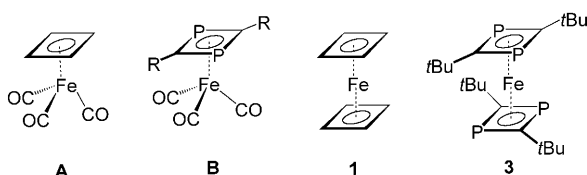


A Phosphorus Analogue of Bis(η^4 -cyclobutadiene)iron(0)**

Robert Wolf, J. Chris Slootweg, Andreas W. Ehlers, František Hartl, Bas de Bruin, Martin Lutz, Anthony L. Spek, and Koop Lammertsma*

Iron is a pivotal element in organometallic chemistry, enabling fundamental insights with high-impact applications.^[1] Ferrocene derivatives have countless uses,^[2] and the recent advances in iron catalysis are equally impressive.^[3]

A historic landmark in organoiron chemistry is (η^4 -cyclobutadiene)iron tricarbonyl, $[\text{Fe}(\eta^4\text{-C}_4\text{H}_4)(\text{CO})_3]$ (**A**).



This molecule was predicted on theoretical grounds^[4] and synthesized by Pettit and co-workers,^[5,6] and it undergoes electrophilic substitutions similar to ferrocene.^[7] Still, the number of cyclobutadiene (Cb) iron complexes pales in comparison to the wealth of iron complexes with the ubiquitous cyclopentadienyl (Cp) ring.^[8] This imbalance is also found for the even less developed phosphaaorganometal-

lic complexes of iron. For example, whereas the P_2 analogue of **A**, $[\text{Fe}(\eta^4\text{-P}_2\text{C}_2\text{R}_2)(\text{CO})_3]$ (**B**; $\text{R} = t\text{Bu}$, Mes), is readily prepared by reaction of $\text{RC}\equiv\text{P}$ with $[\text{Fe}_2(\text{CO})_9]$,^[9] iron sandwich complexes with phosphacyclobutadienes remain essentially limited to neutral, heteroleptic species,^[10,11] thereby sharply contrasting the well-developed phosphaferrrocenes used in areas ranging from catalysis to supramolecular chemistry.^[12,13]

Illustrative of the dichotomy in Cp and Cb iron sandwich compounds is the still-elusive 16-electron complex bis(η^4 -cyclobutadiene)iron(0), $[\text{Fe}(\eta^4\text{-C}_4\text{H}_4)_2]$ (**1**),^[14] which DFT calculations indicate to have a stable D_{4h} -symmetric structure (Figure 1) with a triplet ground state (see below).^[15] In our pursuit of this system we make use of the C/P diagonal relationship in the Periodic Table.

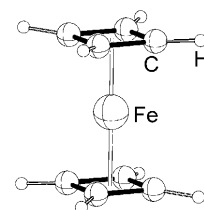


Figure 1. OPBE/TZ2P structure of **1** (D_{4h} symmetry). Bond lengths [Å]: Fe–C 2.007, C–C 1.462, C–H 1.085.

Recently, we showed that reaction of phosphaaalkynes with anionic arene complexes of low-valent transition metals is a facile method to prepare homoleptic diphosphacyclobutadiene sandwich anions, such as the diamagnetic 18-electron ion $[\text{Co}(\eta^4\text{-P}_2\text{C}_2t\text{Bu}_2)_2]^-$, which displays a unique reactivity pattern with electrophiles.^[16] We now report on the synthesis and structural characterization of the d^9 17-electron anionic iron complex $[\text{Fe}(\eta^4\text{-P}_2\text{C}_2t\text{Bu}_2)_2]^-$ (**2**) and the neutral d^8 16-electron $[\text{Fe}(\eta^4\text{-P}_2\text{C}_2t\text{Bu}_2)_2]$ (**3**) as a phosphorus analogue of homoleptic $[\text{Fe}(\eta^4\text{-C}_4\text{H}_4)_2]$ (**1**).

$[\text{K}([18]\text{crown-6})(\text{thf})_2][\text{Fe}(\eta^4\text{-P}_2\text{C}_2t\text{Bu}_2)_2]$ (**K2**) was prepared as a yellow-orange solid from the metalate $[\text{K}([18]\text{crown-6})(\text{thf})_2][\text{Fe}(\eta^4\text{-C}_{14}\text{H}_{10})_2]$ ^[17a] and four equivalents $t\text{BuC}\equiv\text{P}$ ^[18] in 75% yield. The X-ray crystal structure (Figure 2)^[19] is comprised of the counterion $[\text{K}([18]\text{crown-6})(\text{thf})_2]^+$ ^[17b] and the homoleptic anion $[\text{Fe}(\eta^4\text{-P}_2\text{C}_2t\text{Bu}_2)_2]^-$ (**2**). The Fe–P and Fe–C separations in **2** are comparable to those in complex **B**^[9,10] and are slightly longer (by 0.03–0.04 Å) than the Co–P and Co–C separations in the isomorphous complex $[\text{K}([18]\text{crown-6})(\text{thf})_2][\text{Co}(\eta^4\text{-P}_2\text{C}_2t\text{Bu}_2)_2]$.^[16] The two η^4 -bound $\text{P}_2\text{C}_2t\text{Bu}_2$ ligands in the anion are in a staggered orientation.

Anion **2** is a paramagnetic d^9 17-electron species with a solution magnetic moment of $1.77\mu_B$, indicating the presence of one unpaired electron. In full agreement, the EPR spectrum of a frozen THF solution of **K2** (40 K) shows the typical pattern for an axially symmetric d^9 species; a satisfactory spectral simulation was obtained with the g values $g_{\parallel} = 2.28$ and $g_{\perp} = 2.026$ (Figure 3).

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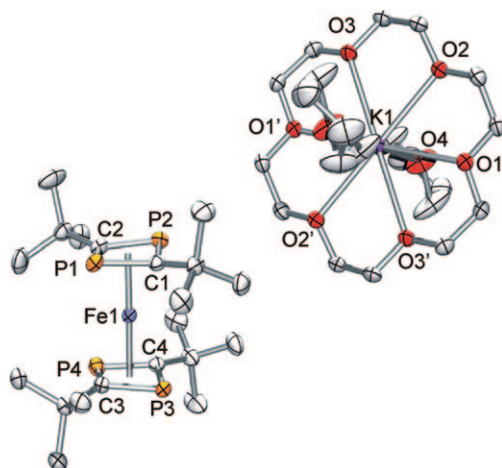


Figure 2. Solid-state structure of **K2**, with displacement ellipsoids at the 50% probability level. H atoms, one of the two crystallographically independent $[\text{K}(\text{18-crown-6})(\text{thf})_2]^+$ cations, and the disorder in the thf molecules are omitted for clarity. Selected bond lengths [Å] and angles [°]: Fe1–P1, P2, P3, P4 2.2969(5)–2.3024(5), Fe1–C1, C2, C3, C4 2.0939(16)–2.1027(16), P1–C1 1.8000(17), P1–C2 1.8024(17), P2–C1 1.8043(17), P2–C2 1.8021(18), P3–C3 1.8048(17), P3–C4 1.8037(18), P4–C3 1.8042(17), P4–C4 1.8013(17); P1–C1–P2 98.72(8), C1–P1–C2 80.94(8).

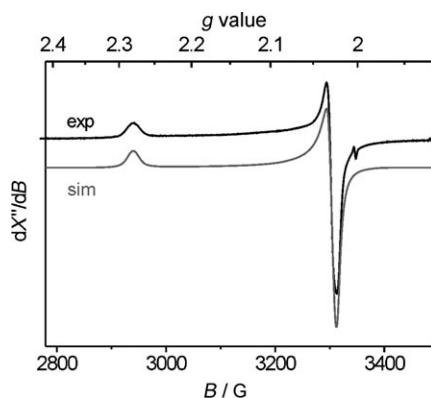


Figure 3. Experimental EPR spectrum of **K2** and its simulation. Microwave frequency 9.38028 GHz, attenuation 30 dB, modulation amplitude 4 G.

The absence of hyperfine coupling and the high-field shift of $g_{\parallel}$ compared to $g_{\perp}$ indicate that the unpaired electron is localized in the $d_{x^2-y^2}$ orbital of the metal.^[20] This conclusion is supported by a molecular orbital analysis of model complex ion $[\text{Fe}(\eta^4\text{-P}_2\text{C}_2\text{Me}_2)_2]^-$ (**2'**, with methyl instead of *tert*-butyl groups), which shows an 84% metal $d_{x^2-y^2}$ contribution in the singly occupied molecular orbital (SOMO), while the highest doubly occupied orbital displays 79% d_{z^2} character. The OPBE/TZ2P DFT calculations^[15] give a significant energetic preference for the doublet state over both the quartet ($\Delta E = 30.4 \text{ kcal mol}^{-1}$) and the sextet ($\Delta E = 64.0 \text{ kcal mol}^{-1}$).

To establish whether **2** is a suitable precursor for the oxidized neutral complex $[\text{Fe}(\eta^4\text{-P}_2\text{C}_2\text{tBu}_2)_2]$ (**3**) or the reduced 18-electron dianion $[\text{Fe}(\eta^4\text{-P}_2\text{C}_2\text{tBu}_2)_2]^{2-}$ (**4**), we examined the redox properties of **K2** (in THF solution) with electrochemical methods. Cyclic voltammetry revealed

anion **2** to be oxidized fully reversibly at a rather low potential, $E_{1/2} = -0.97 \text{ V}$ vs. $[\text{Cp}_2\text{Fe}]/[\text{Cp}_2\text{Fe}]^+$,^[21] but no reduction of **2** was observed in the accessible potential window. UV/Vis monitoring of the oxidation of **K2** in a thin-layer spectroelectrochemical cell showed smooth conversion to a new species (Figure 4) that was identified as oxidized complex **3** by comparison of the UV/Vis absorptions with those of an authentic sample.

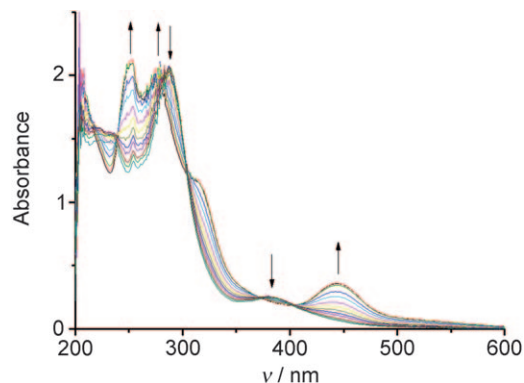


Figure 4. UV/Vis spectral changes accompanying the electrochemical oxidation of **K2** in THF/ $[\text{nBu}_4\text{N}][\text{PF}_6]$ at -0.9 V . The arrows indicate decreasing absorptions of **K2** and increasing absorptions of **3**.

On a preparative scale, **3** was generated by oxidizing **K2** with $[\text{Cp}_2\text{Fe}][\text{PF}_6]$ to give, upon isolation, deep red crystals that are highly soluble in hydrocarbon solvents. The X-ray crystal structure of neutral, 16-electron **3** (Figure 5) revealed a C_2 -symmetric sandwich structure akin to anion **2**.^[19] It is evident that no major structural change occurs upon oxidation.

The effective magnetic moment in C_6D_6 solution ($2.74\mu_B$) indicates that **3** is paramagnetic with two unpaired electrons per molecule. Accordingly, the ^1H NMR spectrum of **3** features a very broad singlet at $\delta = 2.6 \text{ ppm}$ owing to the paramagnetism of the compound.

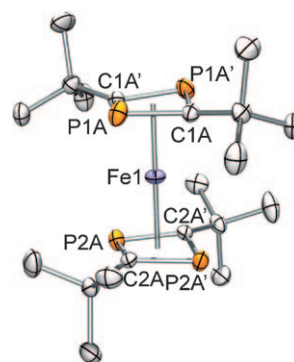


Figure 5. Solid-state structure of **3**, with displacement ellipsoids at the 50% probability level. H atoms and the minor disorder components of the $\text{P}_2\text{C}_2\text{tBu}_2$ ligands are omitted for clarity. Selected bond lengths [Å] and angles [°]: Fe1–P1A 2.3044(10), Fe1–P2A 2.3081(9), Fe1–C1A 2.090(3), Fe1–C2A 2.100(3), P1A–C1A 1.804(3), P1A–C1A' 1.808(3), P2A–C2A 1.802(3), P2A–C2A' 1.796(3), P1A–C1A–P1A' 97.98(15), C1A–P1A–C1A' 81.41(15); P2A–C2A–P2A' 98.61(15), C2A–PA–C2A' 80.91(15).

OPBE/TZ2P geometry optimization of model $[\text{Fe}(\eta^4\text{-P}_2\text{C}_2\text{Me}_2)_2]$ (**3'**, D_{2d} symmetry) gave structural parameters similar to **3**. The triplet ground state of **3'** is favored over the open-shell singlet and the quintet by 20.0 and 37.6 kcal mol⁻¹, respectively. The two singly occupied MOs of the ground state display dominant contributions of the iron orbitals (SOMO-1: 65 % d_{z^2} , SOMO: 65 % $d_{x^2-y^2}$; Figure 6). Thus,

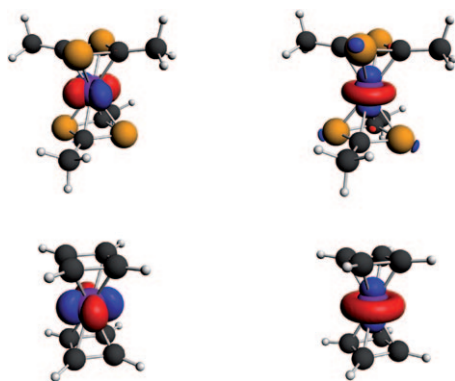


Figure 6. Graphical representations of the SOMO (left) and SOMO-1 (right) of $[\text{Fe}(\eta^4\text{-C}_4\text{H}_4)_2]$ (**1**, bottom) and $[\text{Fe}(\eta^4\text{-P}_2\text{C}_2\text{Me}_2)_2]$ (**3'**, top).

oxidizing **2** results in an open-shell sandwich complex **3** with two unpaired electrons. The oxidized compound **3** displays a similar electronic structure as **2**, but with one electron formally removed from its d_{z^2} -like HOMO.

Formal addition of one electron to model anion **2'** results in the diamagnetic 18-electron dianion $[\text{Fe}(\eta^4\text{-P}_2\text{C}_2\text{Me}_2)_2]^{2-}$ (**4'**). Whereas the theoretical calculations indicate **4'** to be a viable species, no reduction of **K2** could be observed, neither by cyclic voltammetry nor preparatively by using strong reducing agents such as potassium/graphite or potassium/naphthalenide.^[21] We attribute this apparent lack of reduction to the large energy difference between the $d_{x^2-y^2}$ -like HOMO of **4'** (+5.19 eV) and the SOMO of **2'** (0.93 eV), which is caused by the double negative charge.

The DFT calculations reveal a close electronic relationship between the cyclobutadiene sandwich complex $[\text{Fe}(\eta^4\text{-C}_4\text{H}_4)_2]$ (**1**, D_{4h}) and **3'**. Like **3'**, the triplet ground state of **1** is also highly favored over the open-shell singlet ($\Delta E = 20.7$ kcal mol⁻¹) and the quintet ($\Delta E = 47.3$ kcal mol⁻¹). Likewise, the two singly occupied MOs of the ground state of **1** show dominant contributions of the iron atom (SOMO: 88 % $d_{x^2-y^2}$, SOMO-1: 82 % d_{z^2} ; Figure 6). The Mulliken spin population analysis confirms that the unpaired electron density of both resides almost exclusively on the iron center (net spin density polarization on Fe **1**: 2.42 and **3'**: 2.39 versus **2'**: 1.32). The calculations also show that the bond strength of -106.5 kcal mol⁻¹ for a cyclobutadiene ligand of **1** is higher than that of a diphosphacyclobutadiene ligand of **3'** (-98.7 kcal mol⁻¹) and further that the dimerization energy of acetylene to form cyclobutadiene ($\Delta E = -20.5$ kcal mol⁻¹) exceeds that of $\text{MeC}\equiv\text{P}$ ($\Delta E = -12.5$ kcal mol⁻¹). Therefore, from a thermodynamic point of view it appears that the formation of **1** is similarly favorable to that of **3'**.

In summary, the new 17-electron species **2** and 16-electron species **3** are rare examples of readily accessible, open-shell iron sandwich complexes with phosphoorganic ligands. The presented data lead us to conclude that phosphorus derivative **3** is a true analogue of the elusive bis(η^4 -cyclobutadiene)iron(0) compound **1**. Currently, we are investigating whether **1** and its derivatives are likewise accessible. Future studies will focus on a more detailed characterization of the iron oxidation state in **1-3** and the influence of metal coordination on the magnetic and redox properties of these compounds.^[22]

Experimental Section

K2: $t\text{BuC}\equiv\text{P}$ (5 mL, 10.0 mmol, 2 M solution in hexanes) was added dropwise to a deep brown solution of $[\text{K}([18]\text{crown-6})(\text{thf})_2][\text{Fe}(\text{C}_{14}\text{H}_{10})_2]$ (2.13 g, 2.48 mmol) in THF (40 mL) at -78 °C, and the mixture was allowed to warm up to room temperature overnight. The dark orange solution was filtered and concentrated to 10 mL, and toluene (30 mL) was added. $[\text{K}([18]\text{crown-6})(\text{thf})_2][\text{Fe}(\text{P}_2\text{C}_2t\text{Bu}_2)_2]$ was isolated as a yellow-orange crystalline solid after storage at -20 °C overnight, washed with toluene (3 × 15 mL), and dried in vacuo. Crystals suitable for X-ray crystallography were grown by layering a THF solution of **K2** with *n*-pentane. Yield 1.41 g (75 %). Elemental analysis (%) calcd for $\text{C}_{32}\text{H}_{60}\text{O}_6\text{P}_4\text{FeK}$ ($M = 759.66$): C 50.59, H 7.96; found: C 49.74, H 7.95; m.p. > 300 °C (slow dec). ¹H NMR (250.13 MHz, $[\text{D}_8]\text{THF}$): $\delta = -1.9$ (very br s; *t*Bu), 1.73 (br s; THF), 3.72 ppm (br s; THF). Magnetic susceptibility (Evans method, 25 °C, $[\text{D}_8]\text{THF}$): $\mu_{\text{eff}} = 1.77 \mu_{\text{B}}$. UV/Vis (THF) λ_{max} [nm] (ϵ [mol⁻¹ dm³ cm⁻¹]): 296 (48 100), 383 (10 000), 699 (310).

3: $[\text{Cp}_2\text{Fe}][\text{PF}_6]$ (0.050 g, 0.15 mmol) was added to a dark orange solution of **K2** (0.106 g, 0.14 mmol) in THF (6 mL), and the mixture was stirred at room temperature overnight. The solvent was removed completely, the ferrocene byproduct was removed by sublimation (10⁻² torr, 50 °C), and the dark residue was extracted into *n*-pentane (10 mL). Concentrating the orange-red extract to approximately 1 mL yielded red X-ray quality crystals of **3** after storage at -20 °C for several days. Yield 0.023 g (36 %); m.p. 184–186 °C (dark oil). ¹H NMR (250.13 MHz, C_6D_6): $\delta = 2.6$ ppm (very br s; *t*Bu). Magnetic susceptibility (Evans method, 25 °C, C_6D_6): $\mu_{\text{eff}} = 2.74 \mu_{\text{B}}$. UV/Vis (THF) λ_{max} [nm] (ϵ [mol⁻¹ dm³ cm⁻¹]): 275 (65 700), 320 (shoulder), 443 (11 000). HRMS (EI): m/z (%): 456.1 (60), calcd for $\text{C}_{20}\text{H}_{36}\text{P}_4\text{Fe}$: 456.1100, found: 456.1117.

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