ORGANOMETALLICS Cite This: Organometallics XXXX, XXX, XXX-XXX

N-Cobaltocenium Amide as Reactive Nucleophilic Reagent for Donor-Acceptor Bimetallocenes

Maximilian Lauck, Christoph Förster, and Katja Heinze*

Institute of Inorganic Chemistry and Analytical Chemistry, Johannes Gutenberg University of Mainz, Duesbergweg 10-14, D-55128 Mainz, Germany

Supporting Information

ABSTRACT: Deprotonation of the aminocobaltocenium ion $[Cc-NH_2]^+$ ($[H-1]^+$) generates the nucleophilic imine CcNH (1). Reaction of 1 with acid chlorides R–COCl (R = Ph, Fc, and Cc⁺) yields the reference amide [Ph-CO-NH-Cc]⁺ (2⁺) and the amide-linked hetero- and homobimetallocenes [Fc-CO-NH-Cc]⁺ (3⁺) and [Cc-CO-NH-Cc]²⁺ (4²⁺), respectively. Cation–anion interactions of charged amides 2^+-4^{2+} in the solid state and in solution are probed by single crystal X-ray diffraction and NMR and IR spectroscopy. Intramolecular metal–metal interactions in donor–acceptor heterobimetallocene 3^+ and in mixed-valent homobimetallocene 4^+ (prepared electrochemically) are discussed within the Marcus–Hush framework aided by spectroelectrochemical experiments and time-dependent density functional theory calculations.



INTRODUCTION

The ferrocene/ferrocenium couple (Fc/Fc^+) occupies an outstanding position in the metallocene series.¹ This central role in organometallic chemistry is based on its reversible redox behavior and its highly versatile substitution chemistry allowing for strongly electron-withdrawing and -donating substituents. The accessible potential range for the Fc/Fc⁺ redox process spans approximately 1.7 V based on substituent effects.² Furthermore, ferrocene can be conjugated to nearly every conceivable building block, including biomolecules, dyes or electrode surfaces for sensing applications.^{1,3–5} Typically, Fc is introduced in the neutral form, thus acting as an electron-donating unit in photoinduced electron transfer (PET) systems^{4,5} and in charge transfer (CT) complexes.^{6,7}

Electron-poor metallocenes such as $Cp_2Ti(CCR)_2^8$ or $[Cp_2Co]^+$ $(Cc^+)^{6,9}$ were successfully incorporated as electron acceptors in CT systems. Compared to the ubiquitous Fc/Fc⁺ couple, the Cc/Cc⁺ couple has been less often employed in CT and PET schemes.^{6,9,10} This underdeveloped attention is certainly due to the more difficult and less established substitution chemistry of Cc^{+,11} Only in the last years have the groups of Bildstein and Heck put forward reliable routes toward important Cc⁺ key building blocks, such as [Cc-Br]⁺, [Cc-NO₂]⁺, [Cc-NJ₃]⁺, [Cc-COOH]⁺, or [Cc-NH₂]^{+, 12,13}

As our group and others have a strong interest in the development of redox-active oligoferrocene amide foldamers,¹⁴ ferrocene-based redox switches involving classical NH…X and nonclassical NH…Fe hydrogen bonds,¹⁵ ferrocene amide ion sensors,¹⁶ amide-linked ferrocene-chromophore conjugates,^{4i,j,5b,6} and redox-appended enzyme models,¹⁷ we became

strongly interested in the employment of charged cobaltocenium Cc⁺ building blocks in analogous isosteric systems. The positive charges in the parent systems and the expanded redox potential range toward more negative values are attractive assets in these applications.^{2a,12,13b} The now good availability of [Cc-COOH]^{+13a} already allowed us to devise a porphyrincobaltocenium dyad [P-NHCO-Cc⁺]. This chromophore– acceptor system displays photoinduced charge separation after irradiation into the chromophore bands delivering a chargeshifted state with porphyrin radical cation–cobaltocene character [P⁺-NHCO-Cc].¹⁰

In contrast to Fc-NH₂ derivatives,^{4i,j,Sb,7,14,15d,e,18} N-substituted Cc⁺ complexes which would constitute more electronrich Cc⁺ building blocks are rare. In fact, only few reactions toward N-substituted Cc⁺ units are known so far. Starting from N-substituted lithium or sodium cyclopentadienides and CoCl₂ only 1,1'-disubstituted cobaltocenium ions are accessible after oxidation.^{11a,b,e} A unique isonitrile insertion into a cyclopentadienyl pentadienyl cobalt(III) complex gives the amino substituted sterically demanding $[CpCo(\eta^5-C_5Me_4NH^tBu)]^+$ complex.^{11f} Nucleophilic substitution of the nitro group of $[Cc-NO_2]^+$ by *n*-butyl amine gives $[Cc-NH^nBu]^+$.^{12b} Heck reported the formation of the Boc-protected [Cp*Co(η^{5} - $C_5H_4NHC(O)O^tBu)$ ⁺ ion with one Cp* ligand starting from $[Cp*Co(\eta^5-C_5H_4COCl)]^+$ and sodium azide, followed by a Curtius reaction in ^tBuOH.^{12a} Versatile key building block $[CcNH_2]^+$ is obtained from $[Cc-COCl]^+$ and NaN_3 in an

Received: October 26, 2017

optimized procedure reported by Bildstein.^{13b} Thanks to the good availability of $[Cc-NH_2]^+$ we are now in the position to construct bimetallocene amides with $[Cc-NHCO-R]^+$ units.

Here we report a strategy to activate $[Cc-NH_2]^+$ toward acylation. After activation of $[Cc-NH_2]^+$, acid chlorides R-COCl were employed as acylating agents with R = Ph, Fc, and Cc⁺. This gives access to Cc-[NHCO-R]⁺ amides with the charged cobaltocenium ion connected to the *N*-side of the amide unit. The metal–metal interaction in the two novel homo- and heterometallic bimetallocenes $[Cc-CONH-Cc]^{2+/+}$ and $[Fc-CONH-Cc]^+$ via the amide unit is probed by optical spectroscopy and UV/vis/NIR spectroelectrochemistry (Scheme 1). The CT properties of the novel heterobimetallo-

Scheme 1. Reported and Unknown Amide Bridged Bimetallocenes with Fc and Cc⁺ Building Blocks.^{6,14d,e,i}



cene [Fc-CONH-Cc]⁺ are compared to those of its [Cc-CONH-Fc]⁺ isomer which shows strongly solvatochromic CT bands (Scheme 1).⁶ The electronic interaction in novel d^{6} -/ d^{7} -mixed-valent cation [Cc-CONH-Cc]⁺ are contrasted to those of the d^{5} -/ d^{6} -mixed-valent cation [Fc-CONH-Fc]⁺.^{14d,e}

RESULTS AND DISCUSSION

The major challenge toward the introduction of $[Cc-NH]^+$ units into amides is the very low basicity and nucleophilicity of the $[Cc-NH_2]^+$ cation with a pK_b value of 15.6.^{11c} In fact, all conventional amide coupling formation reactions with $[Cc-NH_2]^+$ and strong electrophiles or potent coupling reagents failed in our hands. Reduction of positively charged poor nucleophile $[CcNH_2]^+$ to corresponding neutral amino cobaltocene Cc-NH₂ by KC₈ and subsequent acylation by R– COCl was unsuccessful as well due to competing decomposition side reactions. Deprotonation of $[Cc-NH_2]^+$ to CcNH by methyl lithium, potassium bis(trimethylsilyl)amide or *tert*butylimino-tris(dimethylamino)phosphorane and subsequent acylation with R–COCl failed to give the desired pure products in isolable form due to the formation of side products. Finally, sodium hydride proved to be the ideal base for this propose.¹⁹

Preparation and Properties of CcNH (1). Aminocobaltocenium hexafluoridophosphate [H-1][PF₆] prepared according to the Bildstein procedure^{13b} was deprotonated by a slight excess of sodium hydride in THF (Scheme 2). After the

Scheme 2. Deprotonation of $[H-1]^+$ and Resonance Structures of 1^a





color change from yellow to red within a few minutes (Figure 1), the solution was separated from the excess NaH by filtration. Prolonged reaction with NaH leads to decomposition according to the formation of a black insoluble precipitate (see the Experimental Section). All attempts to crystallize neutral complex 1 were unsuccessful. Consequently, red cobalt complex 1 was investigated spectroscopically in solution and by density functional theory (DFT) calculations (B3LYP/def2-TZVP/PCM THF).

Cobaltocenium hexafluoridophosphate exhibits absorption bands at 262, 301, and 404 nm in CH₃CN characteristic for many Cc⁺ complexes (Figure S1).²⁰ The latter two bands are clearly identified as spin-allowed ligand field transitions based on their weak intensity, while the high energy intense band has been assigned ligand-to-metal charge transfer (LMCT) character.^{20a} In THF, the amino substituent in [H-1]⁺ shifts all bands to lower energy, namely, 278, 358, and 414 nm. Deprotonation of [H-1]⁺ to 1 augments the shift to 280, 371, and 440 nm, respectively, and gives a new shoulder around 550 nm (Figure 1). The 440/550 nm bands of 1 account for its red color.

Time-dependent DFT (TD-DFT) calculations find composed bands at 317, 421, and 490 nm for $[H-1]^+$ (Figure S2). The energies are calculated as roughly 0.5 eV too low probably due to the failure of TD-DFT to describe these transitions properly in a quantitative sense. A very weak ligand field transition is calculated at 501 nm. All calculated bands for [H-1]⁺ display essentially ligand field character with the highenergy band at 317 nm featuring some LMCT contribution, originating from the nitrogen lone pair. Bands at 330, 426, 488, and 554 nm are calculated by TD-DFT for 1 (Figure S2). Again, all bands are composed of ligand field transitions but with additional nitrogen lone pair \rightarrow cobalt LMCT character (Figure 1). Although the numerical agreement is far from perfect, the batho- and hyperchromic effects experienced by the first three spin-allowed ligand field bands due to the increased LMCT character in 1 are reproduced well by the calculations (Figures 1 and S2).

The electronic structure of the aminocobaltocenium derivatives is best described with significant iminium ion character showing bond length alternation within the substituted $C_5H_5NH_2$ ring, short exocyclic C–N bond lengths of 1.340(4)–1.372(4) Å, and a tilted substituted ring with the *ipso* carbon atom being at a larger distance from the cobalt center (tilt angles $173.8(3)-175.7(4)^{\circ}$).^{12a,13b,21} DFT calculations on [H-1]⁺ reproduce these numbers reasonably well with a C–N bond length of 1.35 Å and a tilt angle of 173° (Figure S3).

Organometallics



Figure 1. UV/vis spectra of $[H-1][PF_6]$ (black), 1 (red), and 1 with CF₃SO₃H added (blue) in THF. TD-DFT calculated difference electron densities for relevant transitions of $[H-1]^+$ and 1 with contour values of 0.01 a.u.; purple = electron density depletion, orange = electron density gain. CH hydrogen atoms omitted for clarity.

According to DFT calculations on 1, the C–N distance shortens to 1.30 Å and the tilt angle reduces to 163° . Consequently, a description of the *N*-substituted C₅ ligand as 2,4-cyclopentadiene-1-imine coordinated to cobalt(I) is appropriate for 1 with only minor zwitterionic character (Scheme 2; Figure S3).

Proton and carbon NMR shifts are substantially affected by deprotonation of $[H-1]^+$ to 1 (Figures S4–S6). The proton resonances shift to higher field (Figure 2) by 0.88, 0.16, and 0.54 ppm (H³, H², and NH). Even the proton resonances of the unsubstituted Cp ring (H¹) experience a strong shift by 0.51 ppm suggesting significant reorganization of the entire electronic structure. Similarly, the ¹³C resonances for C¹, C², and C³ shift to higher field, while the *ipso* carbon resonance



Figure 2. ¹H NMR spectra of $[H-1][PF_6]$ (black) and 1 (red) in d_8 -THF.

(C⁴) dramatically shifts by 26.5 ppm to lower field from 132.1 to 158.6 ppm. The latter value indicates R_2C =NR' imine character.²²

The change in electron density upon deprotonation should also affect the ⁵⁹Co NMR shift. Hence, attempts to observe ⁵⁹Co NMR resonances of $[H-1]^+$ and 1 in THF were undertaken. The ⁵⁹Co NMR resonance of $[CcH]^+$ has been reported at -2140 ppm,^{23a} while typical (cyclopentadienyl)-bis(olefine) cobalt(I) complexes display ⁵⁹Co NMR resonances in the range from -1100 to -1640 ppm (all referenced against $K_3Co(CN)_6$ in D_2O).^{23b} For $[H-1]^+$, a resonance at -2035 ppm could be found consistent with a cobaltocenium ion (Figure S7). Unfortunately, no ⁵⁹Co NMR resonance could be detected for 1 under our conditions in the chemical shift range from -12000 to +27000 ppm.

Deprotonation of iminium ion $[H-1]^+$ to imine 1 is fully reversible as addition of triflic acid restores the yellow color, the optical spectrum and the ¹H NMR spectrum of $[H-1]^+$ (Figures 1 and S8–S10).

The symmetric and antisymmetric NH stretching vibrations of $[H-1]^+$ and the NH₂ deformation appear at 3444, 3334, and 1639 cm⁻¹, respectively, in the infrared spectrum in THF solution (Figures S11 and S12). Expectedly, a single band for the NH stretching vibration is observed for 1 at 3283 cm⁻¹, while the NH₂ deformation band has vanished in THF. Numerical frequency calculations on the DFT level (B3LYP/ def2-TZVP/PCM THF; scaled by 0.945) calculate these vibrational energies at 3476 and 3374 cm⁻¹ ($[H-1]^+$) and at 3246 cm⁻¹ (1) in reasonable agreement with the experiment lending credence to the imine description of 1 with minor contribution of the zwitterionic resonance structure (Scheme 2). We hypothesized that imine 1 should be nucleophilic enough for acylation reactions.

Preparation and Properties of [R-CONH-Cc]^{*n*+} (2⁺, 3⁺, and 4²⁺). Treatment of imine 1 with acid chlorides R–COCI (R = Ph, Fc, and Cc⁺) yields corresponding amides 2[PF₆], 3[PF₆], and 4[PF₆]₂ in good yields of 62, 89, and 73%, respectively (Scheme 3). In the reaction mixture of 1 with Ph-COCl, the doubly acylated amine [Cc-N(COPh)₂]⁺ was detected by ESI⁺ mass spectrometry, suggesting that smaller electrophiles can attack the nitrogen atom even twice. No double substitution was observed for the larger metallocenyl acid chlorides. All amides were fully characterized by elemental analysis, ESI⁺ and HR-ESI⁺ mass spectrometry, and NMR and IR spectroscopy (Figures S13–S34). Optical and electrochemical properties of bimetallocences 3⁺ and 4²⁺ and reference cobaltocenium amide 2⁺ were probed by UV/vis/NIR Scheme 3. Synthesis of $[CcNH]^+$ Amides $2[PF_6]$, $3[PF_6]$, and $4[PF_6]_2^a$



^{*a*}Atom numbering for NMR assignment.

spectroscopy, electrochemistry, and UV/vis/NIR spectroelectrochemistry. The solid state structures of $2[PF_6]$ and $3[PF_6]$ were ascertained by X-ray crystallography.

The ESI⁺ and HR-ESI⁺ mass spectra display peaks at massto-charge ratios appropriate for the cations 2^+ , 3^+ , and $[4-H]^+$ (see the Experimental Section and Figures S13–S15).

In the multinuclear NMR spectra of $2[PF_6]$, $3[PF_6]$, and 4[PF₆]₂ (¹H, ¹³C, ¹⁹F, and ³¹P; Figures S16-S33) all resonances have been assigned to corresponding nuclei. The 1 H (H¹, H², and H³) and 13 C resonances (C¹, C², and C³) of the Cc^+ units of 2^+ , 3^+ , and 4^{2+} are negligibly affected by the R substituents. The resonance of the C⁴ nuclei shifts to higher field from 114.4 and 113.8 to 111.0 ppm for R = Fc, Ph, and Cc⁺ with increasing electron-withdrawing nature of R. The same trend holds for the carbonyl resonances C^5 with $\delta =$ 170.8, 167.2, and 162.0 ppm for R = Fc, Ph, and Cc⁺, respectively. The NH proton resonance does not follow this trend with δ = 8.41, 9.17, and 8.96 ppm for R = Fc, Ph, and Cc⁺, suggesting other determining factors such as hydrogen bonding. In fact, small variations in the ¹⁹F chemical shifts of the hexafluoridophosphate counterions display a similar trend with $\delta = -72.9$, -73.2, and -73.1 ppm for R = Fc, Ph, and Cc⁺ which might be indicative of ion-pair formation via NH…F hydrogen bonds in acetonitrile solution. Such ion-pair formation has been previously observed in positively charged ferrocenium and cobaltocenium amides, thioamides, ureas and thioureas.^{6,10,14f,15e,24}

NH hydrogen bonding was further probed by IR spectroscopy (Figure S34). In fact, absorption bands for NH stretching and amide I vibrations appear at $\tilde{\nu}_{\rm NH} = 3264$, 3394, and 3305 cm⁻¹ and $\tilde{\nu}_{\rm amideI} = 1654$, 1678, and 1664 cm⁻¹ for R = Fc, Ph, and Cc⁺, respectively. These data suggest the strongest NH hydrogen bond for 3⁺ (R = Fc) and the weakest one for 2⁺ (R = Ph). Charging of the CO substituted metallocene in a formal Fc to Cc⁺ isosteric replacement (3⁺ \rightarrow 4²⁺) diminishes the NH hydrogen bond strength. Neutral diphenylamide Ph–CONH– Ph with $\tilde{\nu}_{\rm NH} = 3345$ cm⁻¹ and $\tilde{\nu}_{\rm amideI} = 1654$ cm⁻¹ only forms intermolecular NH…OC hydrogen bonds due to the absence of counterions and is thus a poor reference compound for charged amides $2^{+}{-}4^{2+}{}^{25}$

Single crystals of $2[PF_6]$ and $3[PF_6]$ suitable for X-ray diffraction analysis were obtained (Figure 3a,b; Table 1).



Figure 3. Molecular structures of (a) $2[PF_6]$ and (b) $3[PF_6] \times 1/_2C_6H_6$ in the solid state including a nearest neighbor molecule and counterions (Thermal ellipsoids at 50% probability. CH hydrogen atoms and solvent omitted; atom numbering modified with respect to the deposited data for clarity).

Table 1. Selected Bond Distances (Å) and Angles (deg) of $2[PF_6]$ and $3[PF_6]^a$

	2[PF ₆]	3[PF ₆]
Cp-Cp (Cc ⁺)	3.275(2)	3.281(3)
Cp-Cp (Fc)		3.303(3)
C1-N1	1.389(3)	1.386(4)
N1-C2	1.371(3)	1.374(4)
C2-O1	1.220(3)	1.223(4)
C2-C3	1.499(3)	1.474(5)
N1…F6	3.070(2)	2.920(19)
F6…H1	2.23	2.19
N1-H1…F6	160.3	140.0
Co1–Fe1		6.069(2)
Cp(Cc)-Cp(Fc) (intermolec.)		3.555(3)
Ph–Ph (intermolec.)	4.041(2)	
Cp-Co1-Cp	179.16(6)	178.95(10)
Cp-Fe1-Cp		177.66(10)
C1-N1-C2	124.13(17)	125.5(3)
N1-C2-C3	116.55(18)	115.0(3)
N1-C2-O1	121.86(19)	122.7(3)

"Cp denotes center of cyclopentadienyl rings; Ph denotes center of phenyl rings.

However, $4[\mathbf{PF}_6]_2$ crystallized under many attempted conditions only as heavily intergrown, sometimes very large crystallites which were unsuitable for single crystal diffraction (Figure S34). The cation of 2^+ forms a NH…F hydrogen bond to a PF₆⁻ counterion with a N…F distance of 3.070(2) Å (Figure 3a, Table 1). 3^+ forms a closer contact to its counterion with a shorter N…F distance of 2.920(19) Å (Figure 3b, Table 1). Although not very pronounced, this difference fits to the results from the NMR and IR data with 3^+ (R = Fc) forming stronger hydrogen bonds than 2^+ (R = Ph). The contact ion pairs $2[\mathbf{PF}_6]$ and $3[\mathbf{PF}_6]$ pack via π stacking of the Ph substituents (center-to-center distance 4.041(2) Å; Figure 3a) or via Cp…Cp contacts (center-to-center distance 3.555(3) Å; Figure 3b), respectively.

Similar to the well-explored Fc/Fc⁺ redox chemistry, the Cc/ Cc⁺ redox potential can be tuned over a wide range, currently from -0.97 V to -2.37 V vs FcH/FcH⁺. Linear correlations with substituent properties apply as well.^{2a,6,12b,13b} The phenyl substituted reference amide 2⁺ is reversibly reduced to the cobaltocene 2 at -1.360 V in the cyclic voltammogram (Figure 4a, Table 2). At $E_p = -2.265$ V an irreversible Co^{II}/Co^I reduction wave^{12b} (likely associated with reductive deprotonation of the amide proton) appears, which gives rise to a followup product that is reoxidized at -1.825 V (Figure 4a). Spectroelectrochemical reduction of 2⁺ to 2 and reoxidation to 2⁺ is reversible as well, provided that the second irreversible reduction is not addressed (Figure S35).

Replacing the Ph substituent in **2**⁺ by the Fc substituent in **3**⁺ barely affects the reversible Cc/Cc⁺ redox process ($E_{1/2} = -1.355$ V) and the irreversible Co^{II}/Co^I reduction/follow-up reaction ($E_p = -2.290$ and -1.840 V), respectively (Figure 4b; Table 2). The reversible Fc/Fc⁺ oxidation of **3**⁺ is observed in the expected range for CO substituted ferrocenes at 0.305 V.^{2a} Compared to the [Cc-CONH-Fc]⁺ isomer (Scheme 1) with an easy-to-reduce Cc⁺ unit ($E_{1/2} = -1.150$ V) and an easy-to-oxidize Fc unit ($E_{1/2} = -0.015$ V), the potential difference between the respective redox processes has increased by more than 0.5 V from 1.135 V in [Cc-CONH-Fc]⁺ to 1.660 V in **3**⁺.⁶

Expectedly, the bicobaltocenium complex 4^{2^+} is reduced reversibly two times (Table 2, Figure 4c) and irreversibly at lower potential ($E_p = -2.100$ V) with an oxidation wave of the follow-up product at $E_p = -1.570$ V (Figure 4c, Table 2). The assignment of the Cc⁺ reduction waves to individual Cc⁺ units in 4^{2^+} is straightforward according to expected substituent effects, reference compounds (2^+ and reported [CcCOR]⁺ derivatives), and DFT calculations (Figure 4c).^{2a,6,10,13b}

For the prototypical symmetric $[Cc-Cc]^{2+}$ bimetallocenium, the potential difference between the reductions has been reported by Weaver as 0.395 V.²⁶ The potential difference of 4^{2+} is with 0.400 V accidentally similar due to compensating Co…Co distance and substituent effects.

The electronic spectrum of $2[PF_6]$ in CH₃CN (Figure 5a) shows a prominent LMCT maximum at 280 nm, a less intense band at 347 nm, and a shoulder at 406 nm. This pattern is characteristic for cobaltocenium ions (see above).²⁰ The bicobaltocenium ion 4^{2+} displays essentially the same pattern ($\lambda = 271$, 346, 406 nm), yet with higher intensity (Figure 5a, Experimental Section).

In the heterobimetallic complex 3^+ the ferrocene can act as donor moiety, similar to its [Cc-CONH-Fc]⁺ isomer (Scheme 1).⁶ The latter isomer with the smaller redox potential gap (and consequently a smaller HOMO–LUMO gap), features a solvatochromic absorption band with MM'CT character at



Figure 4. Cyclic voltammograms of (a) $2[PF_6]$, (b) $3[PF_6]$, and (c) $4[PF_6]_2$ in CH₃CN/[ⁿBu₄N][PF₆] (scan rate 100 mV s⁻¹). DFT calculated spin densities of 4⁺ and 4 with contour values of 0.01 a.u.; CH hydrogen atoms omitted for clarity.

Table 2. Redox Potentials (V) in Acetonitrile/[NBu_4][PF_6] vs FcH/FcH^+

	2[PF ₆]	3[PF ₆]	$4[PF_6]_2$
$E_{1/2}$ (Fc/Fc ⁺)		0.305	
$E_{1/2} (C - Cc / C - Cc^{+})$			-1.020
$E_{1/2}$ (N-Cc/N-Cc ⁺)	-1.360	-1.355	-1.420
<i>E</i> _p (ox; follow-up)	-1.825	-1.840	-1.570
$E_{\rm p}~({\rm Co^{II}/Co^{I}})$	-2.265	-2.290	-2.100

534 nm in CH₃CN.⁶ For 3⁺, the cobaltocenium ligand field band around 406 nm is indeed considerably broadened on the lower energy side. According to TD-DFT calculations on 3⁺, these absorptions represent MM'CT transitions from iron to cobalt (Figure 5a). To distinguish the MM'CT from the normal Cc^+ and Fc absorption pattern, the Cc⁺ pattern of the spectrum of 2⁺ and the spectrum of Fc-COOMe were subtracted from the composed spectrum of 3⁺ (Figure S36). This procedure yields an approximate absorption band for the MM'CT transition in 3⁺ at 471 nm. This MM'CT occurs at considerably higher energy in 3⁺ (by 2500 cm⁻¹) as compared to the MM'CT of the [Cc-CONH-Fc]⁺ isomer which fits well to the electrochemical data (see above).⁶ Hush analysis with the modified Hush formula for closed-shell donor-acceptor systems^{9g} $H_{AB} = 2.05 \times 10^{-2} (0.5 \varepsilon_{max} \Delta_{1/2} \tilde{\nu} \tilde{\nu}_{max})^{1/2} / r$ gives the electronic coupling matrix element $H_{AB} = 584$ cm⁻¹ for the closed-shell mixed-metal system 3⁺ (Table 3).

Further proof that the MM'CT assignment of 3^+ is correct comes from spectroelectrochemistry. Oxidation of 3^+ to the cobaltocenium–ferrocenium complex 3^{2+} bleaches the MM'CT band around 471 nm, while the characteristic ferrocenium absorption of $[Fc-C(O)R]^+$ units at 632 nm grows (Figures 5b and S37).^{20a,27} Likewise, reduction of 3^+ to 3 bleaches the MM'CT band as the Cc⁺ electron acceptor is reduced to cobaltocene (Figure S37). No distinct new bands grow in similar to the reduction of 2^+ to 2 (Figure S35). The overall reduction of 3^+ to 3 is spectroscopically more complicated



Figure 5. (a) UV/vis spectra of $2[PF_6]$, $3[PF_6]$, and $4[PF_6]_2$ in CH₃CN. Changes in the UV/vis/NIR spectra in the course of redox events in CH₃CN/["Bu₄N][PF₆] during OTTLE spectroelectrochemistry: (b) oxidation of $3^+ \rightarrow 3^{2+}$, (c) reduction of $4^{2+} \rightarrow 4^+$, and (d) reduction of $4^+ \rightarrow 4$. TD-DFT calculated difference electron densities with contour values of 0.01 a.u.: purple = electron density depletion, orange = electron density gain. CH hydrogen atoms omitted for clarity.

Table 3. Results of the Hush Analysis of the MM'CT (IV)	CT) Bands of Severa	l Bimetallocenes (Composed of Fc, Fc ⁺	, Cc, and
Cc ⁺ Moieties ^{<i>a</i>}				

	$ ilde{ u}~(\mathrm{cm}^{-1})~(arepsilon~(\mathrm{M}^{-1}~\mathrm{cm}^{-1}))$	$\Delta ilde{ u}_{1/2}~(\mathrm{cm}^{-1})$	$\Delta G^0 \; ({ m cm}^{-1})$	$r (Å)^a$	$H_{\rm AB}~({\rm cm}^{-1})$	α	$\lambda (cm^{-1})$
$[Fc-Fc]^+$ (ref 26a) ^b	5680 (750)	3620	2541	5.0	509	0.090	3139
$[Cc-Fc]^+$ (refs 9a and 9g) ^b	18115 (2480)	4176	12752	5.0	1256	0.069	5363
$[\text{Cc-Cc}]^+ (\text{ref } 26a)^b$	6580 (3500)	3900	3186	5.0	1229	0.187	3394
$[Fc-CH=CH-Fc]^+$ (ref 26b) ^c	4910 (1340)	4360	1371	6.9	503	0.102	3539
$[Fc-CONH-Fc]^+$ (refs 14d and 14e) ^d	9556 (95)	2443	3388	6.9	140	0.015	6168
$[Cc-CONH-Fc]^+$ (ref 6) ^b	18736 (347)	5584	9154	6.9	400	0.021	9582
[Fc-CONH-Cc] ⁺ 3 ⁺	21240 (886)	4113	13389	6.9	584	0.028	7851
[Cc-CONH-Cc] ⁺ 4 ⁺ ^b	12475 (505)	5436	3226	6.9	550	0.044	9249
⁴ Average distances of the two metal centers as estimated by DFT calculations. ^b In CH ₃ CN. ^c In CH ₂ Cl ₂ . ^d In THF.							

involving three individual steps with distinct isosbestic points (Figure S37). We also note some precipitation during electrolysis. However, the overall process $3^+ \rightarrow 3 \rightarrow 3^+$ is reversible (Figure S37).

Reduction of 4^{2+} to 4^+ yields the redox-asymmetric d^7 -Co^{II}/ d⁶-Co^{III} mixed-valence system with the [CcCO]⁺ unit reduced to the cobaltocene moiety (Figure 4c). Spectroelectrochemical reduction delivers a new prominent band at 524 nm and a very broad band at 803 nm (Figure 5c). Both bands bleach upon reoxidation to 4^{2+} and upon further reduction of 4^+ to the Co^{II}Co^{II} complex 4 (Figures S38 and 5d). These findings suggest that these bands are associated with the uncharged [Cc-CO] cobaltocene moiety. Indeed, TD-DFT calculations on 4^+ assign the band at 524 nm to a metal-to-ligand charge transfer (MLCT) from the electron-rich [Cc-CO] cobaltocene moiety to the carbonyl group of the bridge and importantly describe the band at 803 nm as an intervalence charge transfer (IVCT) transition from the electron-rich [Cc-CO] cobaltocene to the electron-deficient [Cc-NH]⁺ cobaltocenium unit.

Gaussian deconvolution of the absorption spectrum of 4⁺ yields the IVCT absorption band data (Table 3; Figure S39). With an (averaged) Co…Co distance of r = 6.9 Å, Hush's formula²⁸ delivers the electronic coupling matrix element $H_{AB} = 2.05 \times 10^{-2} (\varepsilon_{max} \Delta_{1/2} \tilde{\nu} \tilde{\nu}_{max})^{1/2} / r = 550 \text{ cm}^{-1}$ for the open-shell system 4⁺. This is less than half of H_{AB} obtained for the redox-symmetric bimetallocene [Cc-Cc]⁺ lacking the amide unit (Table 3). This decrease is likely due to the redox asymmetry, the larger metal—metal distance, and the less conjugated amide bridge in 4⁺ dramatically decreasing the transition dipole moment for the IVCT transition.

Compared to the d⁶-Fe^{II}/d⁵-Fe^{III} mixed-valent system [Fc-CONH-Fc]⁺, H_{AB} of 4⁺ is approximately four times larger.^{14e} The same trend holds for the electronic mixing coefficients $\alpha = H_{AB}/\tilde{\nu}_{max}$ (Table 3). Clearly, orbital symmetry plays a major role with the mainly iron-centered e orbitals with local δ symmetry interacting only weakly. However, the redox orbitals in the d⁷-Co^{II}/d⁶-Co^{III} system both feature π^* character with both *ipso* carbon atoms involved. Such a symmetry of the redox orbitals enables electronic interaction via the amide bridge (see Figure 5c).

In the heterometallic isomeric bimetallocenes [Cc-CONH-Fc]⁺ and [Fc-CONH-Cc]⁺ (**3**⁺), the electronic mixing coefficient α is larger than that in [Fc-CONH-Fc]⁺ due to the extended Cc⁺ acceptor π system (Figure 5a) but smaller than that in [Cc-CONH-Cc]⁺ (**4**⁺) due to the very localized Fc donor system in the heterometallics (Figure 5a). The electronic mixing coefficient α increases in the series [Fc-CONH-Fc]⁺, [Cc-CONH-Fc]⁺, [Fc-CONH-Cc]⁺, and [Cc-CONH-Cc]⁺ (Table 3).

All amide-bridged bimetallocenes [Mc-NHCO-Mc]⁺ (Mc = Fc and Cc) display MM'CT or IVCT transitions albeit with different intensities due to the different orbital symmetry and all belong clearly to class II of the Robin/Day system. They all exhibit similar nuclear reorganization energies $\lambda = \tilde{\nu}_{max} - \Delta G^0$ (Table 3) which has been discussed before for other linked bimetallocenes based on the similar bond length and vibrational data of the involved metallocenes.^{26a} However, the reorganization energy λ of the amide-bridged bimetallocenes [Mc-NHCO-Mc]⁺ is significantly larger than the reorganization energy of [Fc-Fc]⁺, [Fc-Cc]⁺, and [Cc-Cc]⁺ with a direct link (Table 3). It is also larger than estimated for the vinylene bridged biferrocene [Fc-CH=CH-Fc]⁺ with a similar metalmetal distance.^{26b} It is tempting to attribute this extra effect to the connecting amide unit and especially the hydrogen bonds of counterions to the NH group. Charge transfer across the amide unit and the hydrogen-bonded counterion certainly affects the NH…X bonding situation and contributes to the inner-sphere reorganization energy (if one ascribes the hydrogen-bonded counterion to the inner sphere). More systematic studies on solvent and counterion effects in amidelinked metallocenes are clearly warranted and will be conducted in the future.

CONCLUSIONS

The poor nucleophile $[Cc-NH_2]^+$ $[H-1]^+$ has been successfully activated by deprotonation to the imine CcNH 1 by NaH. Acylation of 1 by R–COCl gave the cobaltocenium amides [R-CONH-Cc]⁺ 2^+ , 3^+ , and 4^{2+} (R = Ph, Fc, and Cc⁺). They form contact ion pairs with hexafluoridophosphate counterions in solution $(2^+, 3^+, and 4^{2+})$ and in the solid state $(2^+, 3^+, and$ likely 4²⁺) via NH…F hydrogen bonds. Both the donoracceptor heterobimetallocene $\tilde{3}^{\scriptscriptstyle +}$ and the mixed-valent Co^{III}/ Co^{II} complex 4⁺ (prepared by spectroelectrochemistry) are Robin/Day class II systems with similar nuclear reorganization energies but different electronic mixing coefficients α . The electronic coupling in the mixed-valent Co^{III}/Co^{II} complex 4⁺ is 4-fold higher than that of the mixed-valent Fe^{III}/Fe^{II} complex [Fc-CONH-Fc]⁺ due to the more favorable π symmetry of the redox orbitals in 4⁺. The reorganization energies λ of the amidebridged bimetallocences are increased by the hydrogen-bonded counterions relative to those of bimetallocenes with a direct link.

On the basis of the availability of suitably substituted aminocobaltocenium complexes and the here developed amidecoupling chemistry, conducting peptidic molecular wires with cobaltocene/cobaltocenium units in the main chain are now within reach. The development of molecular wires, as well as sensing and charge-separating systems with amino-substituted

Organometallics

cobaltocenium electron acceptor units as building blocks is now actively pursued.

EXPERIMENTAL SECTION

Instrumentation. NMR spectra were recorded on a Bruker Avance DRX 400 spectrometer at 400.31 MHz (1H), 100.05 MHz (¹³C{¹H}), 376.67 MHz (¹⁹F), and 162.05 MHz (³¹P) and on a Bruker Avance DSX 400 spectrometer at 94.88 MHz (⁵⁹Co). Chemical shifts are reported on the δ scale in ppm relative to the solvent signal as an internal standard (CD₃CN (¹H: δ = 1.94 ppm; ¹³C: δ = 118.26 ppm), d_8 -THF (¹H: δ = 3.58 ppm; ¹³C: δ = 67.57 ppm))²⁹ or relative to an external standard (¹⁹F: CFCl₃, ³¹P: H₃PO₄, ⁵⁹Co: 1.0 M K₃[Co(CN)₆] in H_2O); s = singlet, d = doublet, and t = triplet. IR spectra were recorded with a Thermo Nicolet 5700 FT-IR as ATR and with a Bruker ALPHA FT-IR spectrometer as KBr disk, and in THF, with signal intensities: s = strong, m = medium, w = weak. ESI and HR ESI mass spectra were recorded on a Micromass Q-TOF-Ultima spectrometer and a Waters Q-Tof Ultima 3 spectrometer, respectively. Cyclic voltammetric measurements were carried out with a BioLogic SP-50 voltammetric analyzer in CH₃CN containing 0.1 M ["Bu₄N]- $[PF_6]$ as supporting electrolyte at a platinum working electrode, a platinum wire as counter electrode, and a 0.01 M Ag/AgNO₃ electrode as the reference electrode. All cyclic voltammetric measurements were recorded at 100 mV s⁻¹ scan rate. Ferrocene or decamethylferrocene were employed as an internal reference redox system. (rev.) = reversible, (irrev.) = irreversible redox process. Spectroelectrochemical experiments were performed using a Specac omni-cell liquid transmission cell with CaF2 windows equipped with a Pt gauze working electrode, a Pt counter electrode, and a Ag pseudoreference electrode, melt-sealed in a polyethylene spacer (path length 0.7 mm).³⁰ UV/vis/NIR absorption spectra were measured on a Varian Cary 5000 spectrometer in 1.0 cm cells (Hellma, Suprasil); sh = shoulder.

Density Functional Calculations. Calculations were carried out with the ORCA 4.0.1/DFT series of programs.³¹ The B3LYP formulation of density functional theory was used for geometry optimizations and numerical frequency calculations employing the ZORA-Def2-tzvp basis set,^{32,33} the RIJCOSX approximation,^{34,35} the zeroth order regular approximation (ZORA),^{36,37} and the KDIIS algorithm³⁸ at GRID5. No symmetry constraints were imposed on the molecules. Solvent modeling was done employing the conductor-like continuum polarization model (CPCM CH₃CN, and THF).³⁹

Crystal Štructure Determinations. Intensity data were collected with a STOE IPDS-2T diffractometer using Mo K α radiation (λ = 0.71073 Å). The diffraction frames were integrated using the STOE X-RED package and most were corrected for absorption with MULABS of the PLATON software package.^{40–42} The structure was solved by direct methods and refined by the full-matrix method based on F^2 using the SHELX software package.^{43,44} All non-hydrogen atoms were refined anisotropically, while the positions of all hydrogen atoms were generated with appropriate geometric constraints and allowed to ride on their respective parent carbon atoms with fixed isotropic thermal parameters.

Crystallographic Data of **2**[*PF*₆]. C₁₇H₁₅CoF₆NOP (453.20); triclinic, *P*Ī; *a* = 7.6178(15) Å, *b* = 9.4454(19) Å, *c* = 12.203(2) Å, α = 73.80(3)°, β = 85.77(3)°, γ = 81.08(3)°, *V* = 832.6(3) Å³, *Z* = 2; density, calcd. = 1.808 g cm⁻³, *T* = 100 K, μ = 1.198 mm⁻¹; *F*(000) = 456; crystal size 0.140 × 0.117 × 0.090 mm³; θ = 2.268–28.127°; -10 $\leq h \leq 10, -10 \leq k \leq 12, -16 \leq l \leq 16$; rfln collected = 8491; rfln unique = 4049 [*R*(int) = 0.0383]; completeness to θ = 25.242° = 99.7%; semiempirical absorption correction from equivalents; max. and min transmission 1.19124 and 0.90255; data 4049; restraints 0; parameters 244; goodness-of-fit on *F*² = 1.053; final indices [*I* > 2 σ (*I*)] *R*₁ = 0.0323. w*R*₂ = 0.0736; *R* indices (all data) *R*₁ = 0.0411, w*R*₂ = 0.0791; largest diff. peak and hole 0.478 and -0.429 e Å⁻³.

Cyrstallographic Data of **3**[**PF**_{*a*}] × 1/2C₆H₆. C₂₄H₂₂CoF₆FeNOP (600.17); monoclinic, P2₁/*c*; *a* = 7.5786(15) Å, *b* = 19.480(4) Å, *c* = 15.757(3) Å, $\alpha = 90^{\circ}$, $\beta = 102.42(3)^{\circ}$, $\gamma = 90^{\circ}$, V = 2271.8(8) Å³, Z = 4; density, calcd. = 1.755 g cm⁻³, T = 193 K, $\mu = 1.507$ mm⁻¹; *F*(000)

= 1212; crystal size $0.460 \times 0.287 \times 0.120 \text{ mm}^3$; $\theta = 2.091-28.337^\circ$; -10 $\leq h \leq 10, -25 \leq k \leq 25, -19 \leq l \leq 20$; rfln collected = 13 537; rfln unique = 5541 [R(int) = 0.0466]; completeness to $\theta = 25.242^\circ =$ 99.4%; semiempirical absorption correction from equivalents; max and min transmission 1.31360 and 0.81612; data 5541; restraints 126; parameters 379; goodness-of-fit on $F^2 = 1.052$; final indices [$I > 2\sigma(I)$] $R_1 = 0.0472$. w $R_2 = 0.1121$; R indices (all data) $R_1 = 0.0719$, w $R_2 =$ 0.1323; largest diff. peak and hole 0.636 and -0.393 e Å⁻³. The hexafluoridophosphate counterion is disordered over two positions.

CCDC 1581720 and 1581721 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from Cambridge Crystallographic Data Center via www.ccdc.cam.ac. uk/data request/cif.

Materials. Unless otherwise noted, all chemical reagents were used without any further purification as received from suppliers (Sigma-Aldrich, Acros, Alfa Aesar). Tetrahydrofuran was freshly distilled from potassium, CH₃CN from calcium hydride. For the characterization experiments of **1**, the sodium hydride was freed from mineral oil prior the reaction by washing with absolute THF. Cc[PF₆],^{13a} [H-1][PF₆],^{13b} [Cc-COOH][PF₆],^{13a} and Fc-COOH⁴⁵ were prepared according to literature procedures.

General Procedures. All preparations (until quenching with water) were performed under an inert atmosphere of argon, using an M. Braun glovebox and absolute solvents.

Cc[PF₆]. UV/vis (CH₃CN): λ [nm] (ε [M⁻¹ cm⁻¹]) = 262 (36 140), 301 (1140), 404 (230) consistent with Cc[ClO₄]: UV/vis (H₂O): λ [nm] (ε [M⁻¹ cm⁻¹]) = 263 (38 000), 300 (1200), 407 (220).^{20a}

[H-1][PF₆]. ¹H NMR (d_8 -THF): δ [ppm] = 5.24 (t, 2H, ${}^{3}J_{HH}$ = 1.9 Hz, H³), 5.40 (t, 2H, ${}^{3}J_{HH}$ = 1.9 Hz, H²), 5.45 (s, 5H, H¹), 5.61 (s, 2H, H^{NH}). ¹³C {¹H} NMR (d_8 -THF): δ [ppm] = 66.4 (C³), 79.1 (C²), 84.9 (C¹), 132.1 (C⁴). ⁵⁹Co NMR (THF): δ [ppm] = -2035. UV/vis (THF): λ [nm] (ε [m⁻¹ cm⁻¹]) = 278 (20 180), 358 (4480), 414 (sh, 1220). IR (KBr): $\tilde{\nu}$ [cm⁻¹] = 3503 (s, NH_{asym}), 3402 (s, NH_{sym}), 3244 (s, CH), 3124 (s, CH), 1633 (s, CN), 1538 (s, CN), 1414 (m, C = C), 831 (m, PF), 638, 557 (m, FPF_{def}), 452. IR (KBr): $\tilde{\nu}$ [cm⁻¹] = 3503 (s, NH_{asym}), 3402 (s, NH_{sym}), 1633 (s, NH_{2,def}), 1538 (s, CN), 831 s, PF), 557 (s, PF_{2,def}). IR (THF): $\tilde{\nu}$ [cm⁻¹] = 3444 (s, NH_{asym}), 3334 (s, NH_{sym}), 1639 (s, NH_{2,def}), 1542 (s, CN), 559 (s, PF_{2,def}).

Synthesis of 1. Aminocobaltocenium hexafluoridophosphate [H-1]**PF**₆ (10 mg, 29 μ mol, 1 equiv) was dissolved in THF (5 mL) and NaH (1.4 mg, 58 μ mol, 2 equiv) was added. The solution was stirred and the color changed from orange to red. After 5 min, the solution was filtered through a 0.2 μ m PTFE syringe filter. Prolonged reactions times (ca. 20 min) lead to the formation of a black precipitate, decreasing the yield of 1.

¹H NMR (d_8 -THF): δ [ppm] = 4.19 (s, 2H, H³), 4.94 (s, 5H, H¹), 5.07 (s, 1H, H^{NH}), 5.17 (s, 2H, H²). ¹³C {¹H} NMR (d_8 -THF): δ [ppm] = 60.2 (C³), 76.6 (C²), 81.7 (C¹), 158.6 (C⁴). UV/vis (THF): λ [nm] (ε [M⁻¹ cm⁻¹]) = 280 (17 515), 371 (5660), 440 (2565). IR (THF): $\tilde{\nu}$ [cm⁻¹] = 3283 (m, NH), 1565 (s, CN).

Synthesis of $2[PF_6]$. Aminocobaltocenium hexafluoridophosphate $[H-1][PF_6]$ (187.6 mg, 537 μ mol, 1.0 equiv) was dissolved in THF (25 mL) and NaH (150 mg, 3.75 mmol, 7.0 equiv, 60% dispersion in mineral oil) was added. The solution was stirred and the color shifted from orange to red. After 10 min, CcNH the solution was filtered through a 0.2 μ m PTFE syringe filter.

Benzoyl chloride (80 μ L, 694 μ mol, 1.3 equiv) was dissolved in THF (15 mL) and added dropwise to the CcNH solution over 5 min. The solution was stirred for 3 h at room temperature. Water (80 mL), acetic acid (0.5 mL), and potassium hexafluoridophosphate (500 mg, 2.71 mmol, 5.1 equiv) were added. After 12 h of stirring, the THF was removed under reduced pressure and the solution was extracted with dichloromethane (3 × 50 mL). The solvent was removed under reduced pressure. The solid was washed on a short alumina column with hexane/acetic acid (100:5) and with ethanol. On a second alumina column, the product was removed under reduced pressure. The solvent was removed under reduced pressure. The solid and potassium hexafluoridophosphate (500 mg, 2.71 mmol, 5.1 equiv) were dissolved in acetone (50 mL) and stirred for 5 h.

Water (250 mL) was added, and the solution was extracted with dichloromethane (5 × 30 mL). The organic phase was dried over sodium sulfate. The solvent was removed under reduced pressure yielding a yellow glassy solid. Yield 151 mg (0.333 μ mol, 62%). For further purification, the solid was recrystallized from a benzene solution at 6 °C. These crystals were suitable for X-ray diffraction analysis.

MS (ESI⁺, CH₃CN): m/z (%) = 308.05 (100) [M – PF₆]⁺. HR-MS (ESI⁺, CH₃CN): obs. m/z = 308.0477; calcd. for [M – PF₆]⁺ = 308.0486. ¹H NMR (CD₃CN): δ [ppm] = 5.54 (t, 2H, ³J_{HH} = 2.0 Hz, H²), 5.62 (s, 5H, H¹), 6.16 (t, 2H, ³J_{HH} = 2.0 Hz, H³), 7.59 (t, 2H, ³J_{HH} = 7.6 Hz, H⁸), 7.69 (t, 1H, ³J_{HH} = 7.4 Hz, H⁹), 7.98 (d, 2H, ³J_{HH} = 7.3 Hz, H⁷), 9.17 (s, 1H, H^{NH}). ¹³C {¹H} NMR (CD₃CN): δ [ppm] = 74.4 (C³), 80.8 (C²), 85.8 (C¹), 113.8 (C⁴), 128.7 (C⁷), 129.7 (C⁸), 133.9 (C⁹), 133.8 (C⁶), 167.2 (C⁵). ¹⁹F NMR (CD₃CN): δ [ppm] = -73.2 (d, 6F, ¹J_{PF} = 706 Hz, F^{PF₆}). ³¹P NMR (CD₃CN): δ [ppm] = -143.5 (sept, 1P, ¹J_{PF} = 706 Hz, P^{PF₆}). IR (ATR): $\tilde{\nu}$ [cm⁻¹] = 3394 (s, NH), 3122 (s, CH), 3100 (s, CH), 1678 (s, CO), 1530 (s, NC), 1498, 1485, 1413, 1393, 1361, 1336, 1259 (s), 1099, 820 (m, PF), 704, 651, 553 (m, FPF_{def}), 459. UV/vis (CH₃CN): λ [nm] (ε [M⁻¹ cm⁻¹]) = 244 (13 90), 280 (25 000), 347 (4720), 406 (sh, 970). CV (FcH/FcH⁺, 100 mV⁻¹, CH₃CN, 0.1 M [ⁿBu₄N][PF₆]): $E_{1/2}$ [V] = -1.360 (rev.), -1.825 (irrev. ox.), -2.265 (irrev.). Elemental analysis: Anal. Calcd for C₁₇H₁₅NOCoPF₆ (453.23): C, 45.05; H, 3.34; N, 3.09. Found: C, 44.81; H, 3.65; N, 3.31.

Synthesis of 3[PF₆]. Aminocobaltocenium hexafluoridophosphate [H-1][PF₆] (564 mg, 1.62 mmol, 1.1 equiv) was dissolved in THF (100 mL) and NaH (250 mg, 6.25 mmol, 4.1 equiv, 60% dispersion in mineral oil) was added. The solution was stirred, and the color shifted orange to red. After 90 min, the CcNH solution was filtered through a 0.2 µm PTFE syringe filter. Carboxyferrocene (344 mg, 1.50 mmol, 1.0 equiv) and Ghosez's reagent (0.7 mL, 5.29 mmol, 3.5 equiv) were dissolved in dichloromethane (100 mL), and the solution was refluxed for 18 h. The solvent was removed under reduced pressure, the solid was washed with dichloromethane (50 mL), and the solvent was removed under reduced pressure. The solid was suspended in THF (50 mL), and the CcNH solution was added dropwise over 10 min to the FcCOCl solution. The mixture was stirred for 24 h at room temperature and terminated by adding water (1 mL). The solvent was removed under reduced pressure, and the resulting oil was washed on an alumina column with ethyl acetate and with ethanol. The solution was filtered through a 0.2 μ m PTFE filter, and the solvent was removed under reduced pressure. The solid was dissolved in acetone (30 mL), and potassium hexafluoridophosphate (1.00 g, 5.42 mmol, 3.4 equiv) was added. The solution was stirred for 3 h. Water (250 mL) was added, the solution extracted with dichloromethane (5 \times 50 mL), and the organic phase washed with water $(3 \times 50 \text{ mL})$. The organic phase was dried over sodium sulfate. The solvent was removed under reduced pressure yielding a red powder. Yield 751 mg (1.33 mmol, 89%). For further purification, the product was recrystallized by diffusing diethyl ether in an acetonitrile solution. Crystals suitable for X-ray diffraction analysis were obtained by recrystallization from a benzene solution at 6 °C.

MS (ESI⁺, CH₃CN): *m/z* (%) = 416.03 (100) [M – PF₆]⁺, 977.04 (7) [2*x*M – PF₆]⁺. HR-MS (ESI⁺, CH₃CN): obs. *m/z* = 416.0139; calcd for [M – PF₆]⁺ = 416.0148. ¹H NMR (CD₃CN): δ [ppm] = 4.25 (s, 5H, H⁹), 4.54 (t, 2H, ³*J*_{HH} = 1.6 Hz, H⁸), 4.86 (t, 2H, ³*J*_{HH} = 1.6 Hz, H⁷), 5.49 (t, 2H, ³*J*_{HH} = 1.9 Hz, H²), 5.55 (s, 5H, H¹), 6.08 (t, 2H, ³*J*_{HH} = 1.9 Hz, H³), 8.41 (s, 1H, H^{NH}). ¹³C {¹H} NMR (CD₃CN): δ [ppm] = 69.7 (C⁷), 70.9 (C⁹), 72.8 (C⁸), 73.6 (C³), 74.8 (C⁶), 80.5 (C²), 85.6 (C¹), 114.4 (C⁴), 170.8 (C⁵). ¹⁹F NMR (CD₃CN): δ [ppm] = -72.8 (d, 6F, ¹*J*_{PF} = 707 Hz, P^{PF₆}). ³¹P NMR (CD₃CN): δ [ppm] = -143.4 (sept, 1P, ¹*J*_{PF} = 707 Hz, P^{PF₆}). IR (ATR): $\tilde{\nu}$ [cm⁻¹] = 3364 (s, NH), 3188 (s, CH_{Fc}), 3121 (s, CH), 3100 (s, CH), 1654 (s, amide I), 1533 (s, NC), 1498, 1449, 1418, 1379, 1283 (s), 1139, 823 (m, PF), 644, 555 (m, FPF_{def}), 468. UV/vis (CH₃CN): λ [nm] (ε [M⁻¹ cm⁻¹]) = 281 (21370), 347 (4160), 419 (1600). CV (FcH/FcH⁺, 100 mV⁻¹, CH₃CN, 0.1 M [ⁿBu₄M][PF₆]): $E_{1/2}$ [V] = 0.305 (rev.), -1.355 (rev.), -1.840 (irrev. ox), -2.290 (irrev.). Elemental analysis: Anal. Calcd for C₂₁H₁₉NOFeCoPF₆ (561.13) × 1/2H₂O: C, 44.24; H, 3.54; N, 2.46. Found: C, 44.45; H, 3.88; N, 2.51. The water content was confirmed by 1 H NMR spectroscopy.

Synthesis of 4[PF₆]₂. Amino cobaltocenium hexafluoridophosphate [H-1][PF₆] (106 mg, 304 µmol, 1.0 equiv) was dissolved in THF (15 mL) and NaH (100 mg, 2.50 mmol, 8.2 equiv, 60% dispersion in mineral oil) was added. The solution was stirred, and the color shifted from orange to red. After 30 min, the CcNH solution was filtered through a 0.2 μ m PTFE syringe filter. Carboxycobaltocenium hexafluoridophosphate (116 mg, 307 μ mol, 1.0 equiv) and Ghosez's reagent (0.2 μ L, 1.51 mmol; 4.97 equiv) were dissolved in dichloromethane (50 mL), and the solution was refluxed for 18 h. The solvent was removed under reduced pressure, the solid was washed with dichloromethane (30 mL). The solvent was removed under reduced pressure. The solid was suspended in acetonitrile (25 mL), and the CcNH solution was added dropwise over 2 min. The mixture was stirred for 6 h at room temperature. Ammonium hexafluoridophosphate (330 mg, 2.02 mmol; 6.6 equiv) was added, and the solution was stirred for 14 h. The solvent was removed under reduced pressure, and the solid was washed on a short alumina column with ethyl acetate, ethyl acetate/ethanol (1:2), and acetone. The product was dissolved in acetonitrile (50 mL) and filtered through a 0.2 μ m PTFE filter. The solvent was removed under reduced pressure yielding a yellow powder. Yield 158 mg (223 μ mol, 73%). For further purification, the product was recrystallized by diffusing diethyl ether in an acetonitrile solution.

MS (ESI⁺, CH₃CN): m/z (%) = 209.52 (97) $[M - 2PF_6]^{2+}$, 418.04 $(100) [M - H - 2PF_6]^+, 564.01 (34) [M - PF_6]^+, 1273.03 (16) [2M$ $- PF_6^{+}$. HR-MS (ESI⁺, CH₃CN): obs. m/z = 418.0054; calcd. for [M $- H - 2xPF_6]^+ = 418.0052.$ ¹H NMR (CD₃CN): δ [ppm] = 5.55 (t, 2H, ${}^{3}J_{HH} = 2.1$ Hz, H²), 5.63 (s, 5H, H¹), 5.76 (s, 5H, H⁹), 5.86 (t, 2H, ${}^{3}J_{\text{HH}} = 2.0 \text{ Hz}, \text{H}^{8}$), 6.09 (t, 2H, ${}^{3}J_{\text{HH}} = 2.1 \text{ Hz}, \text{H}^{3}$), 6.19 (t, 2H, ${}^{3}J_{\text{HH}} = 2.0 \text{ Hz}, \text{H}^{7}$), 8.96 (s, 1H, H^{NH}). ${}^{13}\text{C}$ {¹H} NMR (CD₃CN): δ [ppm] = 74.7 (C³), 80.8 (C²), 84.8 (C⁷), 85.7 (C¹), 87.0 (C⁹), 87.1 (C⁸), 92.7 (C⁶), 111.0 (C⁴), 162.0 (C⁵). ¹⁹F NMR (CD₃CN): δ [ppm] = -73.1 (d, 6F, ¹J_{PF} = 706 Hz, F^{PF₆}). ³¹P NMR (CD₃CN): δ [ppm] = -143.5 (sept, 1P, ¹J_{PF} = 706 Hz, P^{PF₆}). IR (ATR): $\tilde{\nu}$ [cm⁻¹] = 3305 (s, NH), 3220 (s, CH_{Cc(C)}), 3129 (s, CH), 3104 (s, CH), 1664 (s, amide I), 1557 (s, NC), 1494, 1464, 1421, 1384, 1384, 1286 (s), 1160, 816 (m, PF), 640, 554 (m, FPF_{def}), 456. UV/vis (CH₃CN): λ [nm] (ε [M⁻¹ cm⁻¹]) = 221 (12980), 271 (39570), 346 (6590), 406 (sh, 1900). CV (FcH/FcH⁺, 100 mV⁻¹, CH₃CN, 0.1 M ["Bu₄N][PF₆]): $E_{1/2}$ [V] = -1.020 (rev.), -1.420 (rev.), -1.570 (irrev. ox.), -1.900 (irrev. ox.), -2.100 (irrev.). Elemental analysis: Anal. Calcd for $C_{21}H_{19}NOCo_2P_2F_{12}$ (709.21) × 1/4CH₃CN: C, 35.89; H, 2.77; N, 2.43. Found: C, 35.89; H, 2.77; N, 2.46. The CH₃CN content was confirmed by ¹H NMR spectroscopy.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organo-met.7b00790.

Cartesian coordinates of DFT optimized geometries (XYZ)

Figures and spectroscopic data (UV/vis, IR, ¹H NMR, ¹³C NMR, ³¹P NMR, ¹⁹F NMR, ⁵⁹Co NMR, ¹H¹H COSY, ¹H¹³C HMBC, UV/vis/NIR spectra during OTTLE spectroelectrochemistry, Gaussian deconvolution of CT bands (PDF)

Accession Codes

CCDC 1581720–1581721 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033. AUTHOR INFORMATION

Corresponding Author

*E-mail: katja.heinze@uni-mainz.de.

ORCID 0

Katja Heinze: 0000-0003-1483-4156

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Parts of this research were conducted using the supercomputer Mogon and advisory services offered by Johannes Gutenberg University Mainz (www.hpc.uni-mainz.de), which is a member of the AHRP and the Gauss Alliance e.V. We thank Dr. Dieter Schollmeyer for collection of the diffraction data and Dr. Mihail Mondeshki for assistance in the NMR spectroscopy facility, especially for recording the ⁵⁹Co NMR spectrum. We thank Min Thu Pham for preparative assistance.

REFERENCES

(1) (a) Štepnička, P. The Multifaceted Chemistry of Ferrocene. Eur. J. Inorg. Chem. 2016, 215–216. (b) Heinze, K.; Lang, H. Thematic issue "Ferrocene-Beauty and Function. Organometallics 2013, 32, 5623–5625. (c) Ferrocenes: Ligands, Materials and Biomolecules; Stepnicka, P., Ed.; Wiley: Chichester, U.K., 2008. (d) Ferrocenes: Homogeneous Catalysis, Organic Synthesis, Materials Science; Togni, A., Hayashi, T., Eds.; VCH: Weinheim, Germany, 1995. (e) Hailes, R. L. N.; Oliver, A. M.; Gwyther, J.; Whittell, G. R.; Manners, I. Chem. Soc. Rev. 2016, 45, 5358–5407. (f) Astruc, D. Eur. J. Inorg. Chem. 2017, 2017, 6–29. (g) Molina, P.; Tárraga, A.; Alfonso, M. Dalton Trans. 2014, 43, 18–29.

(2) (a) Lu, S.; Strelets, V. V.; Ryan, M. F.; Pietro, W. J.; Lever, A. B. P. *Inorg. Chem.* **1996**, 35, 1013–1023. (b) Khobragade, D. A.; Mahamulkar, S. G.; Pospíšil, L.; Císarŏva, I.; Rulíšek, L.; Jahn, U. *Chem. - Eur. J.* **2012**, *18*, 12267–12277. (c) Shafir, A.; Power, M. P.; Whitener, G. D.; Arnold, J. Organometallics **2000**, *19*, 3978–3982.

(3) (a) Kraatz, H.-B.; Lusztyk, J.; Enright, G. D. Inorg. Chem. 1997, 36, 2400–2405. (b) Brosch, O.; Weyhermüller, T.; Metzler-Nolte, N. Inorg. Chem. 1999, 38, 5308–5313. (c) van Staveren, D. R.; Metzler-Nolte, N. Chem. Rev. 2004, 104, 5931–5985. (d) Moriuchi, T.; Hirao, T. Chem. Soc. Rev. 2004, 33, 294–301. (e) Heinze, K.; Beckmann, M. Eur. J. Inorg. Chem. 2005, 2005, 3450–3457. (f) Heinze, K.; Wild, U.; Beckmann, M. Eur. J. Inorg. Chem. 2007, 2007, 617–623. (g) Djaković, S.; Siebler, D.; Semenčić, M. C.; Heinze, K.; Rapić, V. Organometallics 2008, 27, 1447–1453. (h) Lataifeh, A.; Beheshti, S.; Kraatz, H.-B. Eur. J. Inorg. Chem. 2009, 2009, 3205–3218. (i) Semenčić, M. C.; Siebler, D.; Heinze, K.; Rapić, V. Organometallics 2009, 28, 2028–2037. (j) Förster, C.; Kovačević, M.; Barišić, L.; Rapić, V.; Heinze, K. Organometallics 2012, 31, 3683–3694.

(4) (a) Mansour, H.; El-Khouly, M. E.; Shaban, S. Y.; Ito, O.; Jux, N. J. Porphyrins Phthalocyanines 2007, 11, 719-728. (b) Poddutoori, P. K.; Sandanayaka, A. S. D.; Hasobe, T.; Ito, O.; van der Est, A. J. Phys. Chem. B 2010, 114, 14348-14357. (c) Bakar, M. A.; Sergeeva, N. N.; Juillard, T.; Senge, M. O. Organometallics 2011, 30, 3225-3228. (d) Suijkerbuijk, B. M. J. M.; Klein Gebbink, R. J. M. Angew. Chem. 2008, 120, 7506-7532. (e) Suijkerbuijk, B. M. J. M.; Klein Gebbink, R. J. M. Angew. Chem., Int. Ed. 2008, 47, 7396-7421. (f) Dammer, S. J.; Solntsev, P. V.; Sabin, J. R.; Nemykin, V. N. Inorg. Chem. 2013, 52, 9496-9510. (g) Vecchi, A.; Gatto, E.; Floris, B.; Conte, V.; Venanzi, M.; Nemykin, V. N.; Galloni, P. Chem. Commun. 2012, 48, 5145-5147. (h) 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. (i) Melomedov, J.; Ochsmann, J. R.; Meister, M.; Laquai, F.; Heinze, K. Eur. J. Inorg. Chem. 2014, 2014, 1984-2001. (j) Melomedov, J.; Ochsmann, J. R.; Meister, M.; Laquai, F.; Heinze, K. Eur. J. Inorg. Chem. 2014, 2014, 2902-2915.

(5) (a) Siemeling, U.; Vor der Brüggen, J.; Vorfeld, U.; Neumann, B.; Stammler, A.; Stammler, H.-G.; Brockhinke, A.; Plessow, R.; Zanello, P.; Laschi, F.; Fabrizi de Biani, F.; Fontani, M.; Steenken, S.; Stapper, M.; Gurzadyan, G. *Chem. - Eur. J.* **2003**, *9*, 2819–2833. (b) Heinze, K.; Hempel, K.; Beckmann, M. *Eur. J. Inorg. Chem.* **2006**, 2006, 2040– 2050.

(6) Huesmann, H.; Förster, C.; Siebler, D.; Gasi, T.; Heinze, K. Organometallics 2012, 31, 413-427.

(7) (a) Neidlinger, A.; Ksenofontov, V.; Heinze, K. Organometallics 2013, 32, 5955–5965. (b) Neidlinger, A.; Förster, C.; Heinze, K. Eur. J. Inorg. Chem. 2016, 2016, 1274–1286. (c) Neidlinger, A.; Förster, C.; Heinze, K. Eur. J. Org. Chem. 2016, 2016, 4852–4864.

(8) Turlington, M. D.; Pienkos, J. A.; Carlton, E. S.; Wroblewski, K. N.; Myers, A. R.; Trindle, C. O.; Altun, Z.; Rack, J. J.; Wagenknecht, P. S. *Inorg. Chem.* **2016**, *55*, 2200–2211.

(9) (a) Schwarzhans, K.-E.; Stolz, W. Monatsh. Chem. 1987, 118, 875-878. (b) Beer, P. D.; Chen, Z.; Goulden, A. J.; Graydon, A.; Stokes, S. E.; Wear, T. J. Chem. Soc., Chem. Commun. 1993, 1834-1836. (c) Casado, C. M.; González, B.; Cuadrado, I.; Alonso, B.; Morán, M.; Losada, J. Angew. Chem. 2000, 112, 2219-2222. (d) Casado, C. M.; González, B.; Cuadrado, I.; Alonso, B.; Morán, M.; Losada, J. Angew. Chem., Int. Ed. 2000, 39, 2135-2138. (e) Barlow, S. Inorg. Chem. 2001, 40, 7047-7053. (f) Laus, G.; Strasser, C. E.; Holzer, M.; Wurst, K.; Pürstinger, G.; Ongania, K.-H.; Rauch, M.; Bonn, G.; Schottenberger, H. Organometallics 2005, 24, 6085-6093. (g) Warratz, R.; Peters, G.; Studt, F.; Römer, R.-H.; Tuczek, F. Inorg. Chem. 2006, 45, 2531-2542. (g) Ornelas, C.; Ruiz, J.; Astruc, D. Organometallics 2009, 28, 2716-2723. (i) Astruc, D.; Ornelas, C.; Ruiz, J. Chem. - Eur. J. 2009, 15, 8936-8944. (j) Gilroy, J. B.; Patra, S. K.; Mitchels, J. M.; Winnik, M. A.; Manners, I. Angew. Chem. 2011, 123, 5973-5977. (k) Gilroy, J. B.; Patra, S. K.; Mitchels, J. M.; Winnik, M. A.; Manners, I. Angew. Chem., Int. Ed. 2011, 50, 5851-5855.

(10) Lauck, M.; Förster, C.; Gehrig, D.; Heinze, K. J. Organomet. Chem. 2017, 847, 33-40.

(11) (a) Knox, G. R.; Munro, J. D.; Pauson, P. L.; Smith, G. H.; Watts, W. E. J. Chem. Soc. **1961**, 4619–4624. (b) Pauson, P. L.; Knox, G. R. U.S. Patent 3278514, 1966. (c) Sheats, J. E.; Rausch, M. D. J. Org. Chem. **1970**, 35, 3245–3249. (d) Yamazaki, H.; Wakatsuki, Y. Bull. Chem. Soc. Jpn. **1979**, 52, 1239–1240. (e) Stahl, K.; Boche, G.; Massa, W. J. Organomet. Chem. **1984**, 277, 113–125. (f) Butovskii, M. V.; Englert, U.; Herberich, G. E.; Koelle, U. Eur. J. Inorg. Chem. **2005**, 2005, 971–980.

(12) (a) Wolter-Steingrube, A.; Bugenhagen, B. E. C.; Herrmann, C.; Heck, J. *Eur. J. Inorg. Chem.* **2014**, 2014, 4115–4122. (b) Wolter-Steingrube, A.; Cordsen, K.; Heck, J. *Eur. J. Inorg. Chem.* **2017**, 2017, 1314–1319.

(13) (a) Vanicek, S.; Kopacka, H.; Wurst, K.; Müller, T.; Schottenberger, H.; Bildstein, B. *Organometallics* **2014**, *33*, 1152– 1156. (b) Vanicek, S.; Kopacka, H.; Wurst, K.; Müller, T.; Hassenrück, C.; Winter, R.; Bildstein, B. *Organometallics* **2016**, *35*, 2101–2109.

(14) (a) Heinze, K.; Schlenker, M. Eur. J. Inorg. Chem. 2004, 2004, 2974-2988. (b) Chowdhury, S.; Schatte, G.; Kraatz, H.-B. Angew. Chem. 2006, 118, 7036-7038. (c) Chowdhury, S.; Schatte, G.; Kraatz, H. B. Angew. Chem., Int. Ed. 2006, 45, 6882-6884. (d) Heinze, K.; Siebler, D. Z. Z. Anorg. Allg. Chem. 2007, 633, 2223-2233. (e) Siebler, D.; Linseis, M.; Gasi, T.; Carrella, L. M.; Winter, R. F.; Förster, C.; Heinze, K. Chem. - Eur. J. 2011, 17, 4540-4551. (f) Siebler, D.; Förster, C.; Heinze, K. Dalton Trans. 2011, 40, 3558-3575. (g) Siebler, D.; Förster, C.; Gasi, T.; Heinze, K. Organometallics 2011, 30, 313-327. (h) Siebler, D.; Heinze, K. J. Organomet. Chem. 2016, 821, 19-24. (i) Acton, E. M.; Silverstein, R. M. J. Org. Chem. 1959, 24, 1487-1490. (15) (a) Förster, C.; Veit, P.; Ksenofontov, V.; Heinze, K. Chem. Commun. 2015, 51, 1514-1516. (b) Veit, P.; Förster, C.; Seibert, S.; Heinze, K. Z. Anorg. Allg. Chem. 2015, 641, 2083-2092. (c) Veit, P.; Prantl, E.; Förster, C.; Heinze, K. Organometallics 2016, 35, 249-257. (d) Kienz, T.; Förster, C.; Heinze, K. Organometallics 2016, 35, 3681-3691. (e) Hanauer, K.; Pham, M. T.; Förster, C.; Heinze, K. Eur. J. Inorg. Chem. 2017, 2017, 433-445.

- (17) (a) Camara, J. M.; Rauchfuss, T. B. Nat. Chem. 2011, 4, 26–30.
 (b) Hüttinger, K.; Förster, C.; Heinze, K. Chem. Commun. 2014, 50, 4285–4288.
- (18) Sethi, S.; Das, P. K.; Behera, N. J. Organomet. Chem. 2016, 824, 140-165.
- (19) Enk, B.; Kopacka, H.; Wurst, K.; Müller, T.; Bildstein, B. Organometallics 2009, 28, 5575–5586.
- (20) (a) Gray, H. B.; Sohn, Y. S.; Hendrickson, N. J. Am. Chem. Soc. 1971, 93, 3603–3612. (b) el Murr, N. E. J. Organomet. Chem. 1976, 112, 189–199.
- (21) Inyushin, S.; Shafir, A.; Sheats, J. E.; Minihane, M.; Whitten, C. E., Jr.; Arnold, J. *Polyhedron* **2004**, *23*, 2937–2942.
- (22) (a) Lee, J. H.; Gupta, S.; Jeong, W.; Rhee, Y. H.; Park, J. Angew. Chem. 2012, 124, 11009–11013. (b) Lee, J. H.; Gupta, S.; Jeong, W.;
- Rhee, Y. H.; Park, J. Angew. Chem., Int. Ed. 2012, 51, 10851-10855. (23) (a) Lucken, E. A. C.; Noack, K.; Williams, D. F. J. Chem. Soc. A
- **1967**, 148–154. (b) Benn, R.; Cibura, K.; Hofmann, P.; Jonas, K.; Rufinska, A. Organometallics **1985**, *4*, 2214–2221.
- (24) Kienz, T.; Förster, C.; Heinze, K. Organometallics 2014, 33, 4803-4812.
- (25) Gockel, S. N.; Hull, K. L. Org. Lett. 2015, 17, 3236-3239.
- (26) (a) McManis, G. E.; Nielson, R. M.; Weaver, M. J. Inorg. Chem.
- 1988, 27, 1827–1829. (b) Ribou, A.-C.; Launay, J.-P.; Sachtleben, M.
- L.; Li, H.; Spangler, C. W. Inorg. Chem. 1996, 35, 3735-3740.
- (27) Siebler, D.; Förster, C.; Heinze, K. Eur. J. Inorg. Chem. 2010, 2010, 3986–3992.
- (28) Hush, N. S. In Prog. Inorg. Chem.; Cotton, F. A., Ed.; John Wiley & Sons, Inc.: Hoboken, NJ, 1967; pp 391–444.
- (29) Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I. Organometallics **2010**, *29*, 2176–2179.
- (30) Krejcik, M.; Danek, M.; Hartl, F. J. Electroanal. Chem. Interfacial Electrochem. **1991**, 317, 179–187.
- (31) Neese, F. WIREs Comput. Mol. Sci. 2012, 2, 73-78.
- (32) Weigend, F.; Ahlrichs, R. Phys. Chem. Chem. Phys. 2005, 7, 3297-3305.
- (33) Weigend, F. Phys. Chem. Chem. Phys. 2006, 8, 1057-1065.
- (34) Neese, F.; Wennmohs, F.; Hansen, A.; Becker, U. Chem. Phys. 2009, 356, 98–109.
- (35) Izsák, R.; Neese, F. J. Chem. Phys. 2011, 135, 144105.
- (36) van Lenthe, E.; Baerends, E. J.; Snijders, J. G. J. Chem. Phys. 1993, 99, 4597-4610.
- (37) van Wüllen, C. J. J. Chem. Phys. 1998, 109, 392-399.
- (38) Kollmar, C. J. Chem. Phys. 1996, 105, 8204-8212.
- (39) Barone, V.; Cossi, M. J. Phys. Chem. A **1998**, 102, 1995–2001.
- (40) X-red; Stoe & Cie: Darmstadt, Germany, 2002.
- (41) Blessing, R. H. Acta Crystallogr., Sect. A: Found. Crystallogr. 1995, 51, 33–38.
- (42) Spek, A. L. Acta Crystallogr., Sect. D: Biol. Crystallogr. 2009, 65, 148–155.
- (43) Sheldrick, G. M. Acta Crystallogr., Sect. C: Struct. Chem. 2015, 71, 3–8.
- (44) Sheldrick, G. M. SHELXL-2014/7; University of Göttingen, Göttingen, Germany, 2014.
- (45) Rausch, M. D.; Ciappenelli, D. J. J. Organomet. Chem. 1967, 10, 127–136.