P₄ Activation

Influence of the nacnac Ligand in Iron(I)-Mediated P₄ Transformations
Fabian Spitzer, Christian Graßl, Gábor Balázs, Eva M. Zolnhofer, Karsten Meyer, and Manfred Scheer*

Dedicated to Professor Hangeorg Schnöckel on the occasion of his 75th birthday

Abstract: A study of P₄ transformations at low-valent iron is presented using β-diketiminato (L) Fe⁺ complexes [LFe(tol)] (tol = toluene; L = L¹ (1a), L² (1b), L³ (1c)) with different combinations of aromatic and backbone substituents at the ligand. The products {[LFe(m,t,P₄)]} (L = L¹ (2a), L² (2b)) containing a P₄ core were obtained by the reaction of 1a,b with P₄ in toluene at room temperature. Using a slightly more sterically encumbered ligand in 1c results in the formation of {[LFe(m,t,P₄)]} (2c), possessing a cyclo-P₄ moiety. Compounds 2a–c were comprehensively characterized and their electronic structures investigated by SQUID magnetization and ¹³⁷Fe Mössbauer spectroscopy as well as by DFT methods.

The activation of white phosphorus (P₄) with main-group and transition-metal compounds is an ongoing area of research. The latter topic is dominated by Cp³ containing transition-metal complexes. More recently, complexes of the β-diketiminato (nacnac = L) ligand have been employed for P₄ activation as well. For early transition-metal compounds, exclusively Group 5 complexes were used, whereas for electron-rich metals Group 8–10 complexes have been applied so far. Selected examples of P₄ complexes A–D with β-diketiminato ligands of late transition metals are shown in Figure 1. Recently, we reported on the Cu¹ compounds (L)[Cu(m,t,P₄)] (E = P (D), As) and (LCu(t,P₄)), respectively, containing intact E₄ moieties, while all other examples (A–C) contain transformed P₄ units. Also, we investigated the reaction of Fe³ complexes [LFe(tol)] with P₄. When the Driess group recently reported on the formation of the Fe³⁺ complex {[LFe(m,t,P₄)]} (A), containing two diatomic P₄ ligands, we were surprised as our investigations showed quite different results. Since the reaction conditions were identical, we supposed that the reason for the different P₄ activation pathways (and products) was due to the slightly different aromatic flanking groups and α-backbone substituents of our [LFe(tol)] precursors. Therefore, we systematically studied the driving forces for the different outcome of P₄ activation by Fe³⁺ centers.

Herein, we present a comparative study of P₄ activation by Fe¹ [β-diketiminato (L) complexes [LFe(tol)] (L = L¹ (1a), L² (1b), L³ (1c)) with toluene (tol) as a labile leaving group. The starting materials [LFe(tol)] (L = L¹ (1a), L² (1b), L³ (1c)) were synthesized in a one-pot synthesis (see the Supporting Information) and characterized by single-crystal X-ray crystallography (1b and 1c, see the Supporting Information).

The reaction of [L²Fe(tol)] (1a) with 0.5 equivalent of P₄ in toluene at room temperature leads to the formation of a tetranuclear complex, namely {[L²Fe(m,t,P₄)]} (2a), which displays a realgar-type P₄ moiety. Changing the stoichiometry of the reaction does not affect the product formation (ratio [L²Fe(tol)]/[P₄] = 2:1 and 1:2). The formation of a P₄ moiety in 2a is in contrast to the recently reported product, {[L³Fe(m,t,P₄)]} (A), published by the Driess group, which contains two [P₄]²⁺ ligands (Scheme 1). A comparison of ligand L¹ with L², however, displays only small differences in the aromatic (Ph² = dipp (2,6-diisopropylphenyl) or dmp (2,6-dimethylphenyl)) and in the backbone (R) substituents. In both cases the reaction conditions were identical. Therefore, we were interested to understand whether the steric demand or the electronic properties of the aromatic flanking groups Ph² and backbone α-substitu-

Figure 1. Selected examples of P₄ complexes with late transition metals Fe, Co, Ni, and Cu supported by the β-diketiminato ligand.¹⁰,¹¹
precursors and 2.2111(6) to 2.2792(6) (o;3win $^2b_m$ = and between 1.982(2) and 1.990(2) (o;3win $^2b_m$ = Ar epresentation of with ligands $^2a$ in [D $^2b_m$ in C $^2b_m$ the upper value corresponds to $^2a$ and $^2b_m$; and (in $^2b_m$ = 55 under identical conditions For $^2b_m$ was $^2b_m$ for $^2b_m$ is more stable than the nonet $^2a$ for $^2b_m$ moity (nonet spin state) is endothermic in [D $^2b_m$ = for $^2b_m$ is the only product of (Scheme 1). Top: Comparison of $^2a$ with its complete ligands is (Scheme 1). Top: Comparison of $^2a$ with its complete ligands is (Scheme 1).

Scheme 1. Top: Comparison of $^2a$ with ligands $^2a$ $^2b_m$ and $^2a$ containing a variety of different substituents. Bottom: Coordinated $^2a_m$ moieties obtained by $^2a_m$ transformation with different Fe$^2_m$ precursors. The gray numbers in brackets represent the NPA charges at the corresponding atoms.$^{[5]}$ For $^2a,b$ the upper value corresponds to $^2a$.

ents R cause the different reactivity of the Fe$^2$ precursors towards $^2a_m$. According to DFT calculations at the BP86/def2-SVP/def2-TZVP (N, Fe, P) level, the dimerization of the hypothetical complex [(L$^2Fe$)$_2$($mu$-$pi^*$$pi^*Pd$)] (quintet spin state) to $^2a$ (nonet spin state) is endothermic (91.5 kJ mol$^{-1}$). This seems to be in contrast with the experimental results. However, considering that the unrestricted singlet spin state of $^2a$ is more stable than the nonet spin state (102.1 kJ mol$^{-1}$), the reaction becomes exothermic. Furthermore, the natural population analyses (NPA) clearly indicates the presence of Fe$^2$ centers and $[P^2b]$$^4$ ligand in $^2a$.

Accordingly, we decided to additionally synthesize ligand $^2a$ (see Scheme 1, top), representing the missing combination between ligands $^2a_n$ and $^2a_l$, to investigate the steric and electronic effects induced by the different substitution of the chelating N atoms and the ligand backbone. Conducting the reaction of [L$^2Fe$(sol)] (1b) and $^2P_d$ under identical conditions (RT, toluene) and same stoichiometries (2:1 and 1:2) facilitates the clean and selective formation of the $^2P_d$ moiety containing complex [(L$^2Fe$)$_2$($mu$-$pi^*$$pi^*$$pi^*Pd$)] (2b) (Figure 2). Even if a higher local concentration of $^2P_d$ was used by the dropwise addition of 1 equivalent of 1b to a solution of 2 equiv of $^2P_d$ in toluene, 2b is the only product of the reaction. Comparing 2a and 2b, we assume that the methyl flanking groups in dmp are not able to prevent the dimerization reaction to the $^2P_d$ moiety, as the dipp substituents did in [(L$^2Fe$)$_2$($mu$-$pi^*$$pi^*Pd$)] (A). Along with A, $^{[6]}$ possessing two separate $^2P_d$ units, compounds 2a,b are different activation steps of $^2P_d$ (Scheme 1).

A single-crystal X-ray structural analysis reveals that compounds 2a$^2$toluene and 2b$^2$toluene are isostuctural (Figure 2 for 2b). Both compounds contain a realgar-type $^2P_d$ ligand coordinating to four [L$^2Fe$] ($L^2$ = $^2a$). $^2a$ and $^2b$ fragments. All P–P distances are in the range of 2.1918(8) to 2.2813(7) Å in 2a and 2.2111(6) to 2.2792(6) Å in 2b and therefore, are in line with P–P single bonds (for comparison: P–P single bond in white phosphorus determined by electron diffraction: 2.1994(3) Å$^{[8]}$ Raman spectroscopy: 2.2228(5) Å$^{[9]}$ and DFT calculations: 2.1994(3) Å$^{[8,9]}$). The coordination geometry of the Fe metal centers in 2a and 2b, respectively, is best described as distorted tetrahedral. The torsion angles between the Fe–P–P and Fe–N–N planes are between 74.66(6)$^o$ and 84.74(5)$^o$ in 2a and 83.45(4)$^o$ and 84.91(6)$^o$ in 2b. There are no significant differences in the P–P bond distances in 2a,b and those of previously reported related $^2P_d$ ligands in [[(NN$^6$Sc)$_2$P$_4$] $^2$] $^4$[(Cp*Sm)$_2$P$_4$] $^4$[(Cp$^*$$Fe$$_2$(CO)$_2$)$_2$P$_4$] $^4$[(Cp$^*$$Fe$_2$(CO)$_2$)$_2$P$_4$] and [(Cp$^*$$Fe$_2(CO)$_2$)$_2$P$_4$]$^{[10]}$.

The Fe–N distances lie between 1.983(2) and 2.006(2) Å in 2a and between 1.982(2) and 1.990(2) Å in 2b. The distances of Fe and the coordinating phosphorus atoms are in the range of 2.4559(6) and 2.5006(6) Å in 2a and 2.4583(3) and 2.4807(5) Å in 2b, respectively.

No signals were detected in the $^{31}$P[$^1$H] NMR spectra of 2a,b. These solutions (2a in $^2$D$_2$ and 2b in $^2$D$_2$toluene) are also EPR-silent at RT as well as at 10 K, suggesting a higher spin multiplicity or antiferromagnetically coupled iron centers that result in a non-magnetic (EPR-silent) ground state at low temperature. However, the $^1$H NMR spectra of 2a and 2b reveal signals in the range from 273 ppm to $-$29 ppm; thus indicating a paramagnetic spin state for 2a,b. The careful analysis of the spectra enabled us to assign all resonances (see the Supporting Information). The effective magnetic moment ($\mu_{eff}$) at room temperature was determined to be 6.79 $\mu_B$ for 2a in $^2$D$_2$ and 6.71 $\mu_B$ for 2b in $^2$D$_2$THF solution (Evans method). These values are well-confirmed by temperature-dependent SQUID measurements in the solid state. Both complexes exhibit a similar magnetic behavior with a strong
temperature dependency of their effective magnetic moments over a temperature range between 2 and 300 K. At 2 K, the effective magnetic moments amount to 1.14 μB (2a) and 0.54 μB (2b). With increasing temperature, the magnetic moments gradually increase until effective magnetic moments of 7.04 μB (2a) and 6.92 μB (2b) are reached at 300 K (see the Supporting Information). This magnetic behavior is likely caused by an antiferromagnetic coupling. The zero-field 57Fe Mössbauer spectrum of 2b at 77 K shows a doublet with an isomer shift δ of 0.73(1) mm/s and a quadrupole splitting ΔEQ of 1.93(1) mm/s, which is in agreement with a high-spin iron(II) complex. Similar Mössbauer parameters have been observed in the four-coordinate iron(II) complex [PhB-(MesIm),Fe(L=N=PPh3)].[11] The presence of iron(II) centers in 2b is also indicated by NPA analysis.

So far, we assume that the aromatic dmp substituents at the coordinating N atoms of the ligand play a crucial role for the formation of the P4 ligand moieties in 2a and 2b, and the α-substituent of the ligand backbone does not have much influence on the outcome of P3 activation. Regardless, to conclusively address this point, the ligand L4 was synthesized (Scheme 1). While L3 features aromatic dpp groups at the coordinating N atoms (like L2), its ligand backbone is substituted with two Me α-substituents (like L1); and hence, represents the missing hybrid ligand L3 and L4. Owing to steric reasons, the Me substituents at the ligand backbone are restricting the rotational flexibility of the Pr groups in dpp, thus increasing their steric pressure.[12]

The reaction of 1e with 0.5 equivalent of P4 in toluene at 2016 and L3 unit in the product 1c (2.023(3) and 2.025(3) θ;3w), 57 and L4 at 300 K (see the Supporting Information). This magnetic behavior is likely caused by an antiferromagnetic coupling. The zero-field 57Fe Mössbauer spectrum of 2b at 77 K shows a doublet with an isomer shift δ of 0.73(1) mm/s and a quadrupole splitting ΔEQ of 1.93(1) mm/s, which is in agreement with a high-spin iron(II) complex. Similar Mössbauer parameters have been observed in the four-coordinate iron(II) complex [PhB-(MesIm),Fe(L=N=PPh3)].[11] The presence of iron(II) centers in 2b is also indicated by NPA analysis.

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The reaction of 1e with 0.5 equivalent of P4 in toluene at RT leads to the formation of [[(L4Fe)Fe(Nη2-Nη1-P4)] (2c), containing a cyclo-P4 moiety. Again, changing the stoichiometry of the reaction does not have an effect on the product formation ([L4Fe(tol)]/P4 = 2:1 and 1:2). Different from our experience with the complexes of the dmp containing ligands L3 and L4, we now obtain a cyclo-P4 unit in the product 2c, which is also in contrast to Driss’ product A, featuring two separated P4 units (Scheme 1).

Single crystals of 2c suitable for X-ray diffraction were grown from a saturated toluene solution (Figure 3). Compound 2c is a centrosymmetric dinuclear iron complex that consists of two [L4Fe] fragments bridged by a planar cyclo-P4 ligand. The middle deck displays weak disorder (occupancy 97:3; see the Supporting Information). In the following, only the major component of the middle deck is discussed. The P–P distances within the central P4 moiety (P1–P2 and P1–P2') in 2c amount to 2.178(1) and 2.207(1) Å, respectively. These distances are longer than those reported for cyclo-[P4]−ligands (2.146(1)–2.1484(9) Å)[13] and shorter than those reported for cyclo-[P4H]− moieties (2.230(2)–2.259(2) Å).[14] The angles of P2–P1–P2 and P1–P2–P1' are 91.73(3)° and 88.27(3)°, respectively, indicating a slightly distorted ring conformation. The Fe–P distances are between 2.4376(6) and 2.5163(6) Å, comparable to those observed in 2a and 2b. Similarly, the Fe–N distances in 2c (2.018(2) and 2.025(2) Å) are comparable to A (2.023(3) and 2.025(3) Å),[15] but slightly elongated compared to 2a (1.983(2) and 2.006(2) Å) and 2b (1.982(2) and 1.990(2) Å). The Fe1–Fe1’ distance in 2c is 3.902 Å, being significantly elongated compared to compound A (2.777 Å). One of the most remarkable differences between 2c and A is the torsion angle θ between the Fe–Fe axis and the plane formed by the nitrogen atoms and the methine carbon atom in the ligand backbone, which is considerably smaller in 2c (15°) compared to A (33°; Figure 4).

Like in the tetranuclear complexes 2a,b, no resonances were detected in the 31P{[1H]} NMR spectra of 2c and solutions of 2c are EPR-silent at room temperature and at 10 K. However, the 1H NMR spectra of 2c in [D6]THF reveals signals in the range from 7 ppm to –2 ppm. The magnetic moment of 2c in [D6]THF at RT was determined to be 3.09 μB (Evans method). Temperature-dependent SQUID measurements in the solid state are in agreement with this result with an effective magnetic moment of 3.46 μB at 300 K. The magnetism of complex 2c is strongly temperature-dependent. At 2 K, the effective magnetic moment was determined to be 0.54 μB and is rising to 1.00 μB at 20 K. Between 20 and 80 K, it remains roughly constant. Increasing the temperature to 300 K leads to a gradual increase of the effective magnetic moment up to a value of 3.46 μB at 300 K (see the Supporting Information). This magnetic behavior is explained by a Stranski phase transition at low temperatures. This transition is accompanied by a dramatic change in the Mössbauer parameters (see the Supporting Information). A detailed analysis of these parameters will be presented in a forthcoming publication.

Figure 3. Molecular structure of 2c (hydrogen atoms are omitted for clarity; ellipsoids are set at 50% probability). Selected bond lengths [Å] and angles [°]: P1–P2 2.178(1), P1–P2' 2.207(1), Fe1–P1 2.4376(6), Fe1–P2 2.5064(6), Fe1–P1' 2.5163(6), Fe1–P2' 2.5064(6), Fe1–N1 2.018(2), Fe1–N2 2.025(2), Fe1–Fe1' 3.902; P2–P1 91.73(3), P1–P2 88.27(3).

Figure 4. Comparison of the coordination geometry in 2c and A.[14]
0 ground state between 0 and 80 K and antiferromagnetic coupling of the two iron nuclei at higher temperatures. The zero-field $^{57}$Fe Mössbauer spectrum of 2c at 77 K features a doublet with an isomer shift $\delta$ of 0.74(1) mm/s and a quadrupole splitting $\Delta E_Q$ of 1.74(1) mm/s, which is similar to the Mössbauer parameters of 2b and is in accordance with a high-spin iron(II) complex.

The optimized geometry of 2c in the quintet spin state obtained from DFT calculations (BPW91/def2-SVP) is in good agreement with the experimentally found geometric parameters, with a slightly shorter Fe–Fe distance (3.827 Å) and slightly longer P–P distances (2.203–2.250 Å). Notably, the geometry optimization in the unrestricted singlet spin state instead leads to further shortening of the Fe–Fe distance (3.712 Å) and to a planar P$_2$ ring with two shorter and two longer P–P distances (2.181 Å and 2.325 Å, respectively). Since the Fe–Fe distance in A (2.777 Å) is significantly shorter than in 2c, the geometry of 2c (quintet spin state) was optimized with a fixed Fe–Fe distance of 2.777 Å. In the optimized geometry, the cyclo-P$_2$ unit is cleaved into two P$_2$ units and the nacnac ligand shows the same type of folding like the one reported for A. The energy difference between both isomers is 29.19 kJ mol$^{-1}$, favoring the relaxed geometry of 2c. This points towards a flat energy surface and suggests that the outcome of the P$_2$ transformation is mostly determined by the Fe–Fe distance. Broken symmetry calculations (BPW91/def2-SVP/aug-cc-pVTZ (Fe, P)) indicate an antiferromagnetic coupling between the two Fe centers, which increases with the decrease of the Fe–Fe distance.$^{[5]5}$ The Mulliken population analysis for the quintet spin state of 2c shows that the spin density is localized on iron atoms, but no considerable spin density was found on the P$_2$ or nacnac ligands. The Mayer bond order for the P–P bonds vary from 0.81 to 0.87; thus, indicating P–P single bonds.

In conclusion, we have shown that the different reactivity of $\beta$-diketiminato Fe$^1$ complexes [LFe(tol)] ($L = L^1$ (1a), L$^2$ (1b), L$^3$ (1c)) towards P$_2$ is sensitive to minimal changes in the ligand: its flanking groups (Ph$^+$) and its backbone $\alpha$-substituents (R). By conducting the reactions under similar conditions (RT) in the same solvent (toluene), and using exact stoichiometric amounts of P$_2$ ([LFe(tol)]/P$_2 = 2:1$) or even larger amounts of P$_2$ ([LFe(tol)]/P$_2 = 1:2$), a different outcome of P$_2$ activation is realized. By employing the aromatic dmp flanking groups as substituents of the coordinating Na atoms, the formation of a [P$_4$]$^{1+}$ structural motif in the iron(II) compounds $[[\text{LFe}](\mu-$n$_2^2\text{P} \equiv \text{P} \equiv \text{P} \equiv \text{P} )](L = L^1$ (2a), L$ = L^2$ (2b)) is observed.$^{[59]}$ Employing the sterically more demanding dmp substituents leads to the formation of an iron(II) compound $[[\text{LFe}](\mu-$n$_2^2\text{P} \equiv \text{P} \equiv \text{P} )](L = L^1$ (2c), containing a cyclo-[P$_4$]$^{1-}$ moiety. This finding is in contrast to the formation of two separate [P$_4$]$^{1-}$ units observed in the iron(III) complex A, with two H $\alpha$-substituents being located in the ligand backbone instead of Me atoms in 2c. This demonstrates the additional steric influence of the Me groups as $\alpha$-substituents to push the dmp substituents closer together, thereby preventing the opening of the cyclo-P$_2$ ring by relaxing the Fe–Fe distance in 2c in comparison with the rather short distance in A. The discussed ligand dependencies in the $\beta$-diketiminato ligand complexes may foster the systematic study of such dependences in other metal systems for the activation of small molecules in general and in particular for the controlled P$_2$ ligand formation from white phosphorus.

**Acknowledgments**

This work was supported by the Deutsche Forschungsgemeinschaft. The European Research Council (ERC) is acknowledged for the support in the SELFPHOS AdG-339072 project.

**Keywords:** Mössbauer spectroscopy - paramagnetic compounds - small-molecule activation - substituent effects - white phosphorous

**How to cite:** Angew. Chem. Int. Ed. 2016, 55, 4340–4344

Angew. Chem. 2016, 128, 4412–4416


6. The term “realgar-type” P$_2$ moiety for the tricyclo[3.3.0.0$^3$]octaphosphane ligand comes from its analogy to the isoostructural realgar (As$_2$S$_3$) molecule.

7. a) For 2a,b,c calculated at the BP86/def2-SVP level. The NPA charges for A were taken from Ref. [4a]. It should be noted that different basis sets were used; b) For the relationship of the formal oxidation states and the spectroscopic and structural parameters (see the Supporting Information, Table S3).


[15] See the Supporting Information.

Received: January 13, 2016
Published online: February 29, 2016