*C*N); 146.2, 133.5, 132.0, 131.8, 129.8, 129.1, 125.8, and 123.8 (*C*$_6$H$_3$, *C*$_6$H$_5$); 29.7 (*C*H(CH$_3$)$_2$); 26.1 and 23.5 (CH(*C*H$_3$)$_2$) ppm. ^{31}P{^{1}H} NMR (202 MHz, CD$_2$Cl$_2$, 298 K): δ = 332.3 (t, $J_{\mathrm{P–P}}$ = 506 Hz) and 173.7 (d, $J_{\mathrm{P–P}}$ = 506 Hz) ppm. MS (ESI, positive mode): *m*/*z* = 557.3 [**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 P$_4$.

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

Yield: 98% (0.90 g). Mp: 338–341 °C. Elem. anal. (%), calcd for **4b**, C$_{34}$H$_{41}$N$_2$P$_3$, (570.6): C, 71.56; H, 7.24; N 4.91; found C, 70.64; H, 7.33; N 4.68. ^{1}H NMR (500 MHz, CD$_2$Cl$_2$, 298 K): δ = 7.57 (t, J = 7.8 Hz, 2H, *p*-C$_6$*H*$_3$), 7.35 (d, J = 7.8 Hz, 4H, *m*-C$_6$H$_3$), 7.14 (d, J = 7.6 Hz, 1H, *o*-C$_6$*H*$_4$), 7.08 (t, J = 7.8 Hz, 1H, *m*-C$_6$*H*$_4$), 7.02 (s, 1H, *o*-C$_6$*H*$_4$), 6.96 (d, J = 7.8 Hz, 1H, *p*-C$_6$*H*$_4$), 2.60 (sept, J = 6.7 Hz, 4H, C*H*(CH$_3$)$_2$), 2.10 (s, 3H, C*H*$_3$), 1.24 (d, J = 6.7 Hz, 12H, CH(C*H*$_3$)$_2$), and 1.03 (d, J = 6.8 Hz, 12H, CH(C*H*$_3$)$_2$) ppm. ^{13}C{^{1}H} NMR (126 MHz, CD$_2$Cl$_2$, 298 K): δ = 167.5 (d, $J_{\mathrm{P–C}}$ = 84.5 Hz, *C*P); 149.6 (N*C*N); 146.3, 139.3, and 133.6 (i-*C*$_6$H$_4$ and i-, *m*-*C*$_6$H$_3$); 132.7 (*o*-*C*$_6$H$_4$); 131.7 (*p*-*C*$_6$H$_3$); 130.5 (*o*-*C*$_6$H$_4$); 129.5 and 128.9 (*m*-*C*$_6$H$_4$); 126.9, 125.8, and 123.71 (*m*-*C*$_6$H$_3$); 29.7 (*C*(CH$_3$)$_2$); 26.2 and 23.5 (C(*C*H$_3$)$_2$); 21.2 (*C*H$_3$) ppm. ^{31}P{^{1}H} NMR (202 MHz, CD$_2$Cl$_2$, 298 K): δ = 331.1 (t, $J_{\mathrm{P–P}}$ = 506 Hz) and 173.6 (d, $J_{\mathrm{P–P}}$ = 506 Hz) ppm. MS (ESI, positive mode): *m*/*z* = 571.3 [**4b** + H]$^+$. UV-vis (λ/nm ε (M^{-1} cm^{-1})): 280 (25637), 345 (36323), and 361 (36539).

$(\mathrm{ADC^{4\text{-}Tol}})\mathrm{P_3}$ (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 C$_{34}$H$_{41}$N$_2$P$_3$ (570.6): C, 71.56; H, 7.24; N, 4.91; found C, 71.11; H, 7.06; N, 4.65. ^{1}H NMR (500 MHz, CD$_2$Cl$_2$, 298 K): δ = 7.59 (t, J = 7.8 Hz, 2H, *p*-C$_6$*H*$_3$), 7.38 (d, J = 7.8 Hz, 4H, *m*-C$_6$*H*$_3$), 7.05 (d, J = 8.4 Hz, 2H, C$_6$*H*$_4$), 7.02 (d, J = 8.3 Hz, 2H, C$_6$*H*$_4$), 2.61 (sept, J = 6.8 Hz, 4H, C*H*(CH$_3$)$_2$), 2.23 (s, 3H, C*H*$_3$), 1.26 (d, J = 6.7 Hz, 12H, CH(C*H*$_3$)$_2$), and 1.03 (d, J = 6.9 Hz, 12H, CH(C*H*$_3$)$_2$) ppm. ^{13}C{^{1}H} NMR (126 MHz, CD$_2$Cl$_2$, 298 K): δ = 167.5 (d, $J_{\mathrm{P–C}}$ = 84.1 Hz, *C*P); 146.2 (N*C*N); 143.1, 133.7, 131.7, 129.8, 129.7, 125.8, and 120.9 (*C*$_6$H$_3$ and *C*$_6$H$_4$); 29.7 (*C*H(CH$_3$)$_2$); 26.1 and 23.5 (CH(*C*H$_3$)$_2$); 21.7 (*C*H$_3$) ppm. ^{31}P{^{1}H} NMR (202 MHz, CD$_2$Cl$_2$, 298 K): δ = 329.9 (t, $J_{\mathrm{P–P}}$ = 506 Hz) and 173.6 (d, $J_{\mathrm{P–P}}$ = 506 Hz) ppm. MS (ESI, positive mode): *m*/*z* = 571.3 [**4c** + H]$^+$. UV-vis (λ/nm ε (M^{-1} cm^{-1})): 283 (23295), 336 (28771), 346 (29238), and 362 (29676).

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

Yield: 94% (0.93 g). Mp: 270–273 °C (decomp.). Elem. anal. (%), calcd for C$_{35}$H$_{44}$N$_3$P$_3$ (599.3): C, 70.10; H, 7.40; N, 7.01; found: C, 69.66; H, 7.18; N 6.59. ^{1}H NMR (500 MHz, CD$_2$Cl$_2$, 298 K): δ = 7.56 (t, J = 7.8 Hz, 2H, *p*-C$_6$*H*$_3$), 7.35 (d, J = 7.8 Hz, 4H, *m*-C$_6$*H*$_3$), 6.90 (d, J = 9.0 Hz, 2H, C$_6$*H*$_4$), 6.28 (d, J = 9.0 Hz, 2H, C$_6$*H*$_4$), 2.88 (s, 6H, N(C*H*$_3$)$_2$), 2.67 (sept, J = 6.8 Hz, 4H, C*H*(CH$_3$)$_2$), 1.24 (d, J = 6.7 Hz, 12H, CH(C*H*$_3$)$_2$), and 0.97 (d, J = 6.8 Hz, 12H, CH(C*H*$_3$)$_2$) ppm. ^{13}C{^{1}H} NMR (126 MHz, CD$_2$Cl$_2$, 298 K): δ = 167.0 (d, $J_{\mathrm{P–C}}$ = 82.8 Hz, *C*P); 151.9 (N*C*N); 146.2, 138.4, 134.6, 131.4, 130.8, 126.3, 125.8, and 111.1 (*C*$_6$H$_3$ and *C*$_6$H$_4$); 40.0 (N(*C*H$_3$)$_2$); 29.6 (*C*H(CH$_3$)$_2$); 25.7 and 23.5 (CH(*C*H$_3$)$_2$) ppm. ^{31}P

$\{^1H\}$ NMR (202 MHz, CD_2Cl_2, 298 K): $\delta = 319.5$ (t, $J_{P-P} = 504$ Hz) and 173.3 (d, $J_{P-P} = 504$ Hz) ppm. MS (ESI, positive mode): $m/z = 600.3$ $[\mathbf{4d} + H]^+$. 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 Li_3P_7) 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=PH[17] by NMR spectroscopy. ^1H NMR (500 MHz, C_6D_6, 298 K): $\delta = 7.23$ (t, $J = 7.7$ Hz, 2H, p-C_6H_3), 7.14 (d, $J = 7.6$ Hz, 4H, m-C_6H_3), 6.18 (s, 2H, NCH), 3.06 (sept, $J = 6.7$ Hz, 4H, CH($CH_3)_2$), 1.92 (d, $J_{PH} = 165.2$ Hz, 1H, PH), 1.47 (d, $J = 6.8$ Hz, 12H, CH(C$H_3)_2$), and 1.15 (d, $J = 6.9$ Hz, 12H, CH(C$H_3)_2$) ppm. ^{31}P NMR (C_6D_6, 298 K, 500 MHz): $\delta = -134.4$ (d, $J_{P-H} = 165.2$ Hz) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6, 298 K, 500 MHz): $\delta = -134.4$ ppm.

Alternative synthesis of 4a and 4c from iMICs^{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, 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 × 10 mL). The filtrate was dried in a vacuum to obtain **4a**. Yield: 41% (0.4 g).

(ADC$^{4\text{-}Tol}$)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 $Fe_2(CO)_9$ (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 $C_{37}H_{39}FeN_2O_4P_3$ (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, CD_2Cl_2, 298 K): $\delta = 7.60$ (t, $J = 7.8$ Hz, 2H, p-C_6H_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(C$H_3)_2$), and 1.01 (d, $J = 6.8$ Hz, 12H, CH(C$H_3)_2$) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2, 298 K): $\delta = 215.1$ (CO); 161.7 (d, $J_{P-C} = 70.3$ 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. $^{31}P\{^1H\}$ 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): $m/z = 725.1$ $[\mathbf{5a} + H]^+$. UV-vis (λ/nm ε (M^{-1} cm^{-1})): 285 (33061), 328 (31345), and 428 (37184). IR (ATR, diamond): $\tilde{\nu}$/cm^{-1} = 2041, 1966, 1937, and 1919.

[(ADC$^{3\text{-}Tol}$)P$_3$]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 $Fe_2(CO)_9$ (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**, $C_{38}H_{41}FeN_2O_4P_3$ (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-C_6H_3), 7.37 (d, $J = 7.8$ Hz, 4H, m-C_6H_3), 7.15 (d, $J = 7.4$ Hz, 1H, o-C_6H_4), 7.08 (t, $J = 7.7$ Hz, 1H, m-C_6H_4), 7.00 (s, 1H, o-C_6H_4), 6.94 (d, $J = 7.7$ Hz, 1H, p-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(C$H_3)_2$), and 1.04 (d, $J = 6.7$ Hz, 12H, CH(C$H_3)_2$) ppm. $^{13}C\{^1H\}$ 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($CH_3)_2$); 26.1 and 23.6 (CH(CH$_3)_2$); 21.2 (CH$_3$) ppm. $^{31}P\{^1H\}$ NMR (202 MHz, CD_2Cl_2, 298 K): $\delta = 315.5$ (t, $J_{P-P} = 531$ Hz) and 145.4 (d, $J_{P-P} = 532$ Hz) ppm. MS (ESI, positive mode): $m/z = 739.1$ $[\mathbf{5b} + H]^+$. UV-vis (λ/nm ε (M^{-1} cm^{-1})): 282 (35189), 327 (29758), and 416 (37568). IR (ATR, diamond): $\tilde{\nu}$/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**, $C_{38}H_{39}MoN_2O_5P_3$ (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-C_6H_3), 7.38 (d, $J = 7.8$ Hz, 4H, m-C_6H_3), 7.35 (t, $J = 7.6$ Hz, 1H, p-C_6H_5), 7.21 (t, $J = 7.8$ Hz, 2H, m-C_6H_5), 7.17 (d, $J = 7.9$ Hz, 2H, o-C_6H_5), 2.58 (sept, $J = 6.7$ Hz, 4H, CH($CH_3)_2$), 1.27 (d, $J = 6.7$ Hz, 12H, CH(C$H_3)_2$), and 1.02 (d, $J = 6.8$ Hz, 12H, CH(C$H_3)_2$). $^{13}C\{^1H\}$ 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 (C_6H_3 and C_6H_5); 29.8 (CH($CH_3)_2$); 26.0 and 23.6 (CH(CH$_3)_2$) ppm. $^{31}P\{^1H\}$ NMR (202 MHz, CD_2Cl_2, 298 K): $\delta = 299.1$ (t, $J_{P-P} = 510$ Hz) and 160.2 (d, $J_{P-P} = 511$ Hz) ppm. IR (ATR, diamond): $\tilde{\nu}$/cm^{-1} = 2065, 2051, 1945, 1925, and 1911.

[(ADC$^{4\text{-}DMP}$)P$_3$]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**, $C_{40}H_{44}N_3O_5P_3W$ (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, CD_2Cl_2, 298 K): $\delta = 7.61$ (t, $J = 7.8$ Hz, 2H, p-C_6H_3), 7.41 (d, $J = 7.8$ Hz, 4H, m-C_6H_3), 6.91 (d, $J = 9.2$ Hz, 2H, C_6H_4), 6.33 (d, $J = 9.2$ Hz, 2H, C_6H_4), 2.88 (s, 6H, N(C$H_3)_2$), 2.60 (sept, J

= 6.8 Hz, 4H, C*H*(CH_3)$_2$), 1.26 (d, J = 6.9 Hz, 12H, CH(C*H*$_3$)$_2$), and 1.00 (d, J = 6.8 Hz, 12H, CH(C*H*$_3$)$_2$) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2, 298 K): δ = 197.3 and 192.0 (*C*O); 152.1 (N*C*P); 146.1 (N*C*N); 134.3, 131.8, 130.7, 129.9, 126.1, 111.2, and 108.7 (*C*$_6$H$_3$ and *C*$_6$H$_5$); 40.0 (N(CH_3)$_2$); 29.7 (*C*H(CH_3)$_2$); 25.6 and 23.6 (CH(*C*H$_3$)$_2$) ppm. $^{31}P\{^1H\}$ NMR (202 MHz, CD_2Cl_2, 298 K): δ = 250.9 (t, J_{P-P} = 512 Hz, with ^{183}W satellites, J_{W-P} = 202 Hz) and 157.0 (d, J_{P-P} = 505 Hz) ppm. MS (ESI): m/z = 924.2 [**7** + H]$^+$. IR (ATR, diamond): $\tilde{\nu}$/cm^{-1} = 2063, 1978, 1925, and 1907.

Conclusions

In conclusion, the direct functionalization of white phosphorus (P_4) with anionic dicarbenes (ADCs) (**2a–2d**) as well as with mesoionic carbenes (iMICs^{Ar}) (**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 C_2P_3-heterocycles **4a–4d** is unprecedented in the P_4 activation by singlet carbenes and main-group compounds. The formation of **4a–4d** suggests unique [3 + 1] fragmentation of P_4 into P_3^+ and P^-. The former species combines with an ADC to give **4a–4d**, whereas the latter reacts with additional P_4 to form $(P_7)^{3-}$ that can be isolated as Li_3P_7. Electronic structures of **4a–4d** have been analyzed by computational studies, which, along with the crystallographic data, show that both C_3N_2- and C_2P_3-rings of **4a–4d** are 6π-electron aromatic systems. Thus, **4a–4d** can be considered as neutral analogues of cyclopentadienyl anions. The C_2P_3-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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