# **ORGANOMETALLICS**

# Electron-Transfer Processes in 3,4-Diferrocenylpyrroles: Insight into a Missing Piece of the Polyferrocenyl-Containing Pyrroles Family

Wil R. Goetsch, Pavlo V. Solntsev, Casey Van Stappen, Anatolii A. Purchel, Semen V. Dudkin, and Victor N. Nemykin\*

Department of Chemistry and Biochemistry, University of Minnesota Duluth, 1039 University Drive, Duluth, Minnesota 55812, United States

**S** Supporting Information

**ABSTRACT:** 3,4-Diiodo-1-(triisopropylsilyl)-1*H*-pyrrole (1), 3,4-diferrocenyl-1-(triisopropylsilyl)-1*H*-pyrrole (2), and 3,4-diferrocenyl-1*H*-pyrrole (3) were prepared and characterized using spectroscopic methods and X-ray crystallography. UV-vis spectra of 2 and 3 were correlated with their density functional theory (DFT)-calculated electronic structures as well as theoretically predicted by the time-dependent (TD) DFT-calculations vertical excitation energies. Redox properties of 2 and 3 were investigated using cyclic voltammetry, differential pulse voltammetry, and spectroelectrochemical approaches. Ferrocene-centered oxidation processes in 2 and 3 were found to be separated by ~180 and ~300 mV in DCM/TBAP and DCM/



 $(NBu_4)[B(C_6F_5)_4]$  systems, respectively. Stepwise spectroelectrochemical oxidation of 2 and 3 allowed us to obtain spectroscopic signatures of the mixed-valence  $[2]^+$  and  $[3]^+$  cations. Hush analysis of the intervalence charge-transfer band in  $[2]^+$  and  $[3]^+$  is suggestive of class II (in Robin and Day classification) mixed-valence behavior. Electronic structures of neutral and spin-localized/delocalized single-electron oxidized mixed-valence cations of 2,5-di-, 3,4-di-, and 2,3,4,5-tetraferrocenylpyrroles were investigated by DFT calculations to resolve current uncertainties regarding the first oxidation process of tetraferrocenylpyrrole.

# INTRODUCTION

Preparation of nanometer-scale molecular systems with controllable redox or electronic conductivity properties is of great interest for modern technology.<sup>1</sup> Because of their welldefined redox properties and robust structure, mono- and poly(ferrocene)-containing compounds were proposed as candidates for potential application in molecular photonics, (opto)electronics, redox-driven fluorescence markers, and sensors for toxic ions.<sup>2</sup> Among these organometallic platforms, compounds with strong metal-metal coupling are particularly interesting from fundamental and practical points of view. Such systems have been intensely studied in recent decades because of their fundamentally interesting multiredox and electronic communication properties.<sup>4</sup> From a practical point of view, such molecular modules could have potential applications in molecular electronics, quantum cellular automata, and optoelectronic materials for use in high-speed photonic or redox-switchable devices.<sup>5</sup> Often, formation of the mixedvalence states in metallocenyl-containing molecules is responsible for the aforementioned properties. Mixed-valence polyferrocene derivatives have been known for several decades, and the factors affecting their redox and electronic communication properties have been thoroughly investigated.<sup>3-13</sup> In the majority of cases, the metal-metal coupling is facilitated by a bridging ligand between the ferrocene groups as well as by the intermetal distance in these compounds. In cases involving relatively large metal-metal distances (10-15 Å), the nature of the bridging ligand become crucial for longrange metal-metal coupling; in the majority of these cases  $\pi$ conjugated ligands are used. Among the poly(ferrocene)containing systems, the most studied bridging ligands are (poly)ethynes,<sup>11</sup> (poly)ethenes,<sup>9,10</sup> porphyrines,<sup>14</sup> aromatic heterocycles,<sup>15,16</sup> and carbocycles.<sup>17</sup> While the (poly)ethyne and (poly)ethene bridges have been known for decades, the porphyrins and the heterocyclic platforms have attracted attention only in recent years. For instance, in a series of excellent publications, Lang and co-workers reported the synthesis, electrochemical and spectroelectrochemical studies of a series of 2,5-diferrocenyl- and supercrowded 2,3,4,5tetraferrocenyl-containing pyrroles, furanes, and thiophenes.<sup>15</sup> They demonstrated that the (poly)ferrocenyl-containing heterocycles can be sequentially oxidized, forming a set of mixed-valence spin-localized cations. On the basis of similarities in electrochemical data between 2,5-diferrocene and 2,3,4,5tetraferrocene derivatives, these authors suggested that the first oxidation process observed in 2,3,4,5-tetraferrocene-substituted pyrroles, furanes, and thiophenes is localized at the ferrocene group connected to the pyrrolic  $\alpha$ -position.<sup>15</sup> Such assignment, however, could potentially suffer from the lack of redox property data on 3,4-diferrocenyl pyrroles, furanes, and thiophenes, which, to the best of our knowledge, have never been reported. In order to improve the current understanding of redox properties and electronic communications in

Received: September 9, 2013

# Scheme 1. Synthesis of Target Ferrocene-Containing Pyrroles



polyferrocene pyrroles, furanes, and thiophenes, we have prepared and characterized the redox properties of the missing members of the group -3,4-diferrocenyl-1-(triisopropylsilyl)-1*H*-pyrrole (**2**) and 3,4-diferrocenyl-1*H*-pyrrole (**3**). We also conducted extensive density functional theory (DFT) and timedependent (TD) DFT calculations on neutral and mixedvalence cations of 2,5-diferrocenyl-, 3,4-diferrocenyl-, and 2,3,4,5-tetraferrocenylpyrroles in order to clarify their redox behavior and spin localization properties.

#### RESULTS AND DISCUSSION

Synthesis and Characterization of 3,4-Diferrocenyl-1-(triisopropylsilyl)-1H-pyrrole (2) and 3,4-Diferrocenyl-1H-pyrrole (3). It is well known that pyrrole undergoes predominant electrophilic substitution at the  $\alpha$ -position, while preparation of  $\beta$ -substituted pyrroles is more challenging.<sup>18</sup> The most common synthetic pathways for preparation of  $\beta$ substituted pyrroles include, but are not limited to, (i) utilization of a removable deactivating group at  $\alpha$ -substituted pyrroles to direct the entry of an electrophile to the  $\beta$ position,<sup>19</sup> (ii) acid-mediated isomerization of the easily available  $\alpha$ -isomers,<sup>20</sup> and (iii) direct substitution of an *N*-(phenylsulfonyl)pyrrole with certain electrophiles, described, for instance, by Anderson and co-workers<sup>21</sup> and Rokach and co-workers.<sup>22</sup> Another approach to the synthesis of  $\beta$ substituted pyrroles is based on the use of a bulky protecting group at the nitrogen atom, such as triisopropylsilyl, to obstruct electrophilic attack at the  $\alpha$ -position.<sup>23</sup> Considerable selectivity for the  $\beta$ -pyrrolic position is indeed observed, and the process of removing the protecting group is easily attainable with the use of tetraalkylammonium fluoride.<sup>24</sup>

Following a previous report by Bray and co-workers,<sup>23</sup> we used a bulky triisopropylsilyl protecting group at the pyrrolic nitrogen atom to obstruct halogenation in the 2,5-pyrrolic positions. Indeed, reaction of *N*-(triisopropylsilyl)pyrrole with either bromine or iodine at low temperature results in formation of 3-mono- as well as 3,4-dihalopyrrole. In our hands, the bromination reaction resulted in formation of the mixture of 3-bromo- and 3,4-dibromopyrrole, which was challenging to separate in required large quantities using conventional chromatography methods. Iodination of *N*-(triisopropylsilyl)pyrrole in the presence of mercuric acetate, however, yielded almost pure 3,4-diiodo-1-(triisopropylsilyl)-1*H*-pyrrole (1), which was further purified using standard techniques (Scheme 1).

Two different strategies were explored for conversion of 1 to the 3,4-diferrocenyl-1-(triisopropylsilyl)-1*H*-pyrrole (2). First, we explored palladium-catalyzed coupling reaction between bis(ferrocenyl)mercury and 1, following methodology described earlier by Beletskaya<sup>25</sup> and co-workers, which was successfully used for the preparation of several ferrocenecontaining derivatives in our laboratory.<sup>26</sup> This reaction, unfortunately, reproducibly resulted in formation of only trace quantities of 2. In the second approach, we explored the reaction between ferrocenyl-zinc chloride and 1, following a procedure reported by Lang and co-workers for the preparation of 2,3,4,5-tetraferrocenylpyrrole.<sup>15</sup> Using this approach, 2 was successfully prepared in 7% to 52% yields in several trials. An optimal yield of 2 could be achieved by heating the reactants for 72 h at 60 °C (Scheme 1) and allows production of target compound 2 in gram quantity. In addition to target compound 2, small amounts of ferrocene, bis(ferrocene), and other byproducts were detected in the reaction mixture. The new diferrocenyl compound 2 is air stable in the solid state and soluble in a variety of organic solvents. Deprotection of 2 can be easily achieved using tetrabutylammonium fluoride<sup>23</sup> in organic solvent to give pure 3,4-diferrocenvl-1*H*-pyrrole (3) after standard purification (Scheme 1). Unlike protected pyrrole derivative 2, compound 3 is not stable in solution and degrades within several days in the majority of organic solvents. This compound, however, could be stored in a solid state for several weeks if refrigerated.

The <sup>1</sup>H and <sup>13</sup>C NMR spectra of **2** and **3** consist of characteristic signals and correlate well with their structures (Figures S1–S4). In particular, <sup>1</sup>H NMR spectra of **2** and **3** consist of one signal of pyrrolic  $\alpha$ -protons and three signals of ferrocene substituents. In addition, two signals of the protecting  $-Si(i-Pr)_3$  group and a pyrrolic NH signal were observed in the <sup>1</sup>H NMR spectra of **2** and **3**, respectively. Similarly, <sup>13</sup>C NMR spectra of pyrroles **2** and **3** consist of two pyrrolic signals and four signals of the protecting  $-Si(i-Pr)_3$  group were observed in the <sup>13</sup>C NMR spectrum of **2**. UV–vis spectra of **2** and **3** are shown in Figure 1 and consist of a weak band at 22 320 cm<sup>-1</sup> (448 nm) or 22 270 cm<sup>-1</sup> (449 nm) and an intense band observed at 36 230 cm<sup>-1</sup> (276 nm) or 36 760 cm<sup>-1</sup> (272 nm) for pyrrole derivatives **2** and **3**, respectively.



**Figure 1.** Experimental (top and middle) and TDDFT-predicted (bottom) UV-vis spectra of compounds **2** and **3**. Vertical bars represent excitation energies and oscillator strengths calculated by the TDDFT approach.

**Crystal Structure Description.** Information regarding the chemical structure of 1 and 2 was obtained on the basis of X-ray crystallography (Figure 2). The results of the X-ray structure refinement of 1 and 2 are presented in Table S1, while selected



**Figure 2.** ORTEP drawings of X-ray structures of compounds **1**, **2**, and **3Ox**. Thermal ellipsoids are at the 50% probability level. Hydrogen atoms are omitted for clarity.

bond distances and angles are shown in Table 1. The pyrrole rings of 1 and 2 are essentially planar. The root-mean-square (RMS) deviations for the planes are 0.002 Å (1) and 0.004 Å (2), respectively, while the largest deviation of the atoms from the corresponding planes is 0.003(2) Å for C(1) and 0.002(4)Å for C(3) for 1 and 2, respectively. The torsion angles N(1)-C(1)-C(2)-C(3) and C(2)-C(3)-C(4)-N(1) are  $0.6(2)^{\circ}$ ,  $(0.1(2)^{\circ})$  and  $(-0.2(4)^{\circ})$ ,  $(-0.5(4)^{\circ})$ , for 1 and 2, respectively. At the same time, out-of-plane deviations of the silicon atoms are different for 1 and 2. Thus, the torsion angles Si(1)-N(1)-C(1)-C(2) and C(2)-C(1)-N(1)-Si(1) are equal to  $-173.4(1)^{\circ}$  and  $163.1(2)^{\circ}$  for 1 and 2, respectively. In addition, the deviation of the silicon atoms and from a leastsquares plane of the pyrrole ring (N(1), C(1), C(2), C(3), andC(4) is 0.170(1) and 0.421(1) Å for 1 and 2, respectively. Iodine atoms in 1 are coplanar with the pyrrole plane. Thus, the deviation of the iodine atoms from the pyrrole plane is -0.098(1) Å for I(1) and -0.066(1) Å for I(2), while torsion angle I(1)-C(2)-C(3)-I(2) is  $-0.8(3)^{\circ}$ . It is worth noting that the torsion angle C(5)-C(2)-C(3)-C(15) in 2 is almost the same and equals  $-1.6(6)^\circ$ , which could not be expected taking into account the bulk character of the ferrocene groups. Indeed, values for the torsion angle in related systems reported in the literature are significantly larger  $(7.24^{\circ} \text{ and } 4.46^{\circ} \text{ for})$ related compounds).<sup>27</sup> Orientation of the ferrocene groups in **2** deviates significantly from the effective C2 symmetry of this ferrocene-containing pyrrole as observed by NMR spectroscopy in solution. Thus, corresponding torsion angles C(1)-C(2)-C(5)-C(9) and C(4)-C(3)-C(15)-C(19) are 141.0(4)° and  $67.4(5)^{\circ}$ , respectively. It is interesting to note that the 2,3,4,5-tetraferrocenyl-pyrrole adopts a similar conformation of the ferrocene groups in the 3- and 4-positions with corresponding torsion angles of 131.74/131.71° and 134.70/ -105.64°.15 A similar conformation of the ferrocenyl substituents with local  $C_2$  symmetry was reported earlier for 3,4-diferrocenemaleoimides, and corresponding torsion angles were found to be -154.84/-141.69°26 and -152.76/-146.02°.15 Fe-C distances in 2 are in the regular range 2.036(4) - 2.071(3) Å, with an average Fe-C distance of 2.049(4) Å.

Because of the low stability of **3** in solution for extended periods of time required for a slow growth of its monocrystals suitable for X-ray crystallography, we were not able to collect single-crystal data on this compound. In the majority of cases, the solution for crystallization became dark and precipitated black micropowders in several days. In one such attempt, however, along with the regular black precipitate, we were able to manually separate several poor-quality dark orange crystals, which were analyzed by X-ray diffraction (Figure 2, Tables S1 and 1) and found to be 5-hydroxy-3,4-diferrocenyl-1*H*-pyrrol-2(5H)-one (**3Ox**, Scheme 1). Formation of the **3Ox** complex can be viewed as a partial oxidation/hydrolysis of **3** in wet toluene in a regular atmosphere.

The crystal structure consists of two molecules of **30x** and two molecules of toluene. Carbon atoms in the 2- and 5positions are not chemically equivalent: one type of carbon atom is sp<sup>3</sup>-hybridized and utilizes an alcohol function (C(4) and C(28)), while the second one is sp<sup>2</sup>-hybridized and may be viewed as a carbonyl component of an amide (C(1) and C(25)). Bond distances for carbonyl component C(1)–O(1) and O(3)–C(25) are 1.21(2) and 1.25(2) Å, respectively, and are very close to another cyclic amide (1.214(4) and 1.204(4) Å) reported earlier.<sup>26</sup> The configuration of the C(4) and C(28)

Compound 1						
I(1)-C(2)	2.066(2)	C(3)-C(2)-I(1)	128.00(15)			
I(2) - C(3)	2.061(2)	C(4)-C(3)-I(2)	125.38(16)			
Si(1)–N(1)	1.791(2)	C(1)-N(1)-C(4)	107.13(17)			
Si(1)-C(8)	1.881(2)	C(1)-N(1)-Si(1)	125.75(14)			
Si(1) - C(5)	1.882(2)	C(4)-N(1)-Si(1)	126.69(14)			
Si(1) - C(11)	1.882(2)	I(1)-C(2)-C(3)-I(2)	-0.8(3)			
Compound 2						
C(25)-Si(1)	1.891(4)	C(1)-C(2)-C(5)	124.2(3)			
C(28)-Si(1)	1.883(4)	C(4) - C(3) - C(15)	125.4(3)			
C(31)-Si(1)	1.879(3)	C(1)-C(2)-C(5)-C(6)	-33.7(5)			
N(1)-Si(1)	1.782(3)	C(4)-C(3)-C(15)-C(19)	67.4(5)			
C(2) - C(5)	1.465(5)	C(2)-C(1)-N(1)-Si(1)	163.1(2)			
C(3)-C(15)	1.480(4)	C(3)-C(4)-N(1)-Si(1)	-163.0(3)			
Fe-C(average)		Fe···π				
	Compor	and 3Ox PhMe				
O(1)-C(1)	1.21(2)	C(1)-C(2)	1.50(2)			
O(2)-C(4)	1.43(1)	C(2)-C(3)	1.37(2)			
N(1)-C(1)	1.38(2)	C(3) - C(4)	1.56(2)			
N(1)-C(4)	1.41(2)	O(3)-C(25)	1.25(2)			
O(4)-C(28)	1.38(1)	N(2)-C(25)	1.33(2)			
N(2)-C(28)	1.47(2)	C(25)-C(26)	1.48(2)			
C(26) - C(27)	1.33(2)	C(27)-C(28)	1.53(2)			
C(1)-N(1)-C(4)	112.4(11)	O(1)-C(1)-N(1)	124.7(12)			
O(1)-C(1)-C(2)	128.8(12)	N(1)-C(1)-C(2)	106.5(12)			
C(3)-C(2)-C(1)	108.4(10)	C(2)-C(3)-C(4)	107.6(10)			
N(1)-C(4)-O(2)	114.2(11)	N(1)-C(4)-C(3)	104.1(11)			
O(2) - C(4) - C(3)	114.3(9)	C(4)-N(1)-C(1)-O(1)	170.1(13)			
O(1)-C(1)-C(2)-C(3)	-169.8(13)	N(1)-C(1)-C(2)-C(3)	10.2(13)			
C(2)-C(3)-C(15)-C(19)	166.2(12)	C(1)-C(2)-C(5)-C(6)	155.1(11)			
C(25)-C(26)-C(29)-C(30)	-152.3(12)	C(28)-C(27)-C(39)-C(40)	16.1(18)			
Fe-C(average)	2.03(1)	Fe···π	1.638(6), 1.651(7),			
			1.651(7), 1.651(6),			
			1.640(7), 1.658(6),			
			1.626(6), 1.633(6)			

Table 1. Selected Bond Distances (Å) and Angles (deg) for Complexes 1, 2, and 30x PhMe Determined by X-ray Crystallography

Chart 1. Structures of Complexes 4Me, 4Ph, 5Me, and 5Ph



atoms differs and corresponds to *S* and *R* type, thus eliminating overall chirality of the crystal (space group *P*1). The oxygen atoms of the hydroxo groups significantly deviate from pyrrole planes (1.02(1) and 0.98(1) Å) built on N(1)–C(1)–C(2)–C(3)–C(4) and N(2)–C(25)–C(26)–C(27)–C(28) atoms, respectively. O–C–C angles for sp<sup>3</sup>-hybridized carbon atoms are 107.6(10)° (O(2)–C(4)–C(3)) and 114.6(9)° (O(4)–C(28)–C(27)), while C–O distances are 1.43(1) Å (O(2)–C(4)) and 1.38(2) Å (O(4)–C(28)). All these geometric parameters ultimately suggest the sp<sup>3</sup>-hybridized state for carbons C(4) and C(28). The distances between carbons in 3 and 4 positions are 1.37(2) and 1.33(2) Å, which are shorter than the same distance in 2 (1.443(5) Å) and correspond to a

carbon–carbon double bond. The orientation of the ferrocenyl groups also differs from that observed in **2**. They adopt local  $C_2$  symmetry, as was previously observed for similar amide systems.<sup>26</sup> In addition, a strong hydrogen bonding between the molecules in a solid state was observed in the crystal structure of **3Ox**. Two molecules of **3Ox** of the same type form a centrosymmetric dimer via hydrogen bonding between amide groups and oxygen atoms of the carbonyl groups (N(1)… O(1)[-x,1-y,-z] = 3.02(1) Å, N–H…O = 153.5° and N(2)… O(3)[1-x,1-y,-z] = 2.98(1) Å, N–H…O = 154.2°). These dimers are additionally bonded by a hydrogen bond between the hydroxo group and the oxygen atom of the carbonyl group (O(1)…O(4)[1-x,y,z]) = 2.74(2) Å and O(3)…O(2) =

2.74(1) Å), forming one-dimensional chains along the crystallographic *a*-axis.

**Electrochemical and Spectroelectrochemical Studies.** In order to investigate redox properties and evaluate the degree of metal-metal coupling in the 3,4-diferrocene-substituted pyrroles, compounds **2** and **3** were studied by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) methods in a low-polarity solvent (DCM) using a common electrochemical electrolyte,  $[N(C_4H_9)_4]ClO_4$  (TBAP), and a noncoordinating electrolyte,  $[N(C_4H_9)_4][B(C_6F_5)_4]$  (TBAF). The latter electrolyte was shown to provide superior resolution for redox waves in numerous coupled systems and in particular for poly(ferrocenyl)pyrroles, furans, thiophenes, and maleoimides.<sup>15,26</sup> Experimental CV and DPV data for pyrrole derivatives **2** and **3** are presented in Figure 3 and summarized



**Figure 3.** CV (blue) and DPV (red) data for compounds **2** and **3** in DCM/0.05 M TBAF (top) and DCM/0.1 M TBAP (bottom) systems at room temperature. CV scan rates are 100 mV/s.

in Table 2. In both electrolyte systems, two clearly defined reversible oxidation processes have been observed. The first oxidation potential in 2 and 3 in both electrolyte systems is significantly lower compared to the parent ferrocene, similar to what has been previously observed for the 2,5-di- and 2,3,4,5-

Table 2. Redox Properties of Pyrroles 2-5 (see Chart1 for Structures 4 and 5)<sup>*a*</sup>

compound	electrolyte	Ox <sub>1</sub> , mV	Ox <sub>2</sub> , mV	$\Delta E$ , mV	$K_{\rm c}$
2	TBAP	-225	-50	175	908
3	TBAP	-150	+30	180	1103
$4Ph^b$	$(NBu_4)[PF_6]$	-198	+117	315	211 039 <sup>d</sup>
5Ph <sup>b</sup>	$(NBu_4)[PF_6]$	-226	-26	200	$2102^{d}$
2	TBAF	-180	+120	300	117 712
3	TBAF	-170	+120	290	79762
$4 Ph^b$	TBAF	-238	+212	450	40 386 252 <sup>d</sup>
4Me <sup>c</sup>	TBAF	-206	+204	410	8 513 809 <sup>d</sup>
5Ph <sup>b</sup>	TBAF	-280	+51	331	393 375 <sup>d</sup>
5Me <sup>c</sup>	TBAF	-280	-15	265	30 146 <sup>d</sup>

<sup>*a*</sup>Potentials vs FcH/FcH<sup>+</sup> (±10 mV), scan rate 100 mV/s at platinum working electrode in dry DCM, 0.1 M TBAP or 0.05 M TBAF electrolyte at room temperature. <sup>*b*</sup>0.1 M TBAF or (NBu<sub>4</sub>)[PF<sub>6</sub>] was used, ref 15a. <sup>*c*</sup>0.1 M TBAF was used, ref 15b. <sup>*d*</sup>K<sub>c</sub> values: this work.

tetrasubstituted pyrroles.<sup>15a-c</sup> Similar to the 2,5-diferrocenyl-pyrrole systems,<sup>15a</sup> two oxidations were assigned to singleelectron ferrocene-centered processes. Because of the welldocumented suppression of the ion-paring for the TBAF electrolyte,<sup>15</sup> the separation between these oxidation waves is smaller ( $\Delta E_{1/2} = 170$  and 180 mV for 2 and 3, respectively) in TBAP electrolyte compared to that observed in TBAF electrolyte ( $\Delta E_{1/2}$  = 300 and 290 mV for **2** and **3**, respectively). Interestingly, the separation between the first two oxidation waves in 2 and 3 in both electrolytes is significantly smaller than similar values reported for 2,5-diferrocenyl-1-phenylpyrrole (315 mV in TBAP and 450 mV in TBAF) or 2,3,4,5tetraferrocenyl-1-phenylpyrrole (330 mV in TFAB).<sup>15a,b</sup> It was unusual to see a decrease in  $\Delta E_{1/2}$  in 2 and 3, as we would expect electronic communication to be improved between two 3,4-disubstituted ferrocenyl ligands, as the distance between the two substituents is smaller than the ferrocene-ferrocene distance in 2,5-disubstituted pyrroles. A large separation between redox waves in 2 and 3 in both electrochemical systems is indicative of the large comproportionation constants  $K_c$  for the 2[2 or 3]<sup>+</sup>  $\rightleftharpoons$  [2 or 3]<sup>0</sup> + [2 or 3]<sup>2+</sup> process.<sup>28</sup> Because of the large values of  $K_{c}$ , one could expect that the spectroscopic signatures of the mixed-valence  $[2]^+$  and  $[3]^+$ might be obtained using a spectroelectrochemical approach.

The UV-vis-NIR spectroscopic signatures of the different oxidized forms of pyrrole derivatives 2 and 3 were obtained using a spectroelectrochemical approach. Stepwise oxidation was performed in DCM/TBAP and DCM/TBAF systems with close results (Figures 4 and 5). Removal of the first electron



**Figure 4.** Spectroelectrochemical oxidation of compound **2** in DCM/ 0.3 M TBAP (top and middle) and DCM/0.15 M TBAF (bottom) systems.

from pyrrole derivative 2 or 3 in both systems results in the appearance of two distinct bands located at ~1000 and ~2200 nm in the NIR region connected by a broad plateau. For both ferrocenyl pyrroles, the former band is about an order of magnitude more intense than the latter band. Upon electrolysis of the mixed-valence  $[2]^+$  or  $[3]^+$  at the second oxidation potential (DCM/TBAP system), the intensity of the weak band observed at ~2200 nm only slightly decreases, the initial band



**Figure 5.** Spectroelectrochemical oxidation of compound 3 in DCM/ 0.3 M TBAP (left) and DCM/0.15 M TBAF (right) systems.

at ~1000 nm undergoes a blue shift to ~900, and the NIR plateau that connects these two bands disappears (Figures 4 and 5). Reduction of  $[2]^{2+}$  is completely reversible in both electrochemical systems studied (Figure S5), and a similar reversibility was observed for  $[3]^{2+}$  in the DCM/TBAP system (Figure S6). Overall, these electrochemical and spectroelectrochemical results for pyrrole derivatives 2 and 3 correlate well with reported data for both the 2,5-diferrocenylpyrroles and 2,3,4,5-tetraferrocenylpyrroles published earlier.<sup>15</sup> The reversibility of the oxidation processes for 3 in the DCM/TBAF system under spectroelectrochemical conditions, however, is quite different. Although, upon the oxidation of  $[3]^+$ , the lowenergy band at ~2200 nm does not lose intensity and the NIR band at ~1000 nm undergoes a blue shift to ~900 nm, the resulting  $[3]^{2+}$  cation cannot be reduced back to the neutral 3 (Figure S6). Such reproducible behavior can be attributed to polymerization of  $[3]^+$  or  $[3]^{2+}$  on the working electrode, which is a typical behavior for numerous  $\alpha$ -unsubstituted NH pyrrole derivatives.<sup>29</sup> In order to test this hypothesis, we conducted several electropolymerization experiments on complex 3 in the DCM/TBAF system (Figure S7). Indeed, when complex 3 was carefully cycled close to the first two ferrocene-based oxidation potentials, no electropolymerization was observed (Figure S7a). When the cycling potential was increased by several hundredths of a millivolt (to mimic the overpotential required by our custom-made spectroelectrochemical cell), electropolymerization was clearly observed in CV experiments (Figure S7b). Such electropolymerization can be initiated only by traces of unidentified impurity present in the electrochemical system because the oxidation potential of the pyrrole fragment in complex 3 is located outside the electrochemical window (Figure S7c). Similar electropolymerization of complex 3 in the DCM/TBAP system was not observed because of the much lower second oxidation potential of ferrocene substituents.

Although signals observed in the inter-valence charge transfer (IVCT) region in the mixed-valence complexes  $[2]^+$  and  $[3]^+$  are rather weak, we were able to conduct a deconvolution analysis for a better resolved and more intense IVCT band region in  $[2]^+$ . The two key parameters for the mixed-valence  $[2]^+$  that could be estimated using the Hush model are the

electronic coupling matrix element  $(H_{ab})$  and the degree of delocalization  $(\alpha^2)$ .<sup>30</sup> These parameters can be estimated using eqs 1 and 2, and the Fe–Fe distances extracted from the corresponding crystal structures or DFT-predicted geometries of neutral compound **2**.

$$H_{\rm ab} = 2.05 \times 10^{-2} [(\nu_{\rm max} \varepsilon_{\rm max} \Delta \nu_{1/2})^{1/2} / r_{\rm ab}]$$
(1)

$$\alpha^{2} = 4.24 \times 10^{-4} [(\varepsilon_{\max} \Delta n_{1/2}) / (r_{ab}^{2} \eta_{\max})]$$
(2)

Both ~1000 and ~2200 nm NIR bands observed in  $[2]^+$  and [3]<sup>+</sup> cannot be assigned as IVCT bands because neither of these would disappear during the second oxidation process. Thus, the broad plateau at ~1800 nm, which increases under  $[2] \rightarrow [2]^+$  or  $[3] \rightarrow [3]^+$  transformation and decays under the  $[2]^+ \rightarrow [2]^{2+}$  or  $[3]^+ \rightarrow [3]^{2+}$  process, was assigned as an IVCT band. Fitting of the IVCT band in  $[2]^+$  with the Gaussian-shape bands (Figure S8) gave the necessary information for calculation of  $H_{ab}$  and  $\alpha^2$  via eqs 1 and 2. The maximum molar absorption coefficient of the IVCT band (143 M<sup>-1</sup> cm<sup>-1</sup>), the energy of  $\nu_{\rm max}$  of 5568 cm<sup>-1</sup> and  $\Delta\nu_{1/2}$  of 3383 cm<sup>-1</sup>, and the crystallographic Fe–Fe distance of 5.934 Å yielded  $H_{\rm ab} = 180 \text{ cm}^{-1}$  and  $\alpha^2 = 1.04 \times 10^{-3}$ . These data along with the  $\Gamma$ -test<sup>30</sup> value (0.046) clearly suggest that 2<sup>+</sup> belongs to a weakly coupled class II mixed-valence system in Robin-Day classification.<sup>31</sup> It should be noted, however, that these values should be treated with caution because the broad and nonprominent nature of the IVCT band could cause some error in the  $\Delta \nu_{1/2}$  value during the fitting procedure. In spite of such possible error, IVCT band deconvolution analysis, which predicts small intramolecular interactions in the mixed-valence  $[2]^+$  and  $[3]^+$ , is in excellent agreement with the electrochemical data on these systems.

DFT and TDDFT Calculations on Neutral Poly-(ferrocenyl)pyrroles. DFT and TDDFT calculations were performed to acquire insight into the nature of the electronic structure, spectroscopy, and redox properties of ferrocenecontaining pyrroles 2 and 3. First, we have studied the influence of the triisopropylsilyl group on the electronic structure and MO composition of 2 and 3. In order to investigate such an influence, we have calculated the electronic structure of 2 at Xray geometry and compared it to those obtained for (i) the geometry-optimized structure of 2 (structure 2a) and (ii) the geometry optimized ( $C_2$  symmetry) structure of 3. The molecular orbital energy diagram, molecular orbital compositions, and representative shapes of important molecular orbitals predicted using the B3LYP exchange-correlation functional with Wachter's full-electron basis set for Fe, the 6-311G(d)basis for C and N, and the 6-31G basis set for H are shown in Figures 6 and 7. MO contribution analysis suggests that in all cases the HOMO is dominated by the contributions from the two ferrocene substituents with a minor contribution coming from the  $\beta$ -pyrrolic and nitrogen atoms. Such MO shape creates a potential orbital electron-transfer pathway for electron transfer from one ferrocene substituent to another. Similar HOMO shapes were observed in the previously reported dimethyl (Z)-2,3-bis(ferrocenyl)-2-butenedioate and (Z)-2,3bis(ferrocenyl)maleimide systems.<sup>26</sup> In addition, the composition of the HOMO in pyrrole derivatives 2 and 3 also suggests that the first oxidation should be ferrocene-centered, in agreement with experimental data. In all cases, the LUMO is again dominated by contributions from the two ferrocene substituents with minor contributions coming from the  $\alpha$ - and



Figure 6. DFT-predicted frontier orbital energies of pyrroles 2 and 3.



Figure 7. Molecular orbital compositions for pyrroles 2 (top) and 3 (bottom) calculated at the DFT level.

 $\beta$ -pyrrolic carbon atoms. In general, our DFT calculations on **2a** and **3** are suggestive of a marginal influence of the triisopropylsilyl protecting group on the MO energies and compositions, and thus in all other calculations the smaller ferrocene-containing pyrrole **3** variant was used. Such results are not surprising because it is expected that the electron-donating properties of proton and triisopropylsilyl substituents should be close to each other.<sup>32</sup>

Accurate prediction of the electronic structure of **3**, which is a truncated version of **2**, allows for the assignment of the experimentally observed bands in the UV–vis spectra of both **2** 

and 3. Indeed, it has been shown that the TDDFT approach can accurately predict both energies and intensities in small ferrocene-containing compounds.<sup>33</sup> The TDDFT-predicted UV-vis spectrum of 3 along with its corresponding vertical excitations is provided in Figure 1 in comparison with the experimental spectra of pyrrole derivatives 2 and 3. TDDFTcalculated vertical excitation energies and expansion coefficients are provided in Table S2. In general, the TDDFT-predicted spectrum of 3 is in very good agreement with the experimental UV-vis spectra of both ferrocene derivatives 2 and 3 (Figure 1). The experimental spectra of 2 and 3 are composed of two primary bands, the first (abbreviated as band 1 below) being weak and broad, centered around 22 320 or 22 270  $\text{cm}^{-1}$  (for 2 and 3, respectively) and spanning from  $\sim 16\,600$  to  $\sim 26\,600$ cm<sup>-1</sup>. TDDFT predicts eight excited states in this spectral envelope. All of these excited states can be viewed as predominantly d-d transitions, but only the first and the fifth excited states contribute significantly to the band 1 profile because excited states 2-4 and 6-8 have negligible intensities (Table S2). In agreement with their predominant d-dcharacter and experimental data, overall TDDFT-predicted intensities for the band 1 spectral envelope are quite low. The second and more prominent band 2 of the experimental spectra of pyrrole derivatives 2 and 3 appears at 36 230 and 36 760 cm<sup>-1</sup>, respectively. TDDFT calculations predict that excited states 9-30 contribute to this band's profile. Out of these contributors, however, only excited states 21, 22, and 25 (Table S2) have significant TDDFT-predicted intensities to form the absorption band profile of the band 2 region. All of these excited states have significant contributions from LMCT and/ or MLCT single-electron transitions in addition to their d-d character. Overall, TDDFT calculations are in good agreement with experimental data and suggest that the band 1 spectral region is dominated by d-d transitions, while the higher energy band 2's spectral region has significant charge-transfer character.

Similar to the 3,4-ferrocene-disubstituted compounds 2 and 3, DFT predicts that the HOMO and the LUMO in 2,5di(ferrocenyl)pyrrole (4) are dominated by the ferrocene substituents, although the contribution from the pyrrole heterocycle to these MOs is significantly higher (~40% for the HOMO and ~20% for the LUMO) than those in 3,4diferrocenyl analogues 2 and 3 (Figure 8). The HOMO and the LUMO in 2,3,4,5-tetraferrocene-1H-pyrrole (5) are also ferrocene-centered, although the HOMO is dominated by contributions from 3,4- while the LUMO is dominated by contributions from the 2,5-ferrocenyl substituents (Figure 8). Thus, DFT calculations predict that the first oxidation in compounds 2-5 should be ferrocene-centered, in agreement with the experimental data. More interestingly, the ground-state DFT calculations predict that the first oxidation in the tetraferrocenylpyrrolic system 5 should be centered at the 3,4-ferrocenyl substituents, which contradicts the earlier electrochemical data-based hypothesis of Lang and co-workers.15

**DFT Calculations on Mixed-Valence Poly(ferrocenyl)pyrrole Cations.** The DFT calculations on the mixed-valence  $[3]^+$  and  $[4]^+$  complexes in localized  $C_1$  and delocalized  $C_2$  symmetries (Table 3) suggest that the localized structures are 5.3 and 34.9 kcal/mol more stable than the corresponding delocalized structures of pyrrole derivatives  $[3]^+$  and  $[4]^+$ , respectively. These findings are in agreement with the IVCT band deconvolution analysis for pyrrole derivatives 2-4,



Figure 8. Molecular orbital compositions for pyrroles 4 (top) and 5 (bottom) calculated at the DFT level.

Table 3. DFT-Predicted Relative Energies and Spin-Densities in  $C_2$  (Delocalized) and  $C_1$  (Localized) Geometries of the Mixed-Valence  $[3]^+$  and  $[4]^+$ 

		spin density			
symmetry	$\Delta E$ , kcal/mol	Fe2	Fe5	Fe3	Fe4
Complex	: <b>[3</b> ] <sup>+</sup>				
$C_2$	5.28			0.64	0.64
$C_1$	0.00			1.28	0.00
Complex	: <b>[4</b> ] <sup>+</sup>				
$C_2$	34.89	0.49	0.49		
$C_1$	0.00	1.15	0.03		

according to which mixed-valence diferrocenes  $[2]^+-[4]^+$  should have localized class II (in Robin–Day classification)<sup>31</sup> character.

In order to resolve the above-mentioned controversy regarding the first oxidation process in 2,3,4,5-tetraferrocenylpyrroles, an extensive set of DFT calculations on relative energies and spin density localization/delocalization in  $[5]^+$ mixed-valence cation were performed. Because the mixedvalence  $[5]^+$  cation, at least theoretically, can adopt localized  $C_1$ (class II in Robin–Day classification)<sup>31</sup> or delocalized  $C_2$  (class III in Robin–Day classification) geometries, both of these possibilities were taken into account. In addition, in the case of localized  $C_1$  symmetry structures, manual localization of the initial spin density on one out of four ferrocene groups was implemented prior to and following geometry optimization. Similarly, in the case of delocalized  $C_2$  symmetry structures of  $[\mathbf{5}]^+$ , we performed three different optimizations: (i) no restrictions on spin density; (ii) spin density at the 2,5-ferrocene groups; (iii) spin density at the 3,4-ferrocene groups. Finally, we also ran a set of DFT calculations on the N-Ph derivate of  $[\mathbf{5}]^+$  (compound **5Ph**) using the experimentally determined geometry for this compound<sup>15</sup> with and without initial spin localization.

The analysis of our data (Table 4 and Figures 9 and 10) is suggestive of the following trends: (i) the global energy

Table 4. DFT-Predicted Relative Energies and Spin Densities for Local and Global Minima in  $C_1$  (Localized) and  $C_2$  (Delocalized) Structures of the Mixed-Valence  $[5]^+$ Complex

			spin density			
symmetry		$\Delta E$ (kcal/mol)	Fe-2	Fe-5	Fe-3	Fe-4
$C_2$	delocalized	7.30	0.33	0.33	0.10	0.10
	Fc-2,5	7.37	0.30	0.30	0.12	0.12
	Fc-3,4	9.70	0.13	0.13	0.20	0.20
	Fc-2,5	3.86	0.33	0.33	0.10	0.10
	Fc-3,4	7.78	0.04	0.04	0.52	0.52
$C_1$	Fc-2	43.14	1.02	0.00	0.00	0.00
	Fc-5	6.50	0.01	1.15	0.01	0.02
	Fc-3	0.00	0.00	0.00	1.27	0.00
	Fc-4	1.20	0.00	0.00	0.00	1.26



**Figure 9.** DFT-predicted energy profiles for  $[\mathbf{5}]^+$  in  $C_2$  and  $C_1$  symmetries.



Figure 10. DFT-predicted energy profiles for  $[5Ph]^+$  in  $C_1$  symmetry.

minimum for all optimized localized and delocalized mixedvalence structures is represented by the complex  $[5]^+$  with electron density localized at one out of two  $\beta$ -pyrrolic ferrocene substituents; (ii) the lowest energy localized  $C_1$  structure in which electron density is localized at  $\alpha$ -pyrrolic ferrocene is 6.5 kcal/mol higher in energy than the global minimum for the  $C_1$ symmetry localized structures; (iii) the minimum energy for the delocalized  $C_2$  symmetry structure belongs to the structure with spin density delocalized over ferrocenes at the 2,5-positions; this structure is 3.89 kcal/mol higher in energy than the global minimum for the localized  $C_1$  structures; (iv) the lowest energy delocalized C<sub>2</sub> symmetry structure in which spin density is delocalized over  $\beta$ -pyrrolic ferrocene groups is 3.92 kcal/mol higher in energy than the  $C_2$  symmetry structure in which spin density is delocalized over  $\alpha$ -pyrrolic ferrocene groups; (v) in the case of the X-ray crystal structure of [5Ph]<sup>+</sup>, DFT calculations again predict that the global minimum should be described by the localized structure in which spin density is localized over one  $\beta$ -pyrrolic ferrocene group, while the lowest energy structure in which spin density is localized over an  $\alpha$ pyrrolic ferrocene group is 3.61 kcal/mol higher in energy. Thus, DFT calculations suggest that the  $\beta$ -ferrocene localized  $C_1$  structure should be more energetically stable than any other mixed-valence singly oxidized species, which is in agreement with the ground-state calculations presented above on neutral 5. Despite this agreement, however, one should be careful about ultimate assignments of the nature of electrochemically or chemically generated  $[5]^+$  because the DFT-predicted energies of the 2,5-delocalized  $C_2$  symmetric and localized  $\alpha$ pyrrolic  $C_1$  symmetric  $[5]^+$  cations are only 3.89 and 6.5 kcal/ mol higher in energy, and this energy order could be easily affected by the electronic and steric properties of the substituent at the nitrogen atom as well as by the polarity of the solvent used for spectroelectrochemical or chemical oxidation experiments. In addition, while the B3LYP exchange-correlation functional could be viewed as a good starting point for DFT calculations on energies of the mixedvalence poly(ferrocenyl)-containing systems,<sup>34</sup> it might be expected that variation of the amount of Hartree-Fock exchange in a given exchange-correlation functional can alter the relative energies and degree of spin density localization/ delocalization in possible spin isomers of  $[5]^{+,3}$ 

The overall problem with providing an accurate assignment of the redox properties in tetraferrocenyl-containing pyrroles, thiophenes, and furans might be even more complex. Indeed, experimental redox data on 2, 4Ph, and 5Ph in TBAP or  $(NBu_4)[PF_6]$  electrolytes (Table 2) cannot resolve such uncertainties as the first oxidation potential of  $2_{1}$ , which appears virtually identical to that of the tetraferrocenyl compound 5Ph, while the first oxidation potential of 4Ph is also close to that in **5Ph** ( $\Delta E_{1/2} \sim 30$  mV). Similarly, in the TBAF/DCM system, the first oxidation potential of 2 is 26 mV higher than the first oxidation potential in 4Me and 58 mV higher than in 4Ph, while all of these are significantly higher than in the tetrasubstituted derivatives 5Me and 5Ph. Moreover, recently Lang and coauthors reported that the oxidation potentials for 2,5-diferrocenyl- and 3,4-diferrocenylthiophenes are exactly the same and differ significantly from the first oxidation potential in 2,3,4,5-tetraferrocenylthiophene.<sup>15</sup>

# CONCLUSIONS

3,4-Diiodo-1-(triisopropylsilyl)-1*H*-pyrrole (1), 3,4-diferrocenyl-1-(triisopropylsilyl)-1*H*-pyrrole (2), and 3,4-diferrocenyl-1*H*pyrrole (3) were prepared and characterized using NMR and UV-vis spectroscopic methods as well as X-ray crystallography and elemental analysis. UV-vis spectra of 2 and 3 were

assigned with the help of their electronic structures, and excited-state energies calculated using DFT and TDDFT methods. It was found that the low-energy, low-intensity band observed in the UV-vis spectra of 2 and 3 can be assigned as ferrocene-centered d-d transitions, while the more intense UV band could be associated with the charge-transfer excitations. Redox properties of 2 and 3 were investigated using cyclic voltammetry, differential pulse voltammetry, and spectroelectrochemical approaches. Ferrocene-centered oxidation processes in 2 and 3 were found to be separated by  $\sim 180$ and ~300 mV in DCM/TBAP and DCM/(NBu<sub>4</sub>)[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] systems, respectively. Stepwise spectroelectrochemical oxidation of 2 and 3 allowed us to obtain spectroscopic signatures of the mixed-valence  $[2]^+$  and  $[3]^+$  cations, which are characterized by two NIR bands observed at ~1000 and ~2200 nm. Hush analysis of the intervalence charge-transfer band in  $[2]^+$ and  $[3]^+$  is suggestive of class II (in Robin and Day classification) mixed-valence behavior. Electronic structures of neutral and spin-localized/delocalized single-electron-oxidized mixed-valence cations 2,5-di- (compound 4), 3,4-di- (compound 3), and 2,3,4,5-tetraferrocenopyrroles (compound 5) were investigated by DFT calculations. DFT predicts that the first electron in 5 should be removed from one of ferrocene groups located at a  $\beta$ -pyrrolic position, although the structure of  $[5]^+$  with spin density localized at one of ferrocene groups at the  $\alpha$ -pyrrolic position is only 6.5 kcal/mol higher in energy.

## EXPERIMENTAL SECTION

**Materials.** *Caution!* All organomercurials are highly toxic. Extreme care is necessary when handling all products and their solutions. All commercial reagents were ACS grade and were used without further purification. Silica gel (60 Å, 63–100  $\mu$ m) and aluminum oxide (activity I, 50–200  $\mu$ m) for column chromatography were purchased from Dynamic Adsorbents, Inc. All reactions were performed under a dry argon atmosphere with flame-dried glassware. Dry toluene and ether were obtained by distillation over sodium, dry DCM was obtained by distillation over sodium, dry DCM was obtained by distillation over Na/K alloy with diphenyl ketone. Tetrabutylammonium tetrakis(pentafluorophenyl)borate ((NBu<sub>4</sub>)[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]) was prepared according to the literature procedure.<sup>36</sup>

**Instrumentation.** A Varian Unity INOVA NMR instrument was used to evaluate spectra taken at 500 MHz frequency for protons and 125 MHz for carbon atoms. Each were referenced to TMS as an internal standard, and chemical shifts were recorded in parts per million. All UV–vis data were obtained on a JASCO-720 spectrophotometer at room temperature. Electrochemical measurements were conducted using a CHI-620C electrochemical analyzer utilizing the three-electrode scheme. Either carbon or platinum working, auxiliary, and reference electrodes were used in a 0.05 M solution of TBAF (or 0.1 M TBAP) in DCM with redox potentials corrected using an internal standard (decamethylferrocene) in all cases. Spectroelectrochemical data were collected using a custom-made 1 mm cell, a working electrode made of platinum mesh, and a 0.30 M solution of TBAP (or 0.15 M TBAF) in DCM. Elemental analysis was performed by Atlantic Microlab, Inc. in Atlanta, GA.

**Synthesis.** Preparation of N-(Triisopropylsilyl)pyrrole. The synthesis of the N-(triisopropylsilyl)pyrrole was performed by a modified method reported by Muchowski.<sup>37</sup> Pyrrole (6.04g, 84.4 mmol) was added dropwise to a solution of potassium-bis-trimethylsilylamide (16.72 g, 83.8 mmol) in anhydrous THF under an argon atmosphere. The reaction mixture was stirred for 18 h. Solvent was evaporated under vacuum, triisopropylsilyl chloride (16.49g, 85.5 mmol) was added dropwise to dry potassium pyrrole salt (83.8 mmol) in anhydrous THF, and the mixture was stirred for 1 h. The solvent was evaporated under vacuum; ether was added to the reaction mixture, which was washed with water. The ether layer was dried over sodium

sulfate, and pure *N*-triisopropylpyrrole (12.73 g, 68% yield) was obtained as a clear oil after vacuum distillation. <sup>1</sup>H NMR of this compound is in agreement with the reported data<sup>37</sup> ( $\delta$ , 500 MHz, CDCl<sub>3</sub>, TMS): 1.09 (d, 18 H, *J* = 7.4 Hz, CH<sub>3</sub>), 1.45 (m, 3 H, *J* = 7.4 Hz, CH), 6.32 (t, 2 H,  $\alpha$ -pyrrolic), 6.80 (t, 2 H,  $\beta$ -pyrrolic).

3,4-Diiodo-1-(triisopropylsilyl)pyrrole, **1**. This compound was prepared following a slightly modified published procedure.<sup>37</sup> Iodine (0.95 g, 4 mmol) in 200 mL of DCM was added dropwise to a mixture of mercuric acetate (1.28 g, 4 mmol) and *N*-(triisopropylsilyl)pyrrole (0.51 g, 2 mmol) in DCM at 0 °C over a period of 1 h. The reaction mixture was stirred for 3.5 h at 0 °C, and the solvent removed under vacuum. The product was washed with hexane, and the solvent was evaporated under reduced pressure to obtain the crude product as an oil (0.494 g, 51% yield). The NMR spectra were identical to those reported by Muchowski,<sup>37</sup> and additional purification has not been applied. <sup>1</sup>H NMR ( $\delta$ , 500 MHz, CDCl<sub>3</sub>, TMS): 1.08 (d, 18H, *J* = 7.49 Hz, CH<sub>3</sub>), 1.41 (sept, 3H, *J* = 7.49 Hz, CH(*i*-Pr)), 6.79 (s, 2H,  $\alpha$ -pyrrolic).

Bis-3,4-ferrocenyl-1-(triisopropylsilyl)pyrrole, 2. To a solution of 2.79 g (15 mmol) of ferrocene and 0.17 g (1.5 mmol) of KOt-Bu in 50 mL of THF was added dropwise 13.8 mL (23.5 mmol) of a 1.6 M solution of tert-butyllithium in n-pentane at -42 °C (dry ice/ acetonitrile) to the reaction mixture. After stirring for 1 h, 6.76 g (24.1 mmol) of ZnCl<sub>2</sub>(THF)<sub>2</sub> was added as a single portion, and the reaction mixture was left to stir for 1 h at -42 °C and an additional 1 h at room temperature. After this period of time, 0.104 g (0.09 mmol) of [Pd(PPh<sub>3</sub>)<sub>4</sub>] along with 2.39 g (5 mmol) of 1,2-diiodo-N-(triisopropylsilyl)pyrrole (1) were added to the reaction mixture. The reaction mixture was refluxed for 72 h. After evaporation of the solvent to dryness, the product was extracted with 500 mL of DCM. The organic layer was washed with water  $(3 \times 150 \text{ mL})$  and dried over MgSO<sub>4</sub>. The solvent was removed under reduced pressure, and the crude product was purified by column chromatography (Al<sub>2</sub>O<sub>3</sub>) using a hexane/toluene (9:1, v/v) mixture as eluent. Additional purification of the product was achieved by fractional crystallization from hexanes, giving 1.54 g (52%) of orange crystals of 2, mp 120-121 °C. Anal. Calcd for  $C_{33}H_{41}Fe_2NSi \cdot 0.4C_6H_{14}$  (traces of hexanes were observed in the <sup>1</sup>H NMR spectrum of 2): C, 67.93; H, 7.50; N, 2.24. Found: C, 67.85; H, 7.51; N, 2.16. <sup>1</sup>H NMR (δ, 500 MHz, CDCl<sub>3</sub>, TMS): 6.81 (s, 2H,  $\alpha$ -pyrrolic), 4.33 (s, 4H,  $\alpha$ -Cp), 4.14 (s, 4H,  $\beta$ -Cp), 4.03 (s, 10H, Cp), 1.52 (sept, 3H, CH, <sup>i</sup>Pr), 1.19 (d, 18H, CH<sub>3</sub>). <sup>13</sup>C NMR,  $\delta$ : 123.5 (α-pyrrole), 122.1 (β-pyrrole), 77.37 (Cipso-Cp), 69.4 (α-Cp), 69.1 (β-Cp), 67.3 (CpH), 18.1 (CH), 12.0 (CH<sub>3</sub>).

*Bis-3,4-ferrocenylpyrrole,* **3**. A solution of tetra-*n*-butylammonium fluoride (0.85 mL of a 1 M solution, 0.85 mmol) in THF was added to a stirred solutions of *N*-(triisopropylsilyl)-3,4-differocenylpyrrole (0.50 g, 0.85 mmol) in THF (3 mL). After 10 min at room temperature, the solution was diluted with ether, and the organic phase was washed with water and dried over MgSO<sub>4</sub>. Then, the organic phase was purified by flash chromatography on neutral alumina with a mixture of DCM-triethylamine (100:1, v/v) as eluent. The first yellow fraction (*R*<sub>f</sub> 0.85) afforded compound **3**, which was recrystallized from DCM-ether. Yield: 0.15 g (41.0%). Mp: 142–143 °C (dec). Anal. Found: C, 65.87; H, 5.37; N, 2.76. Calcd for C<sub>24</sub>H<sub>21</sub>Fe<sub>2</sub>N·0.5C<sub>4</sub>H<sub>10</sub>O: C, 66.14; H, 5.55; N, 2.97. <sup>1</sup>H NMR (ppm, CDCl<sub>3</sub>, TMS, δ): 4.09 (s, 20H, CpH), 4.17 (m, 4H, β-Cp), 4.31 (m, 4H, α-Cp), 6.94 (s, 2H, α-pyrrolic), 8.08 (br, H, NH). <sup>13</sup>C NMR (CDCl<sub>3</sub>, TMS, δ): 120.3 (β-pyrrole), 117.6 (α-pyrrole), 82.17 (C<sub>ipso</sub>Cp), 69.05 (α-Cp), 69.04 (CpH), 67.12. (β-Cp).

**DFT Calculations.** The initial geometry of complex **2** was taken from the X-ray analysis and optimized at the DFT level of theory, using hybrid PBE1PBE<sup>38</sup> or B3LYP<sup>39</sup> exchange–correlation functionals or pure GGA BP86.<sup>40</sup> It was found that the hybrid B3LYP exchange–correlation functional provides the best agreement between theory and experiment for structures of complexes **2** and **3** when tested against pure GGA BP86 and hybrid PBE1PBE exchange–correlation functionals. TDDFT calculations for vertical excitation energies in complexes **2** and **3** were performed using a hybrid B3LYP exchange–correlation functional, which in the series of test calculations outperformed pure BP86 and BPW91<sup>41</sup> GGAs as well

as the hybrid PBE1PBE functional. The first 30 states were calculated for all TDDFT runs. In all calculations, Wachter's full-electron basis set<sup>42</sup> was used for Fe, the  $6-311G(d)^{43}$  for C and N, and the  $6-31G^{44}$  basis for H. Equilibrium geometries were confirmed by frequency calculations and specifically by the absence of the image frequencies. All calculations were performed using Gaussian 03 or Gaussian 09 software.<sup>45</sup> Molecular orbital analysis was conducted using the VMOdes 8.1 program.<sup>46</sup>

Geometries of the mixed-valence  $[\mathbf{2}]^+ - [\mathbf{4}]^+$  were investigated using delocalized  $C_2$  symmetries or localized  $C_1$  symmetries. In the later case, initial guesses for DFT calculations were generated using the spin localization fragmentation procedure available in Gaussian 09. To investigate the spin localization/delocalization properties in the mixed-valence  $[\mathbf{5}]^+$  pyrrole, the spin localization fragmentation procedure available in Gaussian 09 was also used. In the case of  $C_2$  symmetries of pyrrole derivative  $[\mathbf{5}]^+$  initial guesses were generated by delocalization of the spin density over the 3,4- or 2,5-positions. In the case of the localized  $C_1$  symmetries of the mixed-valence pyrrole derivative  $[\mathbf{5}]^+$  initial guesses were generated by localization of spin densities at the 2- or 3-position with consequent geometry optimizations.

X-ray Crystallography. Single crystals suitable for X-ray crystallographic analysis of 1 and 2 were obtained by a slow evaporation of a concentrated hexane solution, while crystals of 3Ox were obtained by a slow evaporation of a toluene/hexane (1:1 v/v) mixture. X-ray diffraction data were collected on a Rigaku Rapid II image plate diffractometer using graphite-monochromated Mo K $\alpha$  radiation ( $\lambda$  = 0.71073 Å) at 123 K. Multiscan absorption corrections were applied to the data using the CrystalClear 2.0 program. The structures were solved by direct methods implemented in SIR-92<sup>47</sup> and refined by a full-matrix least-squares method based on  $F^2$  using SHELXL-97 or SHELXL-2013 and SHELXLE software.<sup>48</sup> All non-hydrogen atoms were refined in anisotropic approximation, while hydrogen atoms were refined in a "riding" mode. The analyses of the structures and visualization of the results were done using PLATON software.<sup>49</sup> The crystal structure of 3Ox was found to be affected by a nonmerohedral twinning, where two components of the twin were related by the transformation matrix -1 0 0 1.25 1 0.826 0 0 -1. This matrix was used to generate a new hkl file in HKLF5 form. The final fraction of twin components after the refinement was 0.22. Additional restraints (SAME, DELU) were used for one toluene solvent molecule.

# ASSOCIATED CONTENT

#### **S** Supporting Information

Experimental <sup>1</sup>H and <sup>13</sup>C NMR spectra and crystallographic and DFT data for compounds **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

#### AUTHOR INFORMATION

#### Corresponding Author

\*E-mail: vnemykin@d.umn.edu. Phone: +1 (218) 7266729.

#### Notes

The authors declare no competing financial interest.

#### ACKNOWLEDGMENTS

Generous support by the NSF CHE-1110455 and NSF MRI CHE-0922366 grants, Minnesota Supercomputing Institute, and University of Minnesota Grant-in-Aid to V.N.N. is greatly appreciated. We wish to acknowledge Yuriy Zatsikha for the help with electropolymerization studies.

# REFERENCES

 (1) (a) Heath, J. R.; Ratner, M. A. Phys. Today 2003, 56, 43-49.
 (b) Chen, J.; Lee, T.; Su, J.; Wang, W.; Reed, M. A. Encycl. Nanosci. Nanotechnol. 2004, 5, 633-662. (c) Weiss, J. Coord. Chem. Rev. 2010, 254, 2247-2248. (d) Nano and Molecular Electronics Handbook; Lyshevski, S. E., Ed.; CRC Press: New York, 2007. (e) Bayley, H. Nature (London, U. K.) 2010, 467, 164-165. (f) Giacalone, F.; Martin, N. Adv. Mater. (Weinheim, Ger.) 2010, 22, 4220-4248. (g) Jurow, M.; Schuckman, A. E.; Batteas, J. D.; Drain, C. M. Coord. Chem. Rev. 2010, 254, 2297-2310. (h) Chung, A.; Deen, J.; Lee, J.-S.; Meyyappan, M. Nanotechnology 2010, 21, 412001/1-412001/22. (i) Belosludov, R. V.; Farajian, A. A.; Baba, H.; Mizuseki, H.; Kawazoe, Y. Ipn. J. Appl. Phys., Part 1 2005, 44, 2823-2825. (j) Belosludov, R. V.; Farajian, A. A.; Kikuchi, Y.; Mizuseki, H.; Kawazoe, Y. Comput. Mater. Sci. 2006, 36, 130-134. (k) Lee, S. U.; Belosludov, R. V.; Mizuseki, H.; Kawazoe, Y. J. Phys. Chem. C 2007, 111, 15397-15403. (1) Lee, S. U.; Belosludov, R. V.; Mizuseki, H.; Kawazoe, Y. Small 2008, 4, 962-969. (2) (a) Fabre, B. Acc. Chem. Res. 2010, 43, 1509-1518. (b) Mizuseki, H.; Belosludov, R. V.; Uehara, T.; Lee, S. U.; Kawazoe, Y. J. Korean Phys. Soc. 2008, 52, 1197-1201. (c) Uehara, T.; Belosludov, R. V.; Farajian, A. A.; Mizuseki, H.; Kawazoe, Y. Jpn. J. Appl. Phys., Part 1 2006, 45, 3768-3771. (d) Kaim, W.; Lahiri, G. K. Angew. Chem., Int. Ed. 2007, 46, 1778-1796. (e) Kaim, W.; Sarkar, B. Coord. Chem. Rev. 2007. 251. 584-594. (f) Chisholm. M. H.: Patmore, N. I. Acc. Chem. Res. 2007, 40, 19-27. (g) Arumainayagam, C. R.; Lee, H.-L.; Nelson, R. B.; Haines, D. R.; Gunawardane, R. P. Surf. Sci. Rep. 2010, 65, 1-44. (3) (a) Astruc, D.; Ornelas, C.; Ruiz Aranzaes, J. J. Inorg. Organomet. Polym. Mater. 2008, 18, 4-17. (b) Santi, S.; Orian, L.; Donoli, A.; Bisello, A.; Scapinello, M.; Benetollo, F.; Ganis, P.; Ceccon, A. Angew. Chem., Int. Ed. 2008, 47, 5331-5334. (c) Cowan, D. O.; LeVanda, C.; Park, J.; Kaufman, F. Acc. Chem. Res. 1973, 6, 1-7.

(4) (a) Kaifer, A. E. Eur. J. Inorg. Chem. 2007, 5015-5027.
(b) Wagner, M. Angew. Chem., Int. Ed. 2006, 45, 5916-5918.
(c) Barlow, S.; O'Hare, D. Chem. Rev. 1997, 97, 637-670. (d) Miller, J. S.; Epstein, A. J. Angew. Chem., Int. Ed. Engl. 1994, 33, 385-415.
(e) Epstein, A. J.; Miller, J. S. Synth. Met. 1996, 80, 231-237.
(f) Barlow, S. Inorg. Chem. 2001, 40, 7047-7053. (g) Giuffrida, G.; Campagna, S. Coord. Chem. Rev. 1994, 135-136, 517-531. (h) Ernst, S.; Kasack, V.; Kaim, W. Inorg. Chem. 1988, 27, 1146-1148.

(5) (a) Ferrocenes: Ligands, Materials and Biomolecules; Stepnicka, P., Ed.; John Wiley & Sons, Ltd.: Chichester, England, 2008. (b) Vlcek, A., Jr. Chemtracts 2001, 14, 1–6. (c) Kowalski, K.; Linseis, M.; Winter, R. F.; Zabel, M.; Zalis, S.; Kelm, H.; Kruger, H.-J.; Sarkar, B.; Kaim, W. Organometallics 2009, 28, 4196–4209. (d) Nakaya, T.; Namiki, K.; Murata, M.; Kanaizuka, K.; Kurashina, M.; Fujita, T.; Nishihara, H. J. Inorg. Organomet. Polym. Mater 2008, 18, 124–130. (e) Nakashima, S. Recent Res. Dev. Pure Appl. Chem 1998, 2, 247–273.

(6) (a) Ding, F.; Wang, H.; Wu, Q.; Van Voorhis, T.; Chen, S.; Konopelski, J. P. J. Phys. Chem. A 2010, 114, 6039-6046. (b) Hadt, R. G.; Nemykin, V. N. Inorg. Chem. 2009, 48, 3982-3992. (c) Santi, S.; Durante, C.; Donoli, A.; Bisello, A.; Orian, L.; Ceccon, A.; Crociani, L.; Benetollo, F. Organometallics 2009, 28, 3319-3326. (d) Masuda, Y.; Shimizu, C. J. Phys. Chem. A 2006, 110, 7019-7027. (e) Mochida, T.; Takazawa, K.; Matsui, H.; Takahashi, M.; Takeda, M.; Sato, M.; Nishio, Y.; Kajita, K.; Mori, H. Inorg. Chem. 2005, 44, 8628-8641. (f) Oda, T.; Nakashima, S.; Okuda, T. Bull. Chem. Soc. Jpn. 2003, 76, 2129-2134. (g) Dong, T.-Y.; Chang, L.-S.; Lee, G.-H.; Peng, S.-M. Organometallics 2002, 21, 4192-4200. (h) Nakashima, S.; Isobe, H.; Okuda, T.; Kai, M. Inorg. Chim. Acta 2000, 306, 215-221. (i) Dong, T.-Y.; Ho, P.-H.; Lai, X.-Q.; Lin, Z.-W.; Lin, K.-J. Organometallics 2000, 19, 1096-1106. (j) Cowan, D. O.; Kaufman, F. J. Am. Chem. Soc. 1970, 92, 219-220. (k) Cowan, D. O.; Levanda, C. J. Am. Chem. Soc. 1972, 94, 9271-9272. (1) Iijima, S.; Saida, R.; Motoyama, I.; Sano, H. Bull. Chem. Soc. Jpn. 1981, 54, 1375-1379. (m) Boehm, M. C.; Gleiter, R.; Delgado-Pena, F.; Cowan, D. O. J. Chem. Phys. 1983, 79, 1154-1165. (n) Dong, T. Y.; Hendrickson, D. N.; Iwai, K.; Cohn, M. J.; Geib, S. J.; Rheingold, A. L.; Sano, H.; Motoyama, I.; Nakashima, S. J. Am. Chem. Soc. 1985, 107, 7996-8008.

(7) (a) Kramer, J. A.; Herbstein, F. H.; Hendrickson, D. N. J. Am. Chem. Soc. 1980, 102, 2293–2301. (b) Jones, S. C.; Barlow, S.; O'Hare, D. Chem.—Eur. J. 2005, 11, 4473–4481. (c) Rulkens, R.; Lough, A. J.; Manners, I.; Lovelace, S. R.; Grant, C.; Geiger, W. E. J. Am. Chem. Soc. 1996, 118, 12683–12695. (d) Yuan, Y.-F.; Zhang, L.-Y.; Hu, A.-G.; Wang, J.-T.; Liu, W.-Y.; Ding, T.-Z. Polyhedron 1999, 18, 1247–1251. (e) Kaufmann, L.; Breunig, J.-M.; Vitze, H.; Schoedel, F.; Nowik, I.; Pichlmaier, M.; Bolte, M.; Lerner, H.-W.; Winter, R. F.; Herber, R. H.; Wagner, M. Dalton Trans. 2009, 2940–2950.

(8) (a) Siemeling, U.; Jutzi, P.; Bill, E.; Trautwein, A. X. J. Organomet. Chem. **1993**, 463, 151–154. (b) Venkatasubbaiah, K.; Doshi, A.; Nowik, I.; Herber, R. H.; Rheingold, A. L.; Jakle, F. Chem.—Eur. J. **2008**, 14, 444–458. (c) Venkatasubbaiah, K.; Nowik, I.; Herber, R. H.; Jaekle, F. Chem. Commun. **2007**, 2154–2156. (d) Venkatasubbaiah, K.; Pakkirisamy, T.; Lalancette, R. A.; Jakle, F. Dalton Trans. **2008**, 4507– 4513. (e) McAdam, C. J.; Robinson, B. H.; Simpson, J.; Tagg, T. Organometallics **2010**, 29, 2474–2483.

(9) (a) Chen, Y. J.; Pan, D.-S.; Chiu, C.-F.; Su, J.-X.; Lin, S. J.; Kwan, K. S. *Inorg. Chem.* 2000, 39, 953–958. (b) Patoux, C.; Coudret, C.; Launay, J.-P.; Joachim, C.; Gourdon, A. *Inorg. Chem.* 1997, 36, 5037–5049. (c) Ribou, A.-C.; Launay, J.-P.; Sachtleben, M. L.; Li, H.; Spangler, C. W. *Inorg. Chem.* 1996, 35, 3735–3740. (d) Dong, T. Y.; Ke, T. J.; Peng, S. M.; Yeh, S. K. *Inorg. Chem.* 1989, 28, 2103–2106. (e) Fry, A. J.; Jain, P. S.; Krieger, R. L. J. Organomet. Chem. 1981, 214, 381–390.

(10) (a) Oton, F.; Ratera, I.; Espinosa, A.; Tarraga, A.; Veciana, J.; Molina, P. *Inorg. Chem.* **2010**, *49*, 3183–3191. (b) Kurosawa, M.; Nankawa, T.; Matsuda, T.; Kubo, K.; Kurihara, M.; Nishihara, H. *Inorg. Chem.* **1999**, *38*, 5113–5123.

(11) (a) Levanda, C.; Bechgaard, K.; Cowan, D. O. J. Org. Chem.
1976, 41, 2700-2704. (b) Powers, M. J.; Meyer, T. J. J. Am. Chem. Soc.
1978, 100, 4393-4398. (c) Plenio, H.; Hermann, J.; Sehring, A. Chem.—Eur. J. 2000, 6, 1820-1829. (d) Blackbourn, R. L.; Hupp, J. T. Chem. Phys. Lett. 1988, 150, 399-405. (e) Cohn, M. J.; Timken, M. D.; Hendrickson, D. N. J. Am. Chem. Soc. 1984, 106, 6683-6689.

(12) (a) Kadish, K. M.; Xu, Q. Y.; Barbe, J. M. Inorg. Chem. **1987**, 26, 2565–2566. (b) Xu, Q. Y.; Barbe, J. M.; Kadish, K. M. Inorg. Chem. **1988**, 27, 2373–2378. (c) Maiya, G. B.; Barbe, J. M.; Kadish, K. M. Inorg. Chem. **1989**, 28, 2524–2527. (d) Solntsev, P. V.; Sabin, J. R.; Dammer, S. J.; Gerasimchuk, N. N.; Nemykin, V. N. Chem. Commun. **2010**, 6581–6583.

(13) (a) Figueira-Duarte, T. M.; Lloveras, V.; Vidal-Gancedo, J.; Gegout, A.; Delavaux-Nicot, B.; Welter, R.; Veciana, J.; Rovira, C.; Nierengarten, J.-F. Chem. Commun. 2007, 4345-4347. (b) Santi, S.; Orian, L.; Durante, C.; Bencze, E. Z.; Bisello, A.; Donoli, A.; Ceccon, A.; Benetollo, F.; Crociani, L. Chem.-Eur. J. 2007, 13, 7933-7947. (c) Horikoshi, T.; Kubo, K.; Nishihara, H. J. Chem. Soc., Dalton Trans. 1999, 3355-3360. (d) Mueller-Westerhoff, U. T.; Eilbracht, P. J. Am. Chem. Soc. 1972, 94, 9272-92744. (e) Morrison, W. H., Jr.; Hendrickson, D. N. J. Chem. Phys. 1973, 59, 380-386. (f) Delgado-Pena, F.; Talham, D. R.; Cowan, D. O. J. Organomet. Chem. 1983, 253, C43-C46. (g) Cohn, M. J.; Timken, M. D.; Hendrickson, D. N. J. Am. Chem. Soc. 1984, 106, 6683-6689. (h) Jiao, J.; Long, G. J.; Rebbouh, L.; Grandjean, F.; Beatty, A. M.; Fehlner, T. P. J. Am. Chem. Soc. 2005, 127, 17819–17831. (i) McAdam, C. J.; Brunton, J. J.; Robinson, B. H.; Simpson, J. J. Chem. Soc., Dalton Trans. 1999, 2487-2496. (j) Diallo, A. K.; Absalon, C.; Ruiz, J.; Astruc, D. J. Am. Chem. Soc. 2011, 133, 629-641. (k) Ochi, Y.; Suzuki, M.; Imaoka, T.; Murata, M.; Nishihara, H.; Einaga, Y.; Yamamoto, K. J. Am. Chem. Soc. 2010, 132, 5061-5069. (1) Sakamoto, R.; Murata, M.; Nishihara, H. Angew. Chim., Int. Ed 2006, 45, 4793-4795. (m) Boyd, D. A.; Cao, Z.; Song, Y.; Wang, T.-W.; Fanwick, P. E.; Crutchley, R. J.; Ren, T. Inorg. Chem. 2010, 49, 11525-11531. (n) Xu, G.-L.; Crutchley, R. J.; DeRosa, M. C.; Pan, Q.-J.; Zhang, H.-X.; Wang, X.; Ren, T. J. Am. Chem. Soc. 2005, 127, 13354-13363.

(14) (a) Jin, Z.; Nolan, K.; McArthur, C. R.; Lever, A. B. P.; Leznoff, C. C. J. Organomet. Chem. 1994, 468, 205–212. (b) Poon, K.-W.; Yan, Y.; Li, X. Y.; Ng, D. K. P. Organometallics 1999, 18, 3528–3533.
(c) Nemykin, V. N.; Lukyanets, E. A. ARKIVOC 2010, i, 136–208.
(d) Nemykin, V. N.; Kobayashi, N. Chem. Commun. 2001, 165–166.
(e) Lukyanets, E. A.; Nemykin, V. N. J. Porphyrins Phthalocyanines 2010, 14, 1–40. (f) Gonzalez-Cabello, A.; Claessens, C. G.; Martin-Fuch, G.; Ledoux-Rack, I.; Vazquez, P.; Zyss, J.; Agullo-Lopez, F.; Torres, T. Synth. Met. 2003, 137, 1487–1488. (g) Loim, N. M.; Abramova, N. V.; Sokolov, V. I. Mendeleev Commun. 1996, 46–47.
(h) Burrell, A. K.; Campbell, W. M.; Jameson, G. B.; Officer, D. L.;

Boyd, P. D. W.; Zhao, Z.; Cocks, P. A.; Gordon, K. C. Chem. Commun. 1999, 637-638. (i) Shoji, O.; Okada, S.; Satake, A.; Kobuke, Y. J. Am. Chem. Soc. 2005, 127, 2201-2210. (j) Kubo, M.; Mori, Y.; Otani, M.; Murakami, M.; Ishibashi, Y.; Yasuda, M.; Hosomizu, K.; Miyasaka, H.; Imahori, H.; Nakashima, S. J. Phys. Chem. A 2007, 111, 5136-5143. (k) Nemykin, V. N.; Barrett, C. D.; Hadt, R. G.; Subbotin, R. I.; Maximov, A. Y.; Polshin, E. V.; Koposov, A. Y. Dalton Trans. 2007, 3378-3389. (1) Nemykin, V. N.; Galloni, P.; Floris, B.; Barrett, C. D.; Hadt, R. G.; Subbotin, R. I.; Marrani, A. G.; Zanoni, R.; Loim, N. M. Dalton Trans. 2008, 4233-4246. (m) Nemykin, V. N.; Rohde, G. T.; Barrett, C. D.; Hadt, R. G.; Bizzarri, C.; Galloni, P.; Floris, B.; Nowik, I.; Herber, R. H.; Marrani, A. G.; Zanoni, R.; Loim, N. M. J. Am. Chem. Soc. 2009, 131, 14969-14978. (n) Galloni, P.; Floris, B.; de Cola, L.; Cecchetto, E.; Williams, R. M. J. Phys. Chem. C 2007, 111, 1517-1523. (o) Nemykin, V. N.; Rohde, G. T.; Barrett, C. D.; Hadt, R. G.; Sabin, J. R.; Reina, G.; Galloni, P.; Floris, B. Inorg. Chem. 2010, 49, 7497-7509. (p) Rohde, G. T.; Sabin, J. R.; Barrett, C. D.; Nemykin, V. N. New J. Chem. 2011, 35, 1440-1448. (q) Vecchi, A.; Gatto, E.; Floris, B.; Conte, V.; Venanzi, M.; Nemykin, V. N.; Galloni, P. Chem. Commun. 2012, 48, 5145-5147. (r) Sharma, R.; Gautam, P.; Mobin, S. M.; Misra, R. Dalton Trans. 2013, 42, 5539-5545. (s) Samanta, S.; Mittra, K.; Sengupta, K.; Chatterjee, S.; Dey, A. Inorg. Chem. 2013, 52, 1443-1453. (t) Bakar, M. A.; Sergeeva, N. N.; Juillard, T.; Senge, M. O. Organometallics 2011, 30, 3225-3228. (u) Subbaiyan, N. K.; Wijesinghe, C. A.; D'Souza, F. J. Am. Chem. Soc. 2009, 131, 14646-14647. (v) Burrell, A. K.; Campbell, W.; Officer, D. L. Tetrahedron Lett. 1997, 38, 1249-1252. (w) Wang, H. J.H.; Jaquinod, L.; Olmstead, M. M.; Vicente, M. G. H.; Kadish, K. M.; Ou, Z.; Smith, K. M. Inorg. Chem. 2007, 46, 2898-2913. (x) Vecchi, A.; Galloni, P.; Floris, B.; Nemykin, V. N. J. Porphyrins Phthalocyanines 2013, 17, 165-196.

(15) (a) Hildebrandt, A.; Schaarschmidt, D.; Lang, H. Organometallics 2011, 30, 556-563. (b) Hildebrandt, A.; Schaarschmidt, D.; Claus, R.; Lang, H. Inorg. Chem. 2011, 50, 10623-10632. (c) Hildebrandt, A.; Lang, H. Dalton Trans. 2011, 40, 11831-11837. (d) Speck, J. M.; Claus, R.; Hildebrandt, A.; Rueffer, T.; Erasmus, E.; van As, L.; Swarts, J. C.; Lang, H. Organometallics 2012, 31, 6373-6380. (e) Hildebrandt, A.; Ruffer, T.; Erasmus, E.; Swarts, J. C.; Lang, H. Organometallics 2010, 29, 4900-4905. (f) Miesel, D.; Hildebrandt, A.; Korb, M.; Low, P. J.; Lang, H. Organometallics 2013, 32, 2993-3002. (g) Pfaff, U.; Hildebrandt, A.; Schaarschmidt, D.; Rüffer, T.; Low, P. J.; Lang, H. Organometallics 2013, 32, 6106-6117. (h) Hildebrandt, A.; Lang, H. Organometallics 2013, 32, 5640-5653. (16) (a) Yang, H.-B.; Ghosh, K.; Zhao, Y.; Northrop, B. H.; Lyndon, M. M.; Muddiman, D. C.; White, H. S.; Stang, P. J. J. Am. Chem. Soc. 2008, 130, 839-841. (b) Hildebrandt, A.; Schaarschmidt, D.; van As, L.; Swarts, J. C.; Lang, H. Inorg. Chim. Acta 2011, 374, 112-118. (c) Pfaff, U.; Hildebrandt, A.; Schaarschmidt, D.; Hahn, T.; Liebing, S.; Kortus, J.; Lang, H. Organometallics 2012, 31, 6761-6771. (d) Lin, J. T.; Yang, M.-F.; Tsai, C.; Wen, Y. S. J. Organomet. Chem. 1998, 564, 257-266. (e) Hildebrandt, A.; Wetzold, N.; Ecorchard, P.; Walfort, B.; Rueffer, T.; Lang, H. Eur. J. Inorg. Chem. 2010, 3615-3627. (f) Inkpen, M. S.; Albrecht, T.; Long, N. J. Organometallics 2013, 32, 6053-6060. (17) (a) Chen, Y. J.; Pan, D. S.; Chiu, C. F.; Su, J. X.; Lin, S. J.; Kwan, K. S. Inorg. Chem. 2000, 39, 953-958. (b) Huang, P.; Jin, B.; Liu, P.; Cheng, L.; Cheng, W.; Zhang, S. J. Organomet. Chem. 2012, 697, 57-64. (c) Steffens, S.; Prosenc, M. H.; Heck, J.; Asselberghs, I.; Clays, K. Eur. J. Inorg. Chem. 2008, 1999-2006. (d) Kaleta, K.; Strehler, F.; Hildebrandt, A.; Beweries, T.; Arndt, P.; Rueffer, T.; Spannenberg, A.; Lang, H.; Rosenthal, U. Chem.-Eur. J. 2012, 18, 12672-12680. (e) Breuer, R.; Schmittel, M. Organometallics 2013, 32, 5980-5987. (18) Anderson, H. J.; Loader, C. E. Synthesis 1985, 353-364.

(18) Anderson, H. J.; Loader, C. E. Synthesis 1985, 353–364.

(19) Loader, C. E.; Anderson, H. J. Can. J. Chem. 1981, 59, 2673–2676.

(20) Carmona, O.; Greenhouse, R.; Landeros, R.; Muchowski, J. M. J. Org. Chem. **1980**, 45, 5336–5339.

(21) Anderson, H. J.; Loader, C. E.; Xu, R.; Le, N.; Gogan, N. J.; McDonald, R.; Edwards, L. G. *Can. J. Chem.* **1985**, *63*, 896–902. (22) (a) Rokach, J.; Hamel, P.; Kakushima, M.; Smith, G. M. *Tetrahedron Lett.* **1981**, 22, 4901–4904. (b) Kakushima, M.; Hamel, P.; Frenette, R.; Rokach, J. *J. Org. Chem.* **1983**, 48, 3214–3219.

(23) Bray, B. L.; Mathies, P. H.; Naef, R.; Solas, D. R.; Tidwell, T. T.; Artis, D. R.; Muchowski, J. M. J. Org. Chem. **1990**, 55, 6317–6328.

(24) Corey, E. J.; Snider, B. B. J. Am. Chem. Soc. **1972**, *94*, 6190–6192.

(25) Beletskaya, I. P.; Tsvetkov, A. V.; Latyshev, G. V.; Tafeenko, V. A; Lukashev, N. V. J. Organomet. Chem. 2001, 637–639, 653–663.

(26) (a) Solntsev, P. V.; Dudkin, S. V.; Sabin, J. R.; Nemykin, V. N. *Organometallics* **2011**, *30*, 3037–3046. (b) Solntsev, P. V.; Goetsch, W. R.; Nemykin, V. N. *Organometallics* **2011**, *30*, 6636–6640. (c) Hildebrandt, A.; Lehrich, S. W.; Schaarschmidt, D.; Jaeschke, R.; Schreiter, K.; Spange, S.; Lang, H. Eur. J. Inorg. Chem. **2012**, 1114–1121.

(27) (a) Klimova, E. I.; Klimova, T.; Backinowsky, L. V.; Flores-Alamo, M.; Ortiz-Frade, L. A.; Garcia, M. M. *Mendeleev Commun.* **2010**, *20*, 312–313. (b) Klimova, E. I.; Beretsneva, T. K.; Toscano, R. A.; Stivalet, J. M. M.; Garcia, M. M. Synth. Commun. **2007**, *37*, 889– 900.

(28) (a) D'Alessandro, D. M.; Keene, F. R. *Chem. Rev.* **2006**, *106*, 2270–2298. (b) D'Alessandro, D. M.; Keene, F. R. *Dalton Trans.* **2004**, 3950–3954.

(29) (a) Sabouraud, G.; Sadki, S.; Brodie, N. Chem. Soc. Rev. 2000, 29, 283–293. (b) Clark, J. C.; Fabre, B.; Fronczek, F. R.; Vicente, M. G. H. J. Porphyrins Phthalocyanines 2005, 9, 803–810. (c) Graczyk-Zajac, M.; Vassiliev, S. Yu.; Vorotyntsev, M. A.; Tsirlina, G. A. J. Solid State Electrochem. 2010, 14, 2039–2048. (d) Martinez, F. J.; Gonzalez, B.; Alonso, B.; Losada, J.; Garcia-Armada, M. P.; Casado, C. M. J. Inorg. Organomet. Polym. Mater. 2008, 18, 51–58. (e) Ouerghi, O.; Senillou, A.; Jaffrezic-Renault, N.; Martelet, C.; Ben Ouada, H.; Cosnier, S. J. Electroanal. Chem. 2001, 501, 62–69.

(30) (a) Hush, N. S. Prog. Inorg. Chem. **1967**, *8*, 391–444. (b) Creutz, C. Prog. Inorg. Chem. **1983**, 30, 1–73. (c) Hush, N. S. Coord. Chem. Rev. **1985**, 64, 135–157.

(31) Robin, M. B.; Day, P. Adv. Radiochem. 1967, 10, 247-422.

(32) (a) Domingo, L. R.; Pérez, P.; Contreras, R. J. Org. Chem. 2003, 68, 6060-6062. (b) Leffler, J. E.; Grunwald, E.Rates and Equilibria of Organic Reactions; Wiley: New York, 1963.

(33) (a) Green, A. G.; Kiesz, M. D.; Oria, J. V.; Elliott, A. G.; Buechler, A. K.; Hohenberger, J.; Meyer, K.; Zink, J. I.; Diaconescu, P. L. Inorg. Chem. 2013, 52, 5603-5610. (b) Plazuk, D.; Zakrzewski, J.; Nakatani, K.; Makal, A.; Wozniak, K.; Domagala, S. RSC Adv. 2012, 2, 3512-3524. (c) Huesmann, H.; Foerster, C.; Siebler, D.; Gasi, T.; Heinze, K. Organometallics 2012, 31, 413-427. (d) Li, Y. L.; Han, L.; Mei, Y.; Zhang, J. Z. H. Chem. Phys. Lett. 2009, 482, 217-222. (e) Fabrizi de Biani, F.; Manca, G.; Marchetti, L.; Leoni, P.; Bruzzone, S.; Guidotti, C.; Atrei, A.; Albinati, A.; Rizzato, S. Inorg. Chem. 2009, 48, 10126-10137. (f) Solntsev, P. V.; Spurgin, K. L.; Sabin, J. R.; Heikal, A. A.; Nemykin, V. N. Inorg. Chem. 2012, 51, 6537-6547. (g) Nemykin, V. N.; Hadt, R. G. J. Phys. Chem. A 2010, 114, 12062-12066. (h) Nemykin, V. N.; Makarova, E. A.; Grosland, J. O.; Hadt, R. G.; Koposov, A. Y. Inorg. Chem. 2007, 46, 9591-9601. (i) Nemykin, V. N.; Maximov, A. Y.; Koposov, A. Y. Organometallics 2007, 26, 3138-3148.

(34) (a) Mohammadi, N.; Ganesan, A.; Chantler, C. T.; Wang, F. J. Organomet. Chem. 2012, 713, 51–59. (b) Zaater, S.; Brahimi, M.; Rahmouni, A. Polyhedron 2012, 31, 29–36. (c) Zapata, F.; Caballero, A.; Espinosa, A.; Tarraga, A.; Molina, P. J. Org. Chem. 2008, 73, 4034– 4044. (d) Zapata, F.; Caballero, A.; Espinosa, A.; Tarraga, A.; Molina, P. Org. Lett. 2008, 10, 41–44. (e) D'Souza, F.; Chitta, R.; Gadde, S.; Islam, D.-M. S.; Schumacher, A. L.; Zandler, M. E.; Araki, Y.; Ito, O. J. Phys. Chem. B 2006, 110, 25240–25250. (f) Vrcek, V.; Buehl, M. Organometallics 2006, 25, 358–367. (g) Siebler, D.; Foerster, C.; Heinze, K. Dalton Trans. 2011, 40, 3558–3575. (h) Hadt, R. G.; Nemykin, V. N. Inorg. Chem. 2009, 48, 3982–3992. (i) Herber, R. H.; Nowik, I.; Grosland, J. O.; Hadt, R. G.; Nemykin, V. N. J. Organomet. Chem. 2008, 693, 1850–1856. (j) Dammer, S. J.; Solntsev, P. V.; Sabin, J. R.; Nemykin, V. N. Inorg. Chem. 2013, 52, 9496–9510. (35) (a) Salzner, U. J. Chem. Theory Comput. 2013, 9, 4064–4073.
(b) Rinkevicius, Z.; Telyatnyk, L.; Salek, P.; Vahtras, O.; Agren, H. J. Chem. Phys. 2003, 119, 10489–10496. (c) Stampfl, C.; Mannstadt, W.; Asahi, R.; Freeman, A. J. Phys. Rev. B 2001, 63, 155106/1–155106/11.
(d) Barone, V.; Bencini, A.; Ciofini, I.; Daul, C. A.; Totti, F. J. Am. Chem. Soc. 1998, 120, 8357–8365. (e) Chou, J. P.; Chen, H. Y. T.; Hsing, C. R.; Chang, C. M.; Cheng, C.; Wei, C. M. Phys. Rev. B 2009, 80, 165412/1–165412/10. (f) Fromager, E.; Knecht, S.; Jensen, H. J. A. J. Chem. Phys. 2013, 138, 084101/1–084101/14. (g) Namazian, M.; Lin, C. Y.; Coote, M. L. J. Chem. Theory Comput. 2010, 6, 2721–2725.
(h) Martin, J.; Baker, J.; Pulay, P. J. Comput. Chem. 2009, 30, 881–883.
(i) Nemykin, V. N.; Hadt, R. G. Inorg. Chem. 2006, 45, 8297–8307.
(j) Nemykin, V. N.; Hadt, R. G.; Belosludov, R. V.; Mizuseki, H.; Kawazoe, Y. J. Phys. Chem. A 2007, 111, 12901–12913. (k) Hadt, R. G.; Nemykin, V. N.; Olsen, J. G.; Basu, P. Phys. Chem. Chem. Phys.

**2009**, *11*, 10377–10384. (36) Barriere, F.; Geiger, W. E. J. Am. Chem. Soc. **2006**, *128*, 3980–3989.

(37) Desales, J.; Greenhouse, R.; Muchowski, J. M. J. Org. Chem. 1982, 47, 3668-3672.

(38) Adamo, C.; Barone, V. J. Chem. Phys. 1999, 110, 6158-6169.
(39) (a) Becke, A. D. J. Chem. Phys. 1993, 98, 5648-5652. (b) Lee, C.; Yang, W.; Parr, R. G. Phys. Rev. B 1988, 37, 785-789.

(40) (a) Becke, A. D. Phys. Rev. A **1988**, 38, 3098-3100. (b) Perdew, J. P. Phys. Rev. B **1986**, 33, 8822-8824.

(41) Perdew, J. P.; Wang, Y. Phys. Rev. B 1992, 45, 13244-13249.

(42) Wachters, A. J. H. J. Chem. Phys. 1970, 52, 1033.

(43) (a) McLean, A. D.; Chandler, G. S. J. Chem. Phys. 1980, 72, 5639–5648. (b) Hay, P. J.; Wadt, W. R. J. Chem. Phys. 1985, 82, 299–310.

(44) Hehre, W. J.; Ditchfield, R.; Pople, J. A. J. Chem. Phys. 1972, 56, 2257-2261.

(45) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; et al. *Gaussian 09*, Revision A.01; Gaussian, Inc.: Wallingford, CT, 2009. For full citation, please see Supporting Information.

(46) Nemykin,V. N.; Basu, P. VMOdes Program, Revision A 7.2; University of Minnesota Duluth and Duquesne University, 2001; 2003; 2005.

(47) Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Burla, M. C.; Polidori, G.; Camalli, M. J. *Appl. Crystallogr.* **1994**, *27*, 435.

(48) Sheldrick, G. M. Acta Crystallogr. 2008, A64, 112.

(49) Burnett, M. N.; Johnson, C. K. ORTEP-III: Oak Ridge Thermal Ellipsoid Plot Program for Crystal Structure Illustrations; Oak Ridge National Laboratory Report ORNL-6895; 1996.