

Cite this: *Chem. Sci.*, 2019, 10, 11078

All publication charges for this article have been paid for by the Royal Society of Chemistry

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

Dennis Rottschäfer,¹ Sebastian Blomeyer,¹ Beate Neumann,¹ Hans-Georg Stammer and Rajendra S. Ghadwal^{1*}

A series of unique C_2P_3 -ring compounds $[(ADC^{Ar})P_3]$ ($ADC^{Ar} = ArC\{(DippN)C\}_2$; Dipp = 2,6-*i*Pr₂C₆H₃; Ar = Ph **4a**, 3-MeC₆H₄ **4b**, 4-MeC₆H₄ **4c**, and 4-Me₂NC₆H₄ **4d**) are readily accessible in an almost quantitative yield by the direct functionalization of white phosphorus (P₄) with appropriate anionic dicarbenes $[Li(ADC^{Ar})]$. The formation of 1,2,3-triphosphol-2-ides (**4a–4d**) suggests unprecedented $[3 + 1]$ fragmentation of P₄ into P₃⁺ and P[−]. The P₃⁺ cation is trapped by the $(ADC^{Ar})^-$ 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 (iMICs^{Ar}) (iMIC^{Ar} = 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 6π-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 $\{[(ADC^{Ar})P_3]M(CO)_n\}$ (M = Fe, *n* = 4, Ar = Ph **5a** or 4-Me-C₆H₄ **5b**; M = Mo, *n* = 5, Ar = Ph **6**; M = W, *n* = 5, Ar = 4-Me₂NC₆H₄ **7**).

Received 3rd September 2019
Accepted 16th October 2019

DOI: 10.1039/c9sc04441h

rsc.li/chemical-science

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 P₄ into PCl₃, a common starting material for OPCs, and thus minimizes the waste and energy consumption.¹ The activation and subsequent functionalization of P₄ has therefore become a topical objective.² Both transition metal³ as well as main-group element⁴ compounds have been shown to activate or functionalize P₄.⁵ 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 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

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 P₄, however, related derivatives containing the [P₂] or [P₃[−]] moiety are accessible by alternative methods.⁹ Sterically demanding 1,3-bis(*t*Bu)imidazol-2-ylidene (IBu^f) activates P₄ in combination with B(C₆F₅)₃ to give **X**.^{6h} This frustrated Lewis pair (FLP) type reactivity¹⁰ led to the transformation of the classical NHC (IBu^f) 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 P₄ has been described so far. This is most likely due to their limited synthetic accessibility.^{11a} 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 P₄ functionalization.^{5i,14} Herein, we showcase the direct functionalization of P₄ *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-*i*Pr₂C₆H₃; Ar = C₆H₅ **4a**, 3-MeC₆H₄ **4b**, 4-MeC₆H₄ **4c**, and 4-Me₂NC₆H₄ **4d**) (Scheme 1).

Molecular Inorganic Chemistry and Catalysis, Inorganic and Structural Chemistry, Center for Molecular Materials, Faculty of Chemistry, Universität Bielefeld, Universitätsstr. 25, Bielefeld, D-33615, Germany. E-mail: rghadwal@uni-bielefeld.de; Web: https://www.ghadwalgroup.de

† Electronic supplementary information (ESI) available. CCDC 1939608–1939615. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c9sc04441h



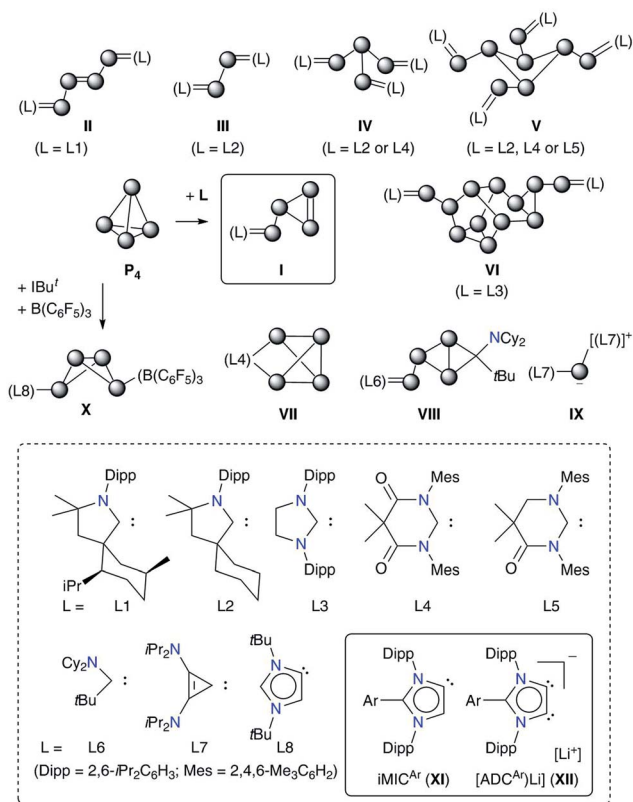
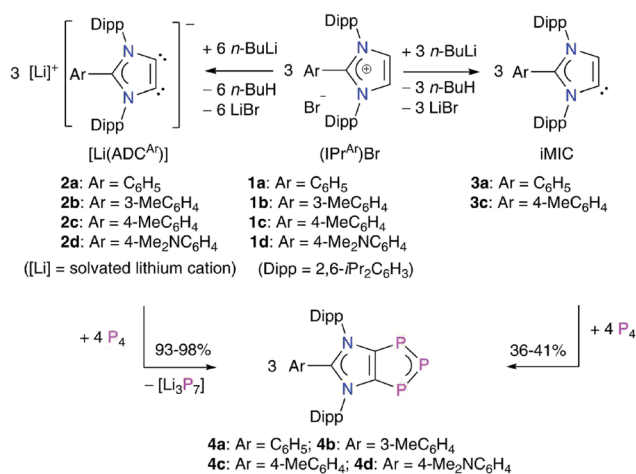


Fig. 1 Singlet carbene-mediated P_4 activation and fragmentation to II–X and a plausible intermediate I. Mesoionic carbenes (iMICs^{Ar}, XI) and anionic dicarbenes (XII) ([Li⁺] = solvated lithium ion) investigated in the current study.



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, 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 iMICs^{Ar} **3a** and **3c** with P_4 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 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. The ¹³C{¹H} NMR resonances for **4a–4d** are fully consistent with their ¹H NMR spectra. The ¹³C{¹H} 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 ³¹P nucleus. The ³¹P{¹H} 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 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 C₂P₃-ring that is coplanar with the imidazole C₃N₂-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

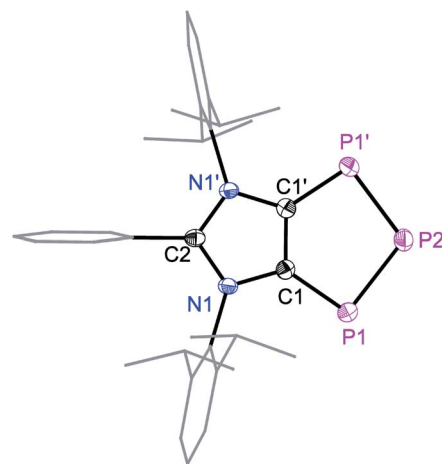
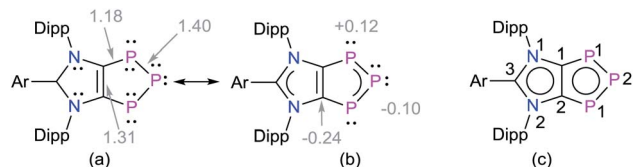


Fig. 2 Solid-state molecular structure of **4a**. Hydrogen atoms are omitted for clarity. Symmetry code: 1 – X, +Y, 3/2 – Z. Selected experimental and calculated [M06-2X/def2SVP] bond lengths (Å) and angles (°): C1–C1' 1.395(5) [1.402], N1–C1 1.404(3) [1.399], P1–C1 1.757(3) [1.764], P1–P2 2.103(1) [2.112], 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 phosphalkenes.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 [P₃C₂R₂]⁻ (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 (-0.10e) 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 6 π -electron C₂P₃ and C₃N₂ aromatic systems (Scheme 2c). The nitrogen atoms contribute 4 π -electrons to the C₃N₃-ring, whereas the P₃ unit shares 4 π -electrons with the C₂P₃-ring. The 2 π -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

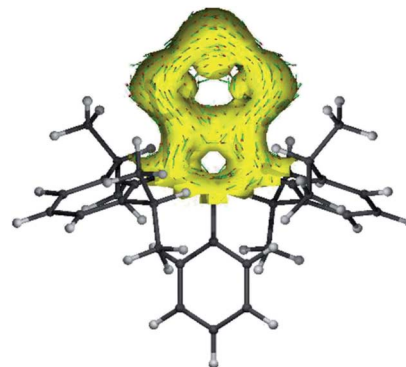


Fig. 3 AICD plot (based on M06-2X/def2-TZVPP//def2-SVP calculations) of the C₃N₂P₃ core of compound **4a**. The isovalue was arbitrarily chosen to be 0.03, the magnetic field is orthogonal to the C₂P₃-plane and points towards the viewer, and thus clockwise ring currents represent aromatic systems, whereas 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 C₃N₂ and the C₂P₃ 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 C₂P₃-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 C₂P₃ 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 6 π -electron η^5 -donors (C₂P₃-ring) like triphospholide²¹ 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)_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 C₃N₂/C₂P₃ units of **4a-4d** at the M06-2X/def2TZVPP//M06-2X/def2SVP level of theory

C ₃ N ₂ /C ₂ P ₃	4a	4b	4c	4d	5a	C ₆ H 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).



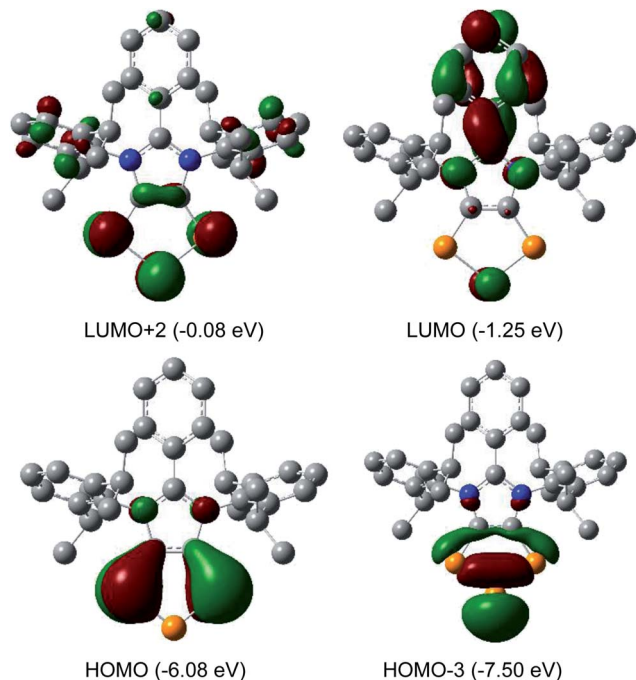
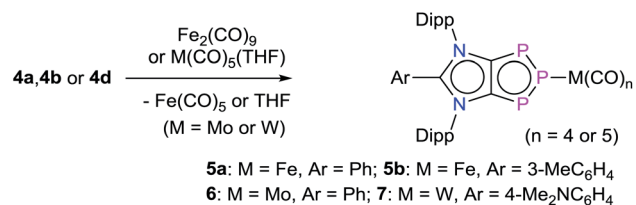


Fig. 4 Selected MOs of **4a** calculated at the M06-2X/def2-TZVPP//def2-SVP level of theory with an isovalue of 0.04. Hydrogen atoms were omitted for clarity.

neighbouring phosphorus atoms. The $^{31}\text{P}\{^1\text{H}\}$ 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 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **7**, the triplet at 250 ppm is accompanied by the ^{183}W satellites ($J_{\text{P-W}} = 202$ 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 $\text{Fe}(\text{CO})_4$ 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 $\{[(\text{ADC}^{\text{Ar}})\text{P}_3]\text{M}(\text{CO})_n\}$ **5a**, **5b**, **6**, and **7**.

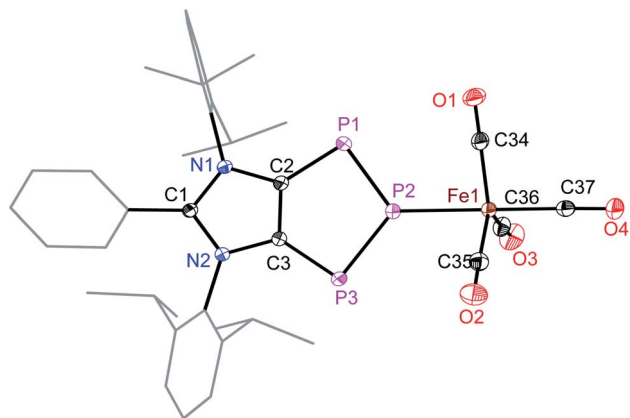


Fig. 5 Solid-state molecular structure of **5a**. Hydrogen atoms and one solvent toluene molecule are omitted for clarity. Selected bond lengths (Å) and angles (°): C2–C3 1.394(2), C2–N1 1.399(1), C3–N2 1.403(1), C2–P1 1.756(1), C3–P3 1.764(1), P1–P2 2.081(1), P2–P3 2.089(1), P2–Fe1 2.240(1), Fe1–C34 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 CD_2Cl_2 : ^1H 5.32; ^{13}C 53.84 and C_6D_6 : ^1H 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



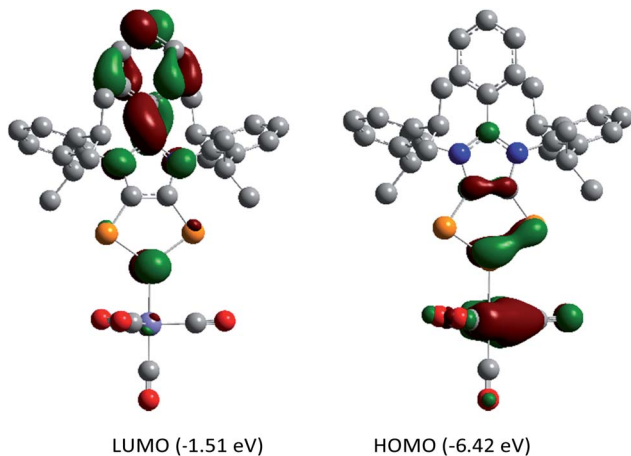


Fig. 6 Frontier molecular orbitals of **5a** calculated at the M06-2X/def2-TZVPP//def2-SVP level of theory. The isovalue was arbitrarily chosen to be 0.04. Hydrogen atoms were omitted for clarity.

with a Büchi B-545 melting point apparatus. (IPr^{Ar})Br salts **1a–1d** (Ar = Ph, 3-MeC₆H₄, 4-MeC₆H₄ or 4-Me₂NC₆H₄) 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 (ADC^{Ph})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 $-40\text{ }^{\circ}\text{C}$. The resulting reaction mixture was stirred at $-20\text{ }^{\circ}\text{C}$ for 1 h and then at room temperature ($25\text{ }^{\circ}\text{C}$) 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 $-24\text{ }^{\circ}\text{C}$ for three days. Mp: $343\text{ }^{\circ}\text{C}$. 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, CD₂Cl₂, 298 K): $\delta = 7.59$ (t, $J = 7.7$ Hz, 2H, *p*-C₆H₃), 7.38 (d, $J = 7.8$ Hz, 4H, *m*-C₆H₃), 7.34 (t, $J = 6.6$ Hz, 1H, *p*-C₆H₃), 7.23–7.18 (m, 4H, *o*-, *m*-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): $\delta = 167.6$ (d, $J_{\text{P-C}} = 84.4$ Hz, CP); 149.2 (NCN); 146.2, 133.5, 132.0, 131.8, 129.8, 129.1, 125.8, and 123.8 (C₆H₃, C₆H₅); 29.7 (CH(CH₃)₂); 26.1 and 23.5 (CH(CH₃)₂) ppm. ³¹P{¹H} NMR (202 MHz, CD₂Cl₂, 298 K): $\delta = 332.3$ (t, $J_{\text{P-P}} = 506$ Hz) and 173.7 (d, $J_{\text{P-P}} = 506$ Hz) ppm. MS (ESI, positive mode): $m/z = 557.3$ [**4a**

+ H]⁺. UV-vis ($\lambda/\text{nm } \epsilon$ (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})P₃ (**4b**)

Yield: 98% (0.90 g). Mp: $338\text{--}341\text{ }^{\circ}\text{C}$. 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, CD₂Cl₂, 298 K): $\delta = 7.57$ (t, $J = 7.8$ Hz, 2H, *p*-C₆H₃), 7.35 (d, $J = 7.8$ Hz, 4H, *m*-C₆H₃), 7.14 (d, $J = 7.6$ Hz, 1H, *o*-C₆H₄), 7.08 (t, $J = 7.8$ Hz, 1H, *m*-C₆H₄), 7.02 (s, 1H, *o*-C₆H₄), 6.96 (d, $J = 7.8$ Hz, 1H, *p*-C₆H₄), 2.60 (sept, $J = 6.7$ Hz, 4H, CH(CH₃)₂), 2.10 (s, 3H, CH₃), 1.24 (d, $J = 6.7$ Hz, 12H, CH(CH₃)₂), and 1.03 (d, $J = 6.8$ Hz, 12H, CH(CH₃)₂) ppm. ¹³C{¹H} NMR (126 MHz, CD₂Cl₂, 298 K): $\delta = 167.5$ (d, $J_{\text{P-C}} = 84.5$ Hz, CP); 149.6 (NCN); 146.3, 139.3, and 133.6 (*i*-C₆H₄ and *i*-, *m*-C₆H₃); 132.7 (*o*-C₆H₄); 131.7 (*p*-C₆H₃); 130.5 (*o*-C₆H₄); 129.5 and 128.9 (*m*-C₆H₄); 126.9, 125.8, and 123.71 (*m*-C₆H₃); 29.7 (C(CH₃)₂); 26.2 and 23.5 (C(CH₃)₂); 21.2 (CH₃) ppm. ³¹P{¹H} NMR (202 MHz, CD₂Cl₂, 298 K): $\delta = 331.1$ (t, $J_{\text{P-P}} = 506$ Hz) and 173.6 (d, $J_{\text{P-P}} = 506$ Hz) ppm. MS (ESI, positive mode): $m/z = 571.3$ [**4b** + H]⁺. UV-vis ($\lambda/\text{nm } \epsilon$ (M⁻¹ cm⁻¹)): 280 (25637), 345 (36323), and 361 (36539).

(ADC^{4-Tol})P₃ (**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 $-24\text{ }^{\circ}\text{C}$. Mp: $339\text{--}343\text{ }^{\circ}\text{C}$. 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, CD₂Cl₂, 298 K): $\delta = 7.59$ (t, $J = 7.8$ Hz, 2H, *p*-C₆H₃), 7.38 (d, $J = 7.8$ Hz, 4H, *m*-C₆H₃), 7.05 (d, $J = 8.4$ Hz, 2H, C₆H₄), 7.02 (d, $J = 8.3$ Hz, 2H, C₆H₄), 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): $\delta = 167.5$ (d, $J_{\text{P-C}} = 84.1$ Hz, CP); 146.2 (NCN); 143.1, 133.7, 131.7, 129.8, 129.7, 125.8, and 120.9 (C₆H₃ and C₆H₄); 29.7 (CH(CH₃)₂); 26.1 and 23.5 (CH(CH₃)₂); 21.7 (CH₃) ppm. ³¹P{¹H} NMR (202 MHz, CD₂Cl₂, 298 K): $\delta = 329.9$ (t, $J_{\text{P-P}} = 506$ Hz) and 173.6 (d, $J_{\text{P-P}} = 506$ Hz) ppm. MS (ESI, positive mode): $m/z = 571.3$ [**4c** + H]⁺. UV-vis ($\lambda/\text{nm } \epsilon$ (M⁻¹ cm⁻¹)): 283 (23295), 336 (28771), 346 (29238), and 362 (29676).

(ADC^{4-DMP})P₃ (**4d**)

Yield: 94% (0.93 g). Mp: $270\text{--}273\text{ }^{\circ}\text{C}$ (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, CD₂Cl₂, 298 K): $\delta = 7.56$ (t, $J = 7.8$ Hz, 2H, *p*-C₆H₃), 7.35 (d, $J = 7.8$ Hz, 4H, *m*-C₆H₃), 6.90 (d, $J = 9.0$ Hz, 2H, C₆H₄), 6.28 (d, $J = 9.0$ Hz, 2H, C₆H₄), 2.88 (s, 6H, N(CH₃)₂), 2.67 (sept, $J = 6.8$ Hz, 4H, CH(CH₃)₂), 1.24 (d, $J = 6.7$ Hz, 12H, CH(CH₃)₂), and 0.97 (d, $J = 6.8$ Hz, 12H, CH(CH₃)₂) ppm. ¹³C{¹H} NMR (126 MHz, CD₂Cl₂, 298 K): $\delta = 167.0$ (d, $J_{\text{P-C}} = 82.8$ Hz, CP); 151.9 (NCN); 146.2, 138.4, 134.6, 131.4, 130.8, 126.3, 125.8, and 111.1 (C₆H₃ and C₆H₄); 40.0 (N(CH₃)₂); 29.6 (CH(CH₃)₂); 25.7 and 23.5 (CH(CH₃)₂) ppm. ³¹P



$\{^1\text{H}\}$ NMR (202 MHz, CD_2Cl_2 , 298 K): $\delta = 319.5$ (t, $J_{\text{P-P}} = 504$ Hz) and 173.3 (d, $J_{\text{P-P}} = 504$ Hz) ppm. MS (ESI, positive mode): $m/z = 600.3$ [$\mathbf{4d} + \text{H}$] $^+$. UV-vis (λ/nm ($\epsilon \text{ M}^{-1} \text{ cm}^{-1}$)): 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) 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 $\text{IPr}=\text{PH}^{17}$ by NMR spectroscopy. ^1H NMR (500 MHz, C_6D_6 , 298 K): $\delta = 7.23$ (t, $J = 7.7$ Hz, 2H, $p\text{-C}_6\text{H}_3$), 7.14 (d, $J = 7.6$ Hz, 4H, $m\text{-C}_6\text{H}_3$), 6.18 (s, 2H, NCH), 3.06 (sept, $J = 6.7$ Hz, 4H, $\text{CH}(\text{CH}_3)_2$), 1.92 (d, $J_{\text{PH}} = 165.2$ Hz, 1H, PH), 1.47 (d, $J = 6.8$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$), and 1.15 (d, $J = 6.9$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$) ppm. ^{31}P NMR (C_6D_6 , 298 K, 500 MHz): $\delta = -134.4$ (d, $J_{\text{P-H}} = 165.2$ Hz) ppm. $^{31}\text{P}\{^1\text{H}\}$ 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), $n\text{-BuLi}$ (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).

$(\text{ADC}^{\text{4-Tol}}\text{P}_3)$ (**4c**). Similarly, treatment of **3c** with P_4 gave **4c**. Yield: 36% (0.4 g).

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

$[(\text{ADC}^{\text{Ph}}\text{P}_3)\text{Fe}(\text{CO})_4]$ (**5a**). To a mixture of **4a** (651 mg, 1.2 mmol) and $\text{Fe}_2(\text{CO})_9$ (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 °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. (%), calcd for $\text{C}_{37}\text{H}_{39}\text{FeN}_2\text{O}_4\text{P}_3$ (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, $p\text{-C}_6\text{H}_3$), 7.38 (d, $J = 7.8$ Hz, 4H, $m\text{-C}_6\text{H}_3$), 7.34 (t, $J = 7.5$ Hz, 1H, $p\text{-C}_6\text{H}_5$), 7.22–7.15 (m, 4H, $o\text{-}, m\text{-C}_6\text{H}_5$), 2.57 (sept, $J = 6.7$ Hz, 4H, $\text{CH}(\text{CH}_3)_2$), 1.27 (d, $J = 6.7$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$), and 1.01 (d, $J = 6.8$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CD_2Cl_2 , 298 K): $\delta = 215.1$ (CO); 161.7 (d, $J_{\text{P-C}} = 70.3$ 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 ($\text{CH}(\text{CH}_3)_2$); 26.0 and 23.5 ($\text{CH}(\text{CH}_3)_2$) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, CD_2Cl_2 , 298 K): $\delta = 316.8$ (t, $J_{\text{P-P}} = 531$ Hz) and 145.4 (d, $J_{\text{P-P}} = 531$ Hz) ppm. MS (ESI, positive mode): $m/z = 725.1$ [$\mathbf{5a} + \text{H}$] $^+$. UV-vis (λ/nm ($\epsilon \text{ M}^{-1} \text{ cm}^{-1}$)): 285 (33061), 328 (31345), and 428 (37184). IR (ATR, diamond): $\tilde{\nu}/\text{cm}^{-1} = 2041, 1966, 1937, \text{ and } 1919$.

$[(\text{ADC}^{\text{3-Tol}}\text{P}_3)\text{Fe}(\text{CO})_4]$ (**5b**). Compound **5b** was synthesized following a similar procedure to that described above for **5a** using **4b** (300 mg, 0.53 mmol) and $\text{Fe}_2(\text{CO})_9$ (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**, $\text{C}_{38}\text{H}_{41}\text{FeN}_2\text{O}_4\text{P}_3$ (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, $p\text{-C}_6\text{H}_3$), 7.37 (d, $J = 7.8$ Hz, 4H, $m\text{-C}_6\text{H}_3$), 7.15 (d, $J = 7.4$ Hz, 1H, $o\text{-C}_6\text{H}_4$), 7.08 (t, $J = 7.7$ Hz, 1H, $m\text{-C}_6\text{H}_4$), 7.00 (s, 1H, $o\text{-C}_6\text{H}_4$), 6.94 (d, $J = 7.7$ Hz, 1H, $p\text{-C}_6\text{H}_4$), 2.56 (sept, $J = 6.6$ Hz, 4H, $\text{CH}(\text{CH}_3)_2$), 2.09 (s, 3H, CH_3), 1.27 (d, $J = 6.6$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$), and 1.04 (d, $J = 6.7$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CD_2Cl_2 , 298 K): $\delta = 215.1$ and 214.9 (CO); 161.6 (d, $J_{\text{P-C}} = 71$ 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 ($\text{CH}(\text{CH}_3)_2$); 26.1 and 23.6 ($\text{CH}(\text{CH}_3)_2$); 21.2 (CH_3) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, CD_2Cl_2 , 298 K): $\delta = 315.5$ (t, $J_{\text{P-P}} = 531$ Hz) and 145.4 (d, $J_{\text{P-P}} = 532$ Hz) ppm. MS (ESI, positive mode): $m/z = 739.1$ [$\mathbf{5b} + \text{H}$] $^+$. UV-vis (λ/nm ($\epsilon \text{ M}^{-1} \text{ cm}^{-1}$)): 282 (35189), 327 (29758), and 416 (37568). IR (ATR, diamond): $\tilde{\nu}/\text{cm}^{-1} = 2039, 2007, 1962, \text{ and } 1921$.

$[(\text{ADC}^{\text{Ph}}\text{P}_3)\text{Mo}(\text{CO})_5]$ (**6**). To a mixture of **4a** (447 mg, 0.8 mmol) and $\text{Mo}(\text{CO})_6$ (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 $n\text{-hexane}$ into a saturated toluene solution of **6**. Elem. anal. (%), calcd for **6**, $\text{C}_{38}\text{H}_{39}\text{MoN}_2\text{O}_5\text{P}_3$ (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, $p\text{-C}_6\text{H}_3$), 7.38 (d, $J = 7.8$ Hz, 4H, $m\text{-C}_6\text{H}_3$), 7.35 (t, $J = 7.6$ Hz, 1H, $p\text{-C}_6\text{H}_5$), 7.21 (t, $J = 7.8$ Hz, 2H, $m\text{-C}_6\text{H}_5$), 7.17 (d, $J = 7.9$ Hz, 2H, $o\text{-C}_6\text{H}_5$), 2.58 (sept, $J = 6.7$ Hz, 4H, $\text{CH}(\text{CH}_3)_2$), 1.27 (d, $J = 6.7$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$), and 1.02 (d, $J = 6.8$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CD_2Cl_2 , 298 K): $\delta = 206.0$ and 201.8 (CO); 164.4 (d, $J_{\text{P-C}} = 73$ 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 ($\text{CH}(\text{CH}_3)_2$); 26.0 and 23.6 ($\text{CH}(\text{CH}_3)_2$) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, CD_2Cl_2 , 298 K): $\delta = 299.1$ (t, $J_{\text{P-P}} = 510$ Hz) and 160.2 (d, $J_{\text{P-P}} = 511$ Hz) ppm. IR (ATR, diamond): $\tilde{\nu}/\text{cm}^{-1} = 2065, 2051, 1945, 1925, \text{ and } 1911$.

$[(\text{ADC}^{\text{4-DMP}}\text{P}_3)\text{W}(\text{CO})_5]$ (**7**). A 10 mL THF solution of $\text{W}(\text{CO})_6$ (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**, $\text{C}_{40}\text{H}_{44}\text{N}_3\text{O}_5\text{P}_3\text{W}$ (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, $p\text{-C}_6\text{H}_3$), 7.41 (d, $J = 7.8$ Hz, 4H, $m\text{-C}_6\text{H}_3$), 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, $\text{N}(\text{CH}_3)_2$), 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, *J*_{P-P} = 505 Hz) ppm. MS (ESI): *m/z* = 924.2 [7 + H]⁺. IR (ATR, diamond): $\tilde{\nu}/\text{cm}^{-1}$ = 2063, 1978, 1925, and 1907.

Conclusions

In conclusion, the direct functionalization of white phosphorus (P₄) with anionic dicarbenes (ADCs) (**2a–2d**) as well as with mesoionic carbenes (iMICs^{At}) (**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 (P₇)^{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.

Acknowledgements

We gratefully acknowledge the support from the Deutsche Forschungsgemeinschaft (DFG) and thank Professor Norbert W. Mitzel for his continuous support. The authors gratefully acknowledge the support by computing time provided by the Paderborn Center for Parallel Computing (PC2).

References

- D. E. C. Corbridge, *Phosphorus: Chemistry, Biochemistry and Technology*, CRC Press, 6th edn, 2016.
- J. M. Lynam, *Angew. Chem., Int. Ed.*, 2008, **47**, 831–833.
- (a) B. M. Cossairt, N. A. Piro and C. C. Cummins, *Chem. Rev.*, 2010, **110**, 4164–4177; (b) M. Caporali, L. Gonsalvi, A. Rossini and M. Peruzzini, *Chem. Rev.*, 2010, **110**, 4178–4235; (c) M. Peruzzini, L. Gonsalvi and A. Romerosa, *Chem. Soc. Rev.*, 2005, **34**, 1038–1047; (d) C. C. Cummins, *Angew. Chem., Int. Ed.*, 2006, **45**, 862–870.
- (a) M. Scheer, G. Balázs and A. Seitz, *Chem. Rev.*, 2010, **110**, 4236–4256; (b) S. Khan, S. S. Sen and H. W. Roesky, *Chem. Commun.*, 2012, **48**, 2169–2179; (c) N. A. Giffin and J. D. Masuda, *Coord. Chem. Rev.*, 2011, **255**, 1342–1359; (d) M. H. Holthausen and J. J. Weigand, *Chem. Soc. Rev.*, 2014, **43**, 6639–6657.
- (a) S. Heinl, S. Reisinger, C. Schwarzmaier, M. Bodensteiner and M. Scheer, *Angew. Chem., Int. Ed.*, 2014, **53**, 7639–7642; (b) W. W. Seidel, O. T. Summerscales, B. O. Patrick and M. D. Fryzuk, *Angew. Chem., Int. Ed.*, 2009, **48**, 115–117; (c) B. M. Cossairt and C. C. Cummins, *Angew. Chem., Int. Ed.*, 2008, **47**, 169–172; (d) B. M. Cossairt and C. C. Cummins, *Angew. Chem., Int. Ed.*, 2008, **47**, 8863–8866; (e) N. A. Piro and C. C. Cummins, *J. Am. Chem. Soc.*, 2008, **130**, 9524–9535; (f) A. R. Fox, C. R. Clough, N. A. Piro and C. C. Cummins, *Angew. Chem., Int. Ed.*, 2007, **46**, 973–976; (g) N. A. Piro, J. S. Figueroa, J. T. McKellar and C. C. Cummins, *Science*, 2006, **313**, 1276–1279; (h) B. M. Cossairt, M.-C. Diawara and C. C. Cummins, *Science*, 2009, **323**, 602; (i) S. Du, J. Yin, Y. Chi, L. Xu and W.-X. Zhang, *Angew. Chem., Int. Ed.*, 2017, **56**, 15886–15890; (j) C. Schwarzmaier, A. Noor, G. Glatz, M. Zabel, A. Y. Timoshkin, B. M. Cossairt, C. C. Cummins, R. Kempe and M. Scheer, *Angew. Chem., Int. Ed.*, 2011, **50**, 7283–7286; (k) C. Camp, L. Maron, R. G. Bergman and J. Arnold, *J. Am. Chem. Soc.*, 2014, **136**, 17652–17661; (l) S. Pelties, D. Herrmann, B. de Bruin, F. Hartl and R. Wolf, *Chem. Commun.*, 2014, **50**, 7014–7016; (m) S. L. Yao, N. Lindenmaier, Y. Xiong, S. Inoue, T. Szilvasi, M. Adelhardt, J. Sutter, K. Meyer and M. Driess, *Angew. Chem., Int. Ed.*, 2015, **54**, 1250–1254; (n) F. Dielmann, A. Timoshkin, M. Piesch, G. Balázs and M. Scheer, *Angew. Chem., Int. Ed.*, 2017, **56**, 1671–1675; (o) F. Spitzer, C. Graßl, G. Balázs, E. M. Zolnhofer, K. Meyer and M. Scheer, *Angew. Chem., Int. Ed.*, 2016, **55**, 4340–4344; (p) F. Spitzer, C. Graßl, G. Balázs, E. Mädl, M. Keilwerth, E. M. Zolnhofer, K. Meyer and M. Scheer, *Chem.–Eur. J.*, 2017, **23**, 2716–2721; (q) B. L. Tran, M. Singhal, H. Park, O. P. Lam, M. Pink, J. Krzystek, A. Ozarowski, J. Telser, K. Meyer and D. J. Mindiola, *Angew. Chem., Int. Ed.*, 2010, **49**, 9871–9875; (r) J. E. Borger, M. S. Bakker, A. W. Ehlers, M. Lutz, J. Chris Slootweg and K. Lammertsma, *Chem. Commun.*, 2016, **52**, 3284–3287.
- (a) S. Khan, R. Michel, J. M. Dieterich, R. A. Mata, H. W. Roesky, J.-P. Demers, A. Lange and D. Stalke, *J. Am. Chem. Soc.*, 2011, **133**, 17889–17894; (b) J. W. Dube, C. M. E. Graham, C. L. B. Macdonald, Z. D. Brown, P. P. Power and P. J. Ragogna, *Chem.–Eur. J.*, 2014, **20**, 6739–6744; (c) R. J. Schwamm, M. Lein, M. P. Coles and C. M. Fitchett, *Angew. Chem., Int. Ed.*, 2016, **55**, 14798–14801; (d) M. Arrowsmith, M. S. Hill, A. L. Johnson, G. Kociok-Köhn and M. F. Mahon, *Angew. Chem., Int. Ed.*, 2015, **54**, 7882–7885; (e) K. X. Bhattacharyya, S. Dreyfuss, N. Saffon-Merceron and N. Mézailles, *Chem. Commun.*, 2016, **52**, 5179–5182; (f) S. Khan, R. Michel, S. S. Sen,



- H. W. Roesky and D. Stalke, *Angew. Chem., Int. Ed.*, 2011, **50**, 11786–11789; (g) W. Lu, K. Xu, Y. Li, H. Hirao and R. Kinjo, *Angew. Chem., Int. Ed.*, 2018, **57**, 15691–15695; (h) D. Holschumacher, T. Bannenberg, K. Ibrom, C. G. Daniliuc, P. G. Jones and M. Tamm, *Dalton Trans.*, 2010, **39**, 10590–10592; (i) J. E. Borger, A. W. Ehlers, M. Lutz, J. C. Slootweg and K. Lammertsma, *Angew. Chem., Int. Ed.*, 2014, **53**, 12836–12839.
- 7 (a) O. Back, G. Kuchenbeiser, B. Donnadiou and G. Bertrand, *Angew. Chem., Int. Ed.*, 2009, **48**, 5530–5533; (b) J. D. Masuda, W. W. Schoeller, B. Donnadiou and G. Bertrand, *Angew. Chem., Int. Ed.*, 2007, **46**, 7052–7055; (c) C. D. Martin, C. M. Weinstein, C. E. Moore, A. L. Rheingold and G. Bertrand, *Chem. Commun.*, 2013, **49**, 4486–4488; (d) C. L. Dorsey, B. M. Squires and T. W. Hudnall, *Angew. Chem., Int. Ed.*, 2013, **52**, 4462–4465; (e) J. D. Masuda, W. W. Schoeller, B. Donnadiou and G. Bertrand, *J. Am. Chem. Soc.*, 2007, **129**, 14180–14181.
- 8 (a) J. E. Borger, A. W. Ehlers, J. C. Slootweg and K. Lammertsma, *Chem.–Eur. J.*, 2017, **23**, 11738–11746; (b) D. Tofan and C. C. Cummins, *Angew. Chem., Int. Ed.*, 2010, **49**, 7516–7518.
- 9 (a) Y. Wang, Y. Xie, P. Wei, R. B. King, H. F. Schaefer III, P. v. R. Schleyer and G. H. Robinson, *J. Am. Chem. Soc.*, 2008, **130**, 14970–14971; (b) M. H. Holthausen, S. K. Surmiak, P. Jerabek, G. Frenking and J. J. Weigand, *Angew. Chem., Int. Ed.*, 2013, **52**, 11078–11082.
- 10 (a) D. W. Stephan, *Science*, 2016, **354**, aaf7229; (b) D. W. Stephan and G. Erker, *Angew. Chem., Int. Ed.*, 2015, **54**, 6400–6441; (c) D. W. Stephan, *Acc. Chem. Res.*, 2015, **48**, 306–316.
- 11 (a) E. Aldeco-Perez, A. J. Rosenthal, B. Donnadiou, P. Parameswaran, G. Frenking and G. Bertrand, *Science*, 2009, **326**, 556–559; (b) D. J. Nelson and S. P. Nolan, *Chem. Soc. Rev.*, 2013, **42**, 6723–6753; (c) G. Ung and G. Bertrand, *Chem.–Eur. J.*, 2011, **17**, 8269–8272; (d) G. Guisado-Barrios, J. Bouffard, B. Donnadiou and G. Bertrand, *Angew. Chem., Int. Ed.*, 2010, **49**, 4759–4762; (e) A. Vivancos, C. Segarra and M. Albrecht, *Chem. Rev.*, 2018, **118**, 9493–9586.
- 12 D. Rottschäfer, F. Ebeler, T. Strothmann, B. Neumann, H.-G. Stammler, A. Mix and R. S. Ghadwal, *Chem.–Eur. J.*, 2018, **24**, 3716–3720.
- 13 (a) N. K. T. Ho, B. Neumann, H.-G. Stammler, V. H. Menezes da Silva, D. G. Watanabe, A. A. C. Braga and R. S. Ghadwal, *Dalton Trans.*, 2017, **46**, 12027–12031; (b) R. S. Ghadwal, S. O. Reichmann and R. Herbst-Irmer, *Chem.–Eur. J.*, 2015, **21**, 4247–4251.
- 14 (a) S. Du, J. Yang, J. Hu, Z. Chai, G. Luo, Y. Luo, W. X. Zhang and Z. Xi, *J. Am. Chem. Soc.*, 2019, **141**, 6843–6847; (b) L. Xu, Y. Chi, S. Du, W.-X. Zhang and Z. Xi, *Angew. Chem., Int. Ed.*, 2016, **55**, 9187–9190.
- 15 M. Baudler and K. Glinka, *Chem. Rev.*, 1993, **93**, 1623–1667.
- 16 M. Baudler, *Angew. Chem., Int. Ed.*, 1987, **26**, 419–441.
- 17 M. Cicač-Hudi, J. Bender, S. H. Schlindwein, M. Bispinghoff, M. Nieger, H. Grützmacher and D. Gudat, *Eur. J. Inorg. Chem.*, 2016, **2016**, 649–658.
- 18 (a) C. L. Boulangé, in *Encyclopedia of Analytical Science (Third Edition)*, ed. P. Worsfold, C. Poole, A. Townshend and M. Miró, Academic Press, Oxford, 2019, pp. 319–327; (b) O. Köhl, *Phosphorus-31 NMR Spectroscopy*, Springer-Verlag Berlin Heidelberg, 2008.
- 19 CCDC 1939608–1939615 contain the supplementary crystallographic data for this paper.†
- 20 P. Pykkö and M. Atsumi, *Chem.–Eur. J.*, 2009, **15**, 12770–12779.
- 21 (a) R. S. P. Turbervill, A. R. Jupp, P. S. B. McCullough, D. Ergöçmen and J. M. Goicoechea, *Organometallics*, 2013, **32**, 2234–2244; (b) R. S. P. Turbervill and J. M. Goicoechea, *Chem. Commun.*, 2012, **48**, 6100–6102.
- 22 P. v. R. Schleyer, C. Maerker, A. Dransfeld, H. Jiao and N. J. R. van Eikema Hommes, *J. Am. Chem. Soc.*, 1996, **118**, 6317–6318.
- 23 D. Geuenich, K. Hess, F. Köhler and R. Herges, *Chem. Rev.*, 2005, **105**, 3758–3772.
- 24 E. P. Kyba, K. L. Hassett, B. Sheikh, J. S. McKennis, R. B. King and R. E. Davis, *Organometallics*, 1985, **4**, 994–1001.

