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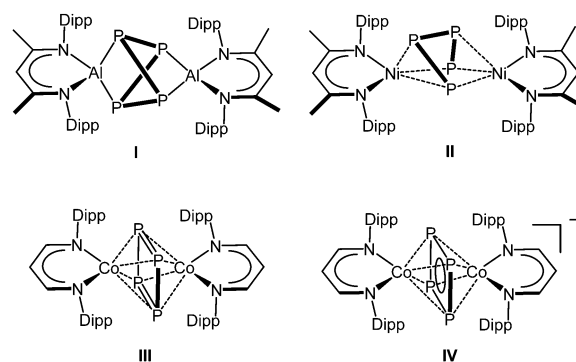
# Reductive cleavage of P<sub>4</sub> by iron(i) centres: synthesis and structural characterisation of Fe<sub>2</sub>(P<sub>2</sub>)<sub>2</sub> complexes with two bridging P<sub>2</sub><sup>2-</sup> ligands†

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The selective transformation of white phosphorus with a β-diketiminato iron(i) toluene complex under mild reaction conditions is reported which furnishes a new dinuclear iron(III) Fe<sub>2</sub>(P<sub>2</sub>)<sub>2</sub> complex with two bridging P<sub>2</sub><sup>2-</sup> ligands. Its reduction with potassium results in the formation of the first delocalised mixed-valent bis-diphosphido iron(II,III) complex which is isostructural with the neutral Fe<sub>2</sub>P<sub>4</sub> precursor.

The exploration of low-valent transition metal (TM) complexes for coordination and subsequent reduction of white phosphorus (P<sub>4</sub>) is an important topic of current interest because metal-catalysed P<sub>4</sub> derivatisation has been suggested to be an environmentally benign synthetic route for the synthesis of desirable organophosphorus compounds.<sup>1</sup> During the past decades, several low-valent TM systems have been examined for transformation of P<sub>4</sub>. With a few exceptions,<sup>1,2</sup> the approaches involve the use of cyclopentadienyl and/or carbonyl TM complexes under harsh conditions (thermal and/or photochemical) resulting in unpredictable P<sub>4</sub> fragmentation. Thus new low-valent metal complex systems that are capable to transform P<sub>4</sub> with high selectivity under mild conditions are highly desired.

Low-valent TM and main group element complexes supported by the β-diketiminato scaffold have been successfully utilised to activate a variety of small molecules, including P<sub>4</sub>.<sup>3</sup> In 2004, Roesky *et al.* described the reduction of P<sub>4</sub> with the monovalent aluminum Me<sup>L</sup>DippAl (Me<sup>L</sup>Dipp = CH[CMeN(2,6-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>]), yielding [(Me<sup>L</sup>Dipp)<sub>2</sub>Al<sub>2</sub>(μ<sub>2</sub>:η<sup>2</sup>,η<sup>2</sup>-P<sub>4</sub>)] (I, Scheme 1) bearing the P<sub>4</sub><sup>4-</sup> ligand.<sup>3d</sup> Recently we



Scheme 1 Selected P<sub>4</sub> transformation products I–IV mediated by low-valent β-diketiminato metals.

communicated the coordination of P<sub>4</sub> by a β-diketiminato ligand supported monovalent nickel species under very mild conditions, leading to the [(Me<sup>L</sup>Dipp)<sub>2</sub>Ni<sub>2</sub>(μ<sub>2</sub>:η<sup>3</sup>,η<sup>3</sup>-P<sub>4</sub>)] complex (II).<sup>3g</sup> Applying a slightly modified β-diketiminato ligand, we developed the corresponding monovalent cobalt complex, which can perform facile transformation of P<sub>4</sub> to afford [(L<sup>Dipp</sup>Co)<sub>2</sub>(μ<sub>2</sub>:η<sup>4</sup>,η<sup>4</sup>-P<sub>4</sub>)] (III, L<sup>Dipp</sup> = CH[CHN(2,6-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>]) as the first complex featuring a neutral, rectangular-planar cyclo-P<sub>4</sub> ligand.<sup>3h</sup> Interestingly, treating III with one molar equivalent of potassium graphite transforms the rectangular cyclo-P<sub>4</sub> moiety to the square-planar cyclo-P<sub>4</sub><sup>2-</sup> in IV as an anion. Similar cyclo-P<sub>4</sub><sup>2-</sup> and cyclo-P<sub>4</sub><sup>4-</sup> inverted sandwich β-diketiminato Nb and Ta complexes were more recently described by Bergman and Arnold *et al.*<sup>3i</sup> In this contribution, we report on the P<sub>4</sub> transformation with a β-diketiminato ligand supported iron(i) species [L<sup>Dipp</sup>Fe-toluene] (2, Scheme 2), affording selectively the dinuclear iron(III) complex [(L<sup>Dipp</sup>Fe)<sub>2</sub>(μ<sub>2</sub>:η<sup>2</sup>,η<sup>2</sup>-P<sub>2</sub>)<sub>2</sub>] (3) with two P<sub>2</sub> dianionic ligands. Remarkably, the reduction of 3 results in the delocalised mixed-valent iron(II,III) complex [(L<sup>Dipp</sup>Fe)<sub>2</sub>(μ<sub>2</sub>:η<sup>2</sup>,η<sup>2</sup>-P<sub>2</sub>)<sub>2</sub>]-[K(thf)<sub>6</sub>] (4) comprising the same diphosphorus ligands of the oxidised species.

The iron(i) precursor complex 2 can be readily prepared in a one-pot synthesis (Scheme 2). The lithiation of the β-diketiminato ligand [L<sup>Dipp</sup>H] (1)<sup>4a</sup> with <sup>n</sup>BuLi in THF, followed by metathesis

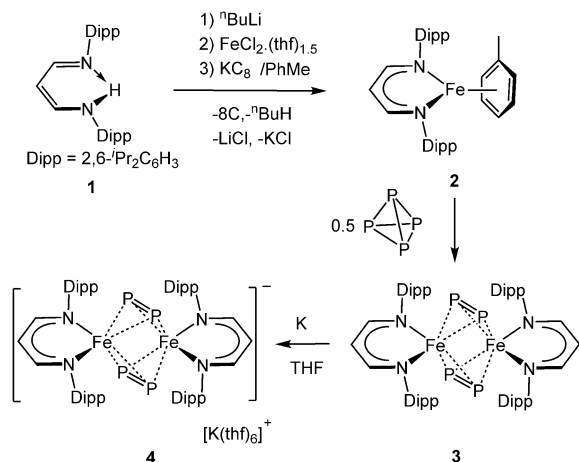
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† Electronic supplementary information (ESI) available: The detailed synthesis, characterisation and crystallographic data of 2, 3, and 4 as well as the computational details of 3 and 4. CCDC 1042230–1042232. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5cc00147a



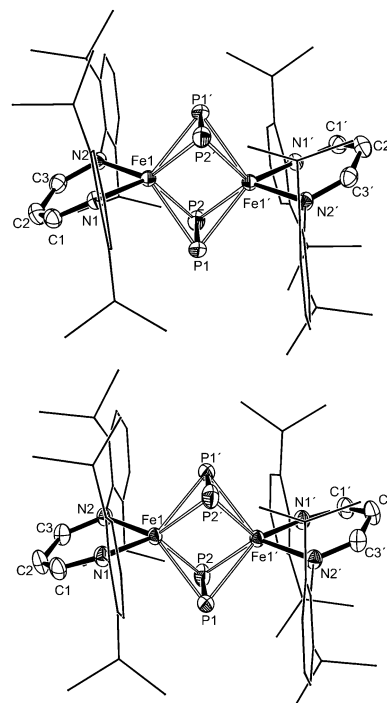


**Scheme 2** Synthesis of  $\beta$ -diketiminato iron(II) complex **2** and the transformation of  $P_4$  to iron complexes **3** and **4**.

with  $FeCl_2(thf)_{1.5}$ ,<sup>4b</sup> leads to a yellow solid after removal of the solvent. Subsequent reduction of this solid dissolved in toluene with potassium graphite furnishes the desired iron(I) toluene complex **2** as dark green crystals in 75% isolated yield after work-up. Complex **2** is paramagnetic as evidenced by the room-temperature magnetic moment of  $1.83 \mu_B$  in solution. The single crystal X-ray diffraction study confirms its constitution (Fig. S1, ESI<sup>†</sup>). It is a mononuclear species with an  $\eta^6$ -toluene ligand bound to the iron centre reminiscent to the low-spin  $\beta$ -diketiminato complex iron(I) [ $MeL^{Dipp}Fe(\eta^6\text{-benzene})$ ], previously reported by Cundari, Rodgers, and Holland *et al.*<sup>5</sup>

Treatment of **2** in toluene solution with half an equivalent of  $P_4$  at room temperature affords a green precipitate of **3** (Scheme 2). After work-up, complex **3** could be isolated as a dark-green solid in approx. 90% yield. It is noteworthy that complex **3** is the only product of this reaction and results even with excess amounts of white phosphorus. Its composition was verified by elemental analysis and ESI mass spectrometry. Single crystals of **3** suitable for X-ray diffraction analysis could be obtained in benzene solutions.

The crystal structure of **3** revealed a centrosymmetric dinuclear iron complex, supported by two puckered  $\beta$ -diketiminato ligands (Fig. 1). The iron centres are bridged by two diphosphorus ligands in a  $\mu_2:\eta^2, \eta^2$ -coordination mode. A similar  $[(Fe)_2(\mu_2:\eta^2, \eta^2-P_2)_2]$  core was previously proposed by Dahl and Barr<sup>6</sup> for  $[(C_5Me_5)_2(Fe)_2(\mu_2:\eta^2, \eta^2-P_2)_2]$  (**V**) but – due to a severe disorder of the diphosphorus ligands – the solid state structure could not be fully refined. The  $Fe \cdots Fe$  distance of  $2.777 \text{ \AA}$  in **3** is significantly longer than that observed in **V** ( $2.585(6) \text{ \AA}$ ) and rules out the presence of an  $Fe-Fe$  bond in the complex. The  $P \cdots P$  distance ( $P2-P1'$  and  $P2'-P1$ ) between the two diphosphorus units ( $3.325 \text{ \AA}$ ) also excludes any attractive  $P \cdots P$  interaction between the two  $P_2$  fragments. This is in contrast to the  $\beta$ -diketiminato cobalt  $P_4$  complex **III**,<sup>3h</sup> for which two long  $P-P$  single bonds ( $2.298(1) \text{ \AA}$ ) along with two short  $P-P$  bonds ( $2.124(1) \text{ \AA}$ ) were observed. In fact, the  $P_4$  unit in **3** has been cleaved into two  $P_2$  moieties. The  $P-P$  distance of **3** ( $2.036(2) \text{ \AA}$ ) within these  $P_2$  moieties are shorter than those typically observed for a  $P-P$  single bond ( $2.20-2.25 \text{ \AA}$ ) and lie in the range of a  $P-P$  double bond ( $2.00-2.05 \text{ \AA}$ ). The latter is slightly shorter than the  $P-P$  bond lengths of



**Fig. 1** Molecular structures of **3** (top) and the anion in **4**-THF (bottom). Hydrogen atoms and solvents molecule are omitted for clarity. Thermal ellipsoids are drawn at 50% probability level. Symmetry transformations used to generate equivalent atoms (') are  $-x + 1, -y + 2, -z$  (for **3**);  $-x + 1, -y + 2, -z + 1$  (for the anion in **4**-THF). Selected distances ( $\text{\AA}$ ) and angles ( $^\circ$ ) for **3**:  $Fe1-N1$   $2.023(3)$ ,  $Fe1-N2$   $2.025(3)$ ,  $Fe1-P1'$   $2.344(1)$ ,  $Fe1-P2'$   $2.356(1)$ ,  $Fe1-P1$   $2.373(1)$ ,  $Fe1-P2$   $2.377(1)$ ,  $P1-P2$   $2.036(2)$ ,  $N1-Fe1-N2$   $93.1(1)$ ,  $Fe1 \cdots Fe1'$   $2.777(2)$ ; selected distances ( $\text{\AA}$ ) and angles ( $^\circ$ ) for the anion of **4**:  $Fe1-N2$   $2.039(2)$ ,  $Fe1-N1$   $2.042(2)$ ,  $Fe1-P2'$   $2.3560(5)$ ,  $Fe1-P1'$   $2.3600(5)$ ,  $Fe1-P1$   $2.3669(5)$ ,  $Fe1-P2$   $2.3738(5)$ ,  $P1-P2$   $2.0353(8)$ ,  $N2-Fe1-N1$   $91.56(6)$ ,  $Fe1 \cdots Fe1'$   $2.871(5)$ .

$[(C_5Me_5)_2(Co)_2(\mu_2:\eta^2, \eta^2-P_2)_2]$  ( $2.053(4)$  and  $2.058(4) \text{ \AA}$ ).<sup>6</sup> It is noteworthy that such  $P_2$  units represent an important type of transformation products resulting from TM-mediated degradation of  $P_4$ .<sup>1</sup> Generally, the  $P_2$  unit may behave as either a four or eight electron donor toward metal centres depending on the coordination environments.<sup>7</sup>

The cyclic voltammogram of **3**, recorded in a THF solution containing  $0.3 \text{ M } nBu_4NPF_6$  as electrolyte at  $295 \text{ K}$ , revealed a reversible redox event centred at  $E_{1/2} = -1.5 \text{ V}$  (*vs.*  $Fc/Fc^+$ ) and additionally one quasi-reversible electron transfer, possibly coupled to a succeeding chemical reaction, at  $E_{1/2} = -2.8 \text{ V}$  (for further details see ESI<sup>†</sup>). Accordingly, we performed the reduction of **3** with one equivalent of potassium in THF at room temperature (Scheme 2). A colour change from green to brown-red was observed during the period of reaction, leading to the formation of reduction product **4** that was isolated in 75% yield as a dark brown crystalline solid. Complex **4** crystallised in THF as a separated ion pair. The potassium cation is coordinated by six disordered THF molecules. Interestingly, the geometric parameters of the anion of **4** are almost identical to those observed for its  $Fe_2P_4$  precursor **3** (Fig. 1 and Table 1). The apparent differences in the molecular structures of **3** and the anion of **4** are the  $P \cdots P$  distance between the two ( $\mu_2:\eta^2, \eta^2-P_2$ )



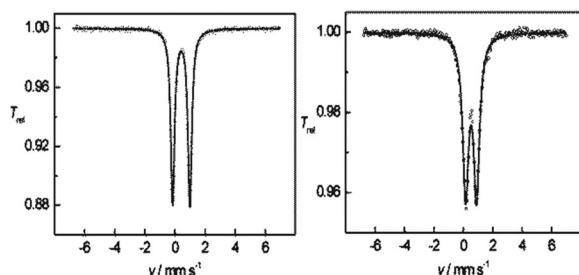
**Table 1** Comparison of the P–P distances and Mayer Bond Order (MBO) in **3**, **4**, and  $[(C_5Me_5)_2Fe_2(\mu_2-\eta^2,\eta^2-P_2)_2] (V)^6$

Complex		<b>3</b>	<b>4</b>	<b>V</b>
P–P distance (short)	Exp. (Å)	2.036(2)	2.0353(8)	—
	Calc. (Å)	2.044	2.033	2.118
	MBO	1.53	1.63	1.39
P··P distance (long)	Exp. (Å)	3.325	3.325	—
	Calc. (Å)	3.243	3.318	3.185
	MBO	0.17	0.05	0.01

subunits (3.158 Å for **4** vs. 3.3235 Å for **3**) and the Fe··Fe distance (2.8713(5) Å for **4** vs. 2.777(2) Å for **3**).

The striking similarity of the two  $\mu_2\eta^2,\eta^2-P_2$  subunits in **3** and **4** prompted us to determine the oxidation states of the iron centres by  $^{57}Fe$  Mössbauer spectroscopy. The Mössbauer spectrum of **3**, recorded at 77 K in a zero-field, exhibits a single quadrupole doublet with a quadrupole splitting ( $\Delta E_Q$ ) of 1.15(1) mm s $^{-1}$  and an isomer shift ( $\delta$ ) of 0.42(1) mm s $^{-1}$ , suggesting the presence of two equivalent high-spin iron(III) centres in **3** (Fig. 2). The Mössbauer spectrum of **4**, recorded under the same conditions, to our surprise, also displayed a single quadrupole doublet with a slightly higher isomer shift and  $\delta = 0.53(1)$  mm s $^{-1}$  and a smaller quadrupole splitting  $\Delta E_Q = 0.74(1)$  mm s $^{-1}$ . Interestingly, the latter isomer shift is intermediate between the values expected for ferric and ferrous localised high-spin iron sites.<sup>8</sup> On the time scale of Mössbauer spectroscopy (*ca.* 10 $^{-7}$  s) no localised Fe(II)/Fe(III) state could be identified suggesting fast charge exchange. It is worth mentioning that such an unusual, delocalised system, evidenced by Mössbauer spectroscopy, is scarce and was previously reported only for  $[(LFe)_2(\mu-OH)_3][ClO_4]_2$  (L = N,N',N''-trimethyl-1,4,7-triazacyclononane) and the porphyrin–phthalocyanine mixed-ligand  $[Fe_2(\mu-N)]$  complex.<sup>9</sup>

Both complexes **3** and **4** are paramagnetic in solution as well as in the solid state. Applying the Evans-method<sup>10</sup> for the determination of the magnetic moment of **3** and **4**, in THF-*d*<sub>8</sub> solution revealed room temperature magnetic moments of 1.12 and 4.50  $\mu_B$ , respectively. Additionally, the solid-state magnetic susceptibility measurements in the temperature range from 300 to 2 K, carried out with an applied magnetic field B of 1.0 T, exhibited a temperature-dependent effective magnetic moment



**Fig. 2** Zero-field  $^{57}Fe$  Mössbauer spectra of **3** (left) and **4** (right) recorded at 77 K. The solid lines are fits of the experimental values with Lorentzian doublets exhibiting isomer shifts,  $\delta$ , quadrupole splittings,  $\Delta E_Q$ , and line-widths,  $\Gamma$ :  $\delta = 0.42(1)$  mm s $^{-1}$ ,  $\Delta E_Q = 1.15(1)$  mm s $^{-1}$ ,  $\Gamma = 0.30(1)$  mm s $^{-1}$  (**3**);  $\delta = 0.53(1)$  mm s $^{-1}$ ,  $\Delta E_Q = 0.74(1)$  mm s $^{-1}$ ,  $\Gamma = 0.48(1)$  mm s $^{-1}$  (**4**).

for both complexes (Fig. S9 and S10 in ESI $^\dagger$ ). For complex **3**, the  $\mu_{eff}$  varies slightly from 1.70 to 1.90  $\mu_B$  at temperatures between 20 and 300 K. In the case of **4**, the effective magnetic moment is significantly more temperature dependent and increases from 2.0 to 3.9  $\mu_B$  as the temperature increases from 2 to 300 K.

The electronic nature of **3** and the the naion of **4** has been elucidated by broken-symmetry DFT calculations at the (B3LYP/6-31G(d)//BP86/6-31G(d) [P, Fe: aug-cc-pVTZ]) levels (see Table 1 and ESI $^\dagger$ ). The calculated metric parameters are in good agreement with those obtained by X-ray diffraction analyses. The Mayer Bond Order (MBO) suggests that the short P–P bonds have significant double bond character (MBO = 1.53 for **3** and 1.63 for **4** (Table 1)) as indicated also by NBO analysis (Fig. S11 and S12, ESI $^\dagger$ ). The negative charge on the P atoms in **3** (−0.16, Table S4, ESI $^\dagger$ ) confirms that the P<sub>2</sub> moiety is best described as dianionic P<sub>2</sub><sup>2−</sup> (P=P dianion) while the NBO analysis indicated that the iron centres are in +3 oxidation state (Fig. S11 and S12, Table S4, ESI $^\dagger$ ). Interestingly, the one electron reduction of **3** does not change the electronic structure of the P<sub>2</sub><sup>2−</sup> moiety (charge: −0.19, Table S4, ESI $^\dagger$ ) but the iron centres since one Fe is reduced to +2 oxidation state which can be monitored from the charge (+0.16 compared to the previous +0.36) and net spin density (2.26 drops to 1.62).

We also calculated the optimised geometry and the electronic structure of the previously proposed  $[(C_5Me_5)Fe(\mu_2-\eta^2,\eta^2-P_2)]_2$  **V** by Dahl and Barr.<sup>6</sup> The short (2.118 Å) and long P–P distances (3.185 Å) are quite similar to that of **3** (Table 1), respectively. However, the Fe–Fe distance (2.552 Å) is significantly shorter than that in **3** (2.778 Å). We found that the P<sub>2</sub> moiety can be regarded as a P<sub>2</sub><sup>2−</sup> unit because it also shows double bonding character as **3** and the P atoms bear partial negative charge (−0.17, Table S4, ESI $^\dagger$ ). The short Fe–Fe distance has, however, an important consequence, namely, the direct exchange interaction becomes dominant between the iron centres and thus the ground state adopts high spin character (Table S4, ESI $^\dagger$ ). NBO analysis even indicates a Fe–Fe bond which clearly distinguishes **V** from **3**.

In summary, the  $\beta$ -diketiminato iron(I) complex **2** reacts readily with P<sub>4</sub> to yield the diiron(III) complex **3** with two P<sub>2</sub><sup>2−</sup> ligands. One-electron reduction of **3** results in the formation of **4** by reducing one Fe(+3) centre to Fe(+2) without significantly changing the geometry of the  $[(Fe)_2(\mu_2-\eta^2,\eta^2-P_2)_2]$  core. Remarkably, the mixed-valent iron(II,III) pair of **4** is delocalised as evidenced by Mössbauer spectroscopy and represents a rare case of that type. The facile and selective transformation of P<sub>4</sub> by  $\beta$ -diketiminato low-valent TM species opens new possibilities to further functionalise the P<sub>2</sub> units; respective investigations are currently pursued by our group.

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