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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<sub>2</sub>P<sub>3</sub>-ring compounds [(ADC<sup>Ar</sup>)P<sub>3</sub>] (ADC<sup>Ar</sup> = ArC{(DippN)C}<sub>2</sub>; Dipp = 2,6-iPr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>; Ar = Ph **4a**, 3-MeC<sub>6</sub>H<sub>4</sub> **4b**, 4-MeC<sub>6</sub>H<sub>4</sub> **4c**, and 4-Me<sub>2</sub>NC<sub>6</sub>H<sub>4</sub> **4d**) are readily accessible in an almost quantitative yield by the direct functionalization of white phosphorus (P<sub>4</sub>) with appropriate anionic dicarbenes [Li(ADC<sup>Ar</sup>)]. The formation of 1,2,3-triphosphol-2-ides (**4a–4d**) suggests unprecedented [3 + 1] fragmentation of P<sub>4</sub> into P<sub>3</sub><sup>+</sup> and P<sup>−</sup>. The P<sub>3</sub><sup>+</sup> cation is trapped by the (ADC<sup>Ar</sup>)<sup>−</sup> to give **4**, while the putative P<sup>−</sup> anion reacts with additional P<sub>4</sub> to yield the Li<sub>3</sub>P<sub>7</sub> species, a useful reagent in the synthesis of organophosphorus compounds. Remarkably, the P<sub>4</sub> fragmentation is also viable with the related mesoionic carbenes (iMICs<sup>Ar</sup>) (iMIC<sup>Ar</sup> = ArC{(DippN)<sub>2</sub>CCH}, i stands for imidazole-based) giving rise to **4**. DFT calculations reveal that both the C<sub>3</sub>N<sub>2</sub> and C<sub>2</sub>P<sub>3</sub>-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<sub>2</sub>P<sub>3</sub>-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<sup>Ar</sup>)P<sub>3</sub>]M(CO)<sub>n</sub> (M = Fe, n = 4, Ar = Ph **5a** or 4-Me-C<sub>6</sub>H<sub>4</sub> **5b**; M = Mo, n = 5, Ar = Ph **6**; M = W, n = 5, Ar = 4-Me<sub>2</sub>NC<sub>6</sub>H<sub>4</sub> **7**).

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## Introduction

The direct conversion of white phosphorus (P<sub>4</sub>) into useful organophosphorus compounds (OPCs) is of significant interest because this excludes the involvement of corrosive Cl<sub>2</sub> gas that is required to convert P<sub>4</sub> into PCl<sub>3</sub>, a common starting material for OPCs, and thus minimizes the waste and energy consumption.<sup>1</sup> The activation and subsequent functionalization of P<sub>4</sub> has therefore become a topical objective.<sup>2</sup> Both transition metal<sup>3</sup> as well as main-group element<sup>4</sup> compounds have been shown to activate or functionalize P<sub>4</sub>.<sup>5</sup> In particular, compounds featuring a low-valent main-group element have made significant advances over the past years.<sup>6</sup>

Among nonmetals, the use of singlet carbenes<sup>7</sup> has given new impetus to the field of P<sub>4</sub> activation as it leads to the direct C–P bond formation (Fig. 1).<sup>8</sup> Several stable carbenes (L1–L7) undergo reactions with P<sub>4</sub> and the fate of P<sub>4</sub> fragmentation to

give P<sub>n</sub> (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.<sup>7</sup> Weakly π-accepting NHCs such as IPr (IPr = C{(DippN)CH}<sub>2</sub>) do not react with P<sub>4</sub>, however, related derivatives containing the [P<sub>2</sub>] or [P<sub>3</sub><sup>−</sup>] moiety are accessible by alternative methods.<sup>9</sup> Sterically demanding 1,3-bis(*t*Bu)imidazol-2-ylidene (IBu<sup>t</sup>) activates P<sub>4</sub> in combination with B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> to give **X**.<sup>6h</sup> This frustrated Lewis pair (FLP) type reactivity<sup>10</sup> led to the transformation of the classical NHC (IBu<sup>t</sup>) 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.<sup>11</sup> Nonetheless, no reaction of an iMIC alone with P<sub>4</sub> has been described so far. This is most likely due to their limited synthetic accessibility.<sup>11a</sup> We recently reported<sup>12</sup> C5-protonated iMICs<sup>Ar</sup> (**XI**) as well as C4/C5-ditopic anionic dicarbenes [Li(ADC<sup>Ar</sup>)] **XII** (Fig. 1) by the deprotonation of C2-arylated 1,3-imidazolium salts.<sup>13</sup> The dicarbenes **XII** feature two adjacent C4/C5-nucleophilic sites, and thus are well endowed to affect unique dual P<sub>4</sub> functionalization.<sup>5i,14</sup> Herein, we showcase the direct functionalization of P<sub>4</sub> via unprecedented [3 + 1] fragmentation with [Li(ADC<sup>Ar</sup>)] and iMICs<sup>Ar</sup> to give the 1,2,3-triphosphol-2-ide derivatives [(ADC<sup>Ar</sup>)P<sub>3</sub>] (ADC<sup>Ar</sup> = ArC{NDipp}C<sub>2</sub>; Dipp = 2,6-iPr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>; Ar = C<sub>6</sub>H<sub>5</sub> **4a**, 3-MeC<sub>6</sub>H<sub>4</sub> **4b**, 4-MeC<sub>6</sub>H<sub>4</sub> **4c**, and 4-Me<sub>2</sub>NC<sub>6</sub>H<sub>4</sub> **4d**) (Scheme 1).

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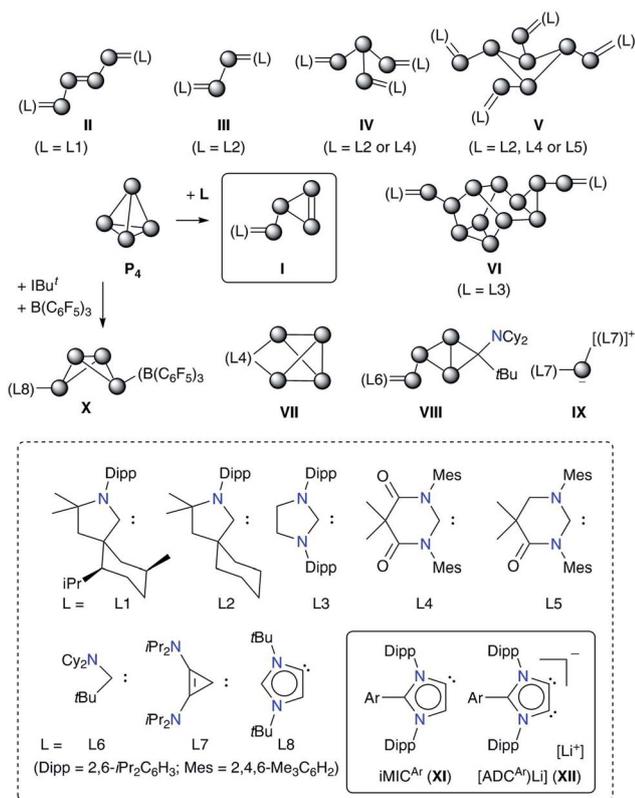
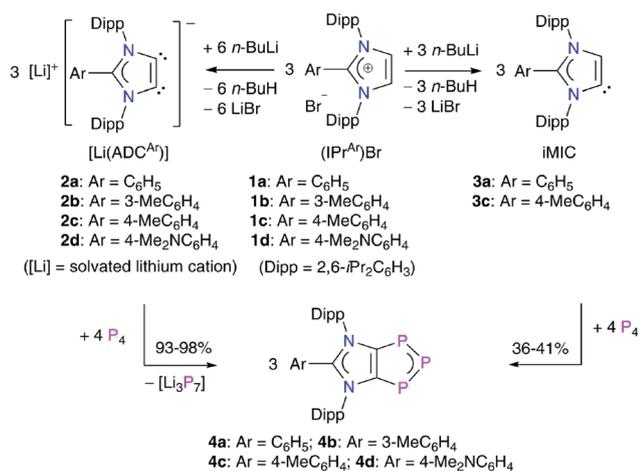


Fig. 1 Singlet carbene-mediated  $P_4$  activation and fragmentation to II–X and a plausible intermediate I. Mesoionic carbenes (iMICs<sup>Ar</sup>, XI) and anionic dicarbenes (XII) ( $[Li]^+$  = solvated lithium ion) investigated in the current study.



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<sup>Ar</sup> **3a** and **3c** with  $P_4$  to form **4a** and **4c**.

## Results and discussion

Treatment of  $[Li(ADC^{Ar})]$  (**2a–2d**),<sup>12</sup> 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 ( $P_7$ )<sup>3-</sup> anion, a very common species in metal mediated fragmentation of  $P_4$ .<sup>15</sup> Indeed,  $Li_3P_7$  can be isolated as a red-brown solid,<sup>15,16</sup> which was confirmed by its reaction with (IPr)HCl to give (IPr)PH, reported previously using  $Na_3P_7$ .<sup>17</sup>

Interestingly, treatment of iMICs<sup>Ar</sup> **3a** and **3c** with  $P_4$  also afforded, *albeit* in a lower yield, the corresponding products **4a** and **4c**, respectively. <sup>1</sup>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<sup>Ar</sup> **3a** and **3b** to 1,3-imidazolium salts **1a** and **1c**. Pure **4a** and **4c** can be extracted from the mixture using toluene.

The <sup>1</sup>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 <sup>13</sup>C{<sup>1</sup>H} NMR resonances for **4a–4d** are fully consistent with their <sup>1</sup>H NMR spectra. The <sup>13</sup>C{<sup>1</sup>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 <sup>31</sup>P nucleus. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of **4a–4d** each shows a doublet at ~73 ppm and a triplet at  $325 \pm 6$  ppm in 2 : 1 ratio ( $J_{P-P} \approx 500$  Hz), indicating the presence of an AB<sub>2</sub> type system with unsaturated P–P bonds.<sup>18</sup>

Solid-state molecular structures<sup>19</sup> of **4a** (Fig. 2), **4b** (Fig. S47<sup>†</sup>), and **4c** (Fig. S48<sup>†</sup>) reveal the presence of a C<sub>2</sub>P<sub>3</sub>-ring that is coplanar with the imidazole C<sub>3</sub>N<sub>2</sub>-ring plane. The metrical parameters of **4a–4c** are comparable (Table S1<sup>†</sup>) 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

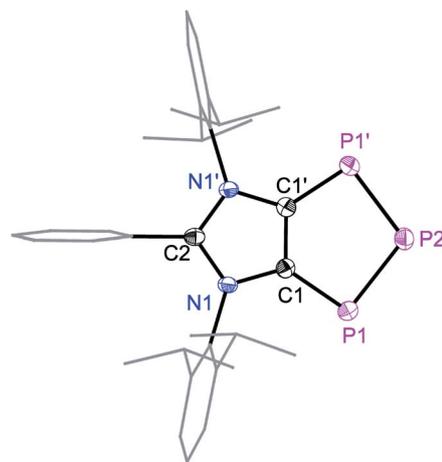
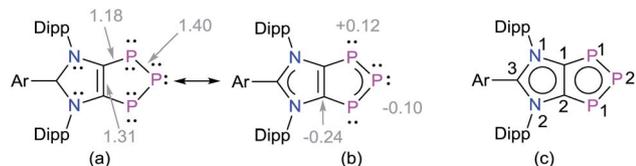


Fig. 2 Solid-state molecular structure of **4a**. Hydrogen atoms are omitted for clarity. Symmetry code: 1 – X, +Y, 3/2 – Z. Selected experimental and calculated [M06-2X/def2SVP] bond lengths (Å) and angles (°): C1–C1' 1.395(5) [1.402], N1–C1 1.404(3) [1.399], P1–C1 1.757(3) [1.764], P1–P2 2.103(1) [2.112], 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,<sup>20</sup> indicating a partial  $\pi$ -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)<sup>15</sup> but compares well with C=P bond lengths (*ca.* 1.75 Å) of inversely polarized phosphalkenes.<sup>17</sup> 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).<sup>13</sup> The C1-C1', C1/C2-P1 and P1-P2 bond lengths of **4a-4c** are comparable with the corresponding bond lengths of triphospholide anions  $[\text{P}_3\text{C}_2\text{R}_2]^-$  (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).<sup>21</sup> 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 $\pi$ -electron  $\text{C}_2\text{P}_3$  and  $\text{C}_3\text{N}_2$  aromatic systems (Scheme 2c). The nitrogen atoms contribute 4 $\pi$ -electrons to the  $\text{C}_3\text{N}_3$ -ring, whereas the  $\text{P}_3$  unit shares 4 $\pi$ -electrons with the  $\text{C}_2\text{P}_3$ -ring. The 2 $\pi$ -electrons of the C1=C2 bond are pooled by both the ring systems. Indeed, calculated nucleus-independent chemical shift (NICS)<sup>22</sup> values for **4a-4d** (Table 1) suggest the aromaticity of the  $\text{C}_3\text{N}_2$ - and  $\text{C}_2\text{P}_3$ -rings. For comparison, we also calculated the NICS values for  $\text{C}_6\text{H}_6$  and cyclobutadiene (CBD) molecules.

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

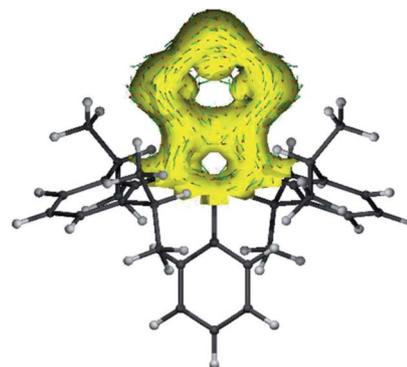


Fig. 3 AICD plot (based on M06-2X/def2-TZVPP//def2-SVP calculations) of the  $\text{C}_3\text{N}_2\text{P}_3$  core of compound **4a**. The isovalue was arbitrarily chosen to be 0.03, the magnetic field is orthogonal to the  $\text{C}_2\text{P}_3$ -plane and points towards the viewer, and thus clockwise ring currents represent aromatic systems, whereas counter-clockwise ring currents are indicative of antiaromatic systems. AICD plots of the complete molecules **4a-4d** are given in the ESI.†

significant delocalization of the  $\pi$ -electrons of both the  $\text{C}_3\text{N}_2$  and the  $\text{C}_2\text{P}_3$  heterocycles, forming one coherent  $\pi$ -system.

The HOMO of compounds **4a** (Fig. 4) and **4b-4c** (Fig. S58-S60†) corresponds to the  $\pi$ -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  $\pi$ -orbitals of the  $\text{P}_3$  and the  $\text{C}_2$  moieties of the  $\text{C}_2\text{P}_3$ -ring. Like in alkali metal 1,2,3-triphospholides,<sup>21b</sup> 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  $\pi$ -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  $\pi^*$  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  $\pi^*$ -orbitals of the  $\text{C}_2\text{P}_3$  unit.

The intriguing electronic structures of **4** prompted us to investigate their ligand properties as they may function as neutral two electron  $\sigma$ -donors (*via* phosphorus atoms) and/or 6 $\pi$ -electron  $\eta^5$ -donors ( $\text{C}_2\text{P}_3$ -ring) like triphospholide<sup>21</sup> and cyclopentadienyl anions. Treatment of **4a**, **4b**, and **4c** with  $\text{Fe}_2(\text{CO})_9$  or  $\text{M}(\text{CO})_5(\text{THF})$  (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  $\sigma$ -donor ligand to bind to the  $\text{M}(\text{CO})_n$  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  $\text{C}_3\text{N}_2/\text{C}_2\text{P}_3$  units of **4a-4d** at the M06-2X/def2TZVPP//M06-2X/def2SVP level of theory

$\text{C}_3\text{N}_2/\text{C}_2\text{P}_3$	<b>4a</b>	<b>4b</b>	<b>4c</b>	<b>4d</b>	<b>5a</b>	$\text{C}_6\text{H}_6/\text{CBD}^a$
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

<sup>a</sup> CBD (cyclobutadiene).



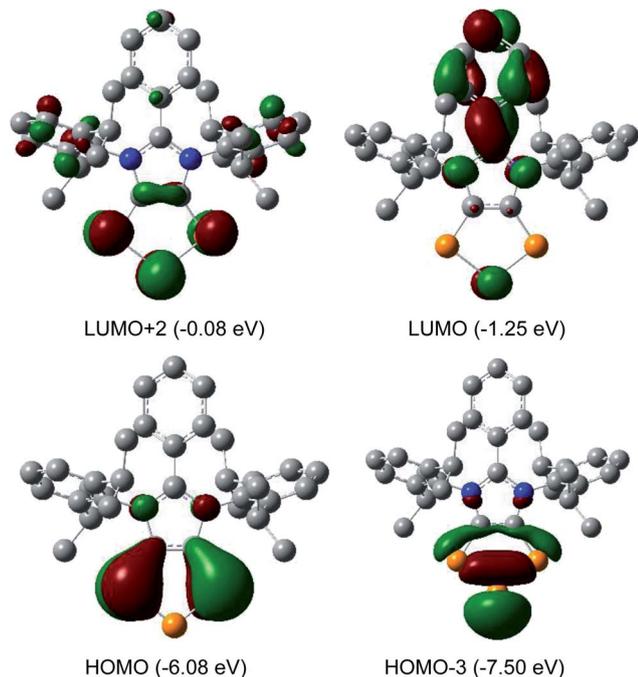
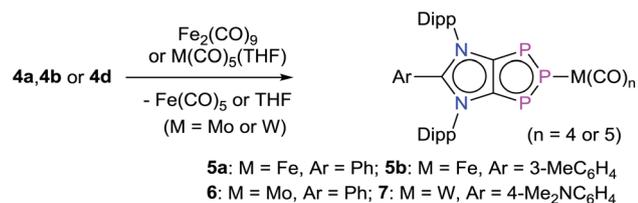


Fig. 4 Selected MOs of **4a** calculated at the M06-2X/def2-TZVPP//def2-SVP level of theory with an isovalue of 0.04. Hydrogen atoms were omitted for clarity.

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  $^{183}\text{W}$  satellites ( $J_{\text{P-W}} = 202$  Hz).

The iron atom in **5a** (Fig. 5) and **5b** (Fig. S49<sup>†</sup>) 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  $\text{P}_3\text{Fe}_3$  iron-carbonyl clusters (av. 2.244 Å).<sup>24</sup> Interestingly, the metrical parameters of the  $\text{C}_3\text{N}_2$ - and  $\text{C}_2\text{P}_3$ -rings of **5a** and **5b** are very similar to those of the precursors **4a** and **4b**, respectively. This indicates that the aromatic  $\pi$ -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<sup>†</sup>) and **7** (Fig. S51<sup>†</sup>) 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**.

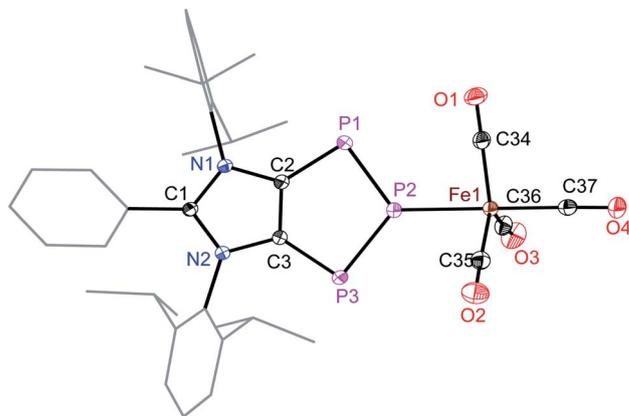


Fig. 5 Solid-state molecular structure of **5a**. Hydrogen atoms and one solvent toluene molecule are omitted for clarity. Selected bond lengths (Å) and angles (°): C2–C3 1.394(2), C2–N1 1.399(1), C3–N2 1.403(1), C2–P1 1.756(1), C3–P3 1.764(1), P1–P2 2.081(1), P2–P3 2.089(1), P2–Fe1 2.240(1), Fe1–C34 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  $\pi$ -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  $\pi$ -back bonding. The aromaticity of the  $\text{C}_2\text{P}_3$  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<sup>†</sup>).

## Experimental

All syntheses and manipulations were carried out under an inert gas atmosphere (Ar or N<sub>2</sub>) 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  $\delta$ , ppm) are referenced to the solvent residual signals of CD<sub>2</sub>Cl<sub>2</sub>:  $^1\text{H}$  5.32;  $^{13}\text{C}$  53.84 and C<sub>6</sub>D<sub>6</sub>:  $^1\text{H}$  7.16;  $^{13}\text{C}$  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<sub>2</sub>Cl<sub>2</sub> 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



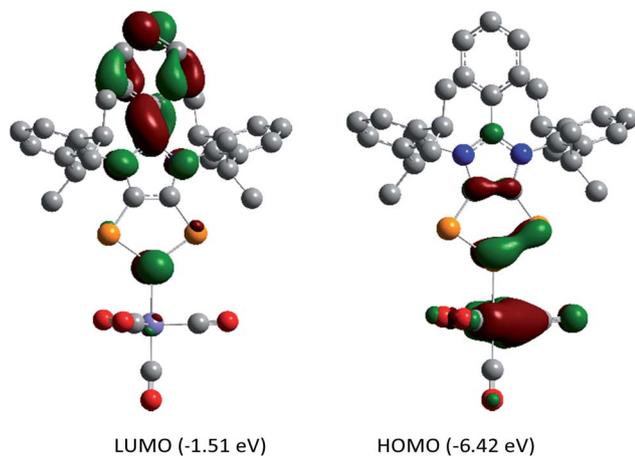


Fig. 6 Frontier molecular orbitals of **5a** calculated at the M06-2X/def2-TZVPP//def2-SVP level of theory. The isovalue was arbitrarily chosen to be 0.04. Hydrogen atoms were omitted for clarity.

with a Büchi B-545 melting point apparatus. (IPr<sup>Ar</sup>)Br salts **1a–1d** (Ar = Ph, 3-MeC<sub>6</sub>H<sub>4</sub>, 4-MeC<sub>6</sub>H<sub>4</sub> or 4-Me<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>) were synthesized following the reported method.<sup>13a</sup> *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<sub>2</sub>(CO)<sub>9</sub> (Sigma-Aldrich), Mo(CO)<sub>6</sub> (Fluorochem), and W(CO)<sub>6</sub> (Sigma-Aldrich) were used as supplied.

#### Synthesis of compound (ADC<sup>Ph</sup>)P<sub>3</sub> (**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**.<sup>12</sup> To this solution, solid P<sub>4</sub> (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<sub>3</sub>P<sub>7</sub> 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 ( $2 \times 10\text{ mL}$ ), 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 C<sub>33</sub>H<sub>39</sub>N<sub>2</sub>P<sub>3</sub> (556.6): C, 71.21; H, 7.06; N, 5.03; found: C, 71.02; H, 6.84; N, 4.87. <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K):  $\delta = 7.59$  (t,  $J = 7.7\text{ Hz}$ , 2H, *p*-C<sub>6</sub>H<sub>3</sub>), 7.38 (d,  $J = 7.8\text{ Hz}$ , 4H, *m*-C<sub>6</sub>H<sub>3</sub>), 7.34 (t,  $J = 6.6\text{ Hz}$ , 1H, *p*-C<sub>6</sub>H<sub>3</sub>), 7.23–7.18 (m, 4H, *o*-, *m*-C<sub>6</sub>H<sub>3</sub>), 2.62 (sept,  $J = 6.6\text{ Hz}$ , 4H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.26 (d,  $J = 6.6\text{ Hz}$ , 12H, CH(CH<sub>3</sub>)<sub>2</sub>), and 1.03 (d,  $J = 6.7\text{ Hz}$ , 12H, CH(CH<sub>3</sub>)<sub>2</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K):  $\delta = 167.6$  (d,  $J_{\text{P-C}} = 84.4\text{ Hz}$ , CP); 149.2 (NCN); 146.2, 133.5, 132.0, 131.8, 129.8, 129.1, 125.8, and 123.8 (C<sub>6</sub>H<sub>3</sub>, C<sub>6</sub>H<sub>5</sub>); 29.7 (CH(CH<sub>3</sub>)<sub>2</sub>); 26.1 and 23.5 (CH(CH<sub>3</sub>)<sub>2</sub>) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K):  $\delta = 332.3$  (t,  $J_{\text{P-P}} = 506\text{ Hz}$ ) and 173.7 (d,  $J_{\text{P-P}} = 506\text{ Hz}$ ) ppm. MS (ESI, positive mode):  $m/z = 557.3$  [**4a**

+ H]<sup>+</sup>. UV-vis ( $\lambda/\text{nm } \epsilon$  (M<sup>-1</sup> cm<sup>-1</sup>)): 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<sub>4</sub>.

#### (ADC<sup>3-Tol</sup>)P<sub>3</sub> (**4b**)

Yield: 98% (0.90 g). Mp:  $338\text{--}341\text{ }^{\circ}\text{C}$ . Elem. anal. (%), calcd for **4b**, C<sub>34</sub>H<sub>41</sub>N<sub>2</sub>P<sub>3</sub>, (570.6): C, 71.56; H, 7.24; N 4.91; found C, 70.64; H, 7.33; N 4.68. <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K):  $\delta = 7.57$  (t,  $J = 7.8\text{ Hz}$ , 2H, *p*-C<sub>6</sub>H<sub>3</sub>), 7.35 (d,  $J = 7.8\text{ Hz}$ , 4H, *m*-C<sub>6</sub>H<sub>3</sub>), 7.14 (d,  $J = 7.6\text{ Hz}$ , 1H, *o*-C<sub>6</sub>H<sub>4</sub>), 7.08 (t,  $J = 7.8\text{ Hz}$ , 1H, *m*-C<sub>6</sub>H<sub>4</sub>), 7.02 (s, 1H, *o*-C<sub>6</sub>H<sub>4</sub>), 6.96 (d,  $J = 7.8\text{ Hz}$ , 1H, *p*-C<sub>6</sub>H<sub>4</sub>), 2.60 (sept,  $J = 6.7\text{ Hz}$ , 4H, CH(CH<sub>3</sub>)<sub>2</sub>), 2.10 (s, 3H, CH<sub>3</sub>), 1.24 (d,  $J = 6.7\text{ Hz}$ , 12H, CH(CH<sub>3</sub>)<sub>2</sub>), and 1.03 (d,  $J = 6.8\text{ Hz}$ , 12H, CH(CH<sub>3</sub>)<sub>2</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K):  $\delta = 167.5$  (d,  $J_{\text{P-C}} = 84.5\text{ Hz}$ , CP); 149.6 (NCN); 146.3, 139.3, and 133.6 (*i*-C<sub>6</sub>H<sub>4</sub> and *i*-, *m*-C<sub>6</sub>H<sub>3</sub>); 132.7 (*o*-C<sub>6</sub>H<sub>4</sub>); 131.7 (*p*-C<sub>6</sub>H<sub>3</sub>); 130.5 (*o*-C<sub>6</sub>H<sub>4</sub>); 129.5 and 128.9 (*m*-C<sub>6</sub>H<sub>4</sub>); 126.9, 125.8, and 123.71 (*m*-C<sub>6</sub>H<sub>3</sub>); 29.7 (C(CH<sub>3</sub>)<sub>2</sub>); 26.2 and 23.5 (C(CH<sub>3</sub>)<sub>2</sub>); 21.2 (CH<sub>3</sub>) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K):  $\delta = 331.1$  (t,  $J_{\text{P-P}} = 506\text{ Hz}$ ) and 173.6 (d,  $J_{\text{P-P}} = 506\text{ Hz}$ ) ppm. MS (ESI, positive mode):  $m/z = 571.3$  [**4b** + H]<sup>+</sup>. UV-vis ( $\lambda/\text{nm } \epsilon$  (M<sup>-1</sup> cm<sup>-1</sup>)): 280 (25637), 345 (36323), and 361 (36539).

#### (ADC<sup>4-Tol</sup>)P<sub>3</sub> (**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 C<sub>34</sub>H<sub>41</sub>N<sub>2</sub>P<sub>3</sub> (570.6): C, 71.56; H, 7.24; N, 4.91; found C, 71.11; H, 7.06; N, 4.65. <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K):  $\delta = 7.59$  (t,  $J = 7.8\text{ Hz}$ , 2H, *p*-C<sub>6</sub>H<sub>3</sub>), 7.38 (d,  $J = 7.8\text{ Hz}$ , 4H, *m*-C<sub>6</sub>H<sub>3</sub>), 7.05 (d,  $J = 8.4\text{ Hz}$ , 2H, C<sub>6</sub>H<sub>4</sub>), 7.02 (d,  $J = 8.3\text{ Hz}$ , 2H, C<sub>6</sub>H<sub>4</sub>), 2.61 (sept,  $J = 6.8\text{ Hz}$ , 4H, CH(CH<sub>3</sub>)<sub>2</sub>), 2.23 (s, 3H, CH<sub>3</sub>), 1.26 (d,  $J = 6.7\text{ Hz}$ , 12H, CH(CH<sub>3</sub>)<sub>2</sub>), and 1.03 (d,  $J = 6.9\text{ Hz}$ , 12H, CH(CH<sub>3</sub>)<sub>2</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K):  $\delta = 167.5$  (d,  $J_{\text{P-C}} = 84.1\text{ Hz}$ , CP); 146.2 (NCN); 143.1, 133.7, 131.7, 129.8, 129.7, 125.8, and 120.9 (C<sub>6</sub>H<sub>3</sub> and C<sub>6</sub>H<sub>4</sub>); 29.7 (CH(CH<sub>3</sub>)<sub>2</sub>); 26.1 and 23.5 (CH(CH<sub>3</sub>)<sub>2</sub>); 21.7 (CH<sub>3</sub>) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K):  $\delta = 329.9$  (t,  $J_{\text{P-P}} = 506\text{ Hz}$ ) and 173.6 (d,  $J_{\text{P-P}} = 506\text{ Hz}$ ) ppm. MS (ESI, positive mode):  $m/z = 571.3$  [**4c** + H]<sup>+</sup>. UV-vis ( $\lambda/\text{nm } \epsilon$  (M<sup>-1</sup> cm<sup>-1</sup>)): 283 (23295), 336 (28771), 346 (29238), and 362 (29676).

#### (ADC<sup>4-DMP</sup>)P<sub>3</sub> (**4d**)

Yield: 94% (0.93 g). Mp:  $270\text{--}273\text{ }^{\circ}\text{C}$  (decomp.). Elem. anal. (%), calcd for C<sub>35</sub>H<sub>44</sub>N<sub>3</sub>P<sub>3</sub> (599.3): C, 70.10; H, 7.40; N, 7.01; found: C, 69.66; H, 7.18; N 6.59. <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K):  $\delta = 7.56$  (t,  $J = 7.8\text{ Hz}$ , 2H, *p*-C<sub>6</sub>H<sub>3</sub>), 7.35 (d,  $J = 7.8\text{ Hz}$ , 4H, *m*-C<sub>6</sub>H<sub>3</sub>), 6.90 (d,  $J = 9.0\text{ Hz}$ , 2H, C<sub>6</sub>H<sub>4</sub>), 6.28 (d,  $J = 9.0\text{ Hz}$ , 2H, C<sub>6</sub>H<sub>4</sub>), 2.88 (s, 6H, N(CH<sub>3</sub>)<sub>2</sub>), 2.67 (sept,  $J = 6.8\text{ Hz}$ , 4H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.24 (d,  $J = 6.7\text{ Hz}$ , 12H, CH(CH<sub>3</sub>)<sub>2</sub>), and 0.97 (d,  $J = 6.8\text{ Hz}$ , 12H, CH(CH<sub>3</sub>)<sub>2</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K):  $\delta = 167.0$  (d,  $J_{\text{P-C}} = 82.8\text{ Hz}$ , CP); 151.9 (NCN); 146.2, 138.4, 134.6, 131.4, 130.8, 126.3, 125.8, and 111.1 (C<sub>6</sub>H<sub>3</sub> and C<sub>6</sub>H<sub>4</sub>); 40.0 (N(CH<sub>3</sub>)<sub>2</sub>); 29.6 (CH(CH<sub>3</sub>)<sub>2</sub>); 25.7 and 23.5 (CH(CH<sub>3</sub>)<sub>2</sub>) ppm. <sup>31</sup>P



$\{^1\text{H}\}$  NMR (202 MHz,  $\text{CD}_2\text{Cl}_2$ , 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):  $m/z = 600.3$  [ $4\text{d} + \text{H}$ ] $^+$ . UV-vis ( $\lambda/\text{nm}$  ( $\epsilon$   $\text{M}^{-1} \text{cm}^{-1}$ )): 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  $\mu\text{mol}$ , calcd for  $\text{Li}_3\text{P}$ ) and  $\text{IPrHCl}$  (80 mg, 188  $\mu\text{mol}$ ) 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.  $^1\text{H}$  NMR (500 MHz,  $\text{C}_6\text{D}_6$ , 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.  $^{31}\text{P}$  NMR ( $\text{C}_6\text{D}_6$ , 298 K, 500 MHz):  $\delta = -134.4$  (d,  $J_{\text{P-H}} = 165.2$  Hz) ppm.  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 298 K, 500 MHz):  $\delta = -134.4$  ppm.

#### Alternative synthesis of 4a and 4c from $i\text{MICs}^{\text{Ar}}$ 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,  $\text{P}_4$  (0.3 g, 2.4 mmol) was added in one portion and the resulting reaction mixture was stirred overnight at rt. The volatiles were removed under vacuum to obtain a dark residue, which was extracted with toluene ( $3 \times 10$  mL). The filtrate was dried in a vacuum to obtain **4a**. Yield: 41% (0.4 g).

$(\text{ADC}^{4\text{-Tol}})_3$  (**4c**). Similarly, treatment of **3c** with  $\text{P}_4$  gave **4c**. Yield: 36% (0.4 g).

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

$[(\text{ADC}^{\text{Ph}})_3]\text{Fe}(\text{CO})_4$  (**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.  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_2\text{Cl}_2$ , 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,  $\text{CD}_2\text{Cl}_2$ , 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 ( $\text{C}_6\text{H}_3$  and  $\text{C}_6\text{H}_5$ ); 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,  $\text{CD}_2\text{Cl}_2$ , 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):  $m/z = 725.1$  [ $5\text{a} + \text{H}$ ] $^+$ . UV-vis ( $\lambda/\text{nm}$  ( $\epsilon$   $\text{M}^{-1} \text{cm}^{-1}$ )): 285 (33061), 328 (31345), and 428 (37184). IR (ATR, diamond):  $\tilde{\nu}/\text{cm}^{-1} = 2041, 1966, 1937, \text{ and } 1919$ .

$[(\text{ADC}^{3\text{-Tol}})_3]\text{Fe}(\text{CO})_4$  (**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.  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_2\text{Cl}_2$ , 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,  $\text{CH}_3$ ), 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,  $\text{CD}_2\text{Cl}_2$ , 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 ( $\text{C}_6\text{H}_3$  and  $\text{C}_6\text{H}_5$ ); 29.8 ( $\text{CH}(\text{CH}_3)_2$ ); 26.1 and 23.6 ( $\text{CH}(\text{CH}_3)_2$ ); 21.2 ( $\text{CH}_3$ ) ppm.  $^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz,  $\text{CD}_2\text{Cl}_2$ , 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):  $m/z = 739.1$  [ $5\text{b} + \text{H}$ ] $^+$ . UV-vis ( $\lambda/\text{nm}$  ( $\epsilon$   $\text{M}^{-1} \text{cm}^{-1}$ )): 282 (35189), 327 (29758), and 416 (37568). IR (ATR, diamond):  $\tilde{\nu}/\text{cm}^{-1} = 2039, 2007, 1962, \text{ and } 1921$ .

$[(\text{ADC}^{\text{Ph}})_3]\text{Mo}(\text{CO})_5$  (**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.  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_2\text{Cl}_2$ , 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,  $\text{CD}_2\text{Cl}_2$ , 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 ( $\text{C}_6\text{H}_3$  and  $\text{C}_6\text{H}_5$ ); 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,  $\text{CD}_2\text{Cl}_2$ , 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):  $\tilde{\nu}/\text{cm}^{-1} = 2065, 2051, 1945, 1925, \text{ and } 1911$ .

$[(\text{ADC}^{4\text{-DMP}})_3]\text{W}(\text{CO})_5$  (**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.  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_2\text{Cl}_2$ , 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,  $\text{C}_6\text{H}_4$ ), 6.33 (d,  $J = 9.2$  Hz, 2H,  $\text{C}_6\text{H}_4$ ), 2.88 (s, 6H,  $\text{N}(\text{CH}_3)_2$ ), 2.60 (sept,  $J$



= 6.8 Hz, 4H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.26 (d, *J* = 6.9 Hz, 12H, CH(CH<sub>3</sub>)<sub>2</sub>), and 1.00 (d, *J* = 6.8 Hz, 12H, CH(CH<sub>3</sub>)<sub>2</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 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 (C<sub>6</sub>H<sub>3</sub> and C<sub>6</sub>H<sub>5</sub>); 40.0 (N(CH<sub>3</sub>)<sub>2</sub>); 29.7 (CH(CH<sub>3</sub>)<sub>2</sub>); 25.6 and 23.6 (CH(CH<sub>3</sub>)<sub>2</sub>) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K): δ = 250.9 (t, *J*<sub>P-P</sub> = 512 Hz, with <sup>183</sup>W satellites, *J*<sub>W-P</sub> = 202 Hz) and 157.0 (d, *J*<sub>P-P</sub> = 505 Hz) ppm. MS (ESI): *m/z* = 924.2 [7 + H]<sup>+</sup>. IR (ATR, diamond):  $\tilde{\nu}/\text{cm}^{-1}$  = 2063, 1978, 1925, and 1907.

## Conclusions

In conclusion, the direct functionalization of white phosphorus (P<sub>4</sub>) with anionic dicarbenes (ADCs) (**2a–2d**) as well as with mesoionic carbenes (iMICs<sup>At</sup>) (**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<sub>2</sub>P<sub>3</sub>-heterocycles **4a–4d** is unprecedented in the P<sub>4</sub> activation by singlet carbenes and main-group compounds. The formation of **4a–4d** suggests unique [3 + 1] fragmentation of P<sub>4</sub> into P<sub>3</sub><sup>+</sup> and P<sup>−</sup>. The former species combines with an ADC to give **4a–4d**, whereas the latter reacts with additional P<sub>4</sub> to form (P<sub>7</sub>)<sup>3−</sup> that can be isolated as Li<sub>3</sub>P<sub>7</sub>. Electronic structures of **4a–4d** have been analyzed by computational studies, which, along with the crystallographic data, show that both C<sub>3</sub>N<sub>2</sub>- and C<sub>2</sub>P<sub>3</sub>-rings of **4a–4d** are 6π-electron aromatic systems. Thus, **4a–4d** can be considered as neutral analogues of cyclopentadienyl anions. The C<sub>2</sub>P<sub>3</sub>-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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## 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.

