

Redox-Active N-Heterocyclic Carbenes: Design, Synthesis, and Evaluation of Their Electronic Properties

Evelyn L. Rosen, C. Daniel Varnado Jr., Andrew G. Tennyson, Dimitri M. Khramov, Justin W. Kamplain, Daphne H. Sung, Philip T. Cresswell, Vincent M. Lynch, and Christopher W. Bielawski*

Department of Chemistry and Biochemistry, The University of Texas at Austin, 1 University Station A5300, Austin, Texas 78712

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To investigate effects of redox-active functional groups on the coordination chemistry and electronic properties of N-heterocyclic carbenes (NHCs), we prepared a series of complexes comprising 1,3-diferrocenylimidazolylidene and -benzimidazolylidene (1 and 2, respectively), 1-ferrocenyl-3-methyl- and 1,3-diphenyl-5-ferrocenylbenzimidazolylidene (3 and 4, respectively), N, N'-diisobutyldiaminocarbene[3]ferrocenophane (FcDAC), and 1,3-dimesitylnaphthoquinoimidazolylidene (NqMes) ligands and coordinated [Ir(COD)Cl] (COD = 1,5-cyclooctadiene), $[Ir(CO)_2Cl]$, and $[M(CO)_5](M = Cr, Mo, W)$ units. The coordination chemistry of the aforementioned NHCs was investigated by X-ray crystallography, and their electronic properties were studied by NMR and IR spectroscopy, as well as electrochemistry. No significant variation in ν_{CO} was observed among metal carbonyl complexes supported by 2-4 and FcDAC, indicating that the number (one vs two) of redoxactive groups, the location (N atom vs backbone) of the redox-active group, and carbene ring identities (strained six-membered, nonaromatic vs five-membered, heteroaromatic) did not have a significant effect on ligand electron-donating ability. Because the shifts in $v_{\rm CO}$ upon oxidation of 1–3 and FcDAC were similar in magnitude but opposite in sign to NqMes, we conclude that the enhancement or attenuation of ligand donating is primarily Coulombic in origin (i.e., due to the molecule acquiring a positive or negative charge).

Introduction

Transition metal-based complexes containing redoxactive ligands have been used in diverse areas,¹ including catalysis,^{2,3} sensing,^{4,5} and optical materials.^{6,7} The appeal of ligands with redox-active functional groups stems from their abilities to change the electronic properties of a metal without the need for further synthetic modifications. In many cases, these ligands exhibit reversible redox processes and therefore enable "switchable" control of the electronic properties of metals by chemical redox agents or bulk electrolysis. Examples of previously reported metal complexes

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with redox-active ligands are shown in Figure 1.^{2,3,8,9} It is important to note that these complexes, as well as many others, contain neutral ligands that are capable of adopting cationic states as well as those that transition to anionic states. Additionally, there are ligand classes where *multiple* oxidation states can be accessed.^{10–13}

Oxidation or reduction of a substitutionally inert ligand can tune the electronic properties of a complex without changing the oxidation state of the metal or steric parameters.^{14–16} These effects can be quantified via ligation to a transition metal–carbonyl complex followed by measurement of the carbonyl stretching frequency (ν_{CO}) as a function of ligand oxidation state. For example, the complexes shown

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^{*}Corresponding author. E-mail: bielawski@cm.utexas.edu.

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Figure 1. Examples of metal complexes supported by redoxactive ligands.

in Figure 2 display shifts in carbonyl stretching energy $(\Delta \nu_{\rm CO})$ of up to 35 cm⁻¹.^{1,17-19} Although correlation between $\Delta \nu_{\rm CO}$ and the characteristics of transition metal com-plexes is not well-understood,^{20,21} ligands with a $\Delta \nu_{\rm CO}$ value in the mid to upper end of this range often result in a measurable influence. For example, a Re carbonyl complex containing a 1,1'-bis(diphenylphosphanyl)cobaltocene ligand shows $\Delta v_{\rm CO}$ values from -11 to -17 cm^{-1.11} As a result, nucleophilic attack on the carbonyl groups was enhanced 200-fold upon oxidation of the metal center.

Despite their unique properties, many classes of redoxactive ligands suffer from a number of practical and fundamental limitations. A large majority of redox-active ligands are either bi- or multidentate; monodentate analogues appear to be much less common.^{18,22,23} Although multidentate ligands can afford stable complexes, the range of possible geometries is often restricted. Other limitations include difficulties associated with metal coordination and/or an inability to impart significant electronic changes at a metal center upon changing the oxidation state of its redox-active ligand. Furthermore, some complexes exhibit irreversible electrochemical behavior, inhibiting widespread use in sensing and catalysis.^{24,25} The development of new classes of redox-active ligands could overcome these limitations. Over the past 50 years,²⁶⁻³¹ N-heterocyclic carbenes

(NHCs)³² and related compounds have become a versatile

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class of ligands for a broad range of transition metals.^{33–43} One reason for this attention is their similar coordination chemistry to phosphines.^{38,44} However, due to their strong electron-donating abilities and unique steric parameters, NHCs often afford complexes that are relatively stable toward ligand displacement and show significantly improved catalyst activities.45,46 Furthermore, NHCs can be synthesized from readily available starting materials⁴⁷ using extensive metal complexation methodology via free NHCs48 or transmetalation via Ag-NHC intermediates.⁴⁹ Despite these advantages, surprisingly few redox-active NHCs and metal complexes thereof have been reported in the literature (see Figure 3 for examples).^{50–59} Bildstein and co-workers reported^{60,61} the first NHC containing *N*-ferrocenyl groups (A and B), but the ability of these redox-active moieties to modulate electronic properties was not explored in detail. Although a [W(CO)₅] complex supported by 1-ferrocenyl-3-methylbenzimidazolylidene has been prepared, its electronic properties were not studied as a function of the ferrocene oxidation state. A variety of NHC-supported complexes bearing N-ferrocenyl substituents have been reported, but

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Figure 2. Selected examples of redox-switchable ligands. The absolute values of the change in metal-carbonyl stretching frequencies $(\Delta \nu_{CO})$ upon oxidation of the neutral ligands shown are indicated. R = Ph; M = Cr, Mo, W; Fc = ferrocene.



Figure 3. Examples of ferrocene-functionalized NHC-based ligands (n = 0, 1, or 2. X = donor group).

these efforts have primarily focused on either chiral modification for asymmetric catalysis or capitalizing on the *steric* parameters of ferrocene rather than its *electrochemical* properties (e.g., C), 56,58,59 with few exceptions (D in Figure 3, **FcDAC** in Figure 4). 62,63

We recently introduced two classes of NHCs containing complementary redox-active moieties. As shown in Figure 4, **FcDAC** is an N,N'-disubstituted diaminocarbene[3]ferrocenophane, whereas **NqMes** features a naphthoquinone annulated to 1,3-dimesitylimidazolylidene. The former can undergo oxidation (ferrocene \Leftrightarrow ferrocenium), whereas the latter can undergo reduction (quinone \Leftrightarrow semiquinone). Expanding the role of NHCs beyond simple phosphine analogues, we showed that both of these ligands can adopt multiple oxidation states and alter the electron density of coordinated metals.⁶³⁻⁶⁵

Herein we report efforts to further explore how the incorporation of redox-active functionalities into NHCs influences their coordination chemistry and electronic properties. As summarized in Figures 4 and 5, we sought to investigate the effects of various structural characteristics: (I) imidazolylidene vs benzimidazolylidene frameworks (e.g., 1 vs 2); (II) incorporating one vs two ferrocene units (e.g., 2 vs 3); (III) attaching a ferrocene unit to an NHC nitrogen atom vs to the backbone of a benzimidazolylidene (e.g., 3 vs 4); (IV) aromatic vs nonaromatic cyclic NHCs (e.g., 2 vs FcDAC); and (V) oxidizable vs reducible redox-active functionalities (e.g., 2 vs NqMes). Fortunately, methodology has already been developed by us and others for preparing metal complexes of 1,⁵⁷ FcDAC,⁶³ and NqMes.⁶⁴ To access the remaining complexes, we improved the overall syntheses for 2^{60} and 3^{61} and developed a route to 4. Given that the spectroscopic, structural, and electrochemical properties of

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D.; Bordner, J.; Samardjiev, I.; Holl, C. D.; Cavallo, L. *Organometallics* **2008**, *27*, 202–210. NHC-supported complexes of [Ir(COD)Cl] (COD = 1,5cyclooctadiene) have been extensively explored,⁶⁶⁻⁷⁰ analogous complexes containing 1–4, FcDAC, and NqMes were studied. Conversion of these complexes to $[Ir(CO)_2Cl]$ analogues was accomplished via treatment with CO(g), enabling more direct measurement of the metal electron density and ligand donicity via IR spectroscopy.^{66,67} We also pursued $[M(CO)_5]$ (M = Cr, Mo, W) complexes supported by 1–4, FcDAC, and NqMes, given that analogous complexes supported by NHCs have been studied extensively by X-ray crystallography and IR spectroscopy.^{61,71–85} Overall, we found that the NHC coordination chemistry and donating ability are most strongly influenced by the NHC backbone

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Figure 4. Complementary redox-active carbenes (R = isobutyl, Ph, or 2-Ad; 63,65 Mes = 2,4,6-trimethylphenyl).



Figure 5. Redox-active NHC-based ligands studied herein.

(i.e., imidazolylidene vs benzimidazolylidene vs nonaromatic). We also discovered that the tunability of these redox-active ligands is primarily determined by Coulombic factors: addition of a positive charge reduces NHC donating ability, whereas a negative charge enhances it. Surprisingly, these effects are largely independent of the location of the redox-active functionality as long as it is in reasonably close proximity to the carbene.

Results and Discussion

Synthesis of N-Heterocyclic Carbene Precursors. Palladium-catalyzed coupling of aminoferrocene⁶⁰ with 1,2-dibromobenzene (Scheme 1A), followed by cyclization with triethylorthoformate and HCl(aq), afforded 1,3-diferrocenylbenzimidazolium chloride, [2H][Cl], in excellent overall yield (91%). Alternatively, aminoferrocene underwent nucleophilic aromatic substitution with 2-fluoronitrobenzene (Scheme 1B), which, following subsequent formylative cyclization and alkylation, produced 1-ferrocenyl-3-methylbenzimidazolium iodide, [3H][I], in 85% overall yield. To access [4H][Cl], we prepared 1,2-dichloro-4-diazoniumbenzene tetrafluoroborate⁸⁶ as a suitable precursor. Reaction of this salt with ferrocene under acidic conditions afforded 1,2-dichloro-4-ferrocenylbenzene (Scheme 1C), which was then subjected to Pd-catalyzed aryl amination and cyclization to give 1,3-diphenyl-5-ferrocenylbenzimidazolium chloride, [4H][Cl], in 20% overall yield after three steps. The spectral properties for [2H][Cl] and [3H][I] obtained by these modified procedures were identical to literature values.^{60,61} Similarly, the ¹H and ¹³C NMR chemical shifts for the 2-position in [4H][Cl] (δ = 10.47 and 142.2 ppm, respectively, in DMSO- d_6) were consistent with analogous compounds reported in the literature.87-89

Synthesis of Iridium Complexes. With the precursors to NHCs 1-4, FcDAC, and NqMes in hand, we pursued their respective [Ir(COD)Cl] (COD = 1,5-cyclooctadiene) complexes, given the abundance of spectroscopic, structural, and

electrochemical information available.⁶⁶⁻⁷⁰ Additionally, the [Ir(COD)Cl] unit subsequently can be converted to $[Ir(CO)_2Cl]$ upon reaction with CO(g), enabling further interrogation of the complex's carbene ligand via IR spectroscopic analysis.^{66,67} Two routes were employed for the preparation of the desired [Ir(COD)Cl] complexes supported by 1-4, FcDAC, and NqMes, depending on the stability of the free NHC. For NHCs that dimerize or decompose in free form (i.e., 1, 3, and 4), deprotonation of the azolium was achieved with Ag₂O followed by transmetalation⁴⁹ to $[Ir(COD)(\mu-Cl)]_2$ (route A, Scheme 2, 99–100% overall yield). Alternatively, the free NHCs 2, FcDAC, and NqMes were successfully generated upon treatment with KO^tBu or NaHMDS and then coordinated⁴⁸ to iridium (route B, 56–100% overall yield). For (1-4)a and 6a, the ¹³C NMR chemical shifts for the 2-position were observed from $\delta =$ 182.2 to 194.6 ppm (Table S5), within the range observed for other NHC-supported [Ir(COD)Cl] complexes ($\delta = 179.6-208.2$ ppm).^{68,90-93} Similarly, the analogous signal observed in the ¹³C NMR spectrum of 5a ($\delta = 213.2$ ppm) was comparable to that observed in its rhodium congener (δ = 225.8 ppm),⁶³ but substantially different from (1-4)a and 6a. Because the carbene nucleus is strongly influenced by the ring system comprising it, apparent by the markedly distinct 13 C NMR chemical shift of **5a** vs (1–4)a and **6a**, we expected that the structural features of **5a** would be similarly unique.

Single crystals of (1-3)a and (5,6)a were obtained and analyzed by X-ray diffraction to obtain their respective structural parameters and enable comparison to crystallographically characterized analogues.⁹⁴ The iridium-NHC distances observed in these complexes (2.022(10) Å for 1a, 2.020(5) Å for 2a, 2.030(7) Å for 3a, 2.068(3) Å for 5a, 2.033(5) Å for 6a) were consistent with other NHC-supported [Ir(COD)Cl] complexes (1.99 to 2.091 Å). $^{67,68,95-100}$ In these complexes, the Ir–COD bond distances trans to the NHC range from 2.134 to 2.227 Å, whereas the distances for the Ir-COD bonds in the cis position range from 2.081 to 2.155 Å. The corresponding lengths in (1-3)a and 6a (2.189(4)-2.191(7) Å) agreed well with these structural features. Only 5a appeared to deviate significantly from the other [Ir(COD)Cl] complexes, judging by ¹³C NMR shifts and N–C–N angles $(121.9(3)^{\circ})$ for **5a** vs 102.8(8)-105.3(4)° for (1-3)a and 6a). In contrast, complexes (1-4)a and 6a shared highly conserved spectroscopic and structural features. We conclude that the distinct

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Scheme 1. Syntheses of Carbene Precursors^a



 a *i*Pr·HCl = 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride



<u>Route A</u>



Route A. For 1: (*i*) 0.5 equiv of Ag₂O, 1,2-dichloroethane, 15 h, 94%; (*ii*) CH₂Cl₂, 6 h, 99%. For 3: (*i*) CH₂Cl₂, 16 h, 91%; (*ii*) CH₂Cl₂, 12 h, 99%. For 4: (*i*) CH₂Cl₂, 2 h, 100%; (*ii*) THF, 7 h, 60 °C, 100%. Route B. For 2: (*i*+*ii*) KO'Bu, THF, 12 h, 60 °C, 100%. For FcDAC: (*i*) Na-HMDS, toluene, 20 min; (*ii*) 2 h, 71%. For NqMes: (*i*) NaHMDS, THF, 20 min; (*ii*) 12 h, 56%. Complexes (1–6)a were obtained by reaction with 0.5 equiv [Ir(COD)Cl]₂. The carbonylation reactions were performed by purging with CO(g) (see Experimental Section for details). Unless specified otherwise, all reactions were performed at ambient temperature. L = 1–4, FcDAC (5), or NqMes (6).

coordination chemistry of **5a** compared to (1-4)a and **6a** reflects the fundamental structural differences between the six-membered, nonaromatic, cyclic **FcDAC** and five-membered, heteroaromatic 1-4 and **NqMes**.

To gain additional insight into the electronic properties and donicity of 1–4, FcDAC, and NqMes via IR spectroscopic analysis, we prepared their metal carbonyl complexes. The [Ir(CO)₂Cl] complexes (1–6)b were obtained in excellent yields (88–100%) by bubbling 1 atm of CO(g) through CH₂Cl₂ solutions of the respective [Ir(COD)Cl] complexes (1–6)a (Scheme 2). Complexes (1–4)b and 6b exhibited a range of values (δ = 180.7–186.9 ppm, CDCl₃),⁹⁴ consistent with known NHC-supported [Ir(CO)₂Cl] complexes (δ = 178.0–202.3 ppm).⁶⁷ A [Rh(CO)₂Cl] complex of FcDAC has been previously reported,⁶³ whose ¹³C chemical shift ($\delta = 212.8$ ppm in CDCl₃) was comparable to that observed in **5b** ($\delta = 202.4$ ppm in CDCl₃).⁹⁴

Interestingly, the ¹³C NMR signals for the 2-position in (1-6)b (180.7–202.4 ppm) were upfield of their respective signals found in (1-6)a (182.2–213.2 ppm),⁹⁴ indicating greater shielding of the carbene nuclei in the [Ir(CO)₂Cl] vs [Ir(COD)Cl] complexes. Replacing COD with more electron-withdrawing, π -acidic carbonyl ligands should decrease the overall metal electron density. As such, a coordinated NHC should donate more electron density to the metal. As the donation increases, the metal–NHC interaction will shift from a simple metal–carbene σ interaction to one that features more multiple-bond character. This phenomenom effectively results in an increase in the shielding of the carbene nucleus and an upfield shift in the ¹³C NMR signal.

Crystal structures were obtained for (1-3)b and (5,6)b, thus enabling comparison to other [Ir(CO)₂Cl] complexes supported by NHCs (see Figures 6-10).94 The iridium-NHC bond lengths in (1-3)b and (5,6)b (2.121(3) Å for 1b, 2.080(4) Å for **2b**, 2.071(3) Å for **3b**, 2.121(3) for **5b**, 2.071(4) Å for **6b**)⁹⁴ agreed well with the values in analogous compounds (2.065-2.122 Å).^{67,69,97} Additionally, the metal-carbonyl distances in (1-3)b and (5,6)b (*trans*: 1.877(4)-1.900(5) Å; cis: 1.827(4) - 1.888(4) Å) were comparable to values observed in related [Ir(CO)₂Cl] complexes (1.854-1.915 and 1.86–1.912 Å for the *trans* and *cis* positions relative to the NHC, respectively). 67,69,97 In general, the metal–carbon bonds trans to the NHC will be longer than those cis due to the strong trans effect of NHCs. Whereas the N1-C1-N2 angles in (1-3)b and 6b varied minimally (105.5(3)- $106.1(3)^{\circ}$), the corresponding value in **5b** was substantially more obtuse $(122.4(2)^\circ)$. Similarly, the chemical shifts for (1-4)b and 6b were conserved, with the signal for 5bsignificantly downfield (202.4 ppm for 5b vs 180.7-186.9 ppm for (1-4)b and 6b).⁹⁴



Figure 6. ORTEP diagram showing 50% probability thermal ellipsoids and selected atom labels for 1b. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Ir-C1, 2.089(6); Ir-C2, 1.892(8); Ir-C3, 1.859(11); C2-O2, 1.143(10); C3-O3, 1.091(12); N1-C1-N2, 105.9(5).



Figure 7. ORTEP diagram showing 50% probability thermal ellipsoids and selected atom labels for **2b**. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Ir-C1, 2.080(4); Ir-C2, 1.894(4); Ir-C3, 1.870(8); C2-O2, 1.127(5); C3-O3, 1.131(8); N1-C1-N2, 106.1(3).

Synthesis of Group 6 Complexes. To gain additional insight into the electron-donating ability of these NHCs comprising redox-active moieties, we prepared a series of $[M(CO)_5]$ complexes⁷² supported by 1–4, FcDAC, and NqMes. Photolysis of the homoleptic carbonyl complexes $[M(CO)_6]$ (M = Cr, Mo, W) in THF afforded $[M(CO)_5(THF)]$,¹⁰¹ where the coordinated THF was readily displaced with free NHC (Scheme 3). Unfortunately, the FcDAC complexes were very unstable and only the tungsten congener 5e was obtained. In contrast, 2c–e and 6c–e were purified via column chromatography and were found to be bench stable for days. The range of ¹³C NMR chemical shifts for the 2-positions of





Figure 8. ORTEP diagram showing 50% probability thermal ellipsoids and selected atom labels for **3b**. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Ir-C2, 1.877(4); Ir-C3, 1.827(4); C2-O2, 1.141(5); C3-O3, 1.142(5).



Figure 9. ORTEP diagram showing 50% probability thermal ellipsoids and selected atom labels for **5b**. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Ir–Cl, 2.3632(8); Ir–Cl, 2.121(3); Ir–C2, 1.891(3); Ir–C3, 1.888(4); C2–O2, 1.136(4); C3–O3, 1.024(4); N1–C1–N2, 122.4(2); N1–C1–Ir–Cl, 78.71(18).



Figure 10. ORTEP diagram showing 50% probability thermal ellipsoids and selected atom labels for **6b**. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Ir-C1, 2.071(4); Ir-C2, 1.900(5); Ir-C3, 1.843(5); C2-O2, 1.120(5); C3-O3, 1.117(5); N1-C1-N2, 105.5(3).



Scheme 3. Synthesis (top) and Structures (bottom) of Various Group 6 Complexes^{*a*}

^{*a*} For these complexes, L = 2, FcDAC, or NqMes.

the NHCs in **2c**-e, **5e**, and **6c**-e (201.4–222.5 ppm, CDCl₃)⁹⁴ was consistent with those observed in previously reported group 6 [M(CO)₅] complexes bearing NHC ligands (188.3–226.1 ppm).^{61,71–85}

Single crystals of the $[M(CO)_5]$ complexes supported by 2 and NqMes were obtained and subjected to X-ray diffraction.⁹⁴ The Cr-NHC distances in 2c and 6c (2.158(3) and 2.125(3) Å, respectively)94 were consistent with those observed in NHC-supported [Cr(CO)₅] complexes (2.098-2.155 Å).^{71–77} Additionally, the *trans* (1.852(4) and 1.857(3) Å) and cis (1.895 and 1.894 Å) chromium-carbonyl bond lengths fell within the range of values observed in analogous complexes (1.840-1.868 and 1.888-1.901 Å for trans and cis, respectively). Although no related structures of $[Mo(CO)_5]$ complexes are known, the metric parameters of **2d** and **6d** (Mo-C_{NHC} = 2.328(2) and 2.257(5) Å; Mo-C_{trans} = 1.975(3) and 1.999(7) Å; Mo-C_{cis} = 2.049 and 2.035 Å; respectively)94 are similar to those of their tungsten congeners $2e(W-C_{NHC} = 2.299(4) \text{ Å}; W-C_{trans} = 1.978(4) \text{ Å}; W-C_{cis} =$ 2.032 Å; see Figure 11) and **6e** (W-C_{NHC} = 2.259(5) Å; $W-C_{trans} = 1.993(5)$ Å; $W-C_{cis} = 2.039$ Å; see Figure 12).

A variety of complexes featuring an NHC coordinated to $[W(CO)_5]$ have been structurally characterized, ^{61,72,73,75,78-85} whose range of values for $W-C_{NHC}$ (2.242–2.296 Å), $W-C_{trans}$ (1.935–2.010 Å), and $W-C_{cis}$ (2.016–2.045 Å) encompass those exhibited by **2e** and **6e**. Overall, the ¹³C NMR chemical shifts and structural features for **2c**–**e** and **6c**–**e** do not vary substantially beyond their different atomic radii of Cr vs Mo and W. Surprisingly, the key structural and NMR spectroscopic features of the aforementioned NHC-supported [M(CO)₅] complexes appear to be independent of the number or nature of the redox-active functionalities present on the NHC scaffold (e.g., two ferrocene units in **2** vs one naphthoquinone moiety in **NqMes**).

Although the ¹³C NMR and crystallographic analyses of the [Ir(CO)₂Cl] and [M(CO)₅] complexes of the imidazolylidene-based NHCs **1–4** and **NqMes** displayed highly conserved features, the Ir– C_{NHC} distance and N–C–N angle in **5b** were significantly longer and more obtuse, respectively, than those observed in (**1–4**)**b** or **6b**. On the basis of these results, we conclude that the intrinsic electronic properties of the carbene nuclei in the aforementioned complexes (as determined by their respective ¹³C NMR chemical shifts) as well as their coordination chemistry (as measured by their respective N1–C1–N2 angles and M–C_{carbene} distances)



Figure 11. ORTEP diagram showing 50% probability thermal ellipsoids and selected atom labels for **2e**. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): W-C1, 2.299(4); W-C2, 1.978(4); W-C3, 2.034(3); W-C4, 2.029(3); W-C5, 2.034(3); W-C6, 2.029(3); O2-C2, 1.164(5); O3-C3, 1.143(4); O4-C4, 1.157(4); O5-C5, 1.143(4); O6-C6, 1.157(4); N1-C1-N2, 103.9(3).



Figure 12. ORTEP diagram showing 50% probability thermal ellipsoids and selected atom labels for **6e**. Hydrogen atoms and solvent molecules have been omitted for clarity. Selected bond lengths (Å) and angles (deg): W–C1, 2.259(5); W–C2, 1.993(5); W–C3, 2.048(5); W–C4, 2.036(6); W–C5, 2.029(6); W–C6, 2.042(6); O2–C2, 1.153(6); O3–C3, 1.128(6); O4–C4, 1.147(7); O5–C5, 1.149(7); O6–C6, 1.143(6); N1–C1–N2, 103.8(4).

are highly sensitive to the features of the cyclic system that comprises it. Compared to the imidazolylidene-derived 1-4 and NqMes, we believe the steric effects of the *N*-mesityl substituents and the six-membered ring in FcDAC cause the carbene hybridization to adopt relatively greater sp-character, resulting in longer bonds to coordinated metals.^{102,103}

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Table 1. Carbonyl Stretching Energies for Complexes (1-6)b, 2c-e, and 6c-e^a



 ${}^{a}ML_{n} = [Ir(CO)_{2}Cl] \text{ for } (1-6)b, [Cr(CO)_{5}] \text{ for } 2c \text{ and } 6c, [Mo(CO)_{5}] \text{ for } 2d \text{ and } 6d, \text{ and } [W(CO)_{5}] \text{ for } 2e \text{ and } 6e.$ For the [M(CO)_{5}] complexes, the A₁⁽²⁾ mode is highest in energy and the A₁⁽¹⁾ mode is denoted with an asterisk (*). Measurements performed in CH₂Cl₂. b Measurements performed in CH₂Cl₃.

Infrared Spectroscopy. Metal-bound carbonyls are useful spectroscopic handles for measuring the electron density at ligated metal centers. Increasing the electron density on a metal will increase its π -back-bonding ability, thus reducing the C–O bond order and stretching frequency (ν_{CO}). For example, a more donating NHC will increase the electron density at the coordinated metal and thus lower the carbonyl stretching energy, allowing measurement of the ligand donicity. Many [Ir(CO)₂CI] complexes supported by NHCs have been prepared for this reason; therefore we sought to determine and compare the donating abilities of 1–4, FcDAC, and NgMes to known NHCs.^{67–70}

Complexes (1-6)b exhibited a range of trans (2058- 2072 cm^{-1}) and *cis* (1982–1988 cm⁻¹) carbonyl stretching energies (see Table 1) consistent with those observed in known NHC-supported [Ir(CO)₂Cl] complexes (*trans*: 2055–2072 cm⁻¹, *cis*: 1971–1989 cm⁻¹).^{67,69,93,97} Some remarkable trends become apparent upon examination of the average values exhibited by (1-6)b ($v_{av} = 2020.0-$ 2030.0 cm^{-1}). The naphthoquinone-annulated NqMes was less electron donating than the other imidazolylidene-based NHCs (1-4), suggesting that the quinone moiety decreased the donating ability of its fused carbene. Imidazolylidene 1 was more donating than benzimidazolylidenes 2-4, further evidence that annulation decreases the electron density at the carbene. Given the narrow range of v_{av} values for 2–4, we conclude that the electron-donating ability of the benzimidazolylidene scaffold does not significantly vary with the number of redox-active groups present in the ligand or their position relative to the carbene atom. Because the carbonyl stretching energies for 1b and 5b are similar, no measurable alteration in carbene electron density is observable between



Figure 13. Representative NHCs with TEP values similar to 1–4, FcDAC, and NqMes.

the five-membered aromatic and strained, six-membered nonaromatic systems. Whereas the cyclic nature of **FcDAC** has a significant impact on *structural* features, it does not appear to greatly affect its ligand donating ability.

To gain more insight into the donating abilities of the aforementioned NHCs, efforts turned toward evaluating their Tolman electronic parameters (TEPs), which can be derived from the metal-carbonyl stretching energies.^{104,105} For [Ir(CO)₂Cl] complexes, Nolan enhanced an equation developed by Crabtree for determining the TEP from the observed ν_{av} , whereby TEP = 0.847 × ν_{av} + 336 cm⁻¹.^{67,70} The TEPs calculated for 1-4, FcDAC, and NqMes $(2046.9-2055.4 \text{ cm}^{-1})$ were consistent with the range observed in other NHC-supported [Ir(CO)2Cl] complexes $(2049.5-2057.3 \text{ cm}^{-1}; \text{ see Figure 13 for representative ex-})$ amples).⁶⁷ For comparison, the TEP for FcDAC compares well to that for IAd (2048.6 vs 2049.5 cm^{-1} , respectively) and NqMes to IPrCl (2055.4 vs 2055.1 cm⁻¹, respectively). Similarly, there are other reported NHCs that exhibit comparable TEPs to the 2046.9 cm⁻¹ measured for 1 (IAd, 2049.5 cm^{-1}), 2050.3 cm⁻¹ for **2** (**ItBu**, 2050.1 cm⁻¹), and 2052.4 and 2052.9 cm⁻¹ for **4** and **3** (SIPr, 2052.2 cm⁻¹). When viewed in the context of previously reported NHCs (i.e., not including 2-4 or 6), 1 and FcDAC were among the most electron-donating, NqMes was among the least, and **2–4** were intermediate in donicity.

Determination of ligand TEP values from group 6 $[M(CO)_5]$ carbonyl stretching energies has not vet been detailed in the literature. Nonetheless, examination of the carbonyl stretching energies in 2c-e, 5e, and 6c-e in comparison to previously reported analogues should enable qualitative evaluation of the donating abilities of 1-4, FcDAC, and NqMes. Prior to this examination, a discussion regarding the number and symmetry of IR-active carbonyl stretching modes is helpful. In an idealized geometry, the $C_{4\nu}$ [M(CO)₅(NHC)] scaffold has two sets of symmetry-inequivalent CO groups in the equatorial (1) and axial (2) positions.¹⁰⁶ For CO_{ax} , the vibrational mode has A_1 symmetry and is IR and Raman active.¹⁰⁷ For CO_{eq} , the irreducible representation for the CO stretching modes is A1, B1, and E, where B₁ is not IR active. To distinguish between the equatorial and axial carbonyls, we will use superscripted (1) and (2) after the relevant irreducible representation.

Because NHCs have a strong σ -donating effect, the CO *trans* to the NHC in the axial position will have the weakest

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Figure 14. Representative cyclic voltammograms (100 mV s⁻¹ scan rate) of Fc* in CH₂Cl₂ with 0.1 M [Bu₄N][PF₆] and 1 mM (A) **2a**, (B) **6a**, (C) **2b**, and (D) **6b**. Features are labeled according to metal oxidation (Fe^{II/III} or Ir^{I/II}), quinone reduction ($Q^{0/-}$), or decamethylferrocene internal standard (Fc*).

Table 2. Electrochemical Properties of (1-6)a and $(1-6)b^a$



[Ir(COD)Cl]			[Ir(CO) ₂ Cl]	
	$E_{1/2}(V)$		$E_{1/2}$ (V)	$\Delta E (\mathrm{mV})^b$
1a 2a 3a 4a 5a 6a	$\begin{array}{c} 0.72, 0.58\\ 0.75, 0.62\\ 0.62\\ 0.53\\ 1.02, 0.76\\ 0.95, -0.66\end{array}$	1b 2b 3b 4b 5b 6b	$\begin{array}{c} 0.78, 0.68 (\mathrm{sh}) \\ 0.79, 0.70 (\mathrm{sh}) \\ 0.71 \\ 0.57 \\ 0.94^c \\ -0.54^c \end{array}$	60, 100 (80) 40, 80 (60) 90 40 180 120

 ${}^{a}ML_{n} = [Ir(COD)Cl]$ for (1–6)a and [Ir(CO)₂Cl] for (1–6)b. Measurements were performed in CH₂Cl₂ containing 0.1 M [Bu₄N][PF₆] at 100 mV s⁻¹ scan rate. ${}^{b}\Delta E = E_{1/2}(IrCO) - E_{1/2}(IrCOD)$. Where two oxidations are present, the averaged value is presented in parentheses. c The iridium-centered oxidation could not be observed within the solvent window.

 π -back-bonding interaction with the metal; thus the $A_1^{(2)}$ mode will be highest in energy.¹⁰⁶ However, the relative ordering of the $A_1^{(1)} + E^{(1)}$ modes varies depending on the nature of the complex, where the $A_1^{(1)}$ mode can vary in energy greatly or be underneath the $E^{(1)}$ band. Correct identification can be achieved by comparing the relative intensities of the bands (in general, the $E^{(1)}$ mode is signifi-

Table 3. Electrochemical Properties of 2c-e and 6c-e^a



$E_{1/2}$ (V)		$E_{1/2}$ (V)
0.67 0.72	6c 6d	0.98, -0.65 1.15, -0.68
0.69	6e	1.15, -0.62
	$\frac{E_{1/2} (\mathrm{V})}{\begin{array}{c} 0.67 \\ 0.72 \\ 0.69 \end{array}}$	E1/2 (V) 0.67 6c 0.72 6d 0.69 6e

 ${}^{a}ML_{n} = [Cr(CO)_{5}]$ for **2c** and **6c**, $[Mo(CO)_{5}]$ for **2d** and **6d**, and $[W(CO)_{5}]$ for **2e** and **6e**. Measurements performed in CH₂Cl₂ containing 0.1 M $[Bu_{4}N][PF_{6}]$ at 100 mV s⁻¹ scan rate.

cantly more intense that the $A_1^{(1)}$ mode).¹⁰⁸⁻¹¹⁰ For the $[M(CO)_5]$ (M = Cr, Mo, W) complexes supported by 2 and NqMes, the $A_1^{(2)}$ stretching energies (2052–2063 cm⁻¹, Table 1) coincided with the range of values observed in other NHC-supported analogues (2048–2064.1 cm⁻¹).^{61,71–85} The $A_1^{(1)}$ modes for the pentacarbonyls supported by 2 (2c, 1887 cm⁻¹; 2d, 1889 cm⁻¹; 2e, 1883 cm⁻¹) and NqMes (6c, 1975 cm⁻¹; 6d, 1980 cm⁻¹; 6e, 1976 cm⁻¹) were consistent with other reported values (1882–1980 cm⁻¹). Similarly, the CO stretching energies for the E⁽¹⁾ modes in 2c–e and 6c–e (1919–1933 cm⁻¹) agreed well with those observed in other NHC-supported [M(CO)₅] complexes (1900–1966 cm⁻¹). These results suggest that either an oxidizable or a reducible functional group could be incorporated into an NHC without significantly altering its fundamental electron-donating ability to [M(CO)₅] fragments comprising group 6 metals.

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Figure 15. Normalized IR difference spectra at 60 s intervals showing the shift in metal carbonyl stretching energies upon oxidation $(E_{app} = +1.2 \text{ V})$ of 2b (A) and 2e (C) or reduction $(E_{app} = -1.2 \text{ V})$ of 6b (B) and 6e (D) in CH₂Cl₂ containing 10 mM analyte and 0.1 M [Bu₄N][PF₆].

Electrochemistry. Complexes **1a** and **2a**, comprising N,N'diferrocenyl NHCs, exhibited two sets of quasi-reversible peaks (**1a**, +0.58 and +0.72 V; **2a**, +0.62 and +0.75 V; see Figures S10, and 14A, respectively, as well as Table 2) in CH₂Cl₂,⁹⁴ which were attributed to the oxidation of their first and second ferrocene units, respectively. The potential separation between the two couples of 140 mV for **1a** and 130 mV for **2a** is consistent with other reported diferrocenylfunctionalized NHCs.^{57,60,61,82} As expected, complexes **3a** and **4a**, supported by monoferrocenyl-functionalized NHCs, exhibited only one ferrocene-based oxidation at +0.62 and +0.53 V, respectively.⁹⁴ None of the iridium-based oxidations could be observed within the solvent window for (**1**-**4**)**a**.

In contrast, 5a and 6a exhibit quasi-reversible redox processes at +1.02 and +0.95 V (see Figures S13 and 14B, as well as Table 2)⁹⁴ that were attributed to $Ir^{I/II}$ couples, values that are consistent with other NHC-supported [Ir(COD)CI] complexes.^{111,112} A reduction feature was also observed in 6a at -0.66 V, similar to the quinone reduction observed in the previously reported [Rh(COD)Cl] analogue.⁶⁴ The ferrocene oxidation in **5a** occurs at +0.76 V, higher than the first oxidations in (1-4)a, reflecting the influence of the strained six-membered ring and the inability of the orthogonal nitrogen lone pairs to donate electron density into the Cp rings to which they are linked. Additionally, the 90 mV difference between $Fc^{0/+}$ potentials in **3a** vs 4a revealed that an N-bound ferrocene was more electron deficient than a C-bound ferrocene. However, because the $Fc^{0/+}$ couple in **3a** occurs at an identical potential to the first oxidation observed in 2a (+0.62 V), we conclude that the overall electron density does not depend on the number of ferrocene units within the NHCs. Furthermore,

the small separation between ferrocene oxidations in 1a and 2a (<40 mV) suggests that the imidazolylideneand benzimidazolylidene-based NHC scaffolds exert similar influences on the electronic environment at the iron centers.

The $Fe^{II/III}$ couples in (1-4)b exhibited anodic shifts of 40-100 mV relative to those observed in (1-4)a, reflecting the greater electron-withdrawing character of [Ir(CO)₂Cl] compared to [Ir(COD)Cl] and agreeing with the ¹³C NMR results. Similarly, the ferrocene oxidation in 5b was observed at +0.94 V, a potential 180 mV higher than that observed for the analogous oxidation in 5a. A greater shift for 5 than 1-4 is expected, given that the ferrocene unit in FcDAC is linked to the NHC at two positions instead of one. The quinone reduction in **6b** at -0.54 V was 120 mV higher than in 6a, consistent with the reduced electron density at the metal.⁶⁴ Given the large shift in potentials for the NHC-based oxidations in 5b and 6b, it was not surprising that the Ir^{I/II} couples were shifted beyond the solvent window and could not be observed. These latter results were consistent with the electrochemical properties of related NHC-supported $[M(CO)_2Cl]$ complexes (M = Rh and Ir).66,68,111

As summarized in Table 3, a relatively narrow range of $M^{0/+}$ oxidation potentials was observed for the $[M(CO)_5]$ complexes supported by 2 (Cr: +0.67 V; Mo: +0.72 V; W: +0.69 V).⁹⁴ These values indicate that the electronic interactions between 2 and the $[M(CO)_5]$ fragments are nearly indistinguishable, presumably due to equivalent metal–NHC interactions. Overall, the range of metal-centered oxidation potentials observed in the $[M(CO)_5]$ complexes supported by 2 and NqMes (from +0.67 to +1.15 V) were consistent with values measured in analogous complexes supported by other NHCs (+0.43 to +1.2 V).^{61,82} However, the $M^{0/+}$ couple in 6c (+0.98 V) occurs at a potential substantially lower than its Mo and W congeners (+1.15 V for 6d and 6e, respectively), in contrast to 2.⁹⁴ In general, as the NHC and metal orbital energies converge,

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	[Ir(CO) ₂ Cl]					[M(CO) ₅]		
	$\nu_{\rm CO}^*$	$\nu_{\rm av}*$	TEP*	$\Delta \nu_{\rm av}$	ΔΤΕΡ		$\nu_{\rm CO}^*$	$\Delta \nu A_1^{(1)}$
1b	2072, 1998	2035.0	2059.6	+15	+12.7	2c	2058, 1980 [†] , 1944	+93
2b	2076, 1998	2037.0	2061.3	+13	+11.0	2d	2058, 1980 [†] , 1944	+91
3b	2080, 2000	2040.0	2063.9	+13	+11.0	2e	2064, 1976 [†] , 1936	+93
4b ^b	_	_	_	_	_	6c	2048, 1916, 1882 [†]	-93
5b	2074, 1996	2035.0	2059.6	+13	+11.0	6d	2058, 1920, 1878 [†]	-102
6b	2060, 1975	2017.5	2044.8	-12.5	-10.6	6e	2056, 1914, 1878 [†]	-98

^{*a*}ML_n = [Ir(CO)₂Cl] for (1–6)b, [Cr(CO)₅] for 2c and 6c, [Mo(CO)₅] for 2d and 6d, and [W(CO)₅] for 2e and 6e. Measurements were performed in CH₂Cl₂ containing 0.1 M [Bu₄N][PF₆] under the conditions specified in Figure 15. ^{*b*} This compound was found to decompose under the bulk electrolysis described above, thus its spectroelectrochemical properties could not be determined. Values with an asterisk (*) correspond to the in situ oxidized or reduced complex. The A₁⁽¹⁾ mode is denoted with a cross (†). Values of $\Delta \nu_{av}$, ΔTEP and $\Delta \nu A_1^{(1)}$ were obtained by subtracting the values observed for the neutral complexes from those for the oxidized/reduced complexes.

the extent of their interaction should increase. For a poorly matched combination, the NHC should "experience" the influence from a generic n+ ion (which will not depend on the metal identity). Conversely, well-matched combinations should exhibit more significant interactions and greater dependence on metal identity and associated properties (e.g., electronegativity, electron affinity, ionization potential). Given that the metal oxidation potentials for **6d**,**e** are higher than **6c** and that Mo/W d-orbital energies are lower than Cr, we conclude that **NqMes** is a better energy match with $[Cr(CO)_5]$, whereby the greater interaction increases electron donation to the metal and thus reduces its oxidation potential.

Interestingly, the quinone reductions in 6c-e occurred at higher energies (from -0.62 to -0.68 V) than the corresponding [Ir(CO)₂Cl] complex **6b** (-0.54 V), consistent with a greater NHC-metal interaction in the latter case. Because the NHC ligand is conserved in these complexes, we conclude that the observed variation is due to the difference in d-orbital energy between the mid-transition group 6 metals and the late-transition group 9 iridium, as judged by the relative electron affinities of these metals (Cr: 64.3 kJ mol^{-1} ; Mo: 71.9 kJ mol^{-1} ; W: 78.6 kJ mol^{-1} ; Ir: 151 kJ mol^{-1}).^{113–115}

Spectroelectrochemistry. A powerful method for determining the electronic influence of a redox-active substituent within an NHC at a coordinated metal is IR spectroelectrochemistry.¹⁷⁻¹⁹ Oxidation of the ferrocene units in 1-3 and FcDAC should decrease the donating abilities of the NHCs, thus lowering the electron density at the coordinated metal carbonyls and result in an increased v_{av} . Alternatively, reducing the quinone in complexes supported by NgMes should increase the carbene's electron-donating ability, affording a more electron rich [Ir(CO)₂Cl] or [M(CO)₅] fragment with a concomitant decrease in carbonyl stretching energies. To explore the relationship between oxidation state of the redox-active functionality and donicity of their respective NHCs, we sought to measure the shift in the average ν_{CO} of [Ir(CO)₂Cl] and [M(CO)₅] complexes upon oxidation of the ferrocene units in 1-3 and reduction of NgMes.

Surprisingly, oxidation of (1-3)b and 5b resulted in nearly identical shifts in v_{av} (**1b**: +15 cm⁻¹; **2b**: +13 cm⁻¹; **3b**: +13 cm⁻¹; **5b**: +13 cm⁻¹; for **2b**, see Figure 15A; for the others, see Figures S24–S26; key features are summarized in Table 4)⁹⁴ that corresponded to ΔTEP values ranging from +11.0 to +12.7 cm⁻¹. These results suggest that the scaffold structure (i.e., imidazolylidene vs benzimidazolylidene vs nonaromatic) or the number of ferrocene units (i.e., one vs two) does not obfuscate the redox tunability of NHC donicity when a redox-active group is directly connected via an N substituent. Closely paralleling the ferrocene oxidation measurements, reduction of **6b** afforded a Δv_{av} of -12.5 cm⁻¹, resulting in a decrease of the TEP by 10.6 cm^{-1} (see Figure 15B). Because the values of Δv_{av} and ΔTEP for **6b** are nearly identical in magnitude but opposite in sign to those observed for (1-3)b and 5b, we conclude that the redox tunability of these ligands does not strongly depend on the specific chemical identity of the redox-active functional group. Rather, the overall charge imparted to the molecule upon redox change appears to be the origin of the ligand's enhanced or attenuated donating ability.

Similar shifts were observed in the $A_1^{(1)}$ carbonyl stretching modes for the $[M(CO)_5]$ complexes of **2** and **NqMes**, albeit with dramatically greater magnitude. Oxidation of **2c**–**e** increased the $\nu A_1^{(1)}$ energies 91–93 cm⁻¹ (for **2e**, see Figure 15C; for **2c,d**, see Figures S27–S28; also see Table 4),⁹⁴ consistent with reduced metal electron density and consistent with shifts observed in complexes supported by ferrocene-functionalized phosphines.^{17–19} Conversely, the $\Delta\nu$ $A_1^{(1)}$ values for **6c–e** ranged from –93 to –102 cm⁻¹ (for **6e**, see Figure 15D; for **6c,d**, see Figures S29–S30),⁹⁴ indicative of enhanced donicity upon reduction of **NqMes**. As observed with the [Ir(CO)₂Cl] complexes, the magnitude of $\Delta\nu$ $A_1^{(1)}$ was nearly identical for **2** vs **NqMes**, albeit with opposite signs (positive for oxidation, negative for reduction).

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Overall, the modulation of the ligand donating abilities of 1-3, FcDAC, and NqMes upon electrochemical switching of the redox-active units (by oxidation or reduction) was largely independent of their molecular characteristics, contrary to expectations. No significant dependence on the presence (FcDAC vs 1-3 and NqMes) or extent of an aromatic system (1 vs 2) was observed. Oxidation of one or two of the ferrocene units (2 vs 3) afforded the same change in NHC electron-donating ability, indicating that a second oxidation had marginal impact beyond the first. Furthermore, the magnitude of the enhanced donicity observed for NqMes upon reduction matched the attenuation observed for the ferrocene-functionalized NHCs upon oxidation. Collectively, these results suggest that the changes in electrondonating ability of 1-3, FcDAC, and NqMes are largely due to Coulombic effects, where removal or addition of an electron alters the overall molecular charge.

Conclusions

In sum, we have developed families of [Ir(COD)Cl], [Ir(CO)₂Cl], and [M(CO)₅] (M = Cr, Mo, W) complexes supported by NHCs comprising redox-active ferrocene (1–4 and **FcDAC**) and quinone (**NqMes**) functionalities. Although the ¹³C NMR spectroscopic and structural features of these complexes were consistent with previously reported analogues, those comprising **FcDAC** were notably distinct from the other redox-active NHCs studied (1–4 or **NqMes**), presumably reflecting the greater sp-hybridization of the carbene nucleus in the former.

Measurement of the electron density at the metal, and thus the donating ability of the NHCs, via IR spectroscopic analysis of carbonyl stretching energies revealed different behavior than the X-ray diffraction or ¹³C NMR spectroscopic results. Complexes 1b and 6b exhibited the lowest and highest v_{av} values, respectively, demonstrating that the NHC backbone (imidazolylidene vs benzimidazolylidene vs naphthoquinone) had a significant effect on the donating ability of the respective carbenes. However, the average carbonyl stretching energies for complexes (2-5)b were similar (differences of no more than 3 cm^{-1} were observed), suggesting the benzimidazolylidene scaffold could be functionalized with one or two redox-active moieties at the N atoms or backbone without significantly perturbing its donicity. Relative to previously reported NHCs, 1 and FcDAC were among the most electron-donating, NqMes was comparable with the least, and 2-4 were intermediate. Because electrochemical analyses revealed similar ferrocene oxidation potentials for the [Ir(COD)Cl] and $[Ir(CO)_2Cl]$ complexes supported by 1-3, we conclude that neither the

number of ferrocene units nor the identity of the aromatic backbone strongly influenced the electron density within the NHC. In contrast, the $Fc^{0/+}$ couples in **4a**,**b** and **5a**,**b** were distinct from those observed in 1–3, evidence that both the attachment point of the redox-active group (relative to the carbene nucleus) and the ring comprising the NHC affected the electronic environment at the iron centers in the respective complexes.

Spectroelectrochemical IR analyses revealed a narrow range of Δv_{av} values for (1–3)b and 5b (+13 to +15 cm⁻¹), corresponding to increases in TEPs from 11.0 to 12.7 cm⁻¹, upon oxidation of the ferrocene units. Reduction of the quinone in 6b, however, decreased its v_{av} by 12.5 cm⁻¹, indicating enhanced donation by NqMes (Δ TEP = -10.6 cm⁻¹). Interestingly, the shift for NqMes was nearly equal in magnitude but opposite in sign to the shifts observed for 1–3 and FcDAC. Because the changes in ligand donating abilities did not depend significantly on the NHC characteristics, we surmise that the observed trends primarily reflect Coulombic effects, whereby addition of a positive or negative charge to the ligand alters its TEP by roughly +14 or -11 cm⁻¹, respectively.

On the basis of these results, NHCs with electrochemically tunable electronic properties could be obtained via incorporating a redox-active moiety by the most straightforward synthetic route available, without requiring extensive ligand design. For an NHC that can be electrochemically toggled to a less donating state, it need only feature a functionality that (1) is in close proximity to the carbene and (2) endows the molecule with a positive charge upon oxidation. Conversely, an analogous NHC bearing a redox-active group that acquires a negative charge upon reduction could function as a ligand that can be redox-switched to a more donating state. Ultimately, we believe our findings will simplify the rational design of NHCs for use in redox-switchable applications that employ electrochemical control to attain both enhanced and attenuated electron-donating states.

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Supporting Information Available: Synthetic and experimental details; tables of crystallographic, spectroscopic, and structural data (Tables S1–S7); ORTEP diagrams of (1–3)a, (5,6)a, 2c,d, and 6c,d (Figures S1–S9); CVs of 1a, (3–5)a, 1b, (3–5)b, 2c–e, and 6c–e (Figures S10–S23); spectroelectrochemical spectra for 1b, 3b, 5b, 2c,d, and 6c,d (Figures S24–S30); ¹H and ¹³C NMR spectra; CIFs. This material is available free of charge via the Internet at http://pubs.acs.org.