

PHOSPHORUS-RICH COMPOUNDS

Phosphorus makes inroads

The synthesis of phosphorus-rich analogues of carbon-based compounds is a desirable but challenging endeavour. Now, the synthesis of the anion $[\text{Fe}(\text{P}_4)_2]^{2-}$ is reported, which so far is the most similar all-phosphorus relative to well-known ferrocene, $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2]$.

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Organic compounds constitute the basis of living things and have undisputable importance in various fields. The reason for the ubiquity of these carbon-rich compounds is the large dissociation energy of carbon–carbon bonds. However, even though these bonds have the largest energy of all element–element bonds, other elements also have fairly large dissociation energies. The most prominent example is phosphorus and, as a result, oligophosphorus compounds are also prevalent. These compounds can be rationalized by replacing C–H fragments with P atoms using the isolobal concept, which has led to phosphorus often being referred to as the carbon copy.¹

For over 100 years, chemists have been synthesizing phosphorus-rich molecules spurred by a desire to understand the similarities and differences compared to their organic counterparts. The number of theoretically imaginable phosphorus-rich compounds is limitless and in fact, in the last decades of the 20th century, numerous compounds were prepared by several researchers, the most prominent being Marianne Baudler.²

Nevertheless, the number of known isolable compounds has remained low and is greatly exceeded by the number of predicted ones. Among these, one of the most desired compounds is $[\text{Fe}(\eta^5\text{-P}_5)_2]$, the phosphorus analogue of ferrocene, $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2]$, which was a milestone in organometallic chemistry. In pursuit of this elusive representative, analogous compounds in which carbon is partially replaced by phosphorus have been synthesized (Fig. 1a) and have led to molecules with fascinating properties. In contrast to the titanocene analogue $[\text{Ti}(\eta^5\text{-P}_5)_2]^{2-}$,³ however, $[\text{Fe}(\eta^5\text{-P}_5)_2]$ has not even been detected. Synthetic routes to phosphorus-rich compounds are rarely selective and, more importantly, transformation reactions between different molecules as well as rearrangements typically have low activation energies and thus occur at room temperature or at even lower temperatures, often leading to complex mixtures.⁴

Now, writing in the *Journal of the American Chemical Society*, Sun and co-workers⁵ report the synthesis of $[\text{Fe}(\eta^4\text{-P}_4)_2]$ (**1**), a closely related structure of the desired decaphosphaferrocene by considering the features that typically hamper the preparation of such compounds (Fig. 1a). In most cases, synthetic routes to phosphorus-rich compounds focus on the use of white phosphorus (P_4) as a starting material which, using different agents, is transformed into the target molecule.^{6,7} Despite impressive progress in making use of P_4 ,^{8,9} only a limited number of phosphorus-rich products can be obtained by optimizing the conditions of this particular reaction. In contrast, the method of Sun and co-workers uses a Zintl phase as the phosphorus source, breaking down the polymeric structure by using ion sequestering agents. As a result, the desired ligand is formed in solution and then reacted with an iron salt to yield the target compound **1**, albeit in a mixture with a second sandwich-like complex, $[\text{Fe}(\eta^4\text{-P}_4)(\eta^4\text{-P}_7)]^{3-}$ (**2**), which contains a norbornene-like P_7^{3-} ligand.

More specifically, the Zintl phase KP is used which consists of polymeric chains of negatively charged phosphorus (Fig. 1b) with the oxidation state of -1 for each phosphorus atom. When this phase is dissolved in ethylenediamine using [2.2.2]cryptand, a disproportionation reaction takes place yielding K_3P and the desired K_2P_4 (Fig. 1b). Additionally, P_7^{3-} as well as KPH_2 (from deprotonation of the solvent by K_3P) are formed. However, by optimizing the type and amount of the sequestering agent ([2.2.2]cryptand or 18-crown-6), Sun and co-workers minimized the formation of these side products and maximized the amount of the P_4^{2-} ion in an easier way than other known methods. The second step of the reaction involved the addition of the iron salt which resulted in a mixture of products from which crystals of **1** and **2** could be obtained over a timescale of weeks.

Both compounds are intriguing examples of phosphorus-rich complexes. Quantum chemical calculations reveal π bonding between the 6-electron donor ligand *cyclo*- P_4^{2-} and iron(II), resulting in a very stable 18-electron compound (complex **1**). Indeed, this π bonding arrangement between the ligand and iron centre is similar to that of ferrocene.

Another interesting aspect of the study is the redox chemistry of the reaction. Surprisingly, the best results were obtained using $Fe(O^tBu)_3$, an iron(III) compound, even though the iron atom in complex **1** (and **2**) is in the +2 oxidation state. Using iron(II) salts instead led to complex mixtures containing notably less of product **1**. The nature of the individual processes in this step is not entirely clear but it appears that both the P_7^{3-} anion as well as complex **2** are formed through oxidation of P_4^{2-} or PH_2^- by iron(III) (Fig. 1b). In an attempt to prevent this oxidation, small amounts of potassium were added. However, the addition of potassium seemed to shift the reaction towards the PH_2^- ion with a loss of P_4^{2-} . Although Sun and co-workers have optimized this difficult reaction leading to the P_4^{2-} anion and its iron(II) complex **1**, an improved understanding of the intricate chemistry involved will certainly be useful for future work.

A drawback of the study is that crystals of compounds **1** and **2** were only obtained as mixtures with other species in rather low yields, over several weeks, which is not an efficient outcome of the synthesis. While individual single crystals could be picked for characterization by X-ray diffraction, samples recrystallized for inspection by $^{31}P\{^1H\}$ NMR spectroscopy indicated the presence of additional species in solution. As mentioned in the article, oxidation is a possible explanation; however, it is also possible that rearrangement reactions occur in solution.^{10,11} Further investigations are required to establish the origin of the additional signals observed in the $^{31}P\{^1H\}$ NMR spectra.

Nevertheless, with the synthesis of $[Fe(\eta^4-P_4)_2]^{2-}$, Sun and co-workers have made an important contribution to the area of phosphorus-rich ferrocene analogues, and their achievements in this challenging field is much appreciated. We are looking forward to seeing further exciting molecules using this synthetic combination of Zintl phases and ion sequestering agents, including the elusive $[Fe(\eta^5-P_5)_2]$.

Figure 1. Synthesis and structures of new phosphorus-rich ferrocene analogues. a) Different representatives of phosphorus-rich relatives of ferrocene. b) Reaction to prepare complexes **1** and **2** including the solid-state structure of the starting material, KP. c) Structure and equilibrium of the *cyclo*- P_4^{2-} ion leading to complex **1** after addition of the metal ion. The second isomer is displayed to highlight the structure of the ligand. d) Structure and equilibrium of the P_7^{3-} ion leading to complex **2** after addition of the metal ion. The second isomer is displayed to highlight the structure of the ligand.

Competing interests

The authors declare no competing interests.

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