Cyclobutadiene Ligands

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

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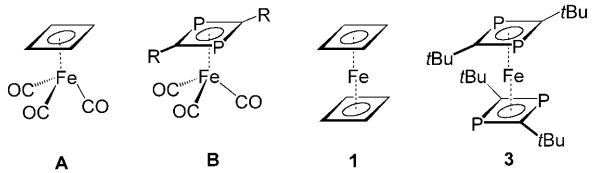
Iron is a pivotal element in organometallic chemistry, enabling fundamental insights with high-impact applications.[1] Ferrocene derivatives have countless uses,[2] and the recent advances in iron catalysis are equally impressive.[3]

A historic landmark in organoiron chemistry is (η^4-cyclobutadiene)iron tricarbonyl, [Fe(η^4-C_4H_4)(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 phosphaorganometallic complexes of iron. For example, whereas the P_2 analogue of **A**, [Fe(η^4-$P_2C_2R_2$)(CO)$_3$] (**B**; R = *t*Bu, Mes), is readily prepared by reaction of RC≡P with [Fe$_2$(CO)$_9$],[9] iron sandwich complexes with phosphacyclobutadienes remain essentially limited to neutral, heteroleptic species,[10,11] thereby sharply contrasting the well-developed phosphaferrocenes used in areas ranging from catalysis to supramolecular chemistry.[12,13]

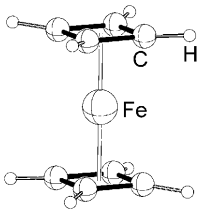


Figure 1. OPBE/TZ2P structure of **1** (D_{4h} symmetry). Bond lengths [Å]: Fe–C 2.007, C–C 1.462, C–H 1.085.

Illustrative of the dichotomy in Cp and Cb iron sandwich compounds is the still-elusive 16-electron complex bis(η^4-cyclobutadiene)iron(0), [Fe(η^4-C_4H_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.

Recently, we showed that reaction of phosphaalkynes 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 [Co(η^4-$P_2C_2t\mathrm{Bu}_2$)$_2$]$^-$, 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 [Fe(η^4-$P_2C_2t\mathrm{Bu}_2$)$_2$]$^-$ (**2**) and the neutral d^8 16-electron [Fe(η^4-$P_2C_2t\mathrm{Bu}_2$)$_2$] (**3**) as a phosphorus analogue of homoleptic [Fe(η^4-C_4H_4)$_2$] (**1**).

[K([18]crown-6)(thf)$_2$][Fe(η^4-$P_2C_2t\mathrm{Bu}_2$)$_2$] (K**2**) was prepared as a yellow-orange solid from the metalate [K([18]crown-6)(thf)$_2$][Fe(η^4-$C_{14}H_{10}$)$_2$][17a] and four equivalents *t*BuC≡P[18] in 75% yield. The X-ray crystal structure (Figure 2)[19] is comprised of the counterion [K([18]crown-6)(thf)$_2$]$^+$[17b] and the homoleptic anion [Fe(η^4-$P_2C_2t\mathrm{Bu}_2$)$_2$]$^-$ (**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 [K([18]crown-6)(thf)$_2$][Co(η^4-$P_2C_2t\mathrm{Bu}_2$)$_2$].[16] The two η^4-bound $P_2C_2t\mathrm{Bu}_2$ 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 μ_B, indicating the presence of one unpaired electron. In full agreement, the EPR spectrum of a frozen THF solution of K**2** (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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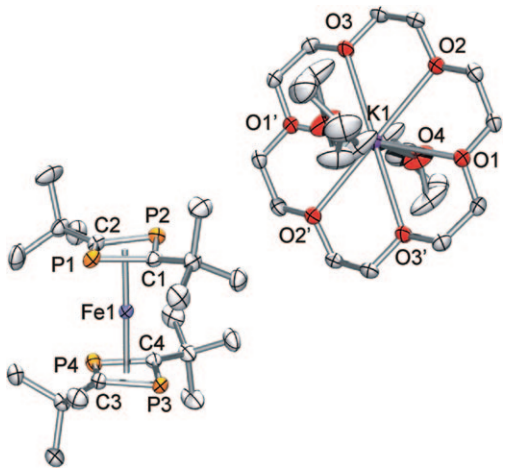

Figure 2. Solid-state structure of K**2**, with displacement ellipsoids at the 50% probability level. H atoms, one of the two crystallographically independent $[K([18]crown\text{-}6)(thf)_2]^+$ cations, and the disorder in the thf molecules are omitted for clarity. Selected bond lengths [Å] and angles [°]: 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).

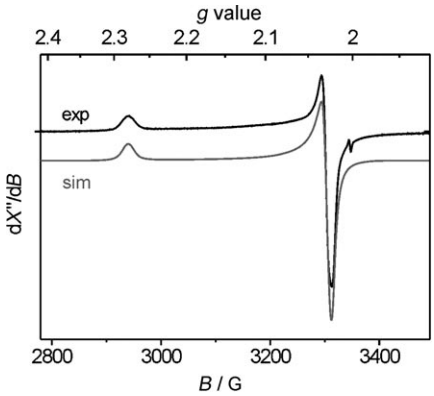

Figure 3. Experimental EPR spectrum of K**2** and its simulation. Microwave frequency 9.38028 GHz, attenuation 30 dB, modulation amplitude 4 G.

The absence of hyperfine coupling and the high-field shift of $g_{\|}$ 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 $[Fe(\eta^4\text{-}P_2C_2Me_2)_2]^-$ (**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 kcal mol^{-1}) and the sextet ($\Delta E = 64.0$ kcal mol^{-1}).

To establish whether **2** is a suitable precursor for the oxidized neutral complex $[Fe(\eta^4\text{-}P_2C_2tBu_2)_2]$ (**3**) or the reduced 18-electron dianion $[Fe(\eta^4\text{-}P_2C_2tBu_2)_2]^{2-}$ (**4**), we examined the redox properties of K**2** (in THF solution) with electrochemical methods. Cyclic voltammetry revealed anion **2** to be oxidized fully reversibly at a rather low potential, $E_{1/2} = -0.97$ V vs. $[Cp_2Fe]/[Cp_2Fe]^+$,[21] but no reduction of **2** was observed in the accessible potential window. UV/Vis monitoring of the oxidation of K**2** 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.

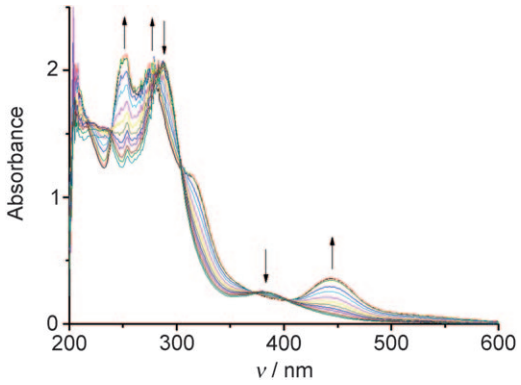

Figure 4. UV/Vis spectral changes accompanying the electrochemical oxidation of K**2** in THF/$[nBu_4N][PF_6]$ at −0.9 V. The arrows indicate decreasing absorptions of K**2** and increasing absorptions of **3**.

On a preparative scale, **3** was generated by oxidizing K**2** with $[Cp_2Fe][PF_6]$ 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 ^{1}H NMR spectrum of **3** features a very broad singlet at $\delta = 2.6$ ppm owing to the paramagnetism of the compound.

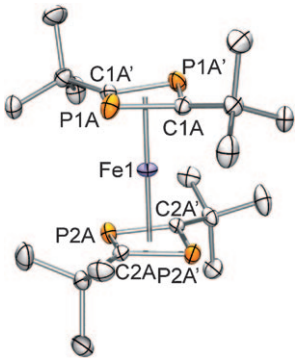

Figure 5. Solid-state structure of **3**, with displacement ellipsoids at the 50% probability level. H atoms and the minor disorder components of the $P_2C_2tBu_2$ ligands are omitted for clarity. Selected bond lengths [Å] and angles [°]: Fe1–P1A 2.3044(10), Fe1–P2A 2.3081(9), Fe1–C1A 2.090(3), Fe1–C2A 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 [Fe(η^4-$P_2C_2Me_2$)$_2$] (**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,

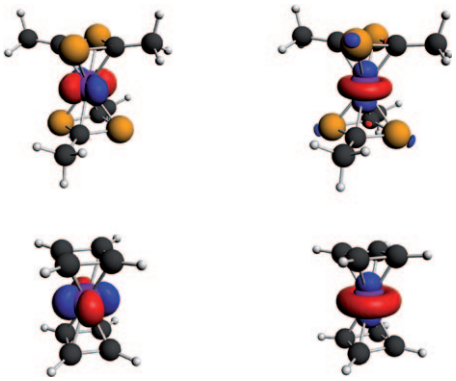

Figure 6. Graphical representations of the SOMO (left) and SOMO−1 (right) of [Fe(η^4-C_4H_4)$_2$] (**1**, bottom) and [Fe(η^4-$P_2C_2Me_2$)$_2$] (**3′**, top).

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 [Fe(η^4-$P_2C_2Me_2$)$_2$]$^{2-}$ (**4′**). Whereas the theoretical calculations indicate **4′** to be a viable species, no reduction of K**2** 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 [Fe(η^4-C_4H_4)$_2$] (**1**, D_{4h}) and **3′**. Like **3′**, the triplet ground state of **1** is also highly favored over the open-shell singlet (ΔE = 20.7 kcal mol^{-1}) and the quintet (ΔE = 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 (ΔE = −20.5 kcal mol^{-1}) exceeds that of MeC≡P (ΔE = −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 phosphaorganic 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

K**2:** *t*BuC≡P (5 mL, 10.0 mmol, 2 M solution in hexanes) was added dropwise to a deep brown solution of [K([18]crown-6)(thf)$_2$][Fe($C_{14}H_{10}$)$_2$] (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. [K([18]crown-6)(thf)$_2$][Fe($P_2C_2tBu_2$)$_2$] 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 K**2** with *n*-pentane. Yield 1.41 g (75%). Elemental analysis (%) calcd for $C_{32}H_{60}O_6P_4FeK$ (M = 759.66): C 50.59, H 7.96; found: C 49.74, H 7.95; m.p. > 300 °C (slow dec). ^{1}H NMR (250.13 MHz, [D$_8$]THF): δ = −1.9 (very br s; *t*Bu), 1.73 (br s; THF), 3.72 ppm (br s; THF). Magnetic susceptibility (Evans method, 25 °C, [D$_8$]THF): μ_{eff} = 1.77 μ_B. UV/Vis (THF) λ_{max} [nm] (ε [mol^{-1} dm^3 cm^{-1}]): 296 (48100), 383 (10000), 699 (310).

3: [Cp$_2$Fe][PF$_6$] (0.050 g, 0.15 mmol) was added to a dark orange solution of K**2** (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). ^{1}H NMR (250.13 MHz, C_6D_6): δ = 2.6 ppm (very br s; *t*Bu). Magnetic susceptibility (Evans method, 25 °C, C_6D_6): μ_{eff} = 2.74 μ_B. UV/Vis (THF) λ_{max} [nm] (ε [mol^{-1} dm^3 cm^{-1}]): 275 (65700), 320 (shoulder), 443 (11000). HRMS (EI): *m*/*z* (%): 456.1 (60), calcd for $C_{20}H_{36}P_4Fe$: 456.1100, found: 456.1117.

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