

Organometallic Chemistry

Organometallic Fe–Fe Interactions: Beyond Common Metal–Metal Bonds and Inverse Mixed-Valent Charge Transfer

Mark R. Ringenberg,*^[a] Max Schwilk,^[b] Florian Wittkamp,^[c] Ulf-Peter Apfel,^[c] and Wolfgang Kaim^[a]

Abstract: The compounds $[Fe(CO)_3(dRpf)]^{n+}$, n=0, 1, 2dRpf = 1,1'-bis(dicyclohexylphosphino)ferrocene and $([1]^{n+})$ or 1,1'-bis(diisopropylphosphino)ferrocene $([2]^{n+})$, were obtained as two-step reversible redox systems by photolytic and redox reactions. The iron-iron distance decreases from about 4 Å to about 3 Å on oxidation, which takes place primarily at the tricarbonyliron moiety. Whereas ferrocene oxidation is calculated to occur only in excited states, the near infrared absorptions of the mixedvalent monocations are due to an unprecedented "inverse" inter-valence charge transfer from the electron-rich iron(II) in the ferrocene backbone to the electron-deficient tricarbonyliron(I). Protonation of complex 1 results in the formation of the structurally characterized hydride [1H]BF4, which reacts with acetone to form the dication, 1^{2+} , and isopropanol. While the hydride [2H]BF₄ was found to be unstable, protonation of 2 in acetone resulted in the clean formation of 2^{2+} formally a hydrogen transfer.

Compounds of iron, the ultimate earth-abundant transition metal, have been increasingly used in organic synthesis.^[1] Ideally, application of iron as a catalyst requires an understanding of electronic structures and skills in manipulating the coordination environment of the metal, especially in those cases where more than one active center is involved, for example, in bifunctional catalysis.^[2] Although organoiron compounds are available from high (Fe^{IV}) to low (Fe^{-II}) oxidation states,^[3] combining two rather different organoiron units has rarely been reported.

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One such example is the Fe⁰Fe^{II} species [Fe(CO)₃(dppf)], dppf = 1,1'-bis(diphenylphosphino)ferrocene, which was obtained as part of a product mixture from the thermal reaction of Fe(CO)₅ with dppf.^[4]

Transition metal complexes of 1,1'-bis(diorganylphosphino)ferrocene (dRpf) ligands have been successfully used as ligands in catalysis.^[5] These complexes are of particular interest due to possible ferrocene iron-metal interactions,^[6] including redox activity,^[7] which can be considered non-innocent behavior.^[8]

Herein we report the remarkable behavior of [Fe-(CO)₃(dchpf)] (1) and [Fe(CO)₃(dⁱppf)] (2), dchpf = 1,1'-bis(dicyclohexylphosphino)ferrocene and dⁱppf = 1,1'-bis(diisopropylphosphino)ferrocene, each containing two organoiron centers with rather different electronic and steric character. Complexes 1 and 2 were synthesized by an improved photolytic method (see Supporting Information). The redox chemistry was studied to establish the electron transfer site and to probe the possibility of iron-iron interaction between the ferrocene-iron (FcFe) and the tricarbonyl-iron (TCFe) centers. Remarkably, the complexes reported herein could be protonated, leading to the formation of a terminal hydride, which in the presence of acid is capable of reducing acetone to 2-propanol, effectively a hydrogen transfer.

The infrared spectra of **1** and **2** exhibit three bands in the CO stretching region, consistent with the molecular structure of **1** (Figure 1), in which the TCFe moiety is part of an approximately bipyramidal arrangement (τ =0.70). The P atoms are in an equatorial position (P2-Fe1-P1 110.41(5)°), and d_{Fe-Fe} = 4.151 Å constitutes a non-bonding distance. Crystals of **2** were



Figure 1. Molecular structure of complex 1 in the crystal; ellipsoids are shown at 50% probability and H atoms are omitted for clarity.

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found to be unstable, decomposing when placed on the diffractometer, however, IR, UV/Vis, and Mössbauer spectra of the two compounds show only minor differences. DFT calculations for compounds 1 and 2 are well supported by the experimental structure of complex 1 (see Supporting Information). Due to the close structural relationship of 1 and 2, we focused on complex 2 for more thorough calculations over 1 to reduce computing time.

The Mössbauer spectrum of **1** (see Figure S1 in the Suppporting Information) indicates two different Fe sites in a 1:1 ratio with isomer shifts of $\delta = 0.45$ (ΔE_q 1.91) and 0.02 (ΔE_q 1.48) mm s⁻¹, revealing no obvious interaction between the two iron centers. Likewise, two different iron sites can be found in complex **2** ($\delta = 0.46$ (ΔE_q 1.94) and -0.01 (ΔE_q 1.44) mm s⁻¹) (see Figure S3). The higher isomer shifts for **1** and **2** are consistent with a low-spin ferrocene backbone, whereas the lower values indicate increased s-electron density on the nucleus, consistent with *trans*-[Fe(CO)₃(*PiP*r₃)₂] and other related TCFe complexes.^[9]

Cyclic voltammetry (CV) of **1** and **2** (Figures 2 and S5 in the Supporting Information) reveals two quasi-reversible oxidation processes, $E_{1/2}[1]^{0/+} = -0.32$ V versus FeCp₂^{0/+} (the standard reference for all potentials reported herein), $E_{1/2}[1]^{+/2+} = 0.12$ V, and $E_{1/2}[2]^{0/+} = -0.26$ V, $E_{1/2}[2]^{+/2+} = 0.14$ V (see Table S1 in the Supporting Information). These potentials correspond to sizeable comproportionation constants $K_{comp} = 10^{7.5}$ and $10^{6.8}$ for the intermediates [1]⁺ and [2]⁺, respectively. These large K_{comp} values allow for well-resolved spectroelectrochemistry of monocation intermediates. The nature of these two redox processes is complicated by the presence of two redox moieties,



Figure 2. Cyclic voltammogram and differential pulse voltammogram of 1 (1 mm) at 0.1 V s⁻¹ in CH₂Cl₂/0.1 m Bu₄NPF₆.



Scheme 1. Electronic structure alternatives for the oxidation of 1 or 2.

FcFe and TCFe. The goal herein is to elucidate which electronic structure outlined in Scheme 1 best describes the redox behavior observed in the CV, using spectroscopic and computational analysis.

The X-band EPR spectra at 298 K of electro-generated [1]⁺ and [2]⁺ exhibit triplet splitting from two equivalent P nuclei $({}^{31}P, I = {}^{1}/_{2})$ (see Figures S10 and S11). The values $g_{iso} = 2.018$ and $a_{p} \approx 11.5$ G for [1]⁺ and [2]⁺ are lower than the parameters for common bisphosphine tricarbonyliron complexes (see Table S2), which have $g_{iso} \approx 2.05$, $a_{p} \approx 19$ G,^[10] suggesting a diminished spin density at the TCFe^I moiety (see Supporting Information). This supports involvement of the ferrocene backbone in stabilizing intermediates [1]⁺ and [2]⁺. Accordingly, the calculated spin densities on TCFe and FcFe in [2]⁺ are + 0.44 and + 0.13 (see Table S3), respectively, corresponding to a dominant pathway 1 in Scheme 1.

Infrared spectroelectrochemical (SEC) response of the [1]^{0/+} and [2]^{0/+} processes results in blue shifts of $\Delta v_{CO} \approx 80 \text{ cm}^{-1}$ (Figures 3, and S12 in the Supporting Information), which is lower than the average $\Delta v_{CO} \approx 100 \text{ cm}^{-1}$ observed for related bisphosphine tricarbonyliron monocations (see Table S4^[10]), supporting a small but notable ferrocene involvement in the redox process.

UV/Vis-NIR SEC response of the oxidations $[1]^{0'+}$ and $[2]^{0'+}$ is accompanied by the appearance of two new long-wavelength absorptions (see Figure 4, and S14 in the Supporting Information). The corresponding transitions were assigned according to TD-DFT calculations for $[2]^n$ (see Supporting Information). The absorptions at λ_{max} =535 nm correspond to a SOMO to LUMO+1 transition, where the SOMO resides primarily on the TCFe-based antibonding orbital between the two Fe atoms and the LUMO+1 (a d orbital on TCFe, see Supporting Information). The absorptions at λ_{max} =790 nm for $[1]^+$ and $[2]^+$ consist of a HOMO-3 to SOMO transition, the former best described as involving a dative bond from the ferrocene iron to TCFe. A further transition to the SOMO was calculated at 1017 nm which, however, does not appear as a strong band in the spectra (see Supporting Information for MOs). The low-



Figure 3. IR spectroelectrochemical response of the transitions [1]^{0/+} (left) and [1]^{+/2+} (right) in CH₂Cl₂/0.1 M Bu₄NPF₆. The end spectrum is shown in red.

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Figure 4. UV/Vis-NIR spectroelectrochemical response of the transitions $[1]^{0'+}$ (left) and $[1]^{+/2+}$ (right) in CH₂Cl₂/0.1 M Bu₄NPF₆.

energy transitions in the cations may thus be described as "inverse" inter-valence charge transfer processes, from Fe^{II}(ferrocene) with a high formal oxidation state to Fe^I(TCFe). Such counterintuitive "inverse" transitions are made possible through the very different ligation, donating for ferrocene iron but π -accepting for TCFe.

The calculated structure for $[2]^+$ suggests a bond order of 0.5 between the ferrocene iron and TCFe. The back donation from the ferrocene iron to TCFe shown in Figure 5 can be best described as a dative bond between the two metal centers. The complex $[Cp*Co(CO)_2]_2[Al(OC(CF_3)_3]_4$ exhibits similar bonding, akin to three-electron σ -bonds.^[11] Although the oxidation is calculated to occur at TCFe for 2, it is clearly supported by interaction with the ferrocene-iron as seen from the SOMO of 2^+ (Figure 5).

Attempts to observe $[1]^+$ or $[2]^+$ by Mössbauer spectroscopy have been unsuccessful due to decomposition of the sample under the extended electrolysis used to generate Fe¹ species. Thus far attempts to isolate Fe¹ species by chemical oxidation have been unsuccessful.

The treatment of 1 with HBF₄ in CH₂Cl₂ results in the formation of the hydride species [1H]BF₄. The observed v_{co} shifts of \approx 100 cm⁻¹ are consistent with the positive charge in the region of the TCFe (see Figure S20). The ³¹P NMR spectrum contains a new doublet at δ = 54 ppm, and the ¹H NMR spectrum contains an upfield triplet at δ = -7.24 ppm (see Figure S21). The molecular structure of $[1H]BF_4$ is shown in Figure 6. While the hydride ligand could not be definitively assigned based on X-ray crystallographic analysis, the facially arranged carbonyl ligands, the phosphorus donors in *cis* position, and the single BF_4^- counter ion are well established. The ligand arrangement and charge balance are consistent with the presence of a sixth ligand (Figure 6), and the anomalous electron density close to the iron center was assigned to the hydride during structural refinement.^[13] The hydride [2H]BF₄ was unstable in solution, forming a complex mixture of products as evident from ³¹P NMR spectroscopy (see Figure S22).



Figure 6. Molecular structure of $[1H]BF_4$ in the crystal; ellipsoids are shown at 50% probability, hydrogen atoms and BF_4^- are omitted for clarity.



Figure 5. Calculated structure of [2]⁺ overlaid with the intrinsic bond orbitals (IBOs) for the Fe–Fe interaction in [2]⁺ (left); SOMO in [2]⁺ (right) visualized using IboView, 80% isosurface.^[12].

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Treatment of 1 or 2 with HBF₄ in acetone produces cherry red products $[1](BF_4)_2$ and $[2](BF_4)_2$ (Scheme 2). ¹H NMR monitoring of this reaction shows that the oxidation is coupled to the formation of isopropanol from acetone through hydride transfer (see Supporting Information). The molecular structure of $[Fe(CO)_3(d^ippf)](BF_4)_{2'}$ [2](BF₄)_{2'} (Figure 7) exhibits an ironiron distance $d_{\text{Fe-Fe}}$ of 2.9634(15) Å and a P1-Fe1-P2 angle of



Scheme 2. Synthesis of dications.

161.98(8)°; crystals of [1](BF₄)₂ were unsuitable for X-ray analysis. The Fe-Fe distance is 0.3 Å longer than the sum of the covalent radii for two low spin ferrous atoms (2.64 Å).^[14] For comparison, unsupported Fe-Fe "bonds" have been reported between 2.39-3.14 Å.^[15] An Fe-Fe bond is also typical for [FeFe]hydrogenase active site models, where bridging thiolates support an average *d*_{Fe-Fe} of 2.51 Å.^[16] Previous studies of bisphosphine tricarbonyliron complexes did not show any formation of dications,^[10] the ferrocene backbone and Fe-Fe interaction being associated with stabilizing the unusual ferrous state of the TCFe moiety.

The ¹H NMR spectra have two signals for the H_{α} and H_{β} protons on the ferrocene group with separations of $\Delta \delta =$ 2.06 ppm and 0.87 ppm for $[1]^{2+}$ and $[2]^{2+}$, respectively, larger than those for neutral **1** and **2** at about $\Delta \delta = 0.10$ ppm. Tamm and co-workers have reported a similar behavior for ferrocene ligands when Fe-Pt or Fe-Ni bonds were formed.^[6]

The IR SEC response for the $[1]^{+/2+}$ and $[2]^{+/2+}$ processes reveals average blue shifts of $\Delta v_{CO} \approx 65 \text{ cm}^{-1}$ with only two discernible v_{co} bands (Figures 3 and S13 in the Supporting Information). This is consistent with a geometry change from free-

coordination (approximately tbp, $\tau = 0.70$) to nearly octahedral (Figure 6) including the Fe–Fe interaction. This change leads to convergence of the two lower energy ν_{CO} bands.

The second oxidation $[1]^{+/2+}$ and $[2]^{+/2+}$ results in a strong absorption at $\lambda_{max} = 500$ nm and in the disappearance of the λ_{max} = 795 nm band (Figures 4 and S15 in the Supporting Information). The absorption at 500 nm is assigned to a charge transfer involving the Fe-Fe bond, represented by the HOMO-3 to LUMO transition involving two corresponding dorbitals on each of the Fe atoms (see Figure S18). The transition thus contains a charge transfer from the ferrocene moiety to the TCFe center, both ferrous sites(!).

Mössbauer spectroscopy was used to assist in the assignment of the oxidation states. The spectra for the dications, $[\mathbf{1}]^{2+}$ $\delta = 0.46$ (ΔE_a 1.90) and 0.40 (ΔE_a 0.35) mm s⁻¹ (Figure S2), and $[\mathbf{2}]^{2+}$ $\delta = 0.46$ (ΔE_a 1.85) and 0.42 (ΔE_a 0.51) mm s⁻¹ (Figure S4), differ considerably from those of 1 and 2. The isomer shifts for the ferrocene part do not change significantly, consistent with a ferrous site. However, the isomer shifts for TCFe are significantly altered. The quadrupole doublets are highly unsymmetric which can be attributed to the altered relaxation of the electrons from different nuclear energy levels, caused by the weak metal-metal interaction. Thus, localized valences with an electron exchange rate $k_e > 10^{-6} \text{ s}^{-1}$ can be expected in the Mössbauer spectra of both dications.

The assignment of oxidation numbers in the ground states of the dications, that is, TCFe^{II}-ferrocene or TCFe^I-ferrocenium (Scheme 1), suggests that the ferrocene remains in the Fe^{II} state. In fact, the computed IBOs reveal that the ferrocene-iron is donating electron density into the d_z^2 orbital of TCFe (Figure 7). Although a similar behavior has been reported for ferrocene-based ligands bound to late transition metals (i.e. Pd or Ni),^[17] to our knowledge this is the first evidence for *ferro*cene iron-to-iron bonding. The ferrocene iron forms a dative bond to TCFe, thus stabilizing its unprecedented ferrous state in the dication.



Figure 7. Molecular structure (left) of the dication 2(BF₄)₂ in the crystal; ellipsoids are shown at 50% probability and hydrogen atoms and both BF₄⁻ anions are omitted for clarity. Calculated structure of $[2]^{2+}$ (right), overlaid with the IBOs for the Fe–Fe bond in $[2]^{2+}$, 80% isosurface.

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Although the oxidation occurs mainly at TCFe, the ferrocene moiety is critical in the redox chemistry of **1** and **2** as it stabilizes the dications, $[1]^{2+}$ or $[2]^{2+}$, as observed by electrochemistry and spectroelectrochemistry. Upon oxidation, the TCFe moiety moves toward the ferrocene iron. A dative bond is formed between the ferrocene-iron and oxidized TCFe, which has been established both crystallographically and computationally. Clearly, the dRpf metallo-ligand is not merely a spectator towards TCFe.

In conclusion, we have demonstrated a redox-dependent intramolecular connection between two different standard organoiron entities, one ferrocene and one tricarbonyliron component (Scheme 3). Two-step single electron transfer is observed,



Scheme 3. Simplified molecular orbitals of different charge states.

concentrated mainly at the Fe(CO)₃ moiety, and resulting in an unusual Class II mixed-valent (Fe^{II}Fe^I) intermediate with a comproportionation constant K_c of about 10⁷ and an *inverse* intervalence charge transfer transition ($Fe^{II} \rightarrow Fe^{I}$) at about 800 nm. Fe^{II}Fe^I (d⁶d⁷) mixed-valent species have been much discussed recently as essential intermediates in [FeFe]-hydrogenase enzymes and their (frequently phosphane-containing) models.^[18] Due to geometrical constraints from the ligands in $[1]^n$ and $[2]^n$ the iron-iron distance varies from a clearly non-bonding 4 Å in the TCFe⁰-ferrocene case with pentacoordinate TCFe to a noticeable interaction below 3 Å for the TCFe^{II}-ferrocene dication species with hexacoordinate tricarbonyliron(II). [FeFe]-Hydrogenases and their models have typical iron-iron distances of 2.5 Å.^[16] Our next efforts will be directed at establishing the available reactivity patterns of such diiron systems for example, in hydrogen-involving conversions. The complexes described herein are of particular interest as candidates for catalysis due to the reversibility of the two-electron process and the apparent hydride transfer to acetone.

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Organometallic Fe–Fe Interactions: Beyond Common Metal–Metal Bonds and Inverse Mixed-Valent Charge Transfer



Two prototypical but very different organoiron moieties, ferrocene and tricarbonyliron, can interact electronically in an intramolecular setting. Unusual oxidation state combinations, structural effects, and redox reactions were observed and analyzed experimentally and theoretically.