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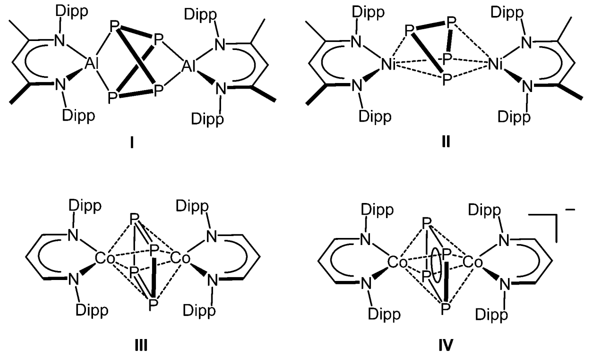
Reductive cleavage of P_4 by iron(I) centres: synthesis and structural characterisation of $Fe_2(P_2)_2$ complexes with two bridging P_2^{2-} ligands†

Shenglai Yao,[a] Tibor Szilvási,[b] Nils Lindenmaier,[a] Yun Xiong,[a] Shigeyoshi Inoue,[a] Mario Adelhardt,[c] Jörg Sutter,[c] Karsten Meyer[c] and Matthias Driess*[a]

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) $Fe_2(P_2)_2$ complex with two bridging P_2^{2-} 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_2P_4 precursor.

The exploration of low-valent transition metal (TM) complexes for coordination and subsequent reduction of white phosphorus (P_4) is an important topic of current interest because metal-catalysed P_4 derivatisation has been suggested to be an environmentally benign synthetic route for the synthesis of desirable organophosphorus compounds.[1] During the past decades, several low-valent TM systems have been examined for transformation of P_4. With a few exceptions,[1,2] the approaches involve the use of cyclopentadienyl and/or carbonyl TM complexes under harsh conditions (thermal and/or photochemical) resulting in unpredictable P_4 fragmentation. Thus new low-valent metal complex systems that are capable to transform P_4 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_4.[3] In 2004, Roesky *et al.* described the reduction of P_4 with the monovalent aluminum $^{Me}L^{Dipp}Al$ ($^{Me}L^{Dipp}$ = $CH[CMeN(2,6\text{-}^iPr_2C_6H_3)]_2$), yielding $[(^{Me}L^{Dipp})_2\text{-}Al_2(\mu\text{:}\eta^2,\eta^2\text{-}P_4)]$ (**I**, Scheme 1) bearing the P_4^{4-} ligand.[3d] Recently we communicated the coordination of P_4 by a β-diketiminato ligand supported monovalent nickel species under very mild conditions, leading to the $[(^{Me}L^{Dipp})_2Ni_2(\mu_2\text{:}\eta^3,\eta^3\text{-}P_4)]$ complex (**II**).[3g] Applying a slightly modified β-diketiminato ligand, we developed the corresponding monovalent cobalt complex, which can perform facile transformation of P_4 to afford $[(L^{Dipp}Co)_2(\mu_2\text{:}\eta^4,\eta^4\text{-}P_4)]$ (**III**, L^{Dipp} = $CH[CHN(2,6\text{-}^iPr_2C_6H_3)]_2$) as the first complex featuring a neutral, rectangular-planar cyclo-P_4 ligand.[3h] Interestingly, treating **III** with one molar equivalent of pottasium graphite transforms the rectangular cyclo-P_4 moiety to the square-planar cyclo-P_4^{2-} in **IV** as an anion. Similar cyclo-P_4^{2-} and cyclo-P_4^{4-} inverted sandwich β-diketiminato Nb and Ta complexes were more recently described by Bergman and Arnold *et al.*[3i] In this contribution, we report on the P_4 transformation with a β-diketiminato ligand supported iron(I) species $[L^{Dipp}Fe\cdot toluene]$ (**2**, Scheme 2), affording selectively the diculear iron(III) complex $[(L^{Dipp}Fe)_2(\mu_2\text{:}\eta^2,\eta^2\text{-}P_2)_2]$ (**3**) with two P_2 dianionic ligands. Remarkably, the reduction of **3** results in the delocalised mixed-valent iron(II,III) complex $[(L^{Dipp}Fe)_2(\mu_2\text{:}\eta^2,\eta^2\text{-}P_2)_2]\text{-}[K(thf)_6]$ (**4**) comprising the same diphosphorus ligands of the oxidised species.



Scheme 1 Selected P_4 transformaiton products **I–IV** mediated by low-valent β-diketiminato metals.

The iron(I) precursor complex **2** can be readily prepared in a one-pot synthesis (Scheme 2). The lithiation of the β-diketiminto ligand $[L^{Dipp}H]$ (**1**)[4a] with ^nBuLi in THF, followed by metathesis

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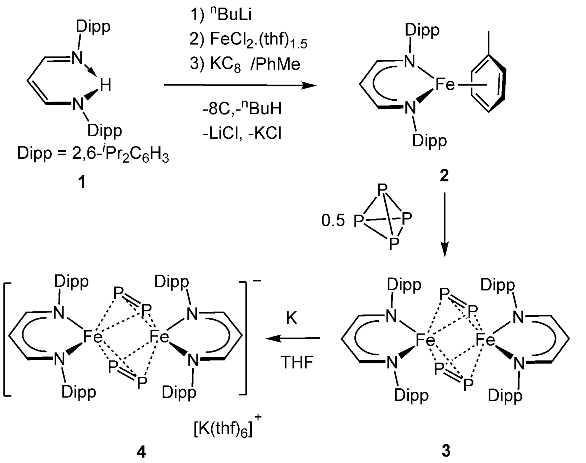
[a] *Technische Universität Berlin, Department of Chemistry: Metalorganics and Inorganic Materials, Sekr. C2, Strasse des 17. Juni 135, D-10623 Berlin, Germany. E-mail: matthias.driess@tu-berlin.de; Fax: +49 (0)30-314-29732; Tel: +49 (0)30-314-29731*

[b] *Department of Inorganic and Analytical Chemistry, Budapest University of Technology and Economics, Szent Gellért tér 4, 1111 Budapest, Hungary*

[c] *Inorganic Chemistry, Department of Chemistry and Pharmacy, Friedrich-Alexander-University Erlangen-Nürnberg (FAU), Egerlandstrasse 1, 91058 Erlangen, Germany*

† 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 β-diketiminato iron(I) complex **2** and the transformation of P_4 to iron complexes **3** and **4**.

with $FeCl_2(thf)_{1.5}$,[4b] 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 μ_B in solution. The single crystal X-ray diffraction study confirms its constitution (Fig. S1, ESI†). It is a mononuclear species with an η^6-toluene ligand bound to the iron centre reminiscent to the low-spin β-diketiminato complex iron(I) [$^{Me}L^{Dipp}Fe(\eta^6$-benzene)], previously reported by Cundari, Rodgers, and Holland *et al.*[5]

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 β-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 [$(Fe)_2(\mu_2{:}\eta^2,\eta^2\text{-}P_2)_2$] core was previously proposed by Dahl and Barr[6] for [$(C_5Me_5)_2(Fe)_2(\mu_2{:}\eta^2,\eta^2\text{-}P_2)_2$] (**V**) but – due to a severe disorder of the diphosphorus ligands – the solid state structure could not be fully refined. The Fe···Fe distance of 2.777 Å in **3** is significantly longer than that observed in **V** (2.585(6) Å) and rules out the presence of an Fe–Fe bond in the complex. The P···P distance (P2–P1′ and P2′–P1) between the two diphosphorus units (3.325 Å) also excludes any attractive P···P interaction between the two P_2 fragments. This is in contrast to the β-diketiminato cobalt P_4 complex **III**,[3h] for which two long P–P single bonds (2.298(1) Å) along with two short P–P bonds (2.124(1) Å) 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) Å) within these P_2 moieties are shorter than those typically observed for a P–P single bond (2.20–2.25 Å) and lie in the range of a P–P double bond (2.00–2.05 Å). The latter is slightly shorter than the P–P bond lengths of [$(C_5Me_5)_2(Co)_2(\mu_2{:}\eta^2,\eta^2\text{-}P_2)_2$] (2.053(4) and 2.058(4) Å).[6] It is noteworthy that such P_2 units represent an important type of transformation products resulting from TM-mediated degradation of P_4.[1] Generally, the P_2 unit may behave as either a four or eight electron donor toward metal centres depending on the coordination environments.[7]

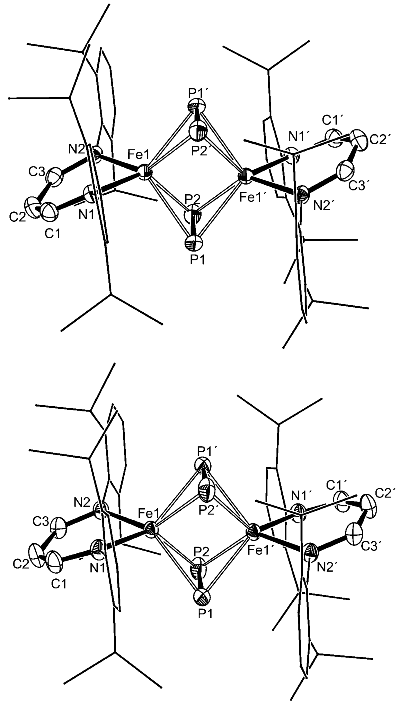


Fig. 1 Molecular structures of **3** (top) and the anion in **4**·THF (bottom). Hydrogen atoms and solvents molecule are omitted for clarity. Thermal ellipsoids are drawn at 50% probability level. Symmetry transformations used to generate equivalent atoms (′) are $-x + 1, -y + 2, -z$ (for **3**); $-x + 1, -y + 2, -z + 1$ (for the anion in **4**·THF). Selected distances (Å) and angles (°) 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···Fe1′ 2.777(2); selected distances (Å) and angles (°) 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···Fe1′ 2.871(5).

The cyclic voltammogram of **3**, recorded in a THF solution containing 0.3 M $^nBu_4NPF_6$ as electrolyte at 295 K, revealed a reversible redox event centred at $E_{1/2} = -1.5$ V (*vs.* Fc/Fc$^+$) and additionally one quasi-reversible electron transfer, possibly coupled to a succeeding chemical reaction, at $E_{1/2} = -2.8$ V (for further details see ESI†). 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···P distance between the two ($\mu{:}\eta^2,\eta^2\text{-}P_2$)

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

Complex		3	4	V
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 $\mu{:}\eta^2,\eta^2\text{-}P_2$ 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 (ΔE_Q) of 1.15(1) mm s^{-1} and an isomer shift (δ) 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 δ = 0.53(1) mm s^{-1} and a smaller quadrupole splitting ΔE_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.[8] 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 $[(LFe)_2(\mu\text{-}OH)_3][(ClO_4)_2]$ (L = *N*,*N*′,*N*″-trimethyl-l,4,7-triazacyclononane) and the porphyrin–phthalocyanine mixed-ligand $[Fe_2(\mu\text{-}N)]$ complex.[9]

Both complexes **3** and **4** are paramagnetic in solution as well as in the solid state. Applying the Evans-method[10] for the determination of the magnetic moment of **3** and **4**, in THF-d_8 solution revealed room temperature magnetic moments of 1.12 and 4.50 μ_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 for both complexes (Fig. S9 and S10 in ESI†). For complex **3**, the μ_{eff} varies slightly from 1.70 to 1.90 μ_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 μ_B as the temperature increases from 2 to 300 K.

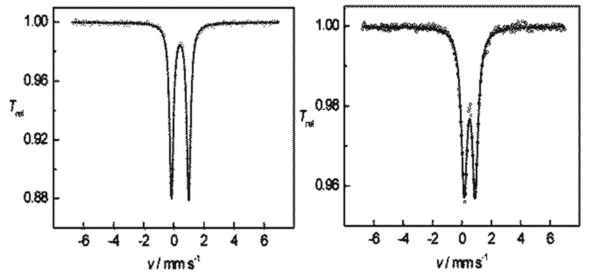


Fig. 2 Zero-field ^{57}Fe Mössbauer spectra of **3** (left) and **4** (right) recorded at 77 K. The solid lines are fits of the experimental values with Lorentzian doublets exhibiting isomer shifts, δ, quadrupole splittings, ΔE_Q, and line-widths, Γ: δ = 0.42(1) mm s^{-1}, ΔE_Q = 1.15(1) mm s^{-1}, Γ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

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†). 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†). The negative charge on the P atoms in **3** (−0.16, Table S4, ESI†) confirms that the P_2 moiety is best described as dianionic P_2^{2-} (P=P dianion) while the NBO analysis indicated that the iron centres are in +3 oxidation state (Fig. S11 and S12, Table S4, ESI†). Interestingly, the one electron reduction of **3** does not change the electronic structure of the P_2^{2-} moiety (charge: −0.19, Table S4, ESI†) 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 optmised geometry and the electronic structure of the previously proposed $[\{(C_5Me_5)Fe(\mu_2{:}\eta^2,\eta^2\text{-}P_2)\}_2]$ **V** by Dahl and Barr.[6] 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_2 moiety can be regarded as a P_2^{2-} unit because it also showes double bonding character as **3** and the P atoms bear partial negative charge (−0.17, Table S4, ESI†). 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†). NBO analysis even indicates a Fe–Fe bond which clearly distinguishes **V** from **3**.

In summary, the β-diketiminato iron(I) complex **2** reacts readily with P_4 to yield the diiron(III) complex **3** with two P_2^{2-} 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 $[(Fe)_2(\mu_2{:}\eta^2,\eta^2\text{-}P_2)_2]$ 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_4 by β-diketiminato low-valent TM species opens new possibilities to further functionalise the P_2 units; respective investigations are currently pursued by our group.

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