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Article

Indirectly Connected Bis(N-Heterocyclic Carbene) Bimetallic Complexes: Dependence of Metal−Metal Electronic Coupling on Linker Geometry

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Reaction of 1,1′,3,3′-tetra(*tert*-amyl)benzobis(imidazolylidene) (**1**) with 2 equiv of FcN_3 or FcNCS afforded bisadducts $[(FcN_3)_2(\mathbf{1})]$ (**2**) or $[(FcNCS)_2(\mathbf{1})]$ (**3**), respectively (Fc = ferrocene). To the best of our knowledge, these represent the first examples of complexes comprising metals indirectly connected to the carbene atoms of N-heterocyclic carbenes (NHCs) via their ligand sets. Cyclic and differential pulse voltammetry indicated that bis(NHC) **1** facilitated significant electronic coupling between ferrocene centers in **2** (ΔE = 140 mV), but not in **3**. We believe the different degrees of electronic interaction are due to geometric factors: the triazene linker in **2** is nearly coplanar with the bis(NHC) scaffold, whereas the isothiocyanate linker is orthogonal, as determined by X-ray crystallography. Employing this "indirect connection" strategy should enable tuning of metal−metal interactions by simple alteration the organic linker between NHC and ML_n fragments rather than complete redesign thereof. Given that NHC-reactive azide or isothiocyanate groups can be incorporated into both organic and inorganic compounds, this approach is envisioned to facilitate access to otherwise inaccessible catalysts and materials.

Introduction

Arduengo's preparation of a stable N-heterocyclic carbene (NHC) was a landmark achievement in modern synthetic chemistry.[1] Since then, organometallic complexes supported by NHCs have filled many roles, ranging from catalysts for polymerization and organic transformations,[2−12] to dopants in emissive materials,[13,14] to antibiotics[15,16] and chemotherapeutics.[17] Variants featuring two or more NHC units have recently emerged[18] and show promise in asymmetric[19−21] and tandem catalysis,[22,23] and in other applications. An important subtype of bis(NHC) comprises two NHC moieties connected via a π-conjugated linker, such as benzobis(imidazolylidene) (**I**),[24,25] triazolyldiylidene (**II**),[26] bitriazolylidene (**III**),[27] pyridylbis(imidazolylidene) (**IV**),[28−30] and

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pyridazinylbis(imidazolylidene) (**V**),[31,32] which enables electronic communication from one carbene-bound species to another (Figure 1). Bis(NHC) **I**, in particular, has been used to prepare phosphorescent bimetallic complexes,[33] luminescent organic[34,35] and conducting organometallic polymers,[25,36] polymeric catalysts,[37] and self-assembled materials.[38]

The utility of ditopic NHCs ultimately depends on how well they facilitate electronic coupling between multiple ligated metals.[39] Electrochemical interactions across bridging ligands can be qualitatively analyzed[40] by measuring the separation in metal-based redox potentials (ΔE) and subsequently classified according to the Robin–Day system.[41] Previously, we[33] and others[42] have shown that bimetallic complexes supported by **I** can be assigned to class I or II, depending on the identity of their ML_n units. For ML_n = [Ir(COD)Cl] (COD = 1,5-cyclooctadiene)[33] or [Fe(Cp)(CO)I] (Cp = cyclopentadienyl),[42] modest interactions (ΔE = 42–80 mV) were observed, identifying these complexes as class II. However, no interaction is measurable ($\Delta E \approx 0$) for ML_n = [Ir(ppy)$_2$] (ppy = 2-phenylpyridyl)[33] or [Ru(*p*-cymene)X$_2$] (X = Br or Cl),[42] revealing these complexes as class I systems.

Because the structures of the aforementioned bis(NHC)-supported bimetallic complexes are nearly identical, the various degrees in metal–metal electronic coupling likely arise from differences in how well the HOMO/LUMO energies of the ML_n fragments match those of the NHCs. For example, the interaction observed between [Ir(COD)Cl] fragments and not [Ir(ppy)$_2$] could be due to the fact that the former comprise Ir(I) centers, whose d-orbitals are higher in energy than those for Ir(III). One obvious drawback to this feature is that it requires judicious selection of the metal centers for maximum interaction. Thus, we sought to eliminate the dependence on ML_n identity and simultaneously enable tuning of metal–metal interactions in bis(NHC)-based systems.

To date, NHC-supported bimetallic complexes have featured bonds *directly* between the carbene functionalities and the metal centers (Figure 2). Such complexes are typically prepared via coordination of the ML_n units to a free bis(NHC) or transmetalation. Tuning the electronic coupling across this construct necessitates modifying the electronics of the bis(NHC) or ML_n fragments and therefore their identities. Because most applications require electronic interaction between *specific* ML_n units, changing these components may not always be possible. An alternative approach would be to modify one of the ligands to react with an NHC, whereby the resulting complex would comprise metals *indirectly* connected to the carbene atom of a bis(NHC) via short, conjugated linkers (–E–, Figure 2). Appropriately designed linkers would facilitate metal–NHC and metal–metal electronic coupling, despite increasing their spatial separation. Tuning of the electronic interactions between NHC-ligated metals could then be effected by changing the identity of the linkers while preserving the identities of both the bis(NHC) and ML_n components.

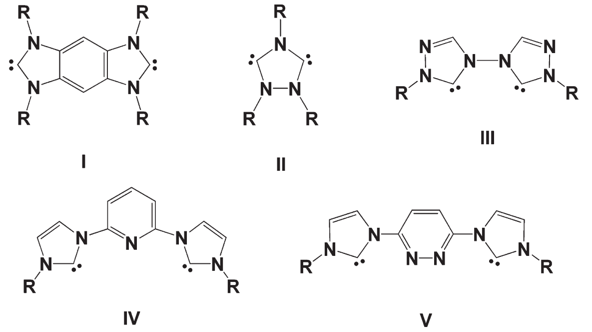

Figure 1. Ditopic NHCs linked by a π-conjugated system.

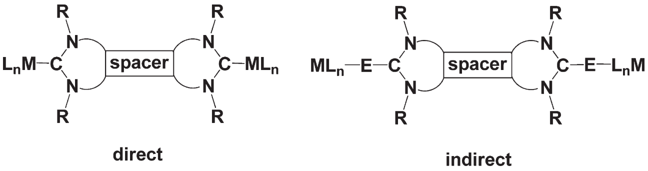

Figure 2. Two different configurations of bis(NHC)-supported bimetallic complexes.

In addition to their ubiquitous organometallic chemistry, NHCs can react with a variety of electrophilic functional groups.[43–47] We have found that azides couple with NHCs to afford acyclic triazenes that exhibit excellent electronic communication across the N_3 linker.[48,49] Isothiocyanates are isoelectronic with azides and have a similarly rich chemistry with NHCs.[43] Because ferrocene can be readily monofunctionalized[50] and is an excellent electrochemical handle, we pursued azido- and isothiocyanatoferrocene as suitable ML_n fragments for preparing indirect bimetallic complexes supported by bis(NHC)s.

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Experimental Section

Materials and Methods. [1,1′,3,3′-Tetra(*tert*-amyl)benzobis(imidazolium)][Cl]$_2$, [**1**H$_2$][Cl]$_2$, was prepared from 1,2,4,5-tetra(*tert*-amylamino)benzene as previously described.[24] Dichloromethane (CH_2Cl_2) and toluene were distilled from CaH_2. Tetrahydrofuran was distilled from Na/benzophenone. Solvents were degassed by three consecutive freeze−pump−thaw cycles. All other reagents were purchased from Aldrich or Acros and used without further purification. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded using a Varian 400 or 500 MHz spectrometer. Chemical shifts δ (in ppm) are referenced to tetramethylsilane using the protio solvent as an internal standard. For ^{1}H NMR: $CDCl_3$, 7.24 ppm; CD_2Cl_2, 5.32 ppm; C_6D_6, 7.15 ppm. For ^{13}C NMR: $CDCl_3$, 77.0 ppm; CD_2Cl_2, 53.8 ppm; C_6D_6, 128.0 ppm. Coupling constants are expressed in hertz (Hz). High-resolution mass spectra (HRMS) were obtained with a VG analytical ZAB2-E instrument (ESI or CI). Unless specified otherwise, all compound syntheses and manipulations were carried out under a nitrogen atmosphere using standard Schlenk or drybox techniques.

Electrochemistry. Electrochemical experiments were conducted on CH Instruments electrochemical workstations (series 660C and 700B) using a gastight, three-electrode cell under an atmosphere of dry nitrogen. The cell was equipped with platinum working and counter electrodes, as well as a silver wire quasi-reference electrode. Unless specified otherwise, measurements were performed on 1.0 mM solutions of analyte in dry CH_2Cl_2 or PhCN with 0.1 M [tetra-*n*-butylammonium][PF_6] as the electrolyte and decamethylferrocene (Fc*) as the internal standard. Differential pulse voltammetry measurements were performed using 50 mV pulse amplitudes and 2 mV data intervals. Chronoamperometry experiments were performed using a 25 μm diameter Au ultramicroelectrode as the working electrode, enabling independent determination of D_0 and n by plotting $i(t)/i_{ss}$ vs $t^{-1/2}$ and using the Cottrell equation.[51] Data deconvolution and fitting were performed using the Origin 8.0 software package. All potentials listed in the text were determined by cyclic voltammetry at 100 mV s^{-1} scan rates and referenced to a saturated calomel electrode (SCE) by shifting $(Fc^*)^{0/+}$ to −0.057 V (CH_2Cl_2) or −0.073 V (PhCN).[52]

1,2,4,5-Tetra(*tert*-amylamino)benzene. To [1,3-bis(2,6-diisopropylphenyl)imidazolium][Cl] (90 mg, 0.21 mmol), Pd(OAc)$_2$ (30 mg, 0.13 mmol), and NaO*t*Bu (35 mg, 0.36 mmol) was added 4 mL of toluene, and the resulting solution was then stirred at room temperature to generate an active coupling catalyst. After 10 min, this clear orange solution was added to a mixture of 1,2,4,5-tetrabromobenzene (1.95 g, 4.95 mmol), *tert*-amyl amine (1.82 g, 20.9 mmol), and NaO*t*Bu (2.33 g, 24.2 mmol) in 40 mL of toluene, and the reaction was then heated to 110 °C for 16 h, resulting in the gradual formation of a dark brown solution with a beige suspensate. This mixture was allowed to cool to room temperature and then filtered through Celite under a cone of nitrogen. The filtrate was concentrated to dryness under reduced pressure, and the solids were then taken up in a minimal amount of hexanes, filtered through Celite, and dried in vacuo to afford 1.5 g (3.6 mmol, 73% yield) of the desired product as a golden powder. Spectral data were consistent with reported literature values.[24]

1,1′,3,3′-Tetra(*tert*-amyl)benzobis(imidazolylidene) (1). To a suspension of [**1**H$_2$][Cl]$_2$ (94 mg, 0.18 mmol) in 2 mL of THF was slowly added lithium diisopropylamide (0.388 M, 0.46 mL, 0.18 mmol). The reaction was then stirred at room temperature, which resulted in a gradual change from a light beige suspension to a dark brown solution. After 15 min, the solvent was removed under reduced pressure to afford a light tan powder. These solids were extracted with 4 × 1 mL portions of toluene and then filtered through a 0.20 μm PTFE filter to remove LiCl and any unreacted starting material. Removal of solvent in vacuo afforded 74 mg (0.17 mmol, 94% yield) of the desired product as a light tan powder. Spectral data were consistent with reported literature values.[24] E_{pa} (PhCN) = +0.37 V (irreversible).

1-Bromoferrocene. To a solution of 1,1′-dibromoferrocene[53] (2.06 g, 6.0 mmol) in 30 mL of THF at −35 °C was dropwise added *n*-BuLi (2.2 M in THF, 2.7 mL, 6.0 mmol), maintaining the internal reaction temperature below −30 °C. After stirring the reaction for 1 h at −35 °C, water (3.0 mL, 0.17 mmol) was added dropwise, and the reaction was allowed to warm to room temperature over the course of 1 h. This mixture was extracted with 10 mL of Et_2O, and the organic layer was then collected, washed 3 × 50 mL of water, and dried with Na_2SO_4. Removal of solvent under reduced pressure afforded 1.5 g (5.7 mmol, 95% yield) of the desired product, which was contaminated with 10% Fc. This material was suitable for subsequent reactions and used without further purification. Spectral data were consistent with reported literature values.[50]

1-Azidoferrocene (FcN$_3$). To a mixture of 1-bromoferrocene (17 g, 90% purity, 58 mmol) and CuCl (7.4 g, 75 mmol) in 400 mL of degassed ethanol was added a solution of NaN_3 (8.2 g, 0.13 mol) in 40 mL of H_2O, and this suspension was then allowed to stir at room temperature. After 24 h, the reaction was filtered through Celite. The filtrate volume was then reduced by 80%, and 1 L of H_2O was added. This orange-brown suspension was then extracted with Et_2O (3 × 200 mL) and the combined organic fractions were washed with water (2 × 300 mL). After drying with Na_2SO_4, the solvent was removed in vacuo to afford 9.0 g (40 mmol, 69% yield) of the desired product as an orange solid. The material was found to retain the 10% Fc from the starting material as an inseparable impurity. ^{1}H NMR (400 MHz, C_6D_6): δ 4.10−3.95 (br m, 7H from product and 3H from Fc), 3.65 (t, J = 1.8, 2H). ^{13}C NMR (75 MHz, C_6D_6): δ 69.3, 68.2, 65.5, 60.9. $E_{1/2}$ (Fe$^{II/III}$) = +0.59 V (quasi-reversible). Spectral data were consistent with reported values.[54]

1-Isothiocyanatoferrocene (FcNCS). 1-Aminoferrocene[50] (0.28 g, 1.4 mmol) and thiocarbonylbisimidazole (0.27 g, tech. 90%, 1.5 mmol) were dissolved in 10 mL of CH_2Cl_2, and the resulting mixture was allowed to stir at room temperature. After 4 h, the reaction was concentrated to 5 mL under reduced pressure, and the resulting residue was then purified by column chromatography (Al_2O_3, 9:1 hexanes/EtOAc, R_f = 0.3) to afford 0.24 g (1.0 mmol, 71% yield) of the desired product as an orange solid after removal of the residual solvent. ^{1}H NMR (300 MHz, C_6D_6): δ 3.93 (t, J = 1.8, 2H), 3.89 (s, 5H), 3.53 (t, J = 1.8, 2H). ^{13}C NMR (75 MHz, C_6D_6): δ 132.8, 85.4, 70.1, 66.2, 65.9. $E_{1/2}$ (Fe$^{II/III}$) = +0.72 V (quasi-reversible). HRMS calcd for $C_{11}H_{10}NSFe$ [M$^+$]: 243.9883. Found: 243.9887. Spectral data were consistent with reported values.[55,56]

[(FcN$_3$)$_2$(1)] (2). To a solution of FcN$_3$ (290 mg, 1.3 mmol) in 2 mL of THF was added a solution of **1** (250 mg, 0.57 mmol) in 3 mL of THF, and the reaction was allowed to stir at room temperature, resulting in the gradual formation of a cloudy, dark red solution. After 16 h, the solvent was removed under reduced pressure. The resulting dark red residue was then washed with 4 × 3 mL portions of Et_2O and then dried in vacuo to afford 320 mg (0.36 mmol, 63% yield) of the desired product

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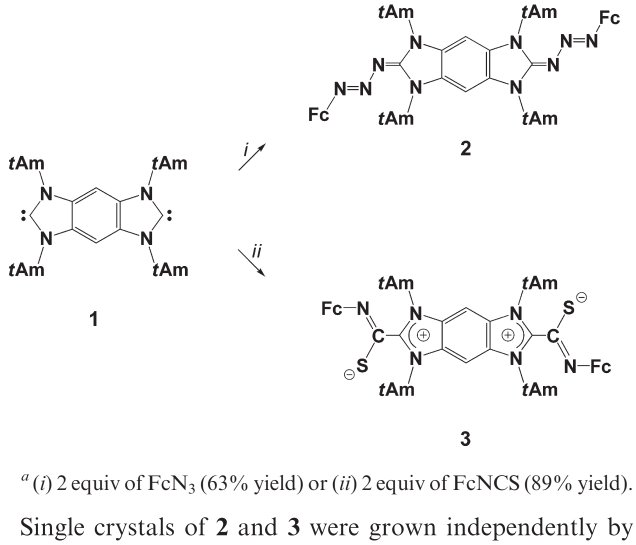
as a brick red solid. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.70 (s, 2H), 4.68 (t, J = 1.8, 4H), 4.28 (t, J = 1.8, 4H), 4.19 (s, 10H), 2.24 (q, J = 7.2, 8H), 1.80 (s, 24H), 0.76 (t, J = 7.2, 12H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 161.0, 127.9, 106.9, 98.9, 69.2, 67.2, 64.5, 63.0, 34.2, 29.2, 8.3. HRMS calcd for $C_{48}H_{64}N_{10}Fe_2$ [M$^+$]: 892.4014. Found: 892.4008. $E_{1/2}$ (Fe$^{II/III}$): +0.52 V (quasi-reversible), +0.66 V (quasi-reversible). CCDC: 729959.[57]

[(FcNCS)$_2$(1)] (3). To a solution of FcNCS (110 mg, 0.43 mmol) in 2 mL of THF was added a solution of **1** (95 mg, 0.22 mmol) in 2 mL of THF, and the reaction mixture was allowed to stir at room temperature, resulting in the gradual formation of a light orange suspension. After 16 h, the solvent was removed under reduced pressure. The resulting light orange residue was then washed with 4 × 3 mL portions of Et_2O and dried in vacuo to afford 180 mg (0.195 mmol, 89% yield) of the desired product as a light orange solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.31 (s, 2H), 5.07 (m, 4H), 4.24–4.22 (m, 14H), 2.40–2.06 (m, 32H), 0.94 (t, J = 7.6, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.8, 153.5, 128.2, 104.3, 103.0, 69.4, 68.4, 65.9, 65.5, 33.9, 28.0, 27.0, 9.0. HRMS calcd for $C_{50}H_{66}N_6Fe_2$ [M$^+$]: 926.3495. Found: 926.3397. $E_{1/2}$ (Fe$^{II/III}$): +0.32 V (quasi-reversible). D_0: $(8.0 \pm 0.3) \times 10^{-6}$ cm^2 s^{-1}, $n = 2.1 \pm 0.1$. CCDC: 729958.[57]

Results and Discussion

Addition of **1**[24] to 2 equiv of FcN_3 or FcNCS (Fc = ferrocene) in THF afforded the adduct [$(FcN_3)_2$(**1**)] (**2**) or [(FcNCS)$_2$(**1**)] (**3**) in 63% or 89% yield, respectively (Scheme 1). The diagnostic ^{13}C NMR signals for the 2,2′-positions shifted from δ = 230.2 ppm (C_6D_6) in **1** to 161.8 ppm (CD_2Cl_2) in **2** and 166.8 ppm ($CDCl_3$) in **3**. Whereas the 4,4′-protons in **2** resonated at nearly the same frequency as in **1** (δ = 7.70 vs 7.89 ppm in C_6D_6 and CD_2Cl_2, respectively), the same signals in **3** were significantly downfield (δ = 8.31 ppm, $CDCl_3$), suggestive of greater positive charge within the benzobis(imidazole) core. For example, the analogous protons in [**1**H_2][Cl]$_2$, featuring a formally dicationic benzobis(imidazolium), are observed at δ = 8.55 ppm (DMSO-d_6).[24]

Scheme 1. Syntheses of Adducts 2 and 3[a]



[a] (*i*) 2 equiv of FcN_3 (63% yield) or (*ii*) 2 equiv of FcNCS (89% yield).

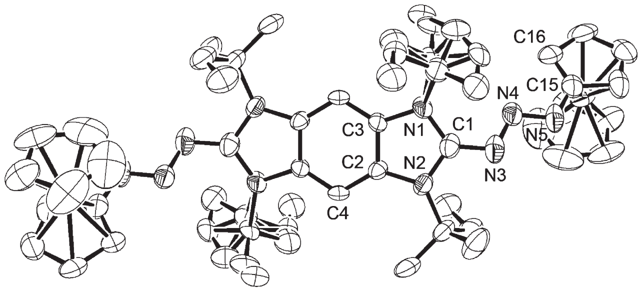


Figure 3. ORTEP diagram showing 50% probability thermal ellipsoids and selected atom labels for **2**. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): N1–C1, 1.381(4); N1–C3, 1.408(4); N2–C1, 1.372(5); N2–C2, 1.410(4); N3–C1, 1.326(5); N3–N4, 1.356(5); N4–N5, 1.269(4); N5–C15, 1.401(6); C2–C3, 1.398(5); C2–C4, 1.376(5); C1–N3–N4, 112.5(3); N1–C1–N2, 109.7(3); N4–N5–C15, 112.1(4); N3–N4–N5, 110.3(3); N1–C1–N3–N4, 31.3(6); N3–N4–N5–C15, 173.0(5); N4–N5–C15–C16, 174.8(6). The Fe–centroid distances for the functionalized and unfunctionalized Cp rings are 1.632 and 1.637 Å, respectively.

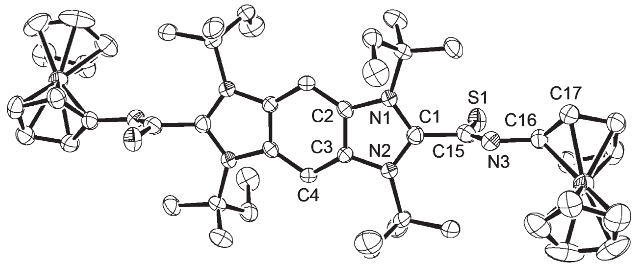


Figure 4. ORTEP diagram showing 50% probability thermal ellipsoids and selected atom labels for **3**. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): N1–C1, 1.361(5); N1–C2, 1.406(5); N2–C1, 1.355(5); N2–C3, 1.407(5); N3–C15, 1.282(5); N3–C16, 1.420(5); S1–C15, 1.716(5); C1–C15, 1.517(5); C2–C3, 1.405(5); C2–C4, 1.394(5); C3–C4, 1.372(5); N1–C1–N2, 110.4(3); C1–C15–N3, 116.3(4); C15–N3–C16, 118.6(4); S1–C15–N3, 135.3(3); N1–C1–C15–N3, 92.6(5); C17–C16–N3–C15, 126.5(6). The Fe–centroid distances for the functionalized and unfunctionalized Cp rings are 1.645 and 1.642 Å, respectively.

Single crystals of **2** and **3** were grown independently by vapor diffusion of hexanes into saturated CH_2Cl_2 solutions, and subsequent analysis by X-ray diffraction confirmed their structures (see Figures 3 and 4). The bis(NHC) cores of **2** or **3** did not show significant deviation from metric parameters observed in other benzobis(imidazolylidene)s.[24] However, the structural features of the FcN_3 units changed significantly upon incorporation into **2**. Most notably, the N3–N4–N5 angle of 110.3(3)° was substantially different from the near-linear value of 172.94(12)° observed in free FcN_3.[58] Although the N4–N5 and N5–C15 bond lengths of 1.269(4) and 1.401(6) Å in **2** differed only slightly from the corresponding values in free FcN_3 (1.2388(12) and 1.4326(13) Å, respectively),[58] the N3–N4 distance was markedly elongated to 1.356(5) Å from 1.1325(14) Å, indicative of a significant decrease in bond order. Additionally, the N4–N5–C15–C16 torsion angle of 174.8(6)° revealed greater triazene–Cp coplanarity than in free FcN_3 (157.82(16)°). Whereas the

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(57) X-ray crystal structure data were collected for **2** and **3** (CCDC 729959 and 729958, respectively) and deposited with the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK.

(58) Walla, P.; Arion, V. B.; Brinker, U. H. *J. Org. Chem.* **2006**, *71*, 3274–3277.

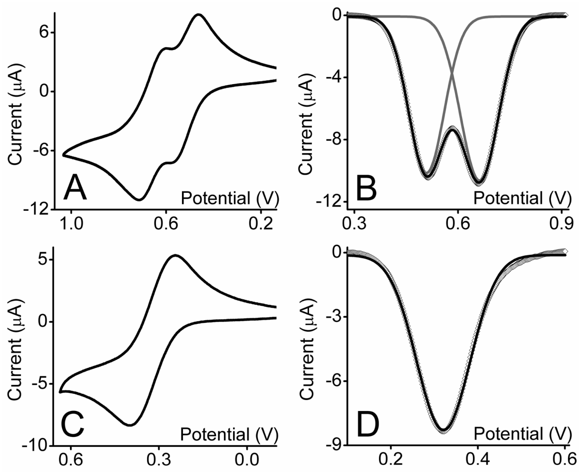

Figure 5. (A) CV of **2** (100 mV s^{-1} scan rate). (B) DPV of the oxidation processes in **2** (◇, 50 mV amplitude, 2 mV interval) showing deconvolution into two peaks (gray lines) and the fitted peak (black line). (C) CV of **3** (100 mV s^{-1} scan rate). (D) DPV of the oxidation process in **3** (◇, 50 mV amplitude, 2 mV interval) showing deconvolution into one peak (black line). All measurements were performed in CH_2Cl_2 solution containing 1 mM analyte and 0.1 M $[Bu_4N][PF_6]$ under an inert atmosphere. Potentials have been adjusted to SCE.

triazene linkers are nearly coplanar with the bis(NHC) unit in **2** (N1−C1−N3−N4 = 31.3(6)°), the isothiocyanate moieties in **3** are nearly perpendicular (N1−C1−C15−N3 = 92.6(5)°). Similarly, the C15−N3−C16−C17 angle of 126.5(6)° in **3** is much more acute than the analogous linker in **2** (N4−N5−C15−C16 = 174.3(6)°). Collectively, these results suggest that electronic coupling between metals across the triazene linkers in **2** should be feasible, whereas the perpendicular isothiocyanate linkers in **3** might interrupt conjugation and preclude any such interactions.

Having elucidated the structures of **2** and **3**, we sought to investigate the electronic interaction between the ferrocene centers therein via electroanalytical methods. Cyclic voltammetry (CV) of **2** in CH_2Cl_2 revealed two overlapping quasi-reversible oxidations at +0.52 and +0.66 V vs SCE (Figure 5A).[59] Because these values are similar to the oxidation potential for FcN_3 (+0.59 V),[56] we conclude that the electronic environment at the iron centers is not significantly perturbed upon adduct formation. Differential pulse voltammetry (DPV) of these oxidations clarified the two overlapping peaks, and the associated ΔE of these two redox processes was determined to be 140 mV (Figure 5B). Deconvolution of the DPV spectrum revealed that the two underlying peaks have nearly identical areas, and thus each peak corresponds to a one-electron oxidation.

The degree of metal−metal interaction in **2** is impressive given that the metals are *indirectly* connected to the carbene atoms of **1** via triazene linkers and are separated by greater than 16.5 Å. Other bimetallic complexes supported by bis(NHC) **I** exhibit much weaker interactions (ΔE = 42−80 mV) despite being having *direct* metal-NHC connections and metal-metal distances of less than 11 Å.[42] Comparable ferrocene−ferrocene interactions (ΔE = 90−126 mV) to **2** have been previously observed, albeit when linked by group 14 or imidazole moieties featuring significantly shorter iron−iron distances (< 9 Å).[50,60]

In contrast to **2**, only one quasi-reversible oxidation was observed in the CV of **3** in CH_2Cl_2 at +0.32 V (Figure 5C). This potential is significantly lower than that in free FcNCS (+0.72 V), suggesting that the iron centers in **3** are more electron rich. This observation supports the zwitterionic formulation of **3**, wherein the electron density of the FcNCS is increased, and complements the ^{1}H NMR data described above. Closer analysis of the oxidation of **3** by DPV and subsequent deconvolution confirmed the presence of only one peak (Figure 5D). Chronoamperometry enabled determination of the diffusion coefficient $D_0 = (8.0 \pm 0.3) \times 10^{-6}$ $cm^2\ s^{-1}$ and number of electrons $n = 2.1 \pm 0.1$ associated with this oxidation process. Thus, the two ferrocene-based oxidations in **3** are occurring at indistinguishable potentials.[61]

The absence of electronic coupling between the ferrocene centers in **3** is believed to be due to the near-orthogonality of the isothiocyanate linkers. In contrast, the triazene linkers in **2** are rotated only 31.3(6)° from the bis(NHC) plane, resulting in better overlap between the NHC moieties and the Cp rings and, as a result, the iron centers. Consequently, the electron density at the metals in **2** will be more sensitive to variations in the electron density within the connecting bis(NHC) unit than those in **3**. To support this notion, the oxidation of the first ferrocene unit in **2** was found to increase the energy of the second oxidation by 140 mV, but the oxidation of one ferrocene unit in **3** did not influence the other, presumably due to the interruption of conjugation.

Summary and Conclusions

Adapting NHC-azide[48,49] and -isothiocyanate[43] coupling chemistries for reaction with bis(NHC) **1** afforded adducts **2** and **3**, respectively. To the best of our knowledge, these are the first examples of complexes featuring metals indirectly connected to the carbene atoms of NHCs. Electrochemical analysis of **2** reveals significant electronic coupling (ΔE = 140 V) between ferrocene units (Fe···Fe > 16.5 Å), but **3** displays no measurable metal−metal interaction. We surmise that the geometry of the linker (i.e., coplanar with vs perpendicular to the NHC moieties) determines the degree of this interaction, whereby increasing coplanarity improves the metal−metal electronic coupling across the bis(NHC) scaffold. These geometry-dependent results build on previous observations that the match between HOMO/LUMO energies of the ML_n fragment and the bis(NHC) apparently influences the extent of interaction.[33,42] This novel "indirect connection" strategy should enable tuning of metal−metal interactions via alteration of the organic linkers between NHC and ML_n fragments while preserving their identities. Given the abundance of NHC-reactive functional groups and relative ease of incorporating them into various substrates,[43,46] tuning of the electronic coupling between metals across bis(NHC) scaffolds could be effected by simply using different linkers (e.g., replacing isothiocyanate with azide). This approach is envisioned to facilitate access to new

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(59) All potentials are reported relative to SCE.

(60) Jones, S. C.; Barlow, S.; O'Hare, D. *Chem.—Eur. J.* **2005**, *11*, 4473–4481.

(61) By indistinguishable, we do not mean identical, merely that the component processes cannot be resolved. Even for two identical, non-interacting redox processes, the statistical separation is 36 mV due to entropic factors. See ref 51, p 246.

bimetallic catalysts and organometallic materials, and allow optimization of existing systems.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra of FcN_3, FcNCS, and compounds **2** and **3**, electrochemical data for FcN_3, FcNCS, **1** and **3**, and X-ray crystallographic data, including tables and CIFs, for **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.