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# Experimental and Theoretical Insights into the Electronic Properties of Anionic N-Heterocyclic Dicarbenes through the Rational Synthesis of Their Transition Metal Complexes

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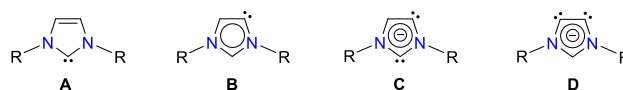
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**ABSTRACT:** The lithiation of the NHC ligand backbone in  $\text{Cp}(\text{CO})_2\text{Mn}(\text{IMes})$  followed by transmetalation on the C4 carbenic position with  $\text{Cp}(\text{CO})_2\text{FeI}$  led to the heterobimetallic complex  $\text{Cp}(\text{CO})_2\text{Mn}(\mu\text{-}d\text{IMes})\text{Fe}(\text{CO})_2\text{Cp}$  bearing the anionic ditopic imidazol-2,4-diylidene  $d\text{IMes}$  ligand. Subsequent treatment of the later with TfOH induced a selective decoordination of the  $[\text{Cp}(\text{CO})_2\text{Mn}]$  fragment to form the cationic abnormal NHC complex  $[\text{Cp}(\text{CO})_2\text{Fe}(a\text{IMes})](\text{OTf})$ , which was further derivatized into the bis(iron)  $d\text{IMes}$  complex  $[\text{Cp}(\text{CO})_2\text{Fe}(\mu\text{-}d\text{IMes})\text{Fe}(\text{CO})_2\text{Cp}](\text{OTf})$  by reaction with  $t\text{AmOK}$  and  $\text{Cp}(\text{CO})_2\text{FeI}$ . The effect of the metallation at the C4 or C2 positions of imidazole ring on the electronic donation properties of the associated C2 and C4 carbenic centers in  $d\text{IMes}$  ligand was quantified through systematic experimental and theoretical studies of  $\text{IMes}$ ,  $a\text{IMes}$  and  $d\text{IMes}$  complexes. The evaluation of the catalytic activity of the series of cationic  $\text{Fe}(\text{II})$  complexes based on  $\text{IMes}$ ,  $a\text{IMes}$ , and  $d\text{IMes}$  ligands in a benchmark ketone hydrosilylation showed the superiority of the bimetallic derivative.

## INTRODUCTION

Since their seminal preparation by Arduengo et al. in 1991<sup>1</sup> stable 2*H*-imidazol-2-ylidenes (**A**, Chart 1) became the most prominent class of N-heterocyclic carbenes (NHCs). Ten years later Crabtree and coworkers reported the first examples of transition metal complexes bearing isomeric imidazol-4-ylidene ligands (**B**)<sup>2</sup> so called “abnormal” NHCs ( $a\text{NHCs}$ ), the first representative free  $a\text{NHC}$  being isolated in the group of Bertrand in 2009.<sup>3</sup> Typically  $a\text{NHC}$  ligands show significantly stronger  $\sigma$ -donor properties than their “normal” NHC analogues and this characteristic feature was successfully exploited in some catalytic processes.<sup>4</sup> In 2006 Arnold et al. reported the preparation of lanthanide complexes supported by a ditopic anionic imidazol-2,4-diylidene (NHDC, **C**) ligands exhibiting normal and abnormal carbenic functions.<sup>5</sup> Shortly after Robinson and coworkers showed that lithium type **C** NHDC complexes could be readily obtained by backbone metallation of free NHCs **A** with  $n\text{BuLi}$ .<sup>6</sup> Finally, Whittlesey and coworkers reported in 2007 the first complex bearing the ditopic anionic imidazol-4,5-diylidene ligand **D**<sup>7</sup> and more recently Ghadwal succeeded generating *in situ* the corresponding lithium dicarbene species, here by double metallation of 2-arylsusbstituted imidazolium salts with two equivalents of  $n\text{BuLi}$ .<sup>8</sup>

**Chart 1. Different Types of Mono- and Ditopic NHCs Derived from Imidazolium Salts**

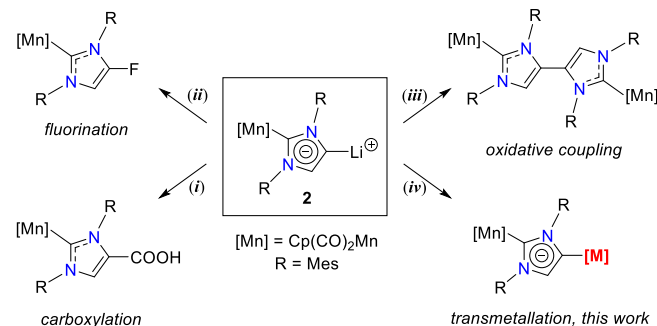


Though the chemistry of NHDC species **C** and their adducts with main group elements have been well developed,<sup>6,9,10</sup> the corresponding binuclear transition metal complexes remain relatively scarce. Bimetallic  $\text{Zn}(\text{II})$ <sup>11</sup> and  $\text{Au}(\text{I})$ <sup>12</sup> NHDC derivatives based on  $\text{IPr}$  skeleton ( $\text{IPr}$  = 1,3-bis(2,6-diisopropylphenyl)-2*H*-imidazol-2-ylidene) were originally obtained by transmetalation of main group metal cations in appropriate precursors with  $\text{ZnEt}_2$  and  $(\text{PPh}_3)\text{AuCl}$ , respectively. Another approach exploiting C–H<sup>13</sup> or C–I<sup>14</sup> NHC backbone bond activation in bidentate and pincer complexes resulted in the formation of binuclear  $\text{Pd}(\text{II})$  or  $\text{Co}(\text{I})$  NHDC complexes. Finally, a variety of heterobimetallic NHDC species associating  $\text{Ru}(\text{II})$  to  $\text{Ag}(\text{I})$ ,  $\text{Au}(\text{I})$ ,  $\text{Pd}(\text{II})$  or  $\text{Ir}(\text{I})$  was prepared from cationic complexes  $[\text{Ru}(\kappa^2\text{-OAc})(\text{L-L})(a\text{NHC-P})]\text{Br}$  ( $\text{L-L}$  = NHC-phosphine, diphosphine), in which the C2 position of  $a\text{NHC}$  ligand remained accessible for metal coordination.<sup>15</sup> Clearly, the lack of sufficiently general preparation methods still hamper the

development of this chemistry and even the electronic properties of the NHC units in ditopic ligands **C** have never been fully quantified by experimental or theoretical means.

We have recently shown that the lithiation of the IMes ligand backbone (IMes = 1,3-bis(2,4,6-trimethylphenyl)-2*H*-imidazol-2-ylidene) in the Mn(I) complex Cp(CO)<sub>2</sub>Mn(IMes) (**1**) with *n*BuLi leads to the quantitative formation of the stable complex Cp(CO)<sub>2</sub>Mn( $\mu$ -*d*IMes)Li (**2**) supported by an imidazol-2,4-diylidene ligand denoted here and below as *d*IMes (Scheme 1).<sup>16</sup> The abnormal carbene function in **2** could readily undergo carboxylation,<sup>16</sup> electrophilic fluorination,<sup>17</sup> or oxidative coupling<sup>18</sup> processes to form the corresponding backbone-decorated IMes derivatives in good yield (Scheme 1, paths *i*–*iii*).

### Scheme 1. Reactivity of the Abnormal Carbene Moiety in Complex Cp(CO)<sub>2</sub>Mn( $\mu$ -*d*IMes)Li (**2**)



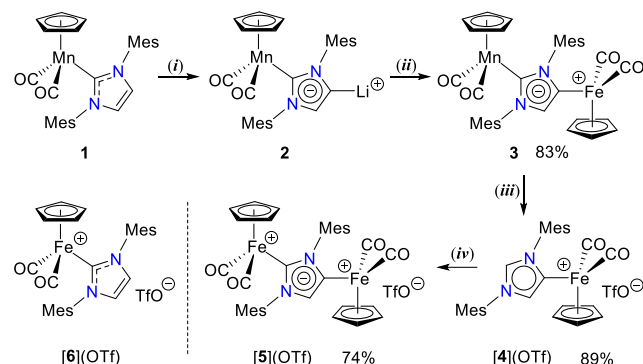
Inspired by the pioneering works of Robinson<sup>11</sup> and Hevia<sup>12</sup> we wondered whether transmetalation at the abnormal carbene position in complex **2** (Scheme 1, path *iv*) could afford a viable route to heterobimetallic transition metal NHDC complexes based on the ubiquitous IMes architecture. We report herein the synthesis of carbonyl-containing Mn(I) and Fe(II) NHDC complexes, the comprehensive study of their electronic structure and the quantification of the donation properties of *d*IMes ligand. Finally the catalytic activity of a unique series of cationic Fe(II) complexes supported by the normal IMes (**A**), the abnormal *a*IMes (**B**) and the anionic ditopic *d*IMes (**C**) ligands (Chart 1, R = Mes) was evaluated in benchmark ketone hydrosilylation.

## RESULTS AND DISCUSSION

**Synthesis and Characterization of Mn(I) and Fe(II) NHC Complexes Based on IMes, *a*IMes and *d*IMes Scaffolds.** We were pleased to find that the reaction of compound **2** with Cp(CO)<sub>2</sub>FeI led to the formation of the corresponding binuclear complex CpMn(CO)<sub>2</sub>( $\mu$ -*d*IMes)Fe(CO)<sub>2</sub>Cp (**3**) in a good yield (Scheme 2). The manganese fragment attached to the normal NHC position in complex **3** was then selectively decoordinates upon protonation with triflic acid according to our recently developed protocol<sup>17,18</sup> to afford the cationic Fe(II) complex [Cp(CO)<sub>2</sub>Fe(*a*IMes)](OTf) (**[4](OTf)**) representing a rare example of mononuclear transition metal complex featuring *a*IMes ligand non-substituted at the C2 position.<sup>19,20</sup> The later complex was further transformed into the binuclear bis(iron) *d*IMes derivative [Cp(CO)<sub>2</sub>Fe( $\mu$ -*d*IMes)Fe(CO)<sub>2</sub>Cp](OTf) (**[5](OTf)**) upon deprotonation of the C2–H bond of the imidazolium moiety with *t*AmOK in the presence of Cp(CO)<sub>2</sub>FeI. Finally, for the sake of comparison of spectral properties, and later on, of catalytic activities, the complex [Cp(CO)<sub>2</sub>Fe(IMes)]

(OTf) (**[6](OTf)**) (Scheme 2, inset) was prepared by an anion exchange in the known [Cp(CO)<sub>2</sub>Fe(IMes)]I<sup>21</sup> salt with NaOTf in CH<sub>2</sub>Cl<sub>2</sub>/water.

### Scheme 2. Synthesis of Normal, Abnormal and Ditopic NHC Complexes of Mn(I) and Fe(II). Mes = 2,4,6-Trimethylphenyl



Reaction conditions: (i) 1.2 equiv. *n*BuLi, THF, r.t., 15 min; (ii) Cp(CO)<sub>2</sub>FeI, toluene, –10°C to r.t., 0.5h; (iii) 1.2 equiv. TfOH, CH<sub>2</sub>Cl<sub>2</sub>, –40°C to r.t., 0.5h; (iv) 1.5 equiv. *t*AmOK, Cp(CO)<sub>2</sub>FeI, THF, –80°C to r.t., 1h.

In contrast to the numerous examples of iron complexes supported by classic 2*H*-imidazol-2-ylidene ligands,<sup>22</sup> only a few compounds featuring imidazol-4-ylidene ligands are known to date.<sup>20f–g,23</sup> The diamagnetic nature of our NHC Fe(II) complexes made possible their full characterization by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy (see Table 1 for selected pertinent NMR data). In particular, the signal of the backbone NHC proton of the *d*IMes ligand in complex **3** is slightly shielded by 0.14 ppm compared to the corresponding value in its IMes antecedent **1** in the same solvent (C<sub>6</sub>D<sub>6</sub>). Similar trend is also observed within the Fe(II) IMes → *a*IMes → *d*IMes series showing the stepwise decrease of the corresponding  $\delta_H$  values by ca. 0.3 ppm in complexes **[6](OTf)**, **[4](OTf)**, and **[5](OTf)** (Table 1). The abnormal carbene atoms coordinated to the Fe(II) centers in complexes **3**, **[4](OTf)**, and **[5](OTf)** are observed by <sup>13</sup>C NMR spectroscopy in a range of  $\delta_{C4}$  124.8–141.8 ppm. Interestingly, the <sup>13</sup>C NMR signals belonging to both normal and abnormal carbene atoms in the cationic *d*IMes complex **[5](OTf)** are shifted by ca. 5 ppm upfield compared to the corresponding signals in the mononuclear derivatives **[6](OTf)** and **[4](OTf)**. Similar difference for  $\delta_{C4}$  carbene resonance values in a range 4.4–12.3 ppm was also observed between related Ru(II) abnormal and NHDC complexes.<sup>15</sup> The observed shielding of the backbone imidazolium protons and carbenic resonances in *d*IMes complexes can

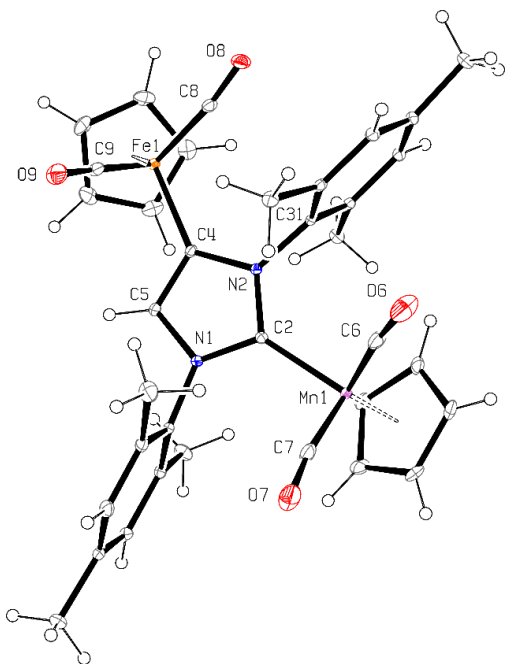
**Table 1. Selected <sup>1</sup>H and <sup>13</sup>C NMR Data for Mn(I) and Fe(II) Complexes Bearing Normal, Abnormal and Ditopic NHC Ligands**

Complex	$\delta_{C5-H}$	$\delta_{C2}$	$\delta_{C4}$	$\delta_{C5}$	$\delta_{CO}$
<b>1</b> <sup>a</sup>	6.18	205.4	123.8	123.8	234.4
<b>[6](OTf)</b> <sup>b</sup>	7.37	171.4	128.1	128.1	209.4
<b>[4](OTf)</b> <sup>b</sup>	7.07	138.2	141.8	132.2	211.8
<b>3</b> <sup>a</sup>	6.04	204.4	124.8	132.9	235.1, 213.8
<b>[5](OTf)</b> <sup>b</sup>	6.79	166.7	136.6	135.7	212.7, 210.3

<sup>a</sup> C<sub>6</sub>D<sub>6</sub> solution; <sup>b</sup> CDCl<sub>3</sub> solution

be ascribed to the higher electron density within the carbenic heterocycle, which is translated in chemical drawings by a formal negative charge delocalized inside the heterocycle.

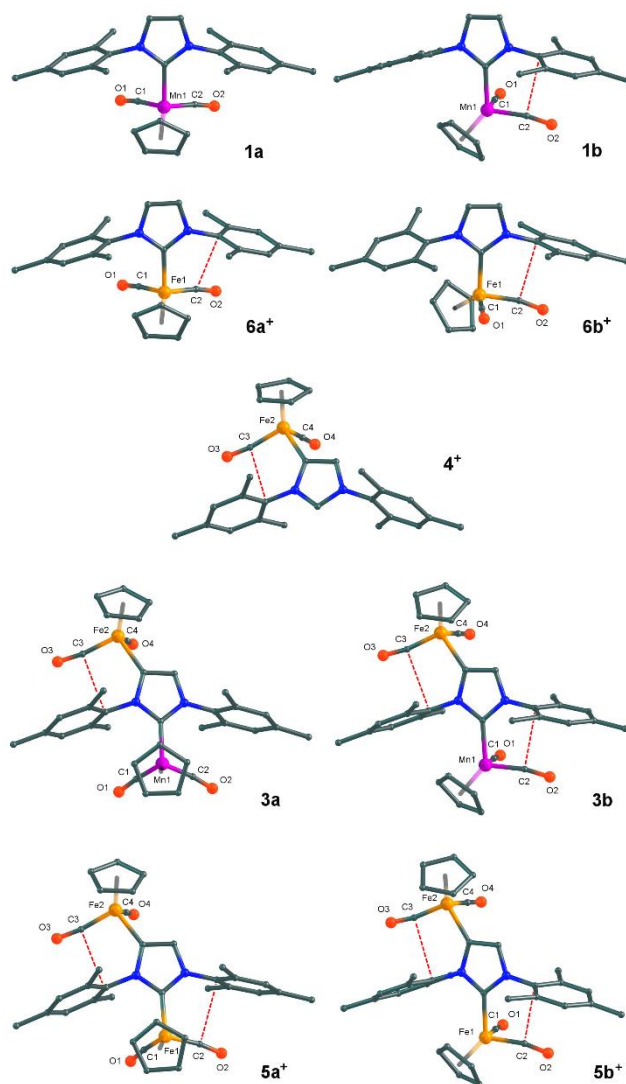
**X-ray diffraction study of the bimetallic NHDC complex 3.** The molecular structure of the heterobimetallic complex **3** was established by single-crystal X-ray diffraction analysis (Figure 1).<sup>24</sup> Both metal centers display an usual piano-stool coordination environment. While the Mn–NHC bond (2.0133(13) Å) in **3** is slightly longer than the corresponding one in the parent IMes complex **1** (2.003[3] Å),<sup>16</sup> the Fe–aNHC bond distance (1.9936(13) Å) is the shortest among other reported anionic NHDC (2.064(2)–2.110(2) Å)<sup>23b,c</sup> or neutral monodentate aNHC iron complexes (2.026(3)–2.117(2) Å),<sup>20g,23a,d</sup> and compares well with those found in structurally similar Fe(II) half-sandwich 1,2,3-triazol-4-ylidene derivatives (1.9744(14)–2.010(6) Å).<sup>25</sup> The normal NHC moiety bonded to Mn1 atom adopts an almost ideal horizontal coordination mode<sup>26</sup> ( $\text{Cp}_{\text{ent}}\text{--Mn1--C2--N2}$   $-80.94(12)^\circ$ ), whereas the abnormal one bonded to Fe1 atom shows an eclipsed conformation, in which the NHC ring becomes almost coplanar with one of the CO ligands ( $\text{C8--Fe1--C4--N2}$   $-23.04(13)^\circ$ ) bringing one of the mesityl group attached to the NHC ring in close proximity to carbonyl carbon atom C8 ( $\text{C8}\cdots\text{C31}$  3.0284(18) Å). Actually, the combination of this  $\text{C}_{\text{ipso}}\cdots\text{C}\equiv\text{O}$  distance being inferior to the sum of the Van der Waals radii (3.4 Å) and the significant bending of the adjacent Fe–C–O fragment ( $\text{Fe1--C8--O8}$   $172.30(12)^\circ$  vs.  $\text{Fe1--C9--O9}$   $178.46(13)^\circ$ ) suggests the occurrence of an attractive interligand and  $\pi(\text{C}=\text{C})\cdots\pi^*(\text{C}=\text{O})$  interaction (*vide infra*) similar to the one previously evidenced in given Fischer-type and NHC complexes.<sup>27</sup>



**Figure 1.** A perspective view of a complex **3** (30% probability ellipsoids).

**Theoretical Investigation of the Electronic Structure of Transition Metal *d*IMes Complexes and the Comparison with Their Mononuclear Congeners.** DFT optimized structures of all relevant Mn(I) and Fe(II) complexes obtained in the gas phase using G09/BP86-D3/def2-TZVP approach are pre-

sented in Figure 2. The most pertinent structural data are provided in Table S1 (see the Supporting Information). While in the case of the Fe(II) *a*IMes complex **4<sup>+</sup>** a single minimum was located on the potential energy surface, two minima were found for both neutral Mn(I) and cationic Fe(II) IMes complexes corresponding to two rotamers exhibiting either an horizontal (**1a**, **6a<sup>+</sup>**) or an eclipsed (**1b**, **6b<sup>+</sup>**) NHC ligand coordination mode. The same situation was also observed in bimetallic NHDC derivatives **3** and **5<sup>+</sup>** (Figure 2). The calculated geometries of **1b** and **3a** show an excellent agreement with the corresponding solid-state structures of complexes **1**<sup>16</sup> and **3** obtained by X-ray diffraction. Since the difference in main thermodynamic characteristics ( $\Delta E$ ,  $\Delta H^{298}$  and  $\Delta G^{298}$ ) between these horizontal and eclipsed isomers (Table S2) does not exceed 1.6 kcal mol<sup>-1</sup>, it is not surprising that either one or both conformations have been observed by single crystal X-ray diffraction in parent



**Figure 2.** DFT optimized geometries for the cationic parts of Mn(I) and Fe(II) IMes, *a*IMes and *d*IMes complexes calculated at G09/BP86-D3/def2-TZVP level. Hydrogen atoms are omitted for clarity, color element codes: C – grey, N – blue, O – red, Mn – rose, Fe – orange. Non-covalent interligand  $\pi(\text{C}=\text{C})\cdots\pi^*(\text{C}=\text{O})$  interactions detected by AIM approach are indicated by red dashed lines.

$[\text{Cp}(\text{CO})_2\text{M}(\text{NHC})]^{n+}$  ( $\text{M} = \text{Mn}$ ,  $n = 0$ ; <sup>16,18,28</sup>  $\text{M} = \text{Fe}$ ,  $n = 1$ <sup>29</sup>) complexes bearing N-aryl-substituted NHC ligands and these rotamers are likely to be in fast exchange in solution.

The calculated metal-NHC bond distances in the bimetallic *d*IMes derivatives are systematically longer by 0.01–0.02 Å than those found in the corresponding conformers of mononuclear IMes and *a*IMes complexes. Taking into account the presence of several short  $\text{C}_{\text{ipso}}\cdots\text{C}\equiv\text{O}$  contacts and associated bent  $\text{M}-\text{C}-\text{O}$  fragments (Figure 2, Table S1) for both normal (2.779–3.084 Å, 166.96–172.43°) and abnormal (2.891–2.932 Å, 169.34–171.29°)  $\text{Cp}(\text{CO})_2\text{M}$ -carbene moieties in these complexes, we investigated the possible occurrence of attractive interligand  $\pi(\text{C}=\text{C})\cdots\pi^*(\text{C}\equiv\text{O})$  interactions<sup>27</sup> using Bader's Atoms In Molecules (AIM) theory<sup>30</sup> (see for details Figures S14–18 and Table S3 in the Supporting information). While such interligand and intramolecular interactions were found only for the eclipsed conformations of the  $\text{Cp}(\text{CO})_2\text{Mn}-\text{NHC}$  moieties in **1b** and **3b** (Figure S14 and Figure S17, respectively) with an interaction energy  $E_{\text{int}}$  of 2.4 kcal mol<sup>−1</sup> in both cases as estimated using the Espinosa-Molins-Lecomte correlation,<sup>31</sup> they are present in all  $\text{Cp}(\text{CO})_2\text{Fe}-\text{NHC}$  fragments regardless the NHC orientation (Figures S15–18), the interaction energy being in the 1.9–2.6 kcal mol<sup>−1</sup> range. According to the bond critical point (BCP) characteristics (Table S3) for the eclipsed conformations of Fe(II) IMes and *a*IMes fragments  $\pi(\text{C}=\text{C})\cdots\pi^*(\text{C}\equiv\text{O})$  interactions are weaker in the latter case (2.6 vs. 2.1–2.2 kcal mol<sup>−1</sup>). Though the estimated interaction energies (1.9–2.0 kcal mol<sup>−1</sup>) found in case of horizontal conformers **5a**<sup>+</sup> and **6a**<sup>+</sup> formally seems to be comparable, these supramolecular bonds show very high values of ellipticity (1.074 and 1.303, respectively vs. 0.122 and 0.088 for the same type of bonding in eclipsed conformers **5b**<sup>+</sup> and **6b**<sup>+</sup>), which clearly indicate their strongly disturbed character.

In contrast to well-studied normal and abnormal carbene derivatives, to the best of our knowledge the electronic structure and bonding situation for bimetallic transition metal NHDC

**Table 2. Selected AIM Charges and Bond Orders (BOs) for Optimized Structures of Mn(I) and Fe(II) Complexes Bearing Normal, Abnormal and Ditopic NHCs**

Comp.	Metal charge	NHC charge <sup>a</sup>	BOs for M–NHC bond
<b>1a</b>	+0.948 (Mn–NHC)	−0.799	0.800 (Mn–NHC)
<b>1b</b>	+0.946 (Mn–NHC)	−0.806	0.813 (Mn–NHC)
<b>6a</b> <sup>+</sup>	+0.845 (Fe–NHC)	−0.647	0.782 (Fe–NHC)
<b>6b</b> <sup>+</sup>	+0.843 (Fe–NHC)	−0.649	0.779 (Fe–NHC)
<b>4</b> <sup>+</sup>	+0.840 (Fe– <i>a</i> NHC)	−0.616	0.799 (Fe– <i>a</i> NHC)
<b>3a</b>	+0.951 (Mn–NHC)	−1.115	0.787 (Mn–NHC)
	+0.838 (Fe– <i>a</i> NHC)		0.791 (Fe– <i>a</i> NHC)
<b>3b</b>	+0.947 (Mn–NHC)	−1.123	0.795 (Mn–NHC)
	+0.840 (Fe– <i>a</i> NHC)		0.787 (Fe– <i>a</i> NHC)
<b>5a</b> <sup>+</sup>	+0.845 (Fe–NHC)	−1.027	0.776 (Fe–NHC)
	+0.840 (Fe– <i>a</i> NHC)		0.792 (Fe– <i>a</i> NHC)
<b>5b</b> <sup>+</sup>	+0.844 (Fe–NHC)	−1.031	0.769 (Fe–NHC)
	+0.841 (Fe– <i>a</i> NHC)		0.789 (Fe– <i>a</i> NHC)

<sup>a</sup> total AIM charge of the heterocyclic moiety without aryl groups ( $\text{C}_3\text{N}_2\text{H}_2$  and  $\text{C}_3\text{N}_2\text{H}_1$  for mono- and ditopic carbenes, respectively)

complexes has never been investigated by theoretical means. Here, DFT calculations data show virtually the same AIM metal charges and metal-carbene bond orders (BOs) in all Mn(I) and Fe(II) IMes, *a*IMes and *d*IMes complexes as well as negatively charged *d*IMes units in bimetallic species **3a-b** and **5a-b**<sup>+</sup> (Table 2). Similar trends in charge distribution can be also deduced from the data obtained by Natural Bond Orbitals (NBO) approach (Table S6).

The metal-carbene bonding in these species was investigated by energy decomposition analysis (EDA)<sup>32</sup> (for details see Experimental section and Table S8 in the Supporting Information). The overall binding energy  $E_{\text{int}}$  of the Fe–NHC bonds is *ca.* 50% higher than for the analogous Mn–NHC interactions mainly due to significantly higher electrostatic contribution  $E_{\text{elst}}$ . In the cationic Fe(II) complexes [**4-6**]<sup>+</sup> the Fe–NHC bonds are always weaker by 3–4% than Fe–*a*NHC ones again owing to slightly greater ionic character for the later, in agreement with literature data.<sup>33</sup> Interestingly, binding energies for both Fe–NHC and Fe–*a*NHC bonds in **5**<sup>+</sup> are systematically *ca.* 6% greater than those found in mononuclear congeners **6**<sup>+</sup> and **4**<sup>+</sup>, respectively. The bonding parameters of iron-*a*NHC bonds in *d*IMes complexes **3** and **5**<sup>+</sup> were then compared with those of classic Fe–C  $\sigma$ -bonds in model Fe(II) complexes  $\text{Cp}(\text{CO})_2\text{Fe}-\text{R}$  ( $\text{R} = \text{Me}$ , 2- and 4-imidazolyl). This study revealed the notable increase of both electrostatic  $E_{\text{elst}}$  component and  $\sigma$ -bonding contribution in  $E_{\text{orb}}$  energy in the series of Fe–*a*NHC  $\rightarrow$  Fe–heteroaryl  $\rightarrow$  Fe–alkyl bonds (for details see the Supporting Information) thus being consistent with a dative nature of the Fe–*a*NHC bonds in NHDC species differing significantly from mainly electrostatically-driven Fe–C interactions with pronounced  $\sigma$ -character in model complexes. The overall results obtained in this theoretical investigation confirm that the NHDC (C, Chart 1) in transition metal complexes really behave as anionic  $\text{L}_2$ -type ligands.

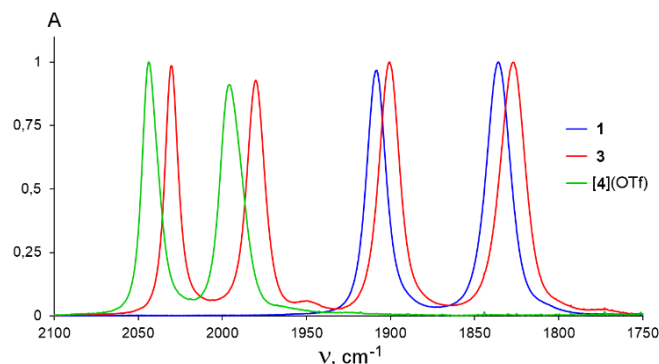
**Experimental Measurement of Relative Electron Donating Properties of *d*IMes Ligand and the Rationalization of the Observed Effects by DFT Calculations.** Having in hands the first examples of NHDC complexes with carbonyl-containing transition metal fragments in both normal and abnormal positions we then turned our attention to the evaluation of electronic donation properties of this type of NHC ligands by IR spectroscopy (Table 3, Figures 3–4). Strikingly, we have observed that in complex **3** the  $\nu_{\text{CO}}$  bands for  $[\text{Cp}(\text{CO})_2\text{Mn}]$  and  $[\text{Cp}(\text{CO})_2\text{Fe}]^+$  moieties are shifted into lower frequency region to *ca.* 8.5 and 15 cm<sup>−1</sup> compared to those of monodentate NHC analogues **1** and [**4**](OTf), respectively (Figure 3). A similar situation is found for the Fe(II) complex [**5**](OTf) (Figure 4) and notably the donicity of the *a*NHC moiety in *d*IMes ligand was found to be sensitive to the nature of the organometallic fragment on the normal NHC position ( $\langle\nu_{\text{CO}}\rangle$  2005.0 and 2014.3 cm<sup>−1</sup> for **3** and [**5**](OTf), respectively) reflecting the occurrence of an efficient electronic delocalization across NHDC ligand scaffold.

DFT calculations of IR data for all these compounds (Table 3) confirm the initial  $\nu_{\text{CO}}$  peaks attribution and show the expected low frequency shift for the conformers with intramolecular  $\pi(\text{C}=\text{C})\cdots\pi^*(\text{C}\equiv\text{O})$  interactions.<sup>27c</sup> The comparison of calculated  $\nu_{\text{CO}}$  data between the *d*IMes complexes and their monocarbene congeners is fully consistent with the experimentally observed trends and  $\Delta\nu_{\text{CO}}$  values within the same series of rotamers were well reproduced.

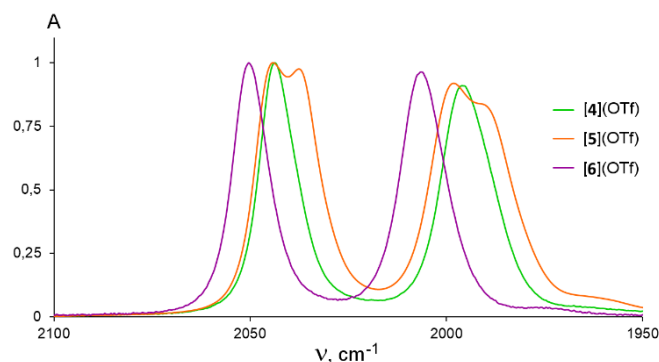


**Table 3. Experimental (CH<sub>2</sub>Cl<sub>2</sub> Solution) and Calculated (G09/BP86-D3/Def2-TZVP, italic) IR Spectroscopy Data for Mn(I) and Fe(II) IMes, *a*IMes and *d*IMes Complexes (Average  $\nu_{\text{CO}}$  Values Are Given in Parenthesis in Red and Blue for Experimental and Theoretical Data, Respectively)**

Comp.	$\nu_{\text{CO}}$ of Cp(CO) <sub>2</sub> M–NHC, cm <sup>−1</sup>	$\nu_{\text{CO}}$ of Cp(CO) <sub>2</sub> M– <i>a</i> NHC, cm <sup>−1</sup>
<b>1</b>	1908.5, 1836 ( <b>1872.3</b> )	
<b>1a</b>	1923, 1875 ( <b>1899</b> )	–
<b>1b</b>	1922, 1872 ( <b>1897</b> )	
[6](OTf)	2050.5, 2006.5 ( <b>2028.5</b> )	
<b>6a<sup>+</sup></b>	2038, 1999 ( <b>2018.5</b> )	–
<b>6b<sup>+</sup></b>	2031, 1993 ( <b>2012</b> )	
[4](OTf)	–	2044, 1996 ( <b>2020</b> )
<b>4<sup>+</sup></b>		2033, 1993 ( <b>2013</b> )
<b>3</b>	1900.5, 1827 ( <b>1867.8</b> )	2030, 1980 ( <b>2005</b> )
<b>3a</b>	1919, 1873 ( <b>1896</b> )	2017, 1975 ( <b>1996</b> )
<b>3b</b>	1918, 1869 ( <b>1893.5</b> )	2016, 1974 ( <b>1995</b> )
[5](OTf)	2044, 1998 ( <b>2021</b> )	2037.5, 1991 ( <b>2014.3</b> )
<b>5a<sup>+</sup></b>	2034, 1994 ( <b>2014</b> )	2026, 1986 ( <b>2006</b> )
<b>5b<sup>+</sup></b>	2029, 1987 ( <b>2008</b> )	2023, 1984 ( <b>2003.5</b> )



**Figure 3.** Superposition of normalized experimental IR spectra of complexes **1**, **3** and [4](OTf) in 2100–1750 cm<sup>−1</sup> range (CH<sub>2</sub>Cl<sub>2</sub>, 0.5 cm<sup>−1</sup> resolution).

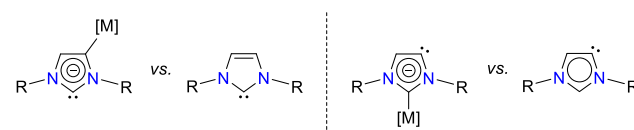


**Figure 4.** Superposition of normalized experimental IR spectra of complexes [4–6](OTf) in 2100–1950 cm<sup>−1</sup> range (CH<sub>2</sub>Cl<sub>2</sub>, 0.5 cm<sup>−1</sup> resolution).

These results seem to indicate that both carbene moieties of *d*IMes are more strongly electron donating than the corresponding normal (IMes) and abnormal (*a*IMes) NHCs (Scheme 3). This proposition is consistent with the decrease of medium

$\langle \nu_{\text{CO}} \rangle$  value for metal–NHC fragments observed by Tamm and coworkers in the rhodium–borane complex (Et<sub>4</sub>N)[((C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>B)(μ-*d*IPr)(Rh(CO)<sub>2</sub>Cl)] ( $\langle \nu_{\text{CO}} \rangle$  2028 cm<sup>−1</sup>) as compared to the classic IPr complex (IPr)Rh(CO)<sub>2</sub>Cl ( $\langle \nu_{\text{CO}} \rangle$  2038 cm<sup>−1</sup>).<sup>34</sup> We also previously observed similar low frequency shift of  $\nu_{\text{CO}}$  bands in IR spectra of manganese complexes Cp(CO)<sub>2</sub>Mn(IMes) ( $\langle \nu_{\text{CO}} \rangle$  1885 cm<sup>−1</sup>) as compared to Cp(CO)<sub>2</sub>Mn(μ-*d*IMes)Li ( $\langle \nu_{\text{CO}} \rangle$  1871 cm<sup>−1</sup>) in Et<sub>2</sub>O solution.<sup>16</sup>

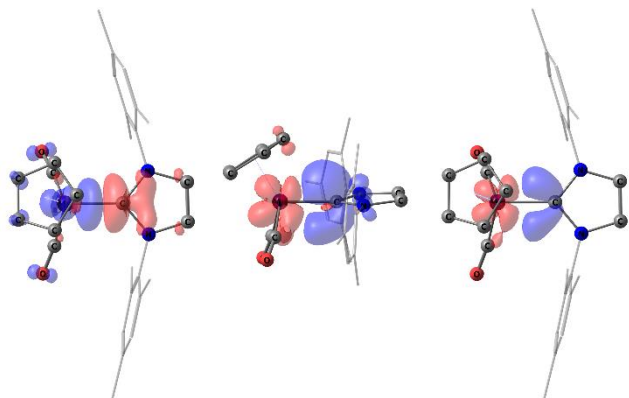
**Scheme 3. The Fragmentation Method Used for the Comparison of Electronic Donation of Anionic *d*IMes Ligand with Those of Related Neutral IMes and *a*IMes Carbenes (R = Mes, [M] = Cp(CO)<sub>2</sub>Mn, Cp(CO)<sub>2</sub>Fe)**



Yet, taking into account that IR measurements for NHC donicity determination are typically carried out on square-planar Rh(I) or Ir(I) complexes and directly correlated with Tolman's electronic parameter (TEP)<sup>35</sup> and being aware of the possible  $\nu_{\text{CO}}$  response perturbations due to interligand interactions in half-sandwich carbene complexes,<sup>27c</sup> we decided to further assess our conclusions by another experimental method. Indeed, the measurement of the oxidation potential of metal NHC complexes constitutes an alternative, which could provide sometimes even higher precision than the TEP approach.<sup>36</sup> While cyclic voltammogram (CV) of Mn(I) IMes complex **1** in acetonitrile reveals a fully reversible one electron oxidation at  $E_{1/2}$  {Mn(I)/Mn(II)} = −0.26 V vs. Fc (Figure S9), its cationic Fe(II) analogue [6](OTf) undergoes under the same conditions an irreversible oxidation at  $E_{\text{p.a.}}$  {Fe(II)/Fe(III)} = +1.44 V (Figure S13) probably due to the occurrence of *ECE*-type process rather typical for this coordinating solvent.<sup>37</sup> The electrochemical behavior of Fe(II) *a*IMes derivative [4](OTf) was found to be intermediate compared to its normal IMes analogues and a quasi-reversible ( $I_{\text{a}}/I_{\text{c}}$  = 0.6) one electron oxidation wave was observed at  $E_{1/2}$  {Fe(II)/Fe(III)} = +1.12 V (Figure S11) in full agreement with a stronger donation of the *a*IMes ligand. The analysis of CVs for *d*IMes complexes (Figures S10 and S12) reveals a similar electrochemical behavior accompanied by a significant decrease of the oxidation potentials for both normal (**3**:  $E_{1/2}$ {Mn(I)/Mn(II)} = −0.39 V; [5](OTf):  $E_{\text{p.a.}}$ {Fe(II)/Fe(III)} = +1.34 V) and especially for abnormal metal–NHC fragments (**3**:  $E_{1/2}$ {Fe(II)/Fe(III)} = +0.71 V; [5](OTf):  $E_{1/2}$ {Fe(II)/Fe(III)} = +0.86 V). Similarly, a significant decrease of Ru(II)/Ru(III) oxidation potential in binuclear RuIr NHDC complex containing the ruthenium atom coordinated to the abnormal NHC position was very recently attributed to the result of efficient electronic coupling *via* the NHDC ligand.<sup>15a</sup> Though an irreversible electrochemical behavior of normal [Cp(CO)<sub>2</sub>Fe(NHC)]<sup>+</sup> moieties precludes a full comparison within the series, lower oxidation potentials observed in the bimetallic *d*IMes complexes reflect the increased donation properties of di-topic carbene ligand thus being in a perfect agreement with the data obtained by IR spectroscopy.

Though this remarkable boosting of the donation properties in NHDC ligands can be intuitively understood in terms of the delocalization of a formal anionic charge within the NHC core, we were pleased to rationalize this phenomenon using theoretical chemistry, namely through the extended transition state natural orbitals for chemical valence (ETS–NOCV) approach.<sup>38</sup>

The summary of the most relevant data for metal-NHC bonding analysis are presented in Table 4 (for details see Table S8 in the Supporting Information). The ETS-NOCV analysis for Mn(I) complex **1a** revealed three primary channels (Figure 5) responsible for IMes  $\sigma$ -donation and two types of  $\pi$ -back bonding – orthogonal and coplanar to the NHC ligand plane further denoted as  $\pi_{\perp}$  and  $\pi_{\parallel}$ , respectively. While the major  $\pi_{\perp}$  component represents a classic back-donation to the  $\pi^*$  orbital of carbene, the minor  $\pi_{\parallel}$  can be described as an overlap of filled metal orbitals with the anti-bonding  $\sigma^*$  orbitals of the NCN moiety.



**Figure 5.** Electron deformation density corresponding to primary NOCV channels for Mn(I) complex **1a** responsible for  $\sigma$ -donation (left) and two types of  $\pi$ -back donation –  $\pi_{\perp}$  (center) and  $\pi_{\parallel}$  (right). Isosurfaces set at 0.003 and 0.001 a.u. for  $\sigma$ - and  $\pi$ -bonding, respectively. Red and blue areas correspond to electron density depletion and concentration, respectively.

**Table 4. Associated Energies of Primary NOCV Channels (kcal mol<sup>-1</sup>) Responsible for the  $\sigma$ -Donation and  $\pi$ -Back Bonding of NHC Ligands in Mn(I) and Fe(II) Complexes Bearing IMes, *a*IMes and *d*IMes Ligands (ADF/BP86-D3/TZP)**

Comp.	Cp(CO) <sub>2</sub> M–NHC bond	Cp(CO) <sub>2</sub> M– <i>a</i> NHC bond
<b>1a</b>	$\sigma$ 38.0, $\pi_{\perp}$ 12.5, $\pi_{\parallel}$ 5.7	–
<b>1b</b>	$\sigma$ 38.8, $\pi_{\perp}$ 13.9, $\pi_{\parallel}$ 5.4	–
<b>6a<sup>+</sup></b>	$\sigma$ 54.3, $\pi_{\perp}$ 9.6, $\pi_{\parallel}$ 3.8	–
<b>6b<sup>+</sup></b>	$\sigma$ 54.9, $\pi_{\perp}$ 9.8, $\pi_{\parallel}$ 4.1 <sup>a</sup>	–
<b>4<sup>+</sup></b>	–	$\sigma$ 64.8, $\pi_{\perp}$ 9.1, $\pi_{\parallel}$ 4.4
<b>3a</b>	$\sigma$ 38.6, $\pi_{\perp}$ 11.2, $\pi_{\parallel}$ 5.7	$\sigma$ 78.2, $\pi_{\perp}$ 8.7, $\pi_{1\parallel}$ 2.5, $\pi_{2\parallel}$ 2.8 <sup>b</sup>
<b>3b</b>	$\sigma$ 39.4, $\pi_{\perp}$ 12.9, $\pi_{\parallel}$ 5.5	$\sigma$ 77.9, $\pi_{\perp}$ 8.9, $\pi_{\parallel}$ 3.5 <sup>c</sup>
<b>5a<sup>+</sup></b>	$\sigma$ 57.3, $\pi_{\perp}$ 9.2, $\pi_{\parallel}$ 4.1	$\sigma$ 71.5, $\pi_{\perp}$ 8.7, $\pi_{\parallel}$ 3.2
<b>5b<sup>+</sup></b>	$\sigma$ 57.5, $\pi_{\perp}$ 9.9, $\pi_{\parallel}$ 4.1 <sup>d</sup>	$\sigma$ 71.3, $\pi_{\perp}$ 9.0, $\pi_{\parallel}$ 3.4

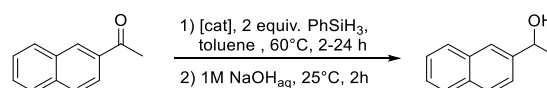
<sup>a</sup> Additional NOCV channel related to metal-*a*NHC  $\pi$ -bonding with the associated energy of 2.2 kcal.mol<sup>-1</sup> was also found (see Figure S25). <sup>b</sup> In this case  $\pi_{\parallel}$  bonding was split in two components and one more NOCV channel related to metal-*a*NHC  $\pi$ -bonding with the associated energy of 4.2 kcal.mol<sup>-1</sup> was also found (see Figure S29). <sup>c</sup> Additional NOCV channel related to metal-*a*NHC  $\pi$ -bonding with the associated energy of 4.0 kcal.mol<sup>-1</sup> was also found (see Figure S30). <sup>d</sup> Additional NOCV channel related to metal-*a*NHC  $\pi$ -bonding with the associated energy of 2.4 kcal.mol<sup>-1</sup> was also found (see Figure S32).

The associated energies of NOCV channels for **1a** (Table 4) are close to calculated alkyl-substituted complex Cp(CO)<sub>2</sub>Mn(IMe) having the same horizontal orientation of the NHC ligand ( $\sigma$  35.0,  $\pi_{\perp}$  14.1,  $\pi_{\parallel}$  5.3 kcal mol<sup>-1</sup>).<sup>39</sup> For the eclipsed isomer **1b**, the energy values for  $\sigma$  and  $\pi_{\perp}$  components are a little bit higher reflecting slightly stronger Mn–NHC bonding (see Table 2 for the bond orders) and additional NOCV channel responsible for  $\pi(\text{C}=\text{C})\dots\pi^*(\text{CO})$  interligand interaction having the associated energy of 1.5 kcal mol<sup>-1</sup> was found (Figure S23). In Fe(II) complexes **6a<sup>+</sup>** and **6b<sup>+</sup>** IMes ligand displays a much stronger  $\sigma$ -bonding energy with a slightly reduced back-donation, which can be explained by a more electron deficient nature of the [Cp(CO)<sub>2</sub>Fe]<sup>+</sup> fragment compared to [Cp(CO)<sub>2</sub>Mn]. As expected, the *a*IMes ligand in Fe(II) derivative **4<sup>+</sup>** shows much greater  $\sigma$ -contribution with again slightly reduced  $\pi_{\perp}$ -bonding being both consistent with higher overall donation properties of *a*NHCs vs. their normal isomers. These results are in agreement with the ETS-NOCV analysis of the bonding of the simplest NHC ligand models IMe and *a*IMe with different transition metal fragments.<sup>40</sup> The energies of NOCV channels responsible for  $\pi(\text{C}=\text{C})\dots\pi^*(\text{CO})$  interactions in Fe(II) NHC cations (3.3–4.3 kcal mol<sup>-1</sup>) are significantly higher than in the corresponding neutral Mn(I) species being consistent with the results of AIM analysis (*vide supra*).

Noteworthy, the data obtained for the *d*IMes complexes within the same series of isomers (Table 4) show a simultaneous increase of the  $\sigma$ -donation and diminution of the  $\pi$ -backdonation for both M–NHC and M–*a*NHC bonding, which is especially pronounced in the latter case for the abnormal carbene fragment. Though the energy differences in most cases are not very significant, the synergy of both effects is clearly responsible for the experimentally observed amplification of NHC donor properties in NHDC derivatives.

**Evaluation of Cationic Fe(II) Complexes Bearing IMes, *a*IMes and *d*IMes Ligands in Ketone Hydrosilylation Catalysis.** In order to look at the possible incidence of improved donation properties of *d*IMes ligand we tested a series of cationic Fe(II) complexes [**4–6**](OTf) in benchmark hydrosilylation of carbonyl substrates.<sup>41</sup> These transformations are well known for half-sandwich Fe(II) complexes bearing normal<sup>22a,b</sup> and abnormal<sup>23a,25</sup> carbene ligands and we have already observed a beneficial effect of increased NHC donation on the catalytic performance in such processes.<sup>27b</sup> We have chosen as a model the hydrosilylation of 2-acetonaphthone with PhSiH<sub>3</sub> (Scheme 4) under the same conditions as previously reported for abnormal 1,2,3-triazol-4-ylidene Fe(II) complex.<sup>25</sup>

#### Scheme 4. Evaluation of Cationic Fe(II) Complexes [**4–6**](OTf) in Hydrosilylation of 2-Acetonaphthone



To our delight, in the presence of 1 mol % of *d*IMes complex [**5**](OTf) a quantitative substrate conversion was achieved after 2 h at 60°C and the corresponding alcohol was isolated in 92% yield after hydrolysis. A decrease of the catalyst charge to 0.5 mol % revealed 94% substrate conversion after 8 h under the same conditions. At the same time *a*IMes complex [**4**](OTf) was found to be much less active affording only 60% conversion after 24 h at 1 mol % loading and complex [**6**](OTf) bearing IMes ligand was totally inactive. To the best of our knowledge, this preliminary study represents the first example

of direct comparison of the catalytic performance for transition metal complexes bearing structurally related normal, abnormal and ditopic NHCs.<sup>42,43</sup>

## CONCLUSION

We have shown that bimetallic transition metal complexes based on imidazol-2,4-diylidene scaffold can be prepared from the emblematic IMes by a rational stepwise metallation approach using  $[\text{Cp}(\text{CO})_2\text{Mn}]$  moiety as protecting group for C2 carbene position. This gave access to an homogeneous series of cationic Fe(II) complexes bearing IMes, *a*IMes, and *d*IMes ligands allowing to show that the donation properties of both normal and abnormal carbenic moieties are actually increased by the metallation at the C4 and C2 positions, respectively. This effect was rationalized by a theoretical study using the ETS-NOCV approach in terms of a simultaneous increase of  $\sigma$ -donation and decrease of  $\pi$ -backdonation being especially pronounced for the abnormal carbenic part. The evaluation of the catalytic properties of the singular series of monometallic Fe(II) IMes and *a*IMes complexes, and bimetallic Fe(II) *d*IMes complex in benchmark ketone hydrosilylation revealed the superiority of the derivative bearing the ditopic *d*IMes ligand. We hope that this contribution will further stimulate the interest to NHDC complexes in the context of homogeneous catalysis.

## EXPERIMENTAL SECTION

**General considerations.** All manipulations were carried out using Schlenk techniques under an atmosphere of dry nitrogen. Dry and oxygen-free organic solvents (THF, Et<sub>2</sub>O, CH<sub>2</sub>Cl<sub>2</sub>, toluene, pentane) were obtained using LabSolv (Innovative Technology) solvent purification system. Acetonitrile for the electrochemical studies was dried by refluxing over P<sub>2</sub>O<sub>5</sub> and distilled under argon prior to use. Solvents used for the purification of organometallic complexes by column chromatography (hexane, toluene, CH<sub>2</sub>Cl<sub>2</sub>, THF) were deoxygenated by nitrogen bubbling during 15–20 min. Deuterated chloroform for NMR experiments was passed through a short column of basic alumina, deoxygenated by three freeze-pump-thaw cycles and kept over 4 Å molecular sieves. A liquid nitrogen/ethanol slush bath was used to maintain samples at the desired low temperature. Chromatographic purification of the compounds was performed on silica (0.060–0.200 mm, 60 Å) obtained from Acros Organics. Complexes  $\text{Cp}(\text{CO})_2\text{Mn}(\text{IMes})$  (**1**),<sup>16</sup>  $[\text{Cp}(\text{CO})_2\text{Fe}(\text{IMes})]\text{I}^{21}$  and  $\text{Cp}(\text{CO})_2\text{FeI}^{44}$  were prepared according to literature procedures. All other reagent grade chemicals purchased from commercial sources were used as received.

Solution IR spectra were recorded in 0.1 mm CaF<sub>2</sub> cells with 0.5 cm<sup>-1</sup> resolution using a Perkin Elmer Frontier FT-IR spectrometer and given in cm<sup>-1</sup> with relative intensity in parentheses. <sup>1</sup>H and <sup>13</sup>C NMR spectra were obtained on Bruker Avance 400 or Avance III HD 400 spectrometers and referenced against the residual signals of deuterated solvents.<sup>45</sup> The signals of quaternary carbon atoms in <sup>13</sup>C NMR spectra were attributed using JMOD and gated <sup>13</sup>C experiments. High-resolution mass spectra (ESI positive mode) were obtained using a Xevo G2 QToF (Waters) spectrometer. Elemental analyses were carried out at the LCC-CNRS (Toulouse) using a Perkin Elmer 2400 series II analyzer.

Cyclic voltammetry and squarewave voltammetry studies were performed using an Autolab PGSTAT100 instrument controlled by GPES 4.09 software in a three-electrode cell consisting of a Pt working electrode (*d* = 0.5 mm), a platinum wire (*S* = 1 cm<sup>2</sup>) as counter electrode, and a SCE electrode as a reference, under Ar atmosphere in acetonitrile solution. 0.1 M solution of Bu<sub>4</sub>NPF<sub>6</sub> was used as the supporting electrolyte and sample concentrations were 1 × 10<sup>-3</sup> M. All peak potentials are calibrated relative to the ferrocene/ferrocenium couple (*E* = +0.40 V vs. SCE in MeCN)<sup>46</sup> by adding ferrocene at the end of the experiments.

**Synthesis of complex 3.** To a solution of complex **1** (640 mg, 1.33 mmol) in THF (5 mL) a 1.6 M solution of *n*BuLi (1.0 mL, 1.6 mmol, 1.2 equiv.) was added dropwise at room temperature. After stirring for

15 min the resulting deep orange solution of complex **2** was evaporated under vacuum and the yellow-brown residue was dissolved in toluene (5 mL). The resulting solution of **2** was then added dropwise for *ca.* 15 min under vigorous stirring to a solution of  $\text{Cp}(\text{CO})_2\text{FeI}$  (404 mg, 1.33 mmol, 1.0 equiv.) in toluene (5 mL) at -10 °C. The cooling bath was removed and the reaction mixture was allowed to reach room temperature. The volatiles were removed under vacuum and the orange residue was purified by column chromatography on silica (2 × 15 cm). The first elution with 1:1 hexane/toluene mixture afforded yellow band containing traces of  $\text{Cp}(\text{CO})_2\text{FeI}$  and starting complex **1** (discarded), followed by a broad orange band of the product **3** contaminated with traces of  $[\text{Cp}(\text{CO})_2\text{Fe}]_2$  eluted with 95:5 toluene/ether mixture. The eluate was evaporated under vacuum and the residue was dissolved in 1:1 THF/heptane mixture (*ca.* 50 mL). The solution was filtered through Celite and concentrated to *ca.* 20 mL under vacuum to induce the crystallization of the target product finished at -20 °C overnight. The supernatant was removed by decantation and the precipitate was washed with hexane (2 × 10 mL) and dried under vacuum to afford complex **3** (725 mg, 83%) as orange microcrystalline solid. Single crystals suitable for X-Ray diffraction experiment were obtained by slow vapor diffusion of hexane into the solution of complex **3** in ether at room temperature. <sup>1</sup>H NMR (400.1 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  6.99 (s, 2H, *CH*<sub>Mes</sub>), 6.97 (s, 2H, *CH*<sub>Mes</sub>), 6.04 (s, 1H, *CH*<sub>Im-5</sub>), 4.09 (s, 5H, Cp-Fe), 3.89 (s, 5H, Cp-Mn), 2.28 (s, 3H, *CH*<sub>3 o-Mes</sub>), 2.23 (s, 9H, *CH*<sub>3 o-Mes</sub>), 2.08 (s, 6H, *CH*<sub>3 p-Mes</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (100.6 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  235.1 (Mn-CO), 213.8 (Fe-CO), 204.4 (Mn-CN<sub>2</sub>), 142.5, 139.7 (*C*<sub>i-Mes</sub>), 138.1, 137.9 (*C*-CH<sub>3 p-Mes</sub>), 137.6, 136.3 (*C*-CH<sub>3 o-Mes</sub>), 132.9 (*CH*<sub>Im-5</sub>), 129.6, 129.3 (*CH*<sub>Mes</sub>), 124.8 (*C*<sub>Im-4</sub>-Fe), 85.3 (Cp-Fe), 81.7 (Cp-Mn), 21.4, 21.2 (*CH*<sub>3 p-Mes</sub>), 19.2, 18.8 (*CH*<sub>3 o-Mes</sub>). IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu_{\text{CO}}$  2030.0 (s), 1980.0 (s), 1900.5 (s), 1827.0 (s) cm<sup>-1</sup>. Elemental analysis calculated (%) for C<sub>35</sub>H<sub>33</sub>FeMnN<sub>2</sub>O<sub>4</sub>: C, 64.05; H, 5.05; N, 4.25; found: C, 64.05; H, 5.30; N, 4.14.

**Synthesis of complex [4](OTf).** To a solution of complex **3** (394 mg, 0.6 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) triflic acid (65  $\mu$ L, 0.72 mmol) was added *via* microsyringe at -40 °C. The orange color of the solution became red-brown and IR spectrum show the transformation of  $\nu_{\text{CO}}$  bands of **3** (2030.0 (s), 1980.0 (s), 1900.5 (s), 1827.0 (s) cm<sup>-1</sup>) into those of the product **[4](OTf)** (2044.0 (s), 1996.0 cm<sup>-1</sup> (s)) and  $\text{CpMn}(\text{CO})_3$  (2022.5 (s), 1935.0 cm<sup>-1</sup> (vs)). The reaction mixture was stirred for 10 min at -40 °C and then allowed to reach room temperature over *ca.* 15–20 min. The resulting brown solution was loaded on a column of silica (2 × 10 cm) and several yellow-brown bands containing  $\text{CpMn}(\text{CO})_3$  and other unidentified impurities were eluted with pure CH<sub>2</sub>Cl<sub>2</sub>. The desired product **[4](OTf)** was then eluted with a CH<sub>2</sub>Cl<sub>2</sub>/THF 20:1 mixture as a yellow band. The eluate was evaporated under vacuum and the residue was dissolved in THF (5 mL). The solution was filtered through Celite, evaporated under vacuum and the product was thoroughly dried under vacuum to afford **[4](OTf)** (337 mg, 89%) as yellow powder. <sup>1</sup>H NMR (400.1 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  8.36 (s, 1H, *CH*<sub>Im-2</sub>), 7.07 (s, 1H, *CH*<sub>Im-5</sub>), 7.04 (s, 2H, *CH*<sub>Mes</sub>), 6.99 (s, 2H, *CH*<sub>Mes</sub>), 5.09 (s, 5H, Cp), 2.35 (s, 3H, *CH*<sub>3 p-Mes</sub>), 2.32 (s, 3H, *CH*<sub>3 p-Mes</sub>), 2.08 (s, 6H, *CH*<sub>3 o-Mes</sub>), 1.97 (s, 6H, *CH*<sub>3 o-Mes</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (100.6 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  211.8 (Fe-CO), 141.8 (*C*<sub>Im-4</sub>-Fe), 141.4, 140.8 (*C*-CH<sub>3 p-Mes</sub>), 138.2 (*CH*<sub>Im-2</sub>), 135.2, 134.0 (*C*-CH<sub>3 o-Mes</sub>), 133.8 (*C*<sub>i-Mes</sub>), 132.2 (*CH*<sub>Im-5</sub>), 131.0 (*C*<sub>i-Mes</sub>), 129.9, 129.7 (*CH*<sub>Mes</sub>), 86.4 (Cp), 21.3, 21.2 (*CH*<sub>3 p-Mes</sub>), 17.6, 17.3 (*CH*<sub>3 o-Mes</sub>). IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu_{\text{CO}}$  2044.0 (s), 1996.0 (s) cm<sup>-1</sup>. Elemental analysis calculated (%) for C<sub>29</sub>H<sub>29</sub>F<sub>3</sub>FeN<sub>2</sub>O<sub>5</sub>S: C, 55.25; H, 4.65; N, 4.45; found: C, 55.11; H, 4.65; N, 4.41.

**Synthesis of complex [5](OTf).** To a solution of **[4](OTf)** (126 mg, 0.2 mmol) and  $\text{Cp}(\text{CO})_2\text{FeI}$  (61 mg, 0.2 mmol) in THF (4 mL) a ~1.7 M solution of *t*AmOK in toluene (175  $\mu$ L, 0.3 mmol) was added dropwise at -80 °C. The reaction mixture was stirred at -80 °C for 30 min and then allowed to warm up to room temperature. IR spectrum showed the formation of **[5](OTf)** ( $\nu_{\text{CO}}$  2035.5 (s), 2027.0 (sh), 1988.0 (s), 1878.5 (sh) cm<sup>-1</sup>) as the main organometallic product. The volatiles were removed under vacuum and the residue was purified by chromatography on silica column (1 × 8 cm). Several yellow-brown bands containing traces of  $\text{Cp}(\text{CO})_2\text{FeI}$  and other unidentified impurities were eluted with pure CH<sub>2</sub>Cl<sub>2</sub>. The product was then eluted with a CH<sub>2</sub>Cl<sub>2</sub>/THF 20:1 mixture as a yellow band. Evaporation of the solvent and drying the residue under vacuum afforded complex **[5](OTf)** (119



mg, 74%) as yellow powder. [5](OTf):  $^1\text{H}$  NMR (400.1 MHz,  $\text{CDCl}_3$ , 25°C):  $\delta$  7.07 (s, 2H,  $\text{CH}_{\text{Mes}}$ ), 7.05 (s, 2H,  $\text{CH}_{\text{Mes}}$ ), 6.79 (s, 1H,  $\text{CH}_{\text{Im-5}}$ ), 4.98 (s, 5H, Cp-Fe), 4.79 (s, 5H, Cp-Fe), 2.39 (s, 3H,  $\text{CH}_3$  *p*-Mes), 2.38 (s, 3H,  $\text{CH}_3$  *p*-Mes), 2.06 (s, 6H,  $\text{CH}_3$  *o*-Mes), 1.96 (s, 6H,  $\text{CH}_3$  *o*-Mes).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100.6 MHz,  $\text{CDCl}_3$ , 25°C):  $\delta$  212.7 (Fe-CO), 210.3 (Fe-CO), 166.7 (Fe-CN<sub>2</sub>), 140.6, 140.3 (C-CH<sub>3</sub> *p*-Mes), 139.9, 137.9 (C-*i*-Mes), 136.7, 136.65 (C-CH<sub>3</sub> *o*-Mes), 136.6 (C<sub>Im-4</sub>-Fe), 135.7 (CH<sub>Im-5</sub>), 130.1, 129.8 (CH<sub>Mes</sub>), 86.2, 86.1 (Cp-Fe), 21.35, 21.3 (CH<sub>3</sub> *p*-Mes), 18.9, 18.4 (CH<sub>3</sub> *o*-Mes). IR ( $\text{CH}_2\text{Cl}_2$ ):  $\nu_{\text{CO}}$  2044.0 (s), 2037.5 (s), 1998.0 (s), 1991.0 (sh)  $\text{cm}^{-1}$ . HRMS (ESI) 657.1141 ( $\text{M}^+$ ), calculated for  $\text{C}_{35}\text{H}_{33}\text{Fe}_2\text{N}_2\text{O}_4$  657.1139 ( $\epsilon_r = 0.3$  ppm).

**Synthesis of complex [6](OTf).** To a solution of  $[\text{Cp}(\text{CO})_2\text{Fe}(\text{IMes})]\text{I}$  (177 mg, 0.25 mmol) in  $\text{CH}_2\text{Cl}_2$  (5 mL) a solution of NaOTf (60 mg, 0.35 mmol) in a nitrogen saturated water (5 mL) was added and the resulting biphasic mixture was vigorously shaken for 2 min. Then the aqueous mixture was removed and the organic mixture was washed with water (5 mL), dried over  $\text{MgSO}_4$  and evaporated to dryness under vacuum. The residue was dissolved in THF (5 mL), filtered through Celite and evaporated to afford after drying under vacuum [6](OTf) (146 mg, 93%) as yellow powder.  $^1\text{H}$  NMR (400.1 MHz,  $\text{CDCl}_3$ , 25°C):  $\delta$  7.37 (s, 2H,  $\text{CH}_{\text{Im-4,5}}$ ), 7.08 (s, 4H,  $\text{CH}_{\text{Mes}}$ ), 4.82 (s, 5H, Cp), 2.38 (s, 6H,  $\text{CH}_3$  *p*-Mes), 2.03 (s, 12H,  $\text{CH}_3$  *o*-Mes);  $^{13}\text{C}\{^1\text{H}\}$  NMR (100.6 MHz,  $\text{CDCl}_3$ , 25°C):  $\delta$  209.4 (Fe-CO), 171.4 (Fe-CN<sub>2</sub>), 141.2 (C-CH<sub>3</sub> *p*-Mes), 135.5 (C-*i*-Mes), 135.4 (C-CH<sub>3</sub> *o*-Mes), 130.1 (CH<sub>Mes</sub>), 128.1 (CH<sub>Im-4,5</sub>), 86.1 (Cp), 21.3 (CH<sub>3</sub> *p*-Mes), 18.1 (CH<sub>3</sub> *o*-Mes). IR ( $\text{CH}_2\text{Cl}_2$ ):  $\nu_{\text{CO}}$  2050.5 (s), 2006.5  $\text{cm}^{-1}$  (s)  $\text{cm}^{-1}$ . Elemental analysis calculated (%) for  $\text{C}_{29}\text{H}_{29}\text{F}_3\text{FeN}_2\text{O}_5\text{S}$ : C, 55.25; H, 4.65; N, 4.45; found: C, 55.03; H, 4.41; N, 4.34.

**X-ray diffraction experiment for complex 3.** X-ray diffraction data were collected on a Bruker D8/APEX II/Incoatec Mo  $\text{I}\mu\text{S}$  Micro-source diffractometer using  $\text{MoK}\alpha$  radiation ( $\lambda = 0.71073$  Å, graphite monochromator). All calculations were performed on a PC compatible computer using the WinGX system.<sup>47</sup> The structures were solved using the SIR92 program,<sup>48</sup> which revealed in each instance the position of most of the non-hydrogen atoms. All the remaining non-hydrogen atoms were located by the usual combination of full matrix least-squares refinement and difference electron density syntheses using the SHELX program.<sup>49</sup> Atomic scattering factors were taken from the usual tabulations. Anomalous dispersion terms for Mn and Fe atoms were included in Fc. All non-hydrogen atoms were allowed to vibrate anisotropically. The hydrogen atoms were set in idealized positions ( $\text{R}_3\text{CH}$ , C-H = 0.96 Å;  $\text{R}_2\text{CH}_2$ , C-H = 0.97 Å;  $\text{RCH}_3$ , C-H = 0.98 Å;  $\text{C}(\text{sp}^2)\text{-H}$  = 0.93 Å;  $U_{\text{iso}}$  1.2 or 1.5 times greater than the  $U_{\text{eq}}$  of the carbon atom to which the hydrogen atom is attached) and their positions refined as “riding” atoms.

**Computational details.** Calculations were performed with the Gaussian 09<sup>50</sup> package with the BP86<sup>51</sup> functional with D3 version of Grimme's dispersion<sup>52</sup> (DFT/BP86-D3) without any ligand simplification. For all atoms the Def2-TZVP<sup>53</sup> basis set was applied. The structures of the all complexes were fully optimized on this level without any symmetry restrictions applying ultrafine integration grid and a tight SCF option. Vibrational frequencies were calculated at the same theory level and reported without applying any scaling factors.

Topological analysis of the electron-density distribution function  $\rho(r)$  was performed using the AIMALL<sup>54</sup> and Multiwfn v3.6<sup>55</sup> program packages based on the wave function obtained by the BP86 calculations. The energies of non-covalent interactions were calculated using the correlation between the binding energy ( $E_{\text{BCP}}$ ) and the value of the density-functional potential energy  $V_{\text{C}}(r)$  in the corresponding critical point (3, -1):  $E = 0.5 \cdot V_{\text{C}}(r)$ .<sup>31</sup> Bond ellipticity,  $\epsilon$  was defined as  $\epsilon = (\lambda_1/\lambda_2 - 1)$ , where  $\lambda_1$  and  $\lambda_2$  are the negative eigenvalues of the Hessian of the electron density at the bond critical point ordered such that  $\lambda_1 < \lambda_2 < 0$ .<sup>30</sup> NBO analysis performed with the NBOPro 6.0 program.<sup>56</sup>

For bonding analysis all complexes were fully reoptimized with the ADF2014<sup>57</sup> program using BP86-D3 functional and TZP<sup>58</sup> basis set. The overall geometry of complexes, as well as relative vibrational frequencies (Table S7) are similar to those of G09/BP86-D3/def2-TZVP calculations. With the energy decomposition analysis (EDA)<sup>32</sup> method, the fragments interaction energy,  $\Delta E_{\text{int}}$ , was decomposed into terms  $\Delta E_{\text{int}} = \Delta E_{\text{elst}} + \Delta E_{\text{Pauli}} + \Delta E_{\text{orb}^+} + \Delta E_{\text{disp}}$ .  $\Delta E_{\text{orb}}$  was further

decomposed with ETS-NOCV approach to the electron density transfer channels,  $\Delta\rho_i(r)$ .<sup>38</sup>

**Hydrosilylation of 2-acetonaphthone catalyzed by Fe(II) NHC complexes [4-6](OTf).** A 10 mL oven-dried Schlenk tube containing a stirring bar, was charged with catalyst, 2-acetonaphthone (85.1 mg, 0.5 mmol),  $\text{PhSiH}_3$  and toluene (1 mL, C = 0.5 M). The reaction mixture was placed in a pre-heated oil bath at 60°C and stirred for the indicated time. After cooling to room temperature MeOH (1 mL) and 1M aqueous NaOH solution (2 mL) were added. The reaction mixture was vigorously stirred for 2 hours at room temperature and then extracted with  $\text{Et}_2\text{O}$  ( $3 \times 10$  mL). The combined organic layers were dried over  $\text{MgSO}_4$ , filtered and evaporated under vacuum. The conversion was determined by  $^1\text{H}$  NMR spectroscopy in the crude mixture by the ratio of proton signals at  $\delta_{\text{H}}$  of 8.47 ppm of 2-acetonaphthone (s, 1H,  $\text{CH}_{\text{Ar}}$ ) and  $\delta_{\text{H}}$  of 5.08 ppm of  $\alpha$ -methyl-2-naphthylmethanol (q, 1H,  $\text{CHCH}_3$ ). The isolation of the product was carried out by column chromatography on silica ( $5 \times 1$  cm) using a 4:1 petroleum ether / EtOAc mixture to afford after drying under vacuum  $\alpha$ -methyl-2-naphthylmethanol (78 mg, 92%).

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

$^1\text{H}$ ,  $^{13}\text{C}$  NMR spectra and cyclic voltammograms for all NHC complexes, additional DFT calculations data (PDF).

Cartesian coordinates for all G09 and ADF optimized structures (xyz).

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### Notes

The authors declare no competing financial interest.

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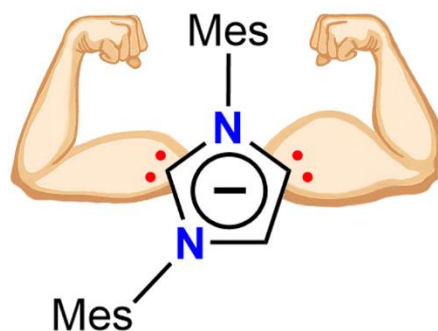
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## Table of Contents artwork and text



Superior electronic donation of imidazol-2,4-diylidene ligand *vs.* the monocarbenic ligands was quantified by IR spectroscopy and cyclic voltammetry on the corresponding mono- and bimetallic Mn(I) and Fe(II) complexes. The observed effect was rationalized by DFT calculations in terms of a synergy between increased  $\sigma$ -donation and decreased  $\pi$ -backdonation of both normal and abnormal carbene fragments being especially pronounced in the latter case.

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