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Bis-Ferrocenyl-Pyridinediimine Trinuclear Mixed-Valent Complexes with Metal-Binding Dependent Electronic Coupling: Synthesis, Structures, and Redox-Spectroscopic Characterization

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ABSTRACT: A family of metal dichloride complexes having a bisferrocenyl-substituted pyridinediimine ligand was systematically synthesized ((Fc₂PDI)MCl₂, M = Mg, Zn, Fe, and Co) and characterized crystallographically, spectroscopically, electrochemically, and computationally. Electronic coupling between the ligand ferrocene units is switched on upon binding to a MCl₂ fragment, as evidenced by both sequential oxidation of the ferrocenes in cyclic voltammetry ($\Delta E_{ox} \approx 200 \text{ mV}$) and by Inter-Valence Charge Transfer electronic excitations in the near IR. Additionally, UV–vis spectra are used to directly observe orbital mixing between the ferrocenyl units and the imine π system since breaking of the orbital symmetry results in allowed transitions ($\epsilon = 2800 \text{ M}^{-1}\text{cm}^{-1}$ vs $\epsilon \approx 200 \text{ M}^{-1}\text{cm}^{-1}$ in free ferrocene) as well as broadening and red-shifting of the ferrocenyl

Trinuclear class II mixed-valent complexes Metallation "switches on" Fc-Fc electronic coupling



transitions—indicating organic character in formerly pure metal-centered transitions. DFT analysis reveals that interaction between the ferrocenes and the MCl₂ fragment is small and suggests that communication is mediated by better energy matching between the ferrocene and organic π^* orbitals upon coordination, allowing superexchange coupling through the LUMO. Furthermore, single crystal diffraction data obtained from oxidation of one *and* both ferrocenes show distortions, introducing the empty d_{xy}/d_{x2-y2} orbitals into the secondary coordination sphere of the MCl₂ fragment. Such structural rearrangements are infrequent in ferrocenyl mixedvalent compounds, and implications for catalysis as well as electronic communication are discussed.

INTRODUCTION

Traditional paradigms in understanding the reactivity of coordination complexes focus predominantly on metal identity and formal oxidation state.¹ In catalysis, the metal center is conventionally viewed as the primary site of reactivity, and this metal-centric view is fruitful when the metal center's properties and its interactions with substrates can be reliably predicted as is often the case in second- or third-row transition metals where strong ligand fields tend to localize frontier orbitals on either the metal or ligand.^{1,2} However, there is growing recognition that this view is not generalizable to all complexes, particularly those of first-row metals with highly conjugated ligands.⁴ The combination of weak ligand fields and highly delocalized frontier orbitals generates complexes with properties not uniquely defined by metal identity and oxidation state, as the frontier orbitals involve substantial mixing with the π ligand backbone.⁵ As such, these catalytic systems can be viewed as being electronically coupled between the metal and ligand—as delocalization of frontier orbitals across the metal and ligand causes changes at one site to perturb the chemistry at the other.⁶

An increasing number of catalysts take advantage of such "non-innocent" ligands 7 that are electronically coupled to

metal centers. Although most ligands can become "noninnocent" under the appropriate conditions,^{4,6} the pyridinediimine ("PDI"; Scheme 1) ligand family has become a prominent example in noninnocent ligand catalysis.⁸ PDI ligands can act as electron reservoirs to store electrons or other reducing equivalents (e.g., hydrides or alkyls at electrophilic sites)⁹ during catalytic cycles,^{7c,10} permitting first-row metal complexes to both emulate the 2-electron chemistry of noble metals, as well as access highly reduced states.^{7c} While the reactivity of such metal-ligand coupled systems has been extensively studied, challenges remain in defining electron localization/delocalization throughout the complex, and reliably predicting which scaffolds will exhibit strong delocalization. Such questions are central to the study of mixed-valent compounds, which contain multiple metal centers in different oxidation states connected by π -linkers that serve

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as a conduit for delocalization.¹¹ Diverse spectroscopic and theoretical tools have been developed for quantifying and characterizing the degree of coupling and delocalization in mixed-valent systems such as NMR, XPS, EPR, UV/vis–NIR, CV, DSC, Mössbauer, and IR/Raman techniques.^{10e,11c,d,12}

Mixed-valent compounds have attracted attention from both physical and synthetic chemists for their interesting electronic structures and electron transfer properties, resulting in a wide diversity of synthetic and structural data to utilize in molecular design.^{11d} The impetus for such longstanding interest is driven by potential applications in molecular wires,¹³ nonlinear optics,¹⁴ catalysis,¹⁵ and testing models for electron transfer.¹⁴ However, the application of mixed-valency in structures capable of acting as ligands toward other transition metals is rare. Indeed, there is great interest in metal-ligand redox and reactivity cooperativity and metallo-ligand mediated electronic coupling between metals in the chemistry community. Despite interest, the application of mixed valency toward exploring the effects of electronically coupled binuclear scaffolds that could be applied to catalysis has been challenging,¹⁷ due to issues of (A) chemical stability in different redox states;¹⁸ (B) establishing clear design criteria for engendering strong coupling, as similar structures often exhibit different coupling strengths as a result of the balance between geometric and electronic factors that lead to coupling;^{11b,19} and (C) designing scaffolds that are modular enough to retain coupling while parametrizing steric and electronic properties to optimize catalysis. Most mixed-valent catalysts capitalize on cooperative effects between metals that have different chemistries in different oxidation states (e.g., using Class I mixed valent structures with little to no delocalization between metals), or otherwise do not well characterize the effect of metal delocalization on reactivity.^{17b,20} However, work in direct metal-metal interactions between ferrocene and d⁰ metals has revealed promising electronic structures and catalytic activity.²¹ We are exploring electronically coupled metal sites as an opportunity to engineer gated electron transfer and multielectron redox events, binuclear mechanisms, strong electric field gradients, and other properties that feature prominently in efficient biological and abiotic catalysts.²² Despite this open question in inorganic chemistry, mixed valent motifs with known Class II or III behavior exist prominently in biological

systems. Notably, iron sulfur clusters are ubiquitous in proteins and serve as both electron buffers and electron transfer conduits for intermediates in enzymatic catalysis.²³ Given mixed valency's ubiquity in nature, inorganic catalysis could benefit from the detailed examination of how electronic coupling affects catalyst structure and reactivity. Under this lens, mixed valency provides an opportunity to explore chemical space in noninnocent ligand catalysis while capitalizing on well-characterized electronic structures, synthetic strategies, and established theoretical frameworks. Nevertheless, such systems are challenging to create in a reliable, modular way, and the chemical space explored remains insufficient to deduce general principles.^{17b,18,19,24}

Thus, we sought to construct ferrocene-based ligand frameworks with well-understood electronic structures to better characterize the interactions between metals and their mechanisms of interaction. The PDI ligand structure (Scheme 1) was targeted because heteroaromatics such as pyrrole and pyridine are known to enhance coupling between ferrocenyl groups.^{11b,19b,25} Furthermore, both ferrocenes and the central metal share bonding with the imines, providing close throughbond connectivity, and a low-lying π^* network^{8c} to mix the metal orbitals-both important for strong electronic communication.^{11a,26} Note that thus far only the main group coordination chemistry of ferrocene-substituted PDI ligands has been reported,²⁷ and the transition metal chemistry remains unexplored. Here we report the synthesis, solid state structural, and spectroelectrochemical characterizations of a series of s- and d-block ferrocenyl PDI ("Fc₂PDI") complexes (Scheme 1). Intriguingly we find the electronics of these complexes to be largely independent of the central metal ion identity, yet that metal binding is required for coupling between ferrocenes. This finding is further explained by DFT computation, showing that the frontier orbitals are primarily ferrocene- and PDI- based, featuring little MCl₂ character. Electronic characterizations suggest that M(II) binding stabilizes the ligand π -system which increases mixing of the Fc moiety and imine π -orbitals, providing a conduit for delocalization. Notably a 3-state IVCT mechanism involving mutual coupling from the Fc units to the pyridine aryl system in the excited state is suggested as the mode of coupling. Furthermore, crystallography and DFT analysis performed on

the neutral, mixed valent (Fc/Fc⁺), and doubly oxidized (Fc⁺/ Fc⁺) species indicate significant structural changes upon oxidation, which may limit the degree of coupling but presents the Fe(III) ferrocenium close to the MCl₂ center, suggesting opportunities for catalysis.

EXPERIMENTAL SECTION

General Considerations. All procedures for air- and moisturesensitive compounds were carried out with rigorous exclusion of O₂ and moisture in flame or oven-dried Schlenk-type glassware interfaced to a dual-manifold Schlenk line or Ar fed high-vacuum $(10^{-6} - 10^{-7})$ Torr) line using an oil diffusion pump, or in an Ar-filled MBraun glovebox with a high capacity recirculator (<0.5 ppm of O₂). Argon for high-vacuum lines (Airgas, UHP grade) was purified by passage through MnO/vermiculite and Davison 4 Å molecular sieve columns. All solvents were degassed by freeze-pump-thaw techniques, excepting tetrahydrofuran (THF) and diethyl ether (Et₂O) which were freshly distilled from sodium using benzophenone indicator (persistent purple). All solvents were stored under inert atmosphere in a Teflon-sealed solvent flask for syringe or vacuum transfer. Dichloromethane (DCM) was distilled off CaH2. Methanol and ethanol were dried over 3 Å molecular sieves and filtered through a cannula (oven-dried with a glass fiber filter). NMR solvents were purchased from Cambridge Isotope Laboratories (>99 atom % D). CD₂Cl₂ used for NMR characterization of complexes was distilled off CaH₂, degassed by freeze-pump-thaw method, and vacuum transferred as needed into Teflon valve-sealed NMR tubes (dried in an oven overnight). Iodoferrocene²⁸ and aminoferrocene²⁹ were synthesized according to literature procedures. Electrodes were purchased from Bioanalytical Services in West Lafayette, IN.

Physical and Analytical Measurements. Solution ¹H and ¹³C NMR spectra were recorded on a 500 MHz Bruker Avance III HD system equipped with a TXO Prodigy probe. Chemical shifts for ¹H and ¹³C spectra were referenced using internal solvent resonances and are reported relative to tetramethylsilane (TMS). UV–vis measurements were taken on a PerkinElmer LAMBDA 1050 double beam spectrophotometer, using a 1 cm quartz cuvette in dry-degassed DCM. Fitting of the UV–vis spectra was done using Fityk software³⁰ using pure Gaussian peaks. Elemental analyses were performed in an air free glovebox by Midwest Microlab, Indianapolis, Indiana for % C, N, H. Crystallographically observed DCM solvates were included in % C, H, N calculation.

Computational Methods. All quantum chemical calculations were performed using the Gaussian 09.D01 software.³¹ Geometry optimizations of all complexes were carried out at the B3LYP³²/6-31+G(d,p) level of theory. Frequency calculations at the same level were performed to validate each structure as a minimum. The UV–visible spectra of all complexes were calculated using TD-DFT theory at the B3LYP/6-311++G(d,p) level of theory. The dichloromethane solvent effect was calculated by the Polarizable Continuum Model (PCM).³³

Crystallography. Single crystals were mounted in Paratone oil and transferred to a cold nitrogen gas stream of a Bruker Kappa APEX CCD area detector equipped with a MoK α microsource. The crystal was maintained at 100.0 K during data collection. The structures were solved using Olex2³⁴ with the XT structure solution program³⁵ and refined using the ShelXL refinement package³⁶ with full-matrix least-squares procedures.

Electrochemistry. Electrochemistry was performed in drydegassed DCM. The electrolyte, tetrabutylammonium tetrakis[3,5bis(trifluoromethyl)phenyl]borate³⁷ (TBA-BArF) was prepared according to literature procedures.³⁸ CV was performed in the dark under a dynamic blanket of N₂ (100 mM TBA-BArF, 1 mM analyte) using Pt working and counter electrodes, and an Ag wire pseudoreference with a Cp*₂Fe internal standard³⁹ of known concentration. The working electrode was polished with alumina paste, while the counter electrode was flame polished and the silver wire was polished with fine sandpaper. **Spectroelectrochemistry.** Spectroelectrochemistry was performed on a CH Instruments Electrochemical Workstation by bulk electrolysis in a glovebox using a carbon foam working electrode, Pt wire counter electrode, and Ag pseudoreference (prepared as described above). Aliquots were taken and transferred to an ovendried 0.2 cm quartz cuvette sealed with a Teflon valve. Spectra were taken on a Shimadzu UV-36000 plus UV/vis–NIR spectrometer (300–3000 nm). The difference spectra were generated by subtraction of the scan featuring the previous electrochemical species (e.g., neutral/monocation, monocation/dication). Due to solvent evaporation over long electrolysis times, these plots are presented in un-normalized absorbance units. Potential was incremented by 50 mV steps until potentiometry indicated oxidation was sustained at the working electrode and maintained until current became negligible.

Syntheses. Fc₂PDI. para-Toluenesulfonic acid (~2 mg, ~0.01 mmol), 2,6-diacetal pyridine (154 mg, 0.94 mmol), and 399 mg of FcNH₂ (1.98 mmol) were added to a flame-dried Schlenk flask under inert atmosphere. A dry reflux condenser was attached, and the atmosphere was replaced with N2. Then, 10 mL of dry and degassed ethanol was added by syringe, and the reaction was allowed to reflux for 18 h, over which time the solution turned dark red and crystalline material precipitated from solution. The reaction mixture was cooled to 0 °C, concentrated in vacuo, and filtered by cannula. The red crystalline product was washed with cold ethanol and dried. Isolated vield: 292 mg, 58%. Further product can be recovered from the filtrate by recrystallization from DCM/pentane. ¹H NMR (CD₂Cl₂, 500 MHz): 8.27 (d, J = 7.8 Hz, 2H, m-Py), 7.81 (t, J = 7.8 Hz, 1H, p-Py), 4.46 (t, J = 1.9 Hz, 4H, Cp- β), 4.26 (t, J = 1.9 Hz, 4H, Cp- γ), 4.21 (s, 10H), 2.56 (s, 6H, CH₃). ¹³C (CD₂Cl₂, 126 MHz): 166.15(C=N), 157.08(Py-ipso.), 136.95 (Py-p), 121.66 (Py-m), 103.98 (Cp-ipso), 69.93 (Cp), 67.29 (Cp-β), 66.16 (Cp-γ), and 16.82 (CH₃). Anal. Calcd for Fc₂PDI, formula C₂₉H₂₇N₃Fe₂: C, 65.81; H, 5.14; N, 7.94. Found: C, 65.66; H, 4.99; N, 7.87.

 $(Fc_2PDI)CoCl_2$. Fc_2PDI (50 mg, 0.094 mmol) and 12 mg (0.094 mmol) of anhydrous CoCl₂ were added to a flame-dried Schlenk flask in a glovebox. Then, 10 mL of DCM was added via syringe and the reaction was allowed to stir at room temperature for 24 h as it turned from red to blue. Over this time blue crystals fell from solution. The solution was diluted with DCM to dissolve all the blue solids and filtered by cannula. The filtrate was subsequently concentrated and diluted with Et_2Oto precipitate the product. The product (Fc_2PDI)-CoCl₂ was washed with Et_2O under inert atmosphere until the filtrate was clear and recrystallized by DCM/Et₂O layering at -40 °C. Isolated yield: 42 mg of blue crystals 68%. Anal. Calcd for (Fc_2PDI)CoCl₂·DCM (1 crystallographic DCM per unit cell), formula $C_{30}H_{29}N_3Fe_2CoCl_4$: C, 45.43; H, 3.74; N, 5.08. Found: C, 44.92; H, 3.77; N, 5.07.

(*Fc*₂*PDI*)*FeCl*₂. **Fc**₂**PDI** (100 mg, 0.0198 mmol) and 24 mg (0.0198 mmol) of anhydrous FeCl₂ were added to a flame-dried Schlenk flask under inert atmosphere. Five mL of freshly distilled THF was added by syringe, and the reaction was allowed to stir at room temperature for 24 h. The solvent was removed under vacuum, and the crude mixture was taken up in minimal DCM and filtered by cannula. Twice the volume in freshly distilled Et₂O was layered on-top and the mixture was allowed to crystallize at -40 °C. The resulting blue crystals were collected by cannula filtration and dried under high vacuum overnight to give (Fc₂PDI)FeCl₂. Isolated yield: 50 mg of blue-crystals (40%). Anal. Calcd for (Fc₂PDI)FeCl₂, formula $C_{29}H_{27}N_3Fe_3N_3Cl_2$: C, 52.73; H, 4.14; N, 6.16. Found: C, 53.10; H, 4.15; N, 6.41.

(*Fc*₂*PDI*)*ZnCl*₂. *Fc*₂*PDI* (400 mg, 0.76 mmol) and 100 mg of ZnCl₂ (0.73 mmol) were added to a flame-dried Schlenk flask under inert atmosphere, and 5 mL of DCM was added. The reaction was allowed to stir overnight at room temperature. The resulting blue solution was filtered by cannula, and the microcrystalline product was washed with Et₂Oto give (*Fc*₂*PDI*)*ZnCl*₂, which was recrystallized by DCM/Et₂O layering at -40 °C. Isolated yield: 260 mg of blue crystals (52%). ¹H NMR (CD₂Cl₂, 500 MHz): 8.29 (pseudodd, *J* = 8.3, 7.6 Hz, 1H, py-*p*), 8.13 (d, *J* = 8.0 Hz, 2H, py-*m*), 5.13 (t, *J* = 2.0 Hz, 4H, Cp- β), 4.51 (t, *J* = 2.0 Hz, 4H, Cp- γ), 4.29 (s, 10H, Cp), 2.82 (s, 6H, CH₃). ¹³C

 $(CD_2Cl_2, 126 \text{ MHz}): 157.44$ (C=N), 151.44 (Py-ipso), 143.68 (Py-*p*), 124.08 (Py-*m*), 97.15 (Cp-ipso), 70.82 (Cp), 70.07 (Cp-β), 69.50 (Cp-γ), 18.88 (CH₃). Anal. Calcd for (**Fc₂PDI)ZnCl₂**·DCM (1 crystallographic DCM per unit cell), formula $C_{30}H_{29}N_3Fe_2ZnCl_4: C$, 48.01; H, 3.89; N, 5.60. Found: C, 48.28; H, 3.78; N, 5.82.

(Fc₂PDI)MqCl₂. Fc₂PDI (212 mg, 0.4 mmol) and 38 mg (0.4 mmol) of anhydrous MgCl₂ were added to a flame-dried Schlenk flask under inert atmosphere. Then, 5 mL of anhydrous DCM and 5 mL of anhydrous MeOH were added by syringe, and the solution was allowed to stir for 24 h at room temperature. The solvent was evaporated under vacuum and the blue/purple solids were redissolved in DCM, then filtered by cannula. The solution was concentrated under vacuum, and the complex was recrystallized overnight by layering with Et₂O at -40 °C. The highly moisture-sensitive crystals were dried under high vacuum overnight to give (Fc2PDI)MgCl2. Isolated yield: 211 mg of blue/purple plate-like crystals (84%). ¹H NMR (CD₂Cl₂, 500 MHz): 8.29 (pseudodd, J = 8.3, 7.7 Hz, 1H, py*p*), 8.07 (d, J = 8.1 Hz, 2H, Py-*m*), 5.11 (t, J = 2.0 Hz, 4H, Cp- γ), 4.52 (t, J = 2.0 Hz, 4H, Cp- β), 4.30 (s, 10H, Cp), 2.85 (s, 6H, CH₃). ¹³C (CD₂Cl₂, 126 MHz): 161.31 (C=N), 153.08 (py-ipso), 143.94 (Py*p*), 123.99 (Py-*m*), 97.72 (Cp-ipso), 70.82 (Cp), 69.89 (Cp-γ), 69.43 $(Cp-\beta)$, 19.10 (CH_3) . Anal. Calcd for $(Fc_2PDI)MgCl_2 \cdot 0.5DCM$, formula C_{30.5}H₂₈N₃Fe₂MgCl₃ C, 53.74; H, 4.72; N, 5.97. Found: C, 53.42; H, 4.55; N, 6.22.

RESULTS

Synthesis. The Fc_2PDI ligand synthesis was modified from literature^{28,29} to streamline the procedure (Scheme 2).





Ferrocene can be selectively monolithiated using t-BuLi and t-BuOK, which was trapped with iodine to afford iodoferrocene (FcI) as a black oily crude that may crystallize on standing if sufficiently pure. After purification through a silica plug and removal of unreacted ferrocene by sublimation (100 °C, 0.1 Torr), pure product was obtained as dark orange needles in 80% isolated yield on scales up to 15 g. Amination of FcI with aqueous ammonia using a Fe₂O₃/CuI catalyst system was carried out following a literature procedure,²⁹ while the amino ferrocene $(FcNH_2)$ was purified by sublimation (90 °C, 0.1 Torr) instead of chromatography. Note that FcNH₂ gradually decomposes in air to an NMR indistinguishable (CDCl₃) brown solid (presumably the N-oxide) at ambient temperature, and therefore should be stored in the freezer under inert atmosphere or in a glovebox. Purification can be readily achieved by sublimation or passage through an alumina plug with hexanes/EtOAc elution (1:1). FcNH₂ was condensed⁴⁰ with diacetylpyridine under reflux in dry degassed ethanol with a catalytic amount of *p*-TsOH to afford the airstable product as a microcrystalline solid. The color of the product ranges from bright red to maroon depending on purity, crystallinity, and crystal polymorph (cations and acids can be coordinated and impart purple coloration). Fc₂PDI was isolated in 58% yield as red/purple microcrystals by filtration and washing with cold ethanol. If required, Fc₂PDI can be recrystallized by DCM/pentane layering.

Next, the Co, Fe, Zn, and Mg complexes of the Fc,PDI ligand were prepared by direct metalation with corresponding MCl₂ precursors, in decent to good isolated yields (Scheme 2). Note that in our hands, we experienced high levels of static electricity which can result in somewhat diminished isolated yields on small scales. The rate of metalation varies with solvent for each MCl₂ species—presumably due to solubility considerations. ZnCl₂ and CoCl₂ react readily with 1.0 equiv of the ligand overnight in DCM affording blue-purple crystalline complexes. For FeCl₂ and MgCl₂, the metalation is prohibitively slow in DCM and requires THF or MeOH for metalation to occur. All complexes were purified by trituration with Et₂O or recrystallization from layered DCM/Et₂O solvent to yield dark blue/purple solids. The complexes exhibit varied stabilities under ambient conditions, as the (Fc₂PDI)CoCl₂ and (Fc₂PDI)ZnCl₂ complexes are reasonably resistant to small amounts of air and moisture for days, while solutions of (Fc₂PDI)FeCl₂ turn brown and precipitate overnight, and (Fc₂PDI)MgCl₂ turns red immediately on exposure to moisture.

CV experiments indicate that oxidation occurs at similar potential to ferrocene, rendering the slightly more oxidizing actylferrocenium and Ag⁺ salts as suitable oxidants to generate the mixed valent species. Initial attempts to oxidize with AgPF₆ were hindered by high insolubility of the product PF₆ salt, preventing further characterization. However, careful layering of a DCM solution of (Fc₂PDI)CoCl₂ on top of a DCM solution of AgPF₆ inside an NMR tube slowed the reaction enough to allow precipitation to occur in the form of single crystals suitable for diffraction. Attempts with other complexes yielded crystalline material not suitable for single crystal X-ray diffraction studies. Using BArF⁻ salts to improve solubility presented unpredicted complications, as multiple attempted oxidations of (Fc₂PDI)FeCl₂ with 1 equiv of [AcFc][BArF] in DCM resulted in a black solution, which was dried and washed with pentane to remove acetylferrocene byproduct, and used directly for crystallization. Interestingly the dication, [(Fc₂PDI)FeCl₂][BArF]₂, rather than the expected monocation, crystallizes from the solution as X-ray suitable crystals (Figure 1F). We believe that a small equilibrium amount of the dication is present due to intermolecular electron transfer (disproportionation constant: $K \approx 0.001$ based on 200 mV separation between first and second oxidations-see electrochemistry below). The dication likely preferentially crystallizes in the nonpolar DCM solvent, permitting isolation in a similar way to that of the crystallization of MgMe2 through the Schlenk equilibrium of Grignards.⁴¹ We emphasize that the mixed-valent species are stable in solution, indicated by CV and spectroelectrochemistry.

NMR Spectroscopy. While $(Fc_2PDI)FeCl_2$ and $(Fc_2PDI)CoCl_2$ are paramagnetic and did not provide informative NMR spectra, the comparison of the free ligand with the corresponding diamagnetic complexes (Fc_2PDI) -MgCl₂ and $(Fc_2PDI)ZnCl_2$ affords interesting insight into the



Figure 1. Single crystal X-ray structures for the free ligand, $(Fc_2PDI)MCl_2$ (M = Co, Fe, Zn, Mg), and oxidized $(Fc_2PDI)MCl_2$ (M = Fe, Co) complexes. Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms and solvent molecules are omitted for clarity. For structure F and G, BArF and PF₆ anions are omitted, respectively.

change in magnetic and electronic environment upon coordination. The *para*-pyridyl protons (relative to N) of the Mg and Zn complexes appear as apparent doublets of doublets rather than triplets, due to second order effects.⁴² The Cp protons shift substantially downfield upon metalation, from δ 4.46 to 5.13 ppm for β -Cp protons, and δ 4.26 to 4.51 ppm for γ -Cp protons distal to the imine (Table 1; Scheme 2). Notably,

Table 1. ¹H NMR Chemical Shift Data (ppm) for Selected Resonances of Fc₂PDI, (Fc₂PDI)ZnCl₂, and (Fc₂PDI)MgCl₂ in CD₂Cl₂ at 25 $^{\circ}$ C

	Fc ₂ PDI	$(Fc_2PDI)ZnCl_2$	(Fc ₂ PDI)MgCl ₂
Py-p	7.81	8.29	8.29
Py-m	8.27	8.13	8.07
Cp-β	4.46	5.13	5.11
Ср-ү	4.26	4.51	4.52

asymmetry in ferrocene Cp magnetic environment (e.g., different resonance frequencies for different Cp protons) has been previously assigned to differential occupation of the d_{xy} d_{x2-y2} and d_{xz}/d_{yz} orbitals caused by donation into or withdrawal from the Fc center.^{21a,h,43} The pyridyl region also exhibits substantial changes, but interestingly with opposite shift trends for meta and para protons (where meta and para are relative to N). Upon coordination, the pyridyl meta protons shift upfield from δ 8.29 to 8.13 ppm, while the para protons shift downfield from δ 7.81 to 8.29 ppm (Table 1). Different shielding effects on the meta and para protons might be explained given that the pyridine based frontier orbitals are largely bonding with respect to the ipso and meta carbons, but antibonding with respect to the meta and para carbons.^{10b,d,44} That is, the different magnetic response at each position may reflect different bonding character at each position. However, the crystallographic data (vide infra) suggest that rotational freedom about the $C_{ipso}-C_{imine}$ bond produces an "open" conformer (Figure 1A) and a "closed" conformer (Figure 1B– G). These conformational changes may also impact the observed chemical shifts, though symmetry (e.g., relative orbital overlaps should be conserved) suggests that orbital interactions and therefore electronic communication should not change between conformers.

Solid State Structures. Single crystals of (Fc₂PDI)MCl₂ (M = Fe, Co, and Zn) complexes suitable for X-ray diffraction studies were grown from DCM/pentane, while diffraction quality crystals of the Mg complex were grown from DCM/ Et₂O. $[(Fc_2PDI)CoCl_2][PF_6]$ was crystallized by layering DCM solutions of AgPF₆ and $(Fc_2PDI)CoCl_2$, while crystals of [(Fc₂PDI)FeCl₂][BArF]₂ were grown from DCM/pentane layering of the crude reaction product prepared by treatment of (Fc₂PDI)FeCl₂ with 1 equiv of [AcFc][BArF] in DCM. Refinement statistics are summarized in the Supporting Information (SI, S1 and S2). Crystal structures are shown in Figure 1 and key structural characteristics are compared in Table 2. All structures have eclipsed ferrocene conformations. The complexes all exhibit slight deviations from Cp-PDI-Cp coplanarity, with torsions between the Cp-imine planes on the order of 7° -30°, which may reflect crystal packing force-s.^{11a,13c,25b,45} The Zn and Co structures also exhibit a distortion of the PDI backbone, manifested as a puckering of the imine carbons above and below the ligand plane. Interestingly, in contrast to other PDI complexes that generally have coordination geometries approaching square pyramidal,^{44b} all structures in this study are distorted trigonal bipyramidal. The ligand bond lengths in all the neutral complexes are essentially equivalent (within the given ESD for each bond) and consistent with a neutral ligand bound to a M(II) fragment.^{10a} The free ligand adopts an "open" conformation in the solid state, likely due to steric factors. The mixed valent compound $[(Fc_2PDI)CoCl_2][PF_6]$ shows a break in symmetry, as the oxidized ferrocene swings to be nearly orthogonal (83°) to the backbone plane. The site of oxidation is assigned by slight elongation of the Fe-Cp distance, and high numbers of close cation-anion distances on inspecting the extended crystal packing which features a sheet of alternating ferrocenium cations and PF_6 anions (see SI). Furthermore, the imine connected to this ferrocenium contracts slightly, and the CoCl₂ center drifts away from the ferrocenium arm. These changes on oxidation are unfavorable for strong coupling, as differences in coordination geometry between metal sites leads to large reorganizational energies, and higher barriers to electron transfer.¹

We point out that stronger ion pairing is known to stabilize localized cations and weaken coupling, motivating crystallization with BArF⁻ anions. While the monocationic BArF⁻ salt Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for Fc_2PDI Ligand and $(Fc_2PDI)MCl_2$ Complexes (M = Zn, Co, Fe, and Mg)^{*a*}

ligand, Fc ₂ PDI					
$C_4 - N_2$	1.285(2)	Cp torsion ^a	22.7°		
			28.1°		
	(Fc ₂ PI	DI)MgCl ₂			
N ₁ -Mg	2.0907(2)	N _{2a} -Mg-N _{2b}	148.19°		
N _{2a} -Mg	2.2826(2)	Cp torsion ^a	13.4°		
N _{2b} -Mg	2.2518(2)		13.9°		
$C_4 - N_2$	1.2909(1)	Cl-Mg-Cl	124.95°		
	(Fc ₂ Pl	DI)ZnCl ₂			
N_1-Zn	2.044(3)	N _{2a} -Zn-N _{2b}	150.00°		
N_{2a} -Zn	2.304(3)	Cp torsion ^a	17.63°		
N _{2b} -Zn	2.255(3)		14.91°		
$C_4 - N_2$	1.289(4)	Cl-Zn-Cl	124.28°		
	(Fc ₂ P)	DI)FeCl ₂			
N ₁ -Fe	2.067(2)	N _{2a} -Fe-N _{2b}	149.1°		
N _{2a} -Fe					
N _{2b} -Fe	2.227(2)	Cp torsion ^a	18.8°		
	2.262(2)		13.5°		
$C_4 - N_2$	1.289(3)	Cl-Fe-Cl	125.7°		
	(Fc ₂ PI	DI)CoCl ₂			
N ₁ -Co	2.003(2)	N _{2a} -Co-N _{2b}	152.98°		
N _{2a} -Co	2.222(2)	Cp torsion ^a	29.49°		
N _{2b} -Co	2.199(2)		8.98°		
$C_4 - N_2$	1.294(3)	$Cl_1-Co-Cl_2$	127.40°		
	[(Fc ₂ PDI)	CoCl ₂][PF ₆]			
N ₁ -Co	2.01247(8)	N_{2a} -Co- N_{2b}	150.94°		
N _{2a} -Co	2.37077(8)	Cp torsion ^a	4.18°		
N _{2b} -Co	2.17412(8)		95.32°		
C_4-N_2	1.28654(5)	Cl_1 -Co- Cl_2	118.37°		
	1.27531(5)				
	[(Fc ₂ PDI)H	FeCl ₂][BArF] ₂			
N ₁ -Fe	2.07669(4)	N_{2a} -Fe- N_{2b}	148.45°		
N_{2a} —Fe	2.29128(5)	Cp torsion ^a	65.82°		
N _{2b} -Fe	2.28597(5)		76.07°		
C_4-N_2	2.29128(5)	Cl_1 –Fe– Cl_2	130.25°		
	2.28597(5)				

^{*a*"}Cp Torsion" is measured between planes defined by the Cp ring and the Cp_{α} - N_{im} and C_{im} = N_{im} bonds.

could not be crystallized, the doubly oxidized structure, $[(Fc_2PDI)FeCl_2][BArF]_2$, shows both ferrocenes canted nearly orthogonal (85°) but with a more symmetric coordination environment about the FeCl₂ center.

Electrochemistry. Due to the highly reversible and stable Fc/Fc⁺ redox couple, electrochemistry is an informative tool in evaluating electronic communication between Fc groups.^{11a-d} For symmetric, uncoupled Fc sites, a single concerted oxidation wave is expected. However, if oxidation of one Fc perturbs the electronic environment of the second, i.e., the metal centers are coupled, then the second oxidation occurs at increased potential, resulting in sequential waves. There are multiple mechanisms that can give rise to split redox waves, ^{11a,c,12b} and the observed ΔE is a net sum of the following: $\Delta E_{obs} = \Delta E_{resonance} + \Delta E_{electrostatic} + \Delta E_{statistical} + \Delta E_{inductive} + \Delta E_{exchange}$. Due to the difficulty in delineating individual contributions to ΔE , it is challenging to quantitatively assess delocalization by CV.^{12b} However, since the exchange and statistical terms are typically small (~36 mV at 25 °C)^{11a} and inductive effects are often assumed to be

small for ferrocenes separated by multiple bonds, electrostatic and resonance effects typically dominate the observed $\Delta E_{1/2}$. Furthermore, because electrostatic effects are dependent on geometry, solvent, and electrolyte; an isostructural series of compounds enables more direct evaluation of delocalization. Thus, the separation between ligand oxidations can be correlated as a function of metalation (e.g., with FeCl₂, CoCl₂, ZnCl₂, or MgCl₂) with the delocalization of charge between the two ferrocene groups.^{11a,b,19b}

With these considerations in mind, CV was performed in DCM because coordinating solvents promote ECE mechanisms in PDI complexes,⁴⁶ while TBA-BArF electrolyte was employed both to improve the electrochemistry in this nonpolar solvent³⁷ and also because the PF_6 salts of these complexes are insoluble, precipitating onto the electrode. Figure 2 shows that the free ligand displays a concerted two-



Figure 2. Cyclic voltammograms of Fc_2PDI , $(Fc_2PDI)FeCl_2$, $(Fc_2PDI)CoCl_2$, $(Fc_2PDI)ZnCl_2$, and $(Fc_2PDI)MgCl_2$ (bottom to top); scan rate: 100 mV/s; 1 mM analyte, 100 mM TBA-BArF in dry degassed DCM under N₂ at 25° in the dark. CVs are referenced to $Cp*_2Fe$ internal standard at 0.0 mV.³⁹ Dotted lines at 564 and 810 mV correspond to Fc_2PDI and $(Fc_2PDI)ZnCl_2$ oxidations for comparison. Reduction waves not presented for Fc_2PDI and $(Fc_2PDI)MgCl_2$ due to rapid decomposition and electrode fouling.

electron wave, suggesting weak to no coupling. Most complexes show sequential 1 e⁻ waves separated by ~200 mV (Table 3). Notably (Fc₂PDI)FeCl₂ exhibits a larger $\Delta E_{1/2}$

Table 3. Cyclic Voltammetry Data for $(Fc_2PDI)MCl_2$ (M = Co, Fe, Mg, Zn), Values in mV vs Cp_2^*Fe

compound	$1^{st}\ E_{1/2}$	$2^{nd}\ E_{1/2}$	$\Delta E_{1/2}$
Fc ₂ PDI	564		
(Fc2PDI)CoCl2	617	820	203
(Fc ₂ PDI)FeCl ₂	584	867	264
(Fc ₂ PDI)MgCl ₂	641	835	194
(Fc ₂ PDI)ZnCl ₂	616	810	194

by 60 mV. The first oxidation is approximately isoenergetic with free Fc in these compounds ($E_{1/2} = 590$ mV vs Cp*₂Fe for Fc),⁴⁷ which suggests that the Fc-based occupied orbitals are not substantially perturbed. Upon complexation, the oxidation shifts slightly to higher potential—an additional 20–80 mV higher potential than Fc₂PDI, reflecting Fc bonding orbital stabilization. Reductions and oxidations are

assigned as primarily being ligand-based, since Zn(I)⁴⁸ and Zn(III)⁴⁹ species are implausible, and the free ligand decomposes at -1.5 V. Note that no additional redox couples are observed within the DCM solvent window of -1.5 to 1.5 V. We propose that when a central metal is coordinated by **Fc₂PDI**, the reduced ligand is stabilized in solution. Note that the (**Fc₂PDI**)**FeCl₂** compound exhibits the largest ΔE , suggesting it for spectroelectrochemical investigation (vide infra).

UV-vis Spectra. Because CV data cannot unambiguously assign the reason for underlying sequential oxidation, redox splitting can be misleading in assessing electronic coupling.^{12b} Therefore, it is more prudent to combine electrochemical data with optical spectroscopy, through both traditional and spectroelectrochemistry experiments. The visible electronic transitions in ferrocene are best considered d-d transitions,⁵ so by exploiting the well understood electronic spectrum of ferrocene, the Fc d-orbital mixing can be tracked as a perturbation of the relevant d-d transitions. For consistency, we refer to the visible region band as "the ferrocenyl band" to remain agnostic as to its character, i.e., d-d, charge transfer (CT), or overlapping d-d and CT transitions. Furthermore, we differentiate between the ferrocenyl iron and the organic pyridine parts of the ligand when describing "metal" versus "ligand" centered processes. The UV-visible spectra of the Fc₂PDI ligand and its (Fc₂PDI)MCl₂ complexes were recorded in DCM, using amino ferrocene (FcNH₂) for comparison.

From the UV-vis data shown in Figure 3, the first observation of note is the substantial increase in ferrocenyl



Figure 3. UV–vis spectra of $FcNH_2$, Fc_2PDI , and $(Fc_2PDI)MCl_2$ (M = Co, Fe, Zn, Mg) in dry, degassed DCM. Inset: enlarged spectrum of $FcNH_2$.

transition intensity in **Fc**₂**PDI**. For simple ferrocene derivatives, the absorptivity of this symmetry-forbidden transition is ~100-200 M⁻¹cm⁻¹.^{50b,51} The ferrocenyl band in FcNH₂ shows an absorptivity of $\epsilon \approx 200$, which increases to $\epsilon \approx 2800$ M⁻¹cm⁻¹, or 1400 per Fc center, for **Fc**₂**PDI**. This absorptivity range is consistent with a symmetry allowed transition, but likely not a full charge transfer which would typically have $\epsilon >$ 5000-10 000 M⁻¹cm⁻¹.⁵¹ Interestingly, the absorptivity of the band does not change significantly upon metalation, except for the (**Fc**₂**PDI**)**ZnCl**₂ complex which shows a greater

absorptivity (\sim 4000 M⁻¹cm⁻¹). The energy of this ferrocenyl band changes between ligand formation and metalation, however. While the FcNH₂ ferrocenyl band is centered at 442 nm—typical for a Fc derivative, Fc₂PDI exhibits a 35 nm redshift to 478 nm. The (Fc2PDI)MCl2 complexes further redshift ~125 nm to ~600 nm. The Zn and Mg complexes display the ferrocenyl band at slightly higher energy (ca. 10 nm) than the Fe and Co complexes (Figure 3). It is interesting that all four (Fc₂PDI)MCl₂ (Co, Fe, Mg, Zn) metal complexes have similar absorption in the range of 600 nm which is not strongly affected by the metal. This suggests that the orbitals responsible for this transition are not localized on the central metal center and are probably mainly ligand centered orbitals. Note also the changes in bandwidth from FcNH₂, to Fc₂PDI, to the (Fc₂PDI)MCl₂ compounds which is another indication of delocalization in the donor/acceptor orbitals. To more concretely analyze these changes, the experimental spectra were fit to gaussians using the known electronic structure of ferrocene. The ferrocenyl band^{50b} (442 nm in FcNH₂) is known to contain two transitions-which can be successfully fit to two Gaussian peaks (Figures S9-S14; Table 4). The full

Table 4. Summary of Experimental UV-vis Band Parameters and Fitting of the Ferrocenyl Band in Figure 3 to Two Gaussians^a

	UV-vis bands		Gaussian fitting			
molecule	λ	absorptivity	λ	absorptivity	fwhm	
FcNH ₂	442	207	468	131	79	
			422	142	70	
Fc ₂ PDI	478	2782	458	1791	102	
			504	1406	100	
(Fc2PDI)CoCl2	616	3120	577	1950	174	
			651	1650	150	
(Fc ₂ PDI)FeCl ₂	605	2517	576	1660	160	
			648	1210	160	
(Fc ₂ PDI)MgCl ₂	590	2601	552	1320	170	
			660	1520	148	
(Fc ₂ PDI)ZnCl ₂	590	4179	568	2200	160	
			612	2200	146	
^a fwhm: full-width-at-half-maximum						

width at half-maximum (fwhm) of each ferrocenyl transition increases from 70 to 80 nm for $FcNH_2$ to 100-102 nm for Fc_2PDI , and to ~160-175 nm for the $(Fc_2PDI)MCl_2$ complexes (Table 3).

To probe the optical spectroscopic assignments further, DFT and time-dependent DFT calculations were carried out. Geometry optimizations for the structures of (Fc₂PDI)MCl₂ (Co, Fe, Mg, Zn) were carried out at the B3LYP/6-31+G(d,p)level of theory and are in excellent agreement with the X-ray structure geometries. B3LYP was applied here based on its success in analogous mixed-valent complexes^{19a,52} and the excellent agreement with our experimental and computed geometries as well as our experimental and computed UV/ visible spectra. According to the DFT calculations, all four complexes have nearly identical frontier molecular orbitals (Figure 4) in which the HOMO is localized in the d-orbitals of the two ferrocene substituents (d_{xy}/d_{x2-y2}) with minor contribution from nitrogen and central metal orbitals. The LUMO, in contrast, is mainly delocalized over the pyridine and imine groups with some contribution from the ferrocene d_{xz} $d_{\nu z}$ orbitals. In other studies, small levels of delocalization have



Figure 4. DFT-computed frontier molecular orbitals of the indicated $(Fc_2PDI)MCl_2$ complexes (M = Co, Fe, Zn, Mg).

been seen even in cases of direct metal–metal interaction from donation of ferrocene into high valent metals.^{21d} In addition, the calculated UV–vis spectra are in good agreement with the experimental values; for more details see the SI. The observed absorption of these complexes in the range of 600 nm is attributed, according to the calculations, to the HOMO \rightarrow LUMO transition. Thus, the DFT calculations support the empirical findings for orbital combinations and bonding.

Spectroelectrochemistry. To reinforce assignments from the UV-vis experiments and DFT, spectroelectrochemistry measurements were employed.53 This technique was performed by measuring the UV-vis spectrum of aliquots taken during bulk electrolysis, and thus detecting electronic structure changes resulting from oxidation.53 Spectroelectrochemistry was performed in a quartz Schlenk cuvette with 100 mM TBA-BArF electrolyte, using carbon foam working and Pt counter electrodes, with an Ag wire pseudo reference. The sharp spectroscopic features near 2000 nm are due to quartz absorptions and solvent vibrational overtones, as demonstrated by solvent blanks (see SI Figure S15). Upon oxidation, Fc₂PDI changes from red to blue/green via a 2 e⁻ event—at constant voltage, 2 equiv of charge are transferred. This correlates with a decrease in the 478 nm ferrocenyl band (Figure 5A), reflecting removal of the electron in the Fc-based donor orbital in this transition. The growth of a broad band at low energy centered around 776 nm (Figure 5A) is also observed, which contrasts with the free Fc⁺ LMCT band, which is comparatively narrow and centered at 625 nm.^{50b}

Given that $(Fc_2PDI)FeCl_2$ displays the largest ΔE in the CV experiments, we decided to explore the spectroelectrochemical properties of this compound. Immediately evident is that the complex becomes black upon oxidation in a 1 e⁻ event. There is a slight decrease in its corresponding ferrocenyl band (at 605 nm) as well as substantial broadening. A new band system at ~850 nm appears, presumably of ferrocenium LMCT character. Interestingly, a very broad transition appears in the



Figure 5. UV–vis-NIR spectra of (A) Fc_2PDI (black) $[Fc_2PDI]^{2+}$ (blue) and change upon oxidation (red dashed); (B) $(Fc_2PDI)FeCl_2$ (black), $[(Fc_2PDI)FeCl_2]^+$ (blue), and (C) $[(Fc_2PDI)FeCl_2]^+$ (blue), $[(Fc_2PDI)FeCl_2]^{2+}$ (green) and change upon oxidation (red dashed) under spectroelectrochemical conditions.

NIR that best assigns to a Inter-Valence charge transfer (IVCT) between the ferrocene and ferrocenium groups. This assignment is confirmed by further oxidation by 1 e- to the $[(Fc_2PDI)FeCl_2]^{2+}$ state, forming a yellow/green solution lacking IVCT features.

DISCUSSION

Metalation-Induced Electronic Coupling. After metalation, electronic coupling between the ferrocenes is observed, as evidenced by the oxidation of one ferrocene perturbing the oxidation potential of the second via cyclic voltammetry. While



Figure 6. Qualitative MO diagram for proposed electronic interactions between the ferrocene and organic π system. The d_{5d} ligand field symmetry labels are used for the ferrocene fragment.

there does seem to be an increase in rigidity of the ligand scaffold upon metalation, rigidity does not explain the lack of coupling in low valent main group Fc₂PDI complexes reported by the Ragogna group.^{27b} Furthermore, we observe increased redox stability, demonstrated through highly reversible oxidation events. In marked contrast, the main group analogs reported previously $2^{26a,b}$ yielded CV data suggestive of decomposition during redox events. These combined observations lead us to conclude that the electronic manifold is different in the transition metal series versus the main group series. This conclusion is further supported by the small ΔE in the more metallic Sn compound, which is absent in the P, Se, S, Te, and Ge complexes, indicating that transition metal chemistry of this ligand is fundamentally different from the nonmetallic main group analogues. If different conformers gave rise to different electrochemistry, we would expect an admixture of signals or an ECE mechanism in the rapid exchanging free ligand-which is not observed. It seems that more acidic heteroatoms in the binding pocket are necessary for this coupling to occur, suggesting that the effect is not due to conformational changes. Conformation changes would explain the data if interaction between the ferrocenes were predominantly electrostatic (e.g., changes in interferrocene distance altering the electrostatic interaction between them). Rather, it appears that the coupling is driven by coordination of Fc₂PDI to a transition metal. Observation of d-elementdriven coupling is not unprecedented, as dithiolato ligands undergo " π -reorganization" upon coordination to transition metals. This reorganization modifies the electronic structure of the dithiolate ligand to promote Proton Coupled Electron Transfer (PCET) chemistry.⁵⁴

Furthermore, the reported lack of coupling in low-valent main group Fc_2PDI complexes provides a clue to the mechanism of coupling. Less acidic P(I), Te(II), Se(II), and S(II) centers do not promote interaction between ferrocenes, while more acidic M(II) ions are likely to stabilize the electronrich Fc_2PDI ligand system, enhancing the energy match between metal and organic π^* orbitals. Lowering the energy of the LUMO would better facilitate a 3-state mechanism for electron transfer, resulting in coupling between metals. This argument is supported by the present crystallographic, CV, UV–vis, and spectroelectrochemistry data. Depiction of the proposed coupling process and the molecular orbital level is then given in Figure 6 and explained below.

XRD. Although one expects that a coplanar conformation would induce optimal coupling, ferrocenyl groups exhibiting substantial torsions in the solid state can still engage in electronic coupling in solution.^{11b,d,25b,45a} This suggests that as long as coplanar geometries are readily sampled at room temperature, then coupling remains intact, even if it is not the sole conformation. We also conclude that changes in conformation ("open" vs "closed") have little bearing on the occupied bonding orbitals, as the ligand bond distances do not significantly vary in any of the compounds studied. This suggests that conformational changes do not appreciably alter the bonding characteristics, which is to be expected based on symmetry-similar orbital overlaps in both conformations. No change in bond lengths suggests that for the neutral species, spectral changes originate largely from orbital interactions occurring in the unoccupied manifold of the MO diagram, which cannot be probed by XRD. This is also evidenced by a more extreme reduction potential for Fc₂PDI compared to the (Fc₂PDI)MCl₂ complexes, suggesting a stabilization of the π^* system upon metalation ($E_{\rm red} \approx -1.5$ V for Fc₂PDI, $E_{\rm red} \approx$ -0.9 to -1.2 V for (Fc₂PDI)MCl₂).

Interestingly, the conformation of the oxidized ferrocene changes, canting inward toward the chloride ligands. The distance between chloride and ferrocenyl iron is ca. 4.2 Å, suggesting an electrostatic attraction rather than formal coordination. This has the added effect of decreasing the intermetallic distance, which leads to uncertainty in extracting an electronic coupling constant using Hush theory, which employs the internuclear distance as a parameter. This distortion also shines light on a complication infrequently discussed in mixed valent studies-that changes in charge distribution upon oxidation can promote rearrangements that may explain why some highly conjugated and promising scaffolds fail to engender strong coupling. In (Fc₂PDI)FeCl₂, this distortion brings the formally Fe(III) center closer to the chlorides in the MCl₂ fragment and likely stabilizes a localized Fe(III) center. Thus, the structure change likely limits the ultimate amount of charge delocalization. This would be akin to ion pair effects known to have strong impacts on degree of delocalization, as probed as a function of supporting electrolyte in CV experiments.^{11a} We focus in this work on suggesting how this conformer presents interesting prospects for reactivity as opposed to how to optimize toward increased delocalization. This structure change, bringing the cationic Fe(III) into

the secondary coordination sphere of the MCl₂ fragment suggests that substrates bound to the central M(II) center can interact—covalently or electrostatically—with the Fe(III) in a cooperative way. Ferrocenium is a useful mild oxidant that given the close distance to ligands on the central metal may undergo facile oxidation of reaction intermediates. Furthermore, a cationic Fe(III) can generate local electric field gradients and polarize substrates, ferrocenium LMCT states have been shown to be useful in photocatalysis,⁵⁵ and it is known to act as a Lewis acid catalyst.⁵⁶ Addition of Lewis acids in the secondary coordination sphere is an attractive strategy in bond activation.⁵⁷ Furthermore, the acceptor orbital in charge transfer transitions for the neutral complexes (see theory section) features a similar ligand centered LUMO that is one of the occupied frontier orbitals in highly reduced PDI structures.^{44b} Based on these interesting excited states, we suggest that an internal electron donor could function as a photoreductant in lieu of aggressive reductants such as NaEt₃BH or Na(Hg). Electronic coupling in excited states is an area of continued interest and exploration⁵⁸ and the easily accessible charge transfer in this system yields only a partial hole (see theory section) at ferrocene, which may reveal interesting properties

Spectroelectrochemistry. In accord with the CV experiments, free Fc_2PDI is not stable in its mixed valent state and cannot be observed by spectroelectrochemistry—constant potential electrolysis continues until $2e^-$ are removed from the molecule. If electrolysis is halted after $1e^-$ is removed, then all species coexist in equilibrium due to disproportionation.

 $(Fc_2PDI)FeCl_2$ is stable in its mixed valent form. Pausing electrolysis after oxidation by one electron reveals a broad low energy feature assignable as an IVCT. Fitting IVCT bands and application of Marcus–Hush theory allows for the electronic coupling of two metal sites to be extracted based on the electron transfer properties. Thus,

$$H_{\rm ab} = \frac{2.06 \times 10^{-2} (\nu_{\rm max} \varepsilon_{\rm max} \Delta \nu_{1/2})^{1/2}}{r_{\rm ab}}$$

where $H_{\rm ab}$ is the Electronic coupling constant, while $\nu_{\rm max},\,\varepsilon_{\rm max}$ $\Delta \nu_{1/2}$, and r_{ab} are the energy of the IVCT band, the extinction coefficient, band fwhm, and distance between metal sites a and b, respectively. Application of this theory gives an electronic coupling of 348 cm⁻¹, taking r_{ab} to be the crystallographically determined distance between ferrocenes in the neutral (all Fe(II)) structure (8.1 Å) and ϵ calculated as an upper bound based on the initial electrolysis concentrations (e.g., ignoring solvent evaporation). This is a modest degree of electronic coupling, indicating Class II behavior, but represents a rare example of a bis-ferrocenyl complex acting as a ligand to another metal fragment that is in a known catalytically active structure (e.g., PDI catalysts). While CV strongly suggests IVCT occurs between ferrocenes (as the second ferrocene is the most easily oxidizable group) on closer inspection, it is interesting that ET occurs between the more disparate metals. This could be explained by a 3-state electron transfer mechanism^{11c} through mutual coupling of each Fc to the ligand π system, providing a mode for electronic coupling through unoccupied orbitals using a superexchange mediated electron transfer mechanism.⁵⁹ This would also explain the lack of decreased intensity for the ferrocenyl band, as 3 state coupling results in an increase in the intensity and broadening of absorption features on the unoxidized metal. It also appears

possible to modify the ancillary chloride ligands (e.g., with larger ligands such as bromide) to allow better energy matching so that the MX_2 fragment participates in the HOMO or LUMO to involve it inside the superexchange mechanism and engender coupling through all three metals. Under this understanding, the calculated H_{ab} is better considered an effective coupling constant, since a two state model is applied. This approximation is invalid in the case of strong coupling,⁶⁰ which does not appear present.

UV/vis-DFT. The orbital interactions can be further understood on the basis of the intensities, energies, and line shapes of the ferrocenyl transitions. Since transitions occur from occupied to unoccupied orbitals, we can infer characteristics of the higher energy orbitals unobservable by X-ray diffraction. In observing a large increase in absorptivity for the ferrocenyl band in the Fc₂PDI ligand relative to ferrocene, it is logical to conclude that the symmetry forbidden transition has become symmetry-allowed. Similar results are seen in Fc-Ru and Fc-Pd/Pt compounds where mixing of Fc orbitals with other ligand or metal orbitals breaks inversion symmetry and leads to absorptivity increases.^{21c,h,55b} We infer that mixing of Fc and imine orbitals can explain a breaking of symmetry, but cannot posit a priori if the organic character is in the HOMO or LUMO. Given that the HOMO energy of the present ferrocenes is not significantly perturbed (see Electrochemistry section), and bond distances do not change substantially (see Crystallography), the mixing likely involves the Fc LUMO, Fe centered d_{rz}/d_{vz} orbitals. Inspection of the DFT results (Figure 4) supports this assertion, as the HOMO is largely Fc d_{xy} / d_{x2-y2} while the LUMO displays d_{xz}/d_{yz} character on the ferrocene units and a large amount of organic PDI character.

To further understand the DFT results, which suggests mixing of Fc d_{xz}/d_{yz} orbitals with the imine π^* instead of π , we consider the effects of each interaction. Donation from the imine π into the unoccupied d_{xz}/d_{yz} orbitals would result in a bonding/antibonding interaction, raising LUMO levels, changing imine bond strengths, and placing more electron density in the ferrocene system. Instead, the electrochemistry supports a largely unperturbed ferrocene HOMO, and the spectroscopy supports a stabilized ligand LUMO (red-shifted absorption). Rather, mixing between the Fc unoccupied d_{xz}/d_{yz} and imine π^* orbitals such that the excited state assumes ligand character and becomes more delocalized (Figure 6) is consistent with the experimental data and DFT results. Similar observations and conclusions have been made that binding of PDI macrocycles to Lewis acids stabilizes the PDI π^* orbitals and leads to better energy matching between metal and organic orbitals, causing greater delocalization.⁶¹ We can thus describe a metal to mixed metal-ligand charge transfer ("MMMLCT") in analogy with mixed metal-ligand to ligand CT ("MMLLCT") excitations.^{54a,62} As shown in Figure 6, this assignment explains the present observations of an unperturbed HOMO and a red-shifted HOMO-LUMO transition.

The red-shift of the ferrocenyl band in Fc_2PDI is relatively small, suggesting the degree of mixing between metal and organic orbitals is too small to produce coupling that can be observed by CV. Nevertheless, the increase in intensity allows us to confidently assign a break in symmetry and demonstrate orbital interaction. Fitting the spectrum to Gaussians reveals two transitions within the 478 nm band, which accounts for both d-d transitions seen in the similar region of free Fc. Furthermore, a weak tail is also observed, which is intuitively assigned to the spin-forbidden counterpart transition, as

observed in ferrocene.^{50b} Partial permission (symmetryallowed, spin forbidden) causes the intensity to increase from 7 $M^{-1}cm^{-1}$ (seen in ferrocene), to ~50–100 $M^{-1}cm^{-1}$. We are unable to model the pure Fc d-d transitions at 442 nm, meaning we are only able to account for all the ligand field transitions by assigning this as a metal to mixed metal/ligand CT rather than a new MLCT to the PDI backbone in addition to the original Fc d-d transitions. This is also in accord with this transition being weaker than expected for a full MLCT (ϵ = 1400 per metal center, rather than $\epsilon > 5000-10000$). This band must be a shift of the Fc d-d transition rather than a new MLCT in addition to the normal Fc transitions. It is uncommon to observe shifts larger than ca. 10-15 nm in simple ferrocenyl compounds, consistent with the donor and acceptor orbitals in ferrocene being metal-centered and insensitive to ligand perturbation.^{50a} In Fc_2PDI , a change in the ligand field appears to take place since it exhibits a much larger shift (36 nm). This is reminiscent of observations by Diaconescu and co-workers, where arylamino substituted ferrocenes show more ligand character in the LUMO, whereas the HOMO is generally still metal-centered, lowering the HOMO-LUMO gap.^{50a}

To find support for the present assignments in the literature, UV/vis spectra of several mixed-valent Fc compounds were also considered. However, since Fc mixed-valent studies typically focus on the NIR region and the related MMCT transitions arising from electronic coupling, it is challenging to directly compare the present results to known Class II and Class III mixed valent compounds. Note however that some Fc conjugated systems have absorbances in the 500–600 nm range, however it is unclear if these represent Fc mixing, MLCT, or π/π^* transitions.^{14a,63} As a further complication, in cases where low energy CT bands are observed, they do not correlate in a consistent way with the degree of coupling. Cases with coupling and no spectral shifts are observed, ^{45b,64} as are cases with spectral shifts and no coupling.⁶⁵

Central Metal Not Directly Engaging in Coupling Pathway. The imine bond lengths do not change significantly upon metalation, suggesting that π bonding between the organic π^* system and MCl₂ d_{π} orbitals is insignificant—as seen in other neutral first row PDI complexes.^{10a,66} The DFT analysis further supports this picture as negligible π -bonding is observed in the frontier orbitals. Elongation of the imine bond is frequently used to estimate the degree of electron density residing in PDI π/π^* networks.^{10a} The unchanged imine bond distances argue that only small amounts of electron density are transferred from the MCl₂ fragment onto the ligand or from the ligand π system into the MCl₂ fragment. For this reason, the Fc delocalization onto the MCl₂ fragment cannot be directly implicated. Small contributions from the MCl₂ fragment are seen in the DFT orbitals, and small spectral/ electrochemical changes are seen, suggesting it is a nonnegligible but weak locus of bonding. Thus, the MCl₂ fragment can be thought of as triggering coupling although it does not participate substantially in the delocalization pathway. Since π bonding does not seem to be important, it is proposed that an electrostatic interaction triggers coupling. Similar interactions are proposed in ferrocenyl polypyridyl complexes, where coordination to Lewis acids creates intense charge transfer transitions from ferrocene and is useful for ion sensing.^{24f,67} Moreover, the present observation of similar electronic properties across a series of metals with diverse coordination chemistries is highly unexpected since mixed-valent compounds typically exhibit high physicochemical sensitivities to substitution and modification. This affords a unique reactivity possibility that the coupling triggered by metal ion binding will be seen with a variety of ions, increasing the versatility of this ligand system. Insensitivity of the interaction toward metal identity in the Fc₂PDI system is further rationalized on similar ionic radii and identical charge numbers, leading to similar electrostatic stabilizations. This suggests that fine-tuning of the coupling interaction is possible by substituting metal ions with different charge densities. Note however that the larger $\Delta E_{1/2}$ for (Fc₂PDI)FeCl₂ vs the other complexes suggests there are further effects to be studied, and that our optical, electrochemical, and crystallographic characterizations do not uniquely define these effects.

CONCLUSIONS

Structural, electrochemical, spectroscopic, and computational evidence argues that metal binding to Fc₂PDI triggers mixing of (Fc₂PDI)MCl₂ (M = Fe, Co, Mg, Zn) ferrocenyl Fc dorbitals with the PDI π^* network, engendering coupling between the two Fc sites. Curiously, this coupling appears dependent on metal ion binding but does not not disappear when different s- or d-block metals are employeddemonstrating the coupling is generalizable and worth exploring further. This is an interesting contrast to p-block analogues which do not exhibit coupling in most cases. CV displays a ~200 mV separation between oxidation of each ferrocene for the Fe, Co, Zn, and Mg complexes, but no separation is seen in the free ligand. Minimal π interaction between the ligand and MCl₂ fragment is evident in the crystal and DFT computed structures, which show no variation in back-bonding into imine π^* orbitals between the free ligand and the complexes. UV-vis spectroscopy shows mixing of Fc d orbitals with ligand π orbitals, with the extent of mixing dependent on metal binding but not appreciably on metal identity. Upon oxidation, broad and low energy ferrocenium transitions appear-indicative of highly delocalized mixed metal-ligand orbitals. Importantly we also observe a very broad IVCT in the NIR, which clearly indicates coupling between the ferrocenes. We assign this as a Class II compound based on the weak ($<5000 \text{ M}^{-1}\text{cm}^{-1}$) and broad (>2000cm⁻¹) IVCT feature. We propose that when Fc₂PDI binds to a Lewis acidic MCl₂ fragment, coupling is promoted by a better energy match between Fc and organic π orbitals. Crystallography suggests that in the mixed valent state the ferrocenium pivots into the MCl₂ coordination sphere, potentially opening doors for cooperative catalysis. Interestingly, this system displays orbital mixing between PDI and Fc orbitals, but most delocalization is seen in unoccupied orbitals. We propose that second and third row transition metals that are known to engage in stronger back bonding into PDI ligands⁶⁸ may place electron density in the orbitals engaged in the delocalized orbitals, leading to stronger coupling and possibly new coordination chemistry.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.0c10015.

UV-vis characterizations, DFT optimized geometries and energies, and calculated UV-vis for these complexes (PDF) Crystal structures (CIF) Crystal structures (CIF)

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Notes

The authors declare no competing financial interest.

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