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Advances in Guanidine Ligand Design: Synthesis of a Strongly Electron-Donating, Imidazolin-2-iminato Functionalized Guanidinate and its Properties on Iron

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Abstract

Imidazolin-2-imines (Im^RN-), derived from *N*-heterocyclic carbenes, have been shown to be strong electron donors when directly coordinated to metals or when used as a substituent in larger ligand frameworks. In an attempt to enhance the electron-donating properties of the popular guanidine ligand class, the effect of appending an Im^RN- backbone onto a guanidinate scaffold was investigated. Addition of 1 equiv of [Li(Et₂O)][Im^{tBu}N] to the aryl carbodiimide (dippN)₂C (dipp = 2,6-diisopropylphenyl) cleanly affords the lithium Im^{tBu}N-functionalized guanidinate [Li(THF)₂][(Im^{tBu}N)C(Ndipp)₂] (**1**). Subsequent metalation of the ligand with FeBr₂ gives the yellow Fe(II) complex {[Im^{tBu}N)C(Ndipp)₂]FeBr}₂ (**4**) in good yield. Solid-state structural analyses of both **1** and **4** shows the Im^{tBu}N- group acts as a non-coordinating backbone substituent. Direct structural comparison of **4** to the closely related guanidinate and ketimine-guanidinate complexes {[X)C(Ndipp)₂]FeBr}₂ (X = ^tBu₂C=N (**5**); N(ⁱPr)₂ (**6**)), differing only in their backbone, reveals a detectable resonance contribution of the Im^{tBu}N- group to the guanidinate ligand electronic structure. Moreover, the Fe(II)/Fe(III) redox couple of **4** (E_{1/2} = -0.67 V) is cathodically shifted by greater than 200 mV from the oxidation potentials of **5** (E_{1/2} = -0.42 V) and **6** (E_{1/2} = -0.45 V), demonstrating the [(Im^{tBu}N)C(Ndipp)₂]⁻ system to be a quantifiably superior electron donor.

Keywords

guanidinate; ketimine-guanidinate; iron; ligand resonance; imidazolin-2-iminato

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Supplementary Data

CCDC1443798 (**1**) and 1443799 (**4**) contain the supplementary crystallographic data. 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.

Supplementary Material

Spectral and electrochemical data and other supplementary information is available online at <http://dx.doi.10.10xxx>

Disclosure Statement

No potential conflict of interest was reported by the authors.

1. Introduction

The treatment of N-heterocyclic carbenes (NHCs) with Me_3SiN_3 yields silylimines that, upon desilylation with MeOH, affords imidazolin-2-imines (Im^{RNH}) featuring a guanidine type motif [1]. The Im^{RN} -ligand class, largely pioneered by Tamm [1–12], has experienced a notable rise in popularity over recent years as these ligands enjoy the modularity of NHCs while exhibiting interesting electronic features [1, 13, 14]. The exocyclic nitrogen of these neutral imines have been shown to be highly basic [1, 15]; yet, Im^{RNH} can be deprotonated using strong alkyl lithium bases to give the monoanionic imidazolin-2-iminato ligands $\text{Im}^{\text{RN-}}$ [16]. These iminic monioanions are impressive electron donors as their NHC core enables an ylidic resonance structure wherein the exocyclic nitrogen adopts imido-like character (Scheme 1, **B**) [1, 5, 8–11, 13, 14]. In this canonical form, the nitrogen can contribute 2σ , 4π -electrons making it isoelectronic to the cyclopentadienyl anion. Impressively, this imidazolium-imido resonance form **B** (Scheme 1) is frequently encountered in $\text{Im}^{\text{RN-}}$, as revealed by X-ray structural analyses, and can manifest itself in both the presence and absence of coordinated metals [1, 5, 8–10]. Indeed, this propensity has been exploited to enhance the electron-donating abilities and basicity of neutral ligand types including bidentate 1,4-diazabutadienes, NNN pincers, and others (Scheme 2) [15, 17–26].

In our laboratory, we have been working towards enhancing the electronic properties of guanidates, another popular ligand class with interesting resonance behavior [27, 28]. Recently, we described our efforts to augment the donor abilities of a guanidate utilizing a ketimine ($\text{R}_2\text{C}=\text{N}-$) backbone as these functional groups can behave as both σ - and π -donors through the imine nitrogen – in principle favoring iminium-diamido or carbonium-diamido resonance forms through conjugation (Scheme 3, **F** and **G**, respectively), thus increasing the relative electron-richness of the coordinating guanidate *N*-atoms [28, 29]. While these ketimine-guanidate ligands displayed interesting steric and structure-reactivity features when coordinated to iron, the ketimine substituent overall provided little to no electronic benefit. Since then, we have redirected our efforts towards examining the chemistry of guanidines with $\text{Im}^{\text{RN-}}$ backbones, used in place of a ketimine, in an attempt to capitalize on the unique donor properties of imidazolin-2-imines. As would be anticipated for a ketimine (Scheme 3, top), when incorporated into a guanidine-like system, the $\text{Im}^{\text{RN-}}$ group foreseeably provides access to four major resonance structures (Scheme 3, **H–K**) wherein the zwitterionic **K** may be favored owing to the readily accessible ylide form **B** of the $\text{Im}^{\text{RN-}}$ group (Scheme 1).

Herein, we describe the synthesis and full characterization of the new $\text{Im}^{\text{BuN-}}$ -guanidine [$(\text{Im}^{\text{BuN}})\text{C}(\text{Ndipp})_2$] $^-$ (dipp = 2,6-diisopropylphenyl) system. Its structural features when coordinated to lithium and iron have been investigated through X-ray crystallographic analyses and the details are fully discussed. As a means to evaluate the relative electron donating properties of the $\text{Im}^{\text{BuN-}}$ -guanidine ligand, its electronic effects on iron have been examined by UV-vis spectroscopy and cyclic voltammetry, the results of which are compared to closely related guanidate and ketimine-guanidate systems of iron previously reported by us [28].

2. Experimental

2.1 General Considerations

All air- and moisture-sensitive operations were performed in an M. Braun drybox under an atmosphere of purified nitrogen or using high-vacuum standard Schlenk techniques. Diethyl ether, hexanes, toluene, and THF were dried using a Pure Process Technology Solvent Purification System and subsequently stored under a dinitrogen atmosphere over activated 4 Å molecular sieves. All deuterated solvents were purchased from Cambridge Isotope Laboratories Inc., degassed by three freeze–pump–thaw cycles, and dried over activated 4 Å molecular sieves for 24 h prior to use. Celite and 4 Å molecular sieves were heated to 150 °C for at least 24 h and then cooled under vacuum. KH [30] was activated and (dippN)₂C [31] and [Li(Et₂O)][Im^{tBu}N] [16] were prepared following literature procedures, while all other reagents were purchased from commercial suppliers and used as received. NMR spectra were recorded on a JEOL ECA 600 MHz or a Bruker AVANCE III 400 MHz. ¹H NMR and ¹³C NMR spectra are referenced to SiMe₄ using the residual ¹H solvent peaks as internal standards or the characteristic ¹³C resonances of the solvent. ⁷Li{¹H} spectra were referenced to external LiCl in D₂O. Resonance assignments in the ¹³C NMR spectra of **1**–**3** were based upon ¹H–¹³C HSQC 2D correlation spectra. IR data were collected using a Thermo Scientific Nicolet iS5 spectrometer. The intensities are reported relative to the most intense peak and are given in parentheses using the following abbreviations: w = weak, m = medium, s = strong. Mass spectrometry (MS) analyses were conducted using a JEOL AccuTOF JMS-T100LC. UV-vis spectra were recorded on a Shimadzu UV-3101PC UV-vis/NIR scanning spectrophotometer.

2.2 Synthesis

2.2.1 Synthesis of [Li(THF)₂][(Im^{tBu}N)C(Ndipp)₂] (1**)**—To a thawing solution of (dippN)₂C (2.2 g, 6.13 mmol) in THF (12 mL) was added [Li(Et₂O)][Im^{tBu}N] (1.7 g, 6.13 mmol) forming a pale yellow solution. The reaction mixture was subsequently allowed to slowly warm to room temperature over several hours. After 12 h, the volatiles were removed under reduced pressure to give a tacky, pale yellow oil. The material was triturated with hexanes (4 mL) and the solvent subsequently removed in vacuo. Addition of hexanes (4 mL) followed by stirring for 30 min resulted in the formation of a solid, white powder. The suspension was filtered over a medium porosity glass frit, and the collected solid was washed with hexanes (3 mL) giving **1** as a white powder. Yield: 1.7 g, 40%. ¹H NMR (25 °C, 400 MHz, C₆D₆): δ 1.12 (br s, 8H, THF), 1.25 (d, 12H, *J*_{HH} = 8 Hz, CHMe₂), 1.48 (d, 12H, *J*_{HH} = 8 Hz, CHMe₂), 1.67 (s, 18H, CCH₃), 3.13 (br s, 8H, THF), 4.05 (sept, 4H, *J*_{HH} = 8 Hz, CHMe₂), 6.22 (s, 2H, ImidH), 6.99 (t, 2H, *J*_{HH} = 8 Hz, ArH), 7.27 (d, 4H, *J*_{HH} = 8 Hz, ArH). ¹³C{¹H} NMR (25 °C, 100.58 MHz, C₆H₆): δ 24.5 (CHMe₂), 24.6 (CHMe₂), 25.2 (THF), 27.9 (CHMe₂), 29.5 (CMe₃), 57.2 (CMe₃), 67.9 (THF), 109.9 (ImidH), 119.9 (aryl), 123.4 (aryl), 143.3 (aryl), 148.1 (^tBuCN₃), 159.8 (dippCN₃), one aryl resonance not observed. ⁷Li{¹H} NMR (25 °C, 155 MHz, C₆D₆): δ −0.8 (s). IR (KBr pellet): 3393 (w), 3196 (w), 3161 (w), 3140 (w), 3108 (w), 3046(m), 3008 (m), 2978 (s), 2957 (s), 2934 (s), 2883 (m), 2863 (s), 2810 (w), 2744 (w), 2700 (w), 2484 (w), 2444 (w), 2398 (w), 2355 (w), 2295 (w), 2158 (w), 2051 (w), 1922 (w), 1897 (w), 1849 (w), 1877 (w), 1785 (w), 1755 (w), 1598 (m), 1589 (m), 1561 (s), 1537 (s), 1480 (s), 1453 (s), 1431 (s), 1424 (s), 1391 (s), 1363

(s), 1349 (s), 1324 (s), 1291 (s), 1240 (s), 1228 (s), 1193 (s), 1159 (m), 1139 (m), 1110 (m), 1087 (m), 1085 (m), 1039 (m), 996 (m), 960 (m), 934 (m), 915 (m), 898 (m), 859 (m), 826 (m), 809 (m), 797 (m), 793 (m), 757 (m), 722 (m), 715 (m), 701 (m), 649 (m), 617 (w), 609 (m), 585 (m), 576 (w), 567 (m), 556 (m), 547 (m), 525 (w), 496 (m), 482 (m), 465 (m), 441 (m), 431 (m), 414 (m), 405 (w).

2.2.2 Synthesis of $(\text{Im}^{\text{tBu}}\text{N})\text{C}(\text{Ndipp})(\text{NHdipp})$ (2)—To a 20 mL scintillation vial equipped with a small magnetic stir bar was added **1** (405 mg, 0.728 mmol) and Et_2O (10 mL). To the stirring solution was added six drops of deionized H_2O and the mixture was vigorously stirred for 30 minutes. The colorless solution was dried over MgSO_4 and subsequently filtered through a medium porosity glass frit. The filter cake was washed with Et_2O (2 mL) and the filtrate was dried under vacuum to give a white solid. Yield: 389 mg, 96% yield. ^1H NMR (25 °C, 400 MHz, C_6D_6): δ 1.02 (d, 6H, $J_{\text{HH}} = 8$ Hz, CHMe_2), 1.33 (d, 6H, $J_{\text{HH}} = 8$ Hz, CHMe_2), 1.39 (d, 6H, CHMe_2 , overlaps with CMe_3 resonance), 1.42 (s, 18H, $J_{\text{HH}} = 8$ Hz, CMe_3), 3.64 (sept, 2H, $J_{\text{HH}} = 8$ Hz, CHMe_2), 3.89 (sept, 2H, $J_{\text{HH}} = 4$ Hz, CHMe_2), 5.69 (s, 1H, NH), 6.15 (s, 2H, ImidH), 7.16–7.19 (m, 4H, aryl), 7.34 (d, 2H $J_{\text{HH}} = 8$ Hz, aryl). $^{13}\text{C}\{^1\text{H}\}$ NMR (25 °C, 100.58 MHz, C_6H_6): δ 22.24 (CHMe_2), 22.94 (CHMe_2), 25.34 (CHMe_2), 25.48 (CHMe_2), 28.79 (CHMe_2), 28.82 (CHMe_2), 28.92 (CMe_3), 58.06 (CMe_3), 111.29 (ImidH), 121.94 (aryl), 122.83 (aryl), 123.52 (aryl), 125.63 (aryl), 137.85 (aryl), 142.12 (aryl), 145.77 (aryl), 147.01, 150.24, 150.36. IR (KBr pellet): 3395 (w, ν NH), 3164 (w), 3067 (w), 3053 (m), 3019 (m), 2976 (s), 2954 (s), 2922 (s), 2886 (m), 2865 (s), 2744 (w), 2711 (w), 2649 (w), 2615 (w), 2597 (w), 2401 (w), 2348 (w), 2295 (w), 1998 (w), 1887 (w), 1854 (w), 1846 (w), 1790 (w), 1724 (w), 1695 (w), 1650 (w), 1601 (s), 1564 (s), 1527 (s), 1477 (s), 1462 (s), 1453 (s), 1428 (s), 1422 (s), 1402 (s), 1383 (s), 1364 (s), 1331 (s), 1318 (s), 1280 (m), 1248 (s), 1232 (s), 1208 (s), 1198 (s), 1177 (m), 1166 (m), 1143 (w), 1112 (s), 1098 (m), 1058 (w), 1045 (w), 1038 (w), 993 (w), 969 (w), 956 (w), 935 (w), 892 (w), 883 (w), 863 (m), 827 (w), 810 (w), 796 (w), 775 (w), 755 (s), 725 (w), 712 (m), 668 (s), 641 (w), 627 (w), 612 (w), 568 (w), 553 (w), 534 (w), 514 (w), 492 (w), 466 (w), 447 (w), 429 (w). ESI-MS: m/z 558.463 ($[\text{M} + \text{H}]^+$; calcd m/z 558.453).

2.2.3 Synthesis of $[\text{K}(\text{THF})][(\text{Im}^{\text{tBu}}\text{NC}(\text{Ndipp})_2]$ (3)—To a stirring solution of **2** (225mg, 0.403 mmol) in THF (6 mL) was added activated KH (81 mg, 2.02 mmol). While stirring, evolution of H_2 was observed and the reaction was allowed to stir for 12 h. The mixture was filtered through celite supported on glass wool to remove excess KH affording a pale yellow solution. Removal of the volatiles in vacuo produced an off-white semisolid that upon trituration with hexanes (3 mL) gave a white powder. Yield: 200 mg, 83%. ^1H NMR (25 °C, 600 MHz, C_6D_6): δ 1.16 (br d, 12H, CHMe_2), 1.39 (d, 4H, THF), 1.46 (d, 12H, $J_{\text{HH}} = 6$ Hz, CHMe_2), 1.68 (s, 18H, CMe_3), 3.52 (t, 4H, THF), 3.99 (br s, 4H, CHMe_2), 6.22 (s, 2H, ImidH), 6.82 (br s, 2H, aryl), 7.11–7.16 (d, 4H, $J_{\text{HH}} = 12$ Hz, aryl). $^{13}\text{C}\{^1\text{H}\}$ NMR (25 °C, 100.58 MHz, C_6H_6): δ 24.33 (CHMe_2), 25.92 (CHMe_2), 27.73 (CHMe_2), 29.06 (THF), 29.87 (CMe_3), 59.17 (CMe_3), 67.95 (THF), 109.81 (ImidH), 122.67 (aryl), 147.53 (tBuCN_3), 157.86 (dippCN_3), three aryl resonances not observed. IR (KBr pellet): 3389 (w), 3153 (w), 3040 (w), 2954 (s), 2921 (m), 2862 (m), 2346 (w), 1327 (w), 1596 (m), 1549 (s), 1538 (s), 1473 (m), 1450 (s), 1416 (s), 1373 (s), 1366 (s), 1348 (s), 1327 (m), 1311 (m), 1295 (m), 1240 (m), 1231 (s), 1189 (m), 1155 (w), 1138 (w), 1098 (w), 1094 (w), 1880 (w),

1045 (w), 1025 (w), 989 (w), 954 (w), 932 (w), 885 (w), 871 (w), 853 (w), 817 (w), 801 (w), 794 (w), 765 (w), 755 (w), 714 (w), 704 (w), 661 (w), 553 (w), 438 (w), 411 (w).

2.2.4 Synthesis of $\{[(\text{Im}^{\text{tBu}}\text{N})\text{C}(\text{Ndipp})_2]\text{FeBr}_2\}_2$ (4**)**—To a 20 mL scintillation vial equipped with a small stir bar was added FeBr_2 (90 mg, 0.312 mmol) and THF (3 mL), and the suspension was stirred for 20 min to ensure complete dissolution of the FeBr_2 to give a brown solution. To this was added a THF (3 mL) solution of **3** (207 mg, 0.347 mmol) slowly dropwise with stirring. Upon addition, the formation of a brown-gray suspension with insoluble gray particulate was observed. The reaction mixture was stirred for 20 h and subsequently filtered through celite supported on glass wool to afford a yellow solution. Removal of the solvent under reduced pressure afforded a bright yellow semi-solid. The solid was triturated with hexanes (2 mL) three times with removal of the solvent under reduced pressure each time, eventually producing **4** as a bright yellow powder. Storage of a toluene (1 mL) and hexane (3 mL) solution at $-20\text{ }^\circ\text{C}$ for 12 h afforded **4** as a yellow crystalline material. Yield: 132 mg (61% yield). ^1H NMR ($25\text{ }^\circ\text{C}$, 400 MHz, C_6D_6): δ -23.48 (s, 2H), -14.82 (s, 4H), -10.24 (s, 12H, CHMe_2), 1.09 (s, 12H, CHMe_2), 6.88 (br s, 18H, CMe_3 , overlaps with NMR solvent resonance), 14.64 (s, 2H), 23.46 (s, 4H). IR (KBr pellet): 3397 (w), 3204 (w), 3166 (w), 3054 (m), 2963 (w), 2929 (m), 2869 (m), 2810 (w), 2758 (w), 2715 (w), 2596 (w), 2281 (w), 2241 (w), 2165 (w), 1914 (w), 1658 (w), 1598 (s), 1563 (s), 1463 (s), 1431 (s), 1419 (m), 1378 (m), 1368 (m), 1323 (s), 1231 (m), 1199 (m), 1164 (w), 1147 (w), 1108 (w), 1085 (w), 1058 (w), 1027 (w), 999 (w), 958 (w), 937 (w), 922 (w), 883 (w), 861 (w), 824 (w), 796 (w), 768 (w), 756 (w), 724 (w), 707 (w), 673 (w), 663 (w), 624 (w), 588 (w), 569 (w), 548 (w), 535 (w), 526 (w), 518 (w), 475 (w), 410 (w), 400 (w). UV-vis (toluene, 0.10 mM , $25\text{ }^\circ\text{C}$, $\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$): 406 ($\epsilon = 1897$).

2.3 Cyclic Voltammetry

Cyclic voltammetric measurements were performed using a CH Instruments 600e potentiostat with a PC unit controlled with CHI software (version 13.12). Experiments were performed in a glovebox under an inert N_2 atmosphere using platinum disks (2 mm diameter) embedded in Kel-F thermoplastic as the counter and working electrodes while the reference electrode consisted of a platinum wire. Solutions utilized in the electrochemical studies were approximately 1 mM in complex with $[\text{NBu}_4][\text{PF}_6]$ (0.1M , THF) as supporting electrolyte. All potentials are reported versus the $[\text{Cp}_2\text{Fe}]^{0/+}$ couple, referenced as internal standard.

2.4 X-ray Structure Solutions and Refinement

X-ray diffraction Data was collected on a Bruker 3-axis platform diffractometer equipped with an APEX I CCD detector using a graphite monochromator with a $\text{Mo K}\alpha$ X-ray source ($\alpha = 0.71073\text{ \AA}$). The crystal was mounted on a Mitigen Kapton loop, coated in NVH oil, and maintained at $100(2)\text{ K}$ under a flow of nitrogen gas during data collection. A hemisphere of data was collected using ω and ϕ scans with 0.3° frame widths. Data collection and cell parameter determination were conducted using the SMART [32] program. Integration of the data and final cell parameter refinements were performed using SAINT [33] software with data absorption correction implemented through SADABS [34]. Structures were solved using direct or charge flipping methods and difference Fourier

techniques. All hydrogen atom positions were idealized and rode on the atom of attachment. Structure solution, refinement, graphics, and creation of publication materials were performed using SHELXTL [35] or the Olex2 [36] crystallographic package.

3. Results and Discussion

3.1 Ligand Synthesis and Characterization

Addition of 1 equiv of $[\text{Li}(\text{Et}_2\text{O})][\text{Im}^{\text{tBu}}\text{N}]$ to a thawing solution of $(\text{dippN})_2\text{C}$ in THF immediately produces a clear, pale-yellow solution. After slowly warming to room temperature and stirring for 12 h, the total removal of the THF followed by addition of hexanes results in the precipitation of $[\text{Li}(\text{THF})_2][(\text{Im}^{\text{tBu}}\text{N})\text{C}(\text{Ndipp})_2]$ (**1**) as a white powder (eq 1). It should be noted that we have found $[\text{Li}(\text{Et}_2\text{O})][\text{Im}^{\text{tBu}}\text{N}]$ to be thermally unstable in THF at room temperature as it decomposes to a number of unidentified products after several hours. Thus, in all cases, ^1H NMR analysis of the crude reaction mixture from **1** reveals incomplete consumption of the $(\text{dippN})_2\text{C}$ carbodiimide, and in our hands, gives mixtures of approximately 4:1 product to carbodiimide. Fortunately, $(\text{dippN})_2\text{C}$ is highly soluble in non-polar solvents and can be removed by washing the product with hexanes to give **1** in 40% yield. Crystalline material of **1** can be grown from the storage of a 5:1 hexanes to THF solution kept at -25°C .

(1)

The ^1H NMR spectrum of **1** in C_6D_6 is well-resolved at room temperature with a sharp, diagnostic resonance from the *tert*-butyl protons at 1.67 ppm. The diastereotopic methyl protons of the isopropyl groups of **1** appear as doublets at 1.25 and 1.48 ppm accompanied by a septet at 4.05 ppm corresponding to the isopropyl methine protons. Also observed in the ^1H NMR spectrum are two peaks at 1.12 and 3.13 ppm which have been assigned to the protons of two lithium-coordinated molecules of THF by integration. In total, **1** clearly adopts a pseudo C_{2v} symmetric geometry on the NMR time scale, implying the $\text{Im}^{\text{tBu}}\text{N}$ -backbone is not locked in position but is instead geometrically dynamic in solution.

Treatment of **1** with excess H_2O in Et_2O gives the protonated species $(\text{Im}^{\text{tBu}}\text{N})\text{C}(\text{Ndipp})(\text{NHdipp})$ (**2**) in nearly quantitative yield. Surprisingly, the room temperature ^1H NMR spectrum of **2** in C_6D_6 reveals a series of sharp, well-defined resonances indicative of only one conformational form in solution. This is contrary to the conformational and tautomeric fluxionality typical of guanidines, including ketimine-guanidines, which often leads to complicated or broad ^1H NMR spectra [27, 28, 37]. The IR spectrum of **2** (KBr pellet) displays a characteristic N-H stretch at 3395 cm^{-1} .

Addition of excess KH to **2** in THF with stirring over several hours gives $[\text{K}(\text{THF})_2][(\text{Im}^{\text{tBu}}\text{N})\text{C}(\text{Ndipp})_2]$ (**3**) which can be isolated in 83% yield as a hexane insoluble white powder. Its ^1H NMR spectrum in C_6D_6 presents one peak set and is qualitatively similar to **1** but does display some moderate peak broadening. For instance, the methyl protons of the isopropyl groups appear as a broad singlet and a sharper doublet at 1.16 and 1.46 ppm, respectively. The reason for this broadening is not known but likely points to some fluxional behavior in solution.

3.2 Synthesis of an Iron $\text{Im}^{\text{R}}\text{N}$ -Guanidinate

In order to probe the structural and electronic features of the new $\text{Im}^{\text{R}}\text{N}$ -guanidinate scaffold $[(\text{Im}^{\text{tBu}}\text{N})\text{C}(\text{Ndipp})_2]^-$, especially any electronic contributions of the $\text{Im}^{\text{tBu}}\text{N}$ - group, we chose to pursue its chemistry with iron in order to make direct comparisons to the related guanidinate and ketimine-guanidinate complexes $\{[(\text{X})\text{C}(\text{Ndipp})_2]\text{FeBr}\}_2$ ($\text{X} = \text{tBu}_2\text{C}=\text{N}$ (**5**); $\text{N}(\text{tPr})_2$ (**6**)), previously reported by us [28], which differ only in their backbone substituent.

Gratifyingly, using a procedure adapted from the synthesis of **5**, the iron $\text{Im}^{\text{tBu}}\text{N}$ -guanidinate $\{[(\text{Im}^{\text{tBu}}\text{N})\text{C}(\text{Ndipp})_2]\text{FeBr}\}_2$ (**4**) can be readily synthesized from the metathesis reaction of **3** with FeBr_2 in THF (eq 2). It should be noted, attempts to produce **4** from the reaction of **1** with FeBr_2 gave a complicated product mixture containing LiBr , **4**, and other unidentified paramagnetic products that proved difficult to separate. Complex **4** is sparingly soluble in non-polar solvents, partially soluble in aromatics, and very soluble in THF, and can be isolated as a light-yellow crystalline solid in 61% yield from the storage of a concentrated 1:3 toluene to hexane mixture at -25°C for 12 h.

(2)

The ^1H NMR spectrum of **4** in C_6D_6 displays seven paramagnetically broadened resonances that range from -23.5 to 23.5 ppm in an approximate 2:4:12:12:18:2:4 ratio. This spectral pattern is suggestive of a C_2 symmetry in solution which indicates a κ^2 -chelation of the Ndipp nitrogen atoms with iron that is accompanied by a geometrically dynamic $\text{Im}^{\text{tBu}}\text{N}$ -backbone – solution-phase behavior not unlike that observed for **1** or that known for its ketimine-guanidinate counterpart **5** [28].

3.3 Structural Comparison and Analyses

Molecular structure analyses of both **1** and **4**, performed through single crystal X-ray diffractometry at 100 K, was undertaken to better understand the effect of the $\text{Im}^{\text{tBu}}\text{N}$ -backbone, if any, on the ligand architecture. Any resonance contributions from the imine nitrogen of the $\text{Im}^{\text{tBu}}\text{N}$ - group (Scheme 3, bottom) to the CN_3 guanidinate ligand core of **1**

and **4** would be anticipated to be observable through X-ray crystallographic analyses, especially when comparing the metrical parameters of **4** to the known structures of **5** and **6**. In particular, contributions from resonance form **K** (Scheme 3) in **1** and **4** should lead to a shorter $N_{Im}-C_{N3}$ bond and longer $C_{N3}-N_{dipp}$ bonds owing to increased dianionic character at the N_{dipp} nitrogens.

The solid-state molecular structures of **1** and **4** are shown in Figure 1. Complex **1** and **4**·C₇H₈ both crystallize in the monoclinic space group $P2_1/c$ as full molecules in the asymmetric unit. The metric parameters of the crystallographically independent iron centers of **4**·C₇H₈ are similar, and for simplicity, only the parameters of one half of the bimetallic unit of **4** will be discussed.

Inspection of the average $N_{dipp}-C_{N3}$ bond lengths (Scheme 4) of **1**, **4**, **5**, and **6** falls in the order of **4** (1.372 Å) > **6** (1.355 Å) $\approx$ **1** (1.352 Å) > **5** (1.345 Å), with the average $N_{dipp}-Fe$ bonds of **4** (2.008 Å) > **6** (2.024 Å) $\approx$ **5** (2.026 Å). As some of the bond metrics do not satisfy the 3σ -criterion, care must be exercised when comparing quantitative differences; however, a qualitative assessment can be made as the general trend is clear overall showing longer $N_{dipp}-C_{N3}$ bonds and slightly shorter $N_{dipp}-Fe$ bonds in **4** suggestive of some ligand diamido resonance character **K** (Scheme 3) that does not appear to manifest itself in **1**. This assertion is further substantiated by comparisons of the $N_{Im}-C_{N3}$ bonds found across **4** ($N3-C1 = 1.335(3)$ Å), **1** ($N3-C1 = 1.366(3)$ Å), and **5** ($N3-C1 = 1.369(2)$ Å) (Scheme 4) which does show a statistically significant shortening in **4** consistent with increased $N_{Im}-C_{N3}$ double bond character. Accordingly, the $N3-C1$ bond in **4** is shorter than the 1.376 Å anticipated for a $C(sp^2)-N(sp^2)$ single bond [38] but is slightly longer than the 1.28(2) Å $N(sp^2)=C(sp^2)$ bond length found in the formerly dianionic guanidinate ligand in [(CyN=C(NCy)₂]Ta(NMe₂)₃ (Cy = cyclohexyl) [39]. Moreover, the $N_{Im}-C_{Im}$ bond of **4** ($N3-C2 = 1.318(3)$ Å) is elongated when compared to that of **1** ($N3-C2 = 1.298(4)$ Å) or **5** (1.274(2) Å). Finally, the $N2-C1-N3-C2 = 4.5^\circ$ torsion angle in **4** approaches zero as would be expected about a $N_{Im}-C_{N3}$ double bond.

Altogether, the metrical parameters undeniably point to a ligand electronic structure in **4** containing an appreciable imidazolium-diamido resonance contribution (Scheme 3, **K**). The differences between the ligand electronic form in **1** and **4**, i.e. $[(Im^{Bu}=N)-C(Ndipp)_2]^-$ respective to $[(Im^{Bu})-N=C(Ndipp)_2]^-$, is not known but does demonstrate the $Im^{Bu}N$ -guanidinate ligand manifold to be electronically flexible.

3.4 Electronic Absorption Spectroscopy

If present, electronic differences between **4** and its counterparts **5** and **6** would be anticipated to reveal themselves in the electronic absorption spectra. Indeed, we previously showed by UV-vis absorption spectroscopy that the electronic structure of iron ketimine-guanidines, e.g. **5**, is more akin to related iron amidinates than guanidines, e.g. **6**, despite the presence of a CN_3 ligand core in both **5** and **6** [28]. As the *N*-amine lone pair on the backbone of guanidines can π -conjugate into the CN_3 ligand system to adopt an iminium-diamido canonical form, as is observed in the structure of **6** [28], it can be imagined that the electronic absorption spectrum of **4**, with its solid-state imidazolium-diamido resonance

characteristics, might be similar to that of **6**. Surprisingly, the UV-vis absorption maximum of **4** ($\lambda_{\text{max}} = 400$ nm) is not significantly different as compared to **5** ($\lambda_{\text{max}} = 402$ nm), both of which are red-shifted from **6** ($\lambda_{\text{max}} = 383$ nm) (Figure 2). A possible explanation is that the electronic structure of **4** in solution is different than that found in the solid-state with potentially less imidazolium-diamido resonance character expressed in the former.

Attempts to further compare the relative electronic properties of **4**, **5**, and **6**, by their magnetic susceptibilities, were made. However, the room-temperature solution-phase magnetic moment of **4** by Evans' method, to compare to that recorded for **5** and **6** [28], were hampered by the limited solubility of pure, crystalline samples of **4**.

3.5 Electrochemistry

In our previous study of **5** and **6** [28], electrochemical analyses revealed ketimine-guanidates to be inferior electron donors to guanidates when ligated to iron. Thus, to further probe the effect of appending an $\text{Im}^{\text{R}}\text{N}$ - group onto a guanidate-type ligand scaffold, the solution-phase redox properties of **4** were examined by cyclic voltammetry. The cyclic voltammogram (CV) of **4**, measured in THF with $[\text{NBu}_4][\text{PF}_6]$ as the supporting electrolyte and internally referenced to the $\text{Fc}^{0/+}$ redox couple, is shown in Figure 3. Qualitatively, the CV of **4** is very similar to that of both **5** and **6** [28] as it displays the same electrochemical features, including an irreversible oxidation wave at higher potentials and an Fe(II)/Fe(III) redox couple that shows increased reversibility at higher scan rates. Notably, the Fe(II)/Fe(III) redox wave of **4** ($E_{1/2} = -0.67$ V) is cathodically shifted by greater than 200 mV from the oxidation potentials of **5** ($E_{1/2} = -0.42$ V) and **6** ($E_{1/2} = -0.45$ V). Additionally, the irreversible oxidation wave in **4** is also shifted by a nearly equal amount from the comparable feature in **5** and **6**.

Comparing the series, the iron metal-center in **4** is clearly more electron-rich than that of the iron centers in either **5** or **6**, which indicates that the $\text{Im}^{\text{Bu}}\text{N}$ -guanidate ligand is superior in its electron donating abilities. Importantly, this points out that, while both ligands in **4** and **5** possess imine backbones, the $\text{Im}^{\text{R}}\text{N}$ - group is a substantially better electron donor over ketimines when used as a guanidate appendage. Indeed, in this case, the $\text{Im}^{\text{Bu}}\text{N}$ - group even appears to provide a greater electronic contribution than the secondary amine Pr_2N -backbone of the guanidate ligand in **6**. This is interesting as this observation does not correlate with the differences observed in their respective electronic absorption spectra (vide supra), suggesting that potential inductive effects cannot be discounted

4. Summary

In our efforts to engineer strongly electron-donating guanidate ligands, we have appended an imidazolin-2-imine $\text{Im}^{\text{R}}\text{N}$ - group onto a guanidine-type framework. The $\text{Im}^{\text{R}}\text{N}$ - group was chosen as it is well-known to exhibit an ylidic imidazolium-imido resonance form which makes it primely suited for π -conjugation into a CN_3 guanidate core – a phenomenon anticipated to greatly enhance ligand donor strength. The $\text{Im}^{\text{R}}\text{N}$ -guanidate $[\text{Li}(\text{THF})_2][(\text{Im}^{\text{Bu}}\text{N})\text{C}(\text{Ndipp})_2]$ (**1**) can be readily synthesized in a single step and subsequently used towards the synthesis of the Fe(II) complex $\{[(\text{Im}^{\text{Bu}}\text{N})\text{C}(\text{Ndipp})_2]\text{FeBr}\}_2$

(4). When directly compared to the related Fe(II) complexes $\{[(X)C(Ndipp)_2]FeBr\}_2$ ($X = tBu_2C=N$ (5); $N(iPr)_2$ (6)), differing from 4 only in their backbone substituent, it is clear from structural and electrochemical analyses that the $Im^R N$ -guanidinate ligand in 4 is both electronically unique and a superior electron donor. In 4, the $Im^{tBu} N$ -guanidinate ligand seemingly adopts dominant imidazolium-diamido resonance character (Scheme 3, K) which greatly enhances the electron-richness of its chelating nitrogen atoms at iron. With this new $Im^R N$ -guanidinate ligand in hand, we are continuing to explore its chemistry on iron and other 3d-metals.

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Figure 1. ORTEP diagram of **1** (top) and **4**·C₇H₈ (bottom). Hydrogen atoms and the co-crystallized molecule of toluene omitted for clarity.

Figure 2. Room temperature electronic absorption spectra for **4** (0.10 mM; blue), **5** (0.09 mM; green), and **6** (0.15 mM; red) [28] in THF.

Figure 3. Cyclic voltammogram of **4** in THF with $[\text{NBu}_4][\text{PF}_6]$ as supporting electrolyte (vs $\text{Fc}^{0/+}$).

Scheme 1.
Resonance forms of the $\text{Im}^{\text{R}}\text{N}^-$ ligand.

Scheme 2.

Examples of neutral ligands incorporating the $\text{Im}^{\text{R}}\text{N}^-$ functionality and their limiting resonance forms.

Scheme 3.

Possible resonance structures of ketimine and Im^RN functionalized guanidines, **D–G** and **H–K**, respectively.

Scheme 4. Comparison of selected bond distances (Å) and angles (deg) in **1** and **4** versus **5** and **6** [28].

Table 1X-ray crystallographic data for **1** and **4**.

	1	4•C₇H₈
empirical formula	C ₄₄ H ₆₄ LiN ₅ O ₂	C ₇₂ H ₁₀₈ Br ₂ Fe ₂ N ₁₀ •C ₇ H ₈
crystal habit, color	plate, colorless	plate, light brown
crystal size (mm)	0.23 × 0.19 × 0.08	0.32 × 0.24 × 0.12
crystal system	monoclinic	monoclinic
space group	<i>P</i> 2 ₁ /c	<i>P</i> 2 ₁ /c
Volume (Å ³)	4161.0(7)	7766.0(6)
a	21.230(2)	19.9200(9)
b	10.9407(11)	19.3080(9)
c	19.1462(19)	21.4082(10)
α	90	90
β	110.663(2)	109.408(1)
γ	90	90
Z	4	4
F _w (g/mol)	702.05	1477.33
density (calcd) (Mg/m ³)	1.140	1.264
abs coeff (mm ⁻¹)	0.069	1.450
F ₀₀₀	1560.0	3128.0
total no. of reflns	10205	21829
unique reflns	5960	12243
final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	R1 = 0.0822, wR2 = 0.2085	R1 = 0.0505, wR2 = 0.1024
largest diff peak and hole (e/ Å ³)	0.65 and -0.66	0.45 and -0.52
GOF	1.041	0.982