

# The Core Difference between a Mesoionic and a Normal *N*-Heterocyclic Carbene

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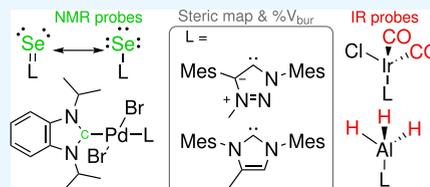


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**ABSTRACT:** The properties of the abnormal *N*-heterocyclic carbene (NHC) 1,4-dimesityl-3-methyl-1,2,3-triazolin-5-ylidene were comprehensively compared to those of the related normal carbene 1,3-dimesitylimidazol-2-ylidene using a range of steric and electronic probe techniques (%  $V_{\text{bur}}$ , steric maps, Tolman electronic parameter, alane, Huynh electronic parameter, selone, and  $pK_a$  values). The two NHCs were determined to be sterically equivalent (isostructural), while the triazolin-5-ylidene was found to be a stronger  $\sigma$ -electron donor and a much weaker  $\pi$ -electron acceptor. These results were used to demonstrate that the electronic properties of these NHCs could affect the stereochemical outcome of an NHC-catalyzed reaction.



## INTRODUCTION

*N*-Heterocyclic carbenes (NHCs) are a useful class of ligand in organometallic chemistry.<sup>1</sup> The first isolated NHC was reported in 1991,<sup>2</sup> which started the widespread investigation into their properties and uses as both stabilizing ligands<sup>3</sup> and organocatalysts.<sup>4</sup> There have been a variety of methods used to probe ligand properties, and an understanding of their strengths and shortcomings is important when assessing the information provided by a particular technique.

One of the first attempts to quantify ligand behavior concluded that it was the steric properties, measured using the eponymously coined Tolman cone angle ( $\theta$ ), that were key to the stability of the complex.<sup>5</sup> Many years later, an alternative method for quantifying the steric properties of ligands was proposed: the solid angle  $\Omega$ .<sup>6</sup> This technique provides useful information but is not intuitive and has had limited success as a result.<sup>7</sup> Subsequently, a new technique was proposed: buried volume (%  $V_{\text{bur}}$ ).<sup>8</sup> This value is calculated from a single crystal X-ray diffraction (SCXRD) structure and is defined as the percentage of a sphere filled by the ligand at a specified distance from the metal center.<sup>9</sup> The catalytic performance of NHCs has been correlated with the %  $V_{\text{bur}}$ .<sup>10</sup> This method provides an intuitive—though simplistic—single number to represent the steric bulk of a given ligand. To capture more complex geometries, the method was extended to include a steric map, providing a visual indication of the 3D nature of the ligand.<sup>11</sup>

Tolman proposed both the cone angle to measure steric properties and the Tolman electronic parameter (TEP)—to measure electronic properties—around the same time.<sup>5,12</sup> The TEP originally required the preparation of nickel carbonyl complexes ( $\text{Ni}(\text{CO})_3(\text{L})$ , where L = the ligand of interest) and was limited to be used with phosphorus-derived ligands.<sup>5</sup> The technique was expanded to use less toxic metal centers ( $\text{MX}(\text{CO})_2(\text{L})$ , where M = Rh, Ir; X = Cl, Br, I) and to

include analysis of other ligand types, including NHCs.<sup>13,14</sup> The  $A_1$  infrared (IR) stretch of the carbonyl group provides an indication of the electron-donating ability of the ligand.

There are three considerations when using TEP values from the literature to compare the electronic properties of NHCs.<sup>14,15</sup> First, the choice of the metal center (commonly Ni, Rh, or Ir) and halide (commonly Br or Cl) affects the TEP values. There are linear regressions to interconvert values obtained with one metal center to another; however, these have evolved with time, and care should be taken to ensure that all conversions have used the same formula. Second, the absorbances are highly dependent on the media used during collection. Whether a sample is evaluated neat, as a Nujol mull, or in solution (including the choice of the solvent) affects the absorbances and must be considered to ensure valid comparisons. Third, the precision is limited compared to other techniques with the resolution of the IR absorbance bands being limited<sup>a</sup> to 0.5–1.5  $\text{cm}^{-1}$ .

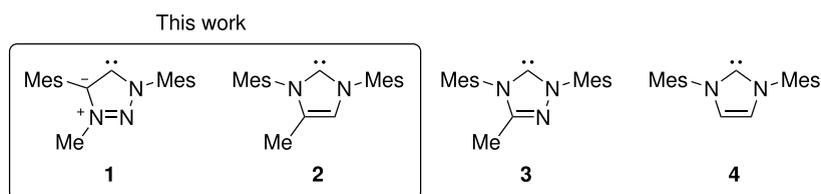
Along with the practical considerations, the TEP technique has several fundamental limitations including the assumption that the ligand does not accept  $\pi$ -electron density.<sup>12</sup> This assumption has been shown to be invalid for NHC ligands.<sup>16</sup> Another issue is that the probe does not adequately distinguish electronic from steric effects.<sup>17</sup> A solution has been proposed to overcome mode–mode coupling to analyze the localized TEP,<sup>18</sup> though the computational method has not seen widespread adoption.

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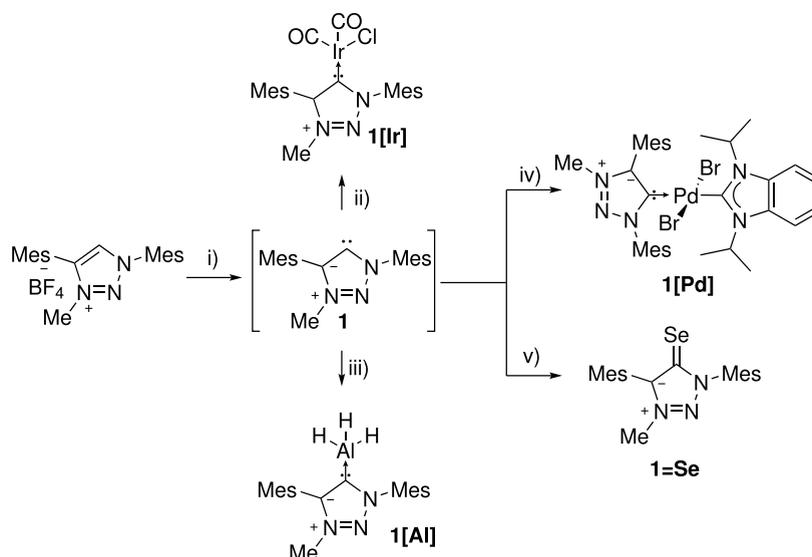
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**Figure 1.** Left, the two carbenes **1** and **2** selected for this study. Right, two related NHCs, 1,2,4-triazolin-5-ylidene **3** and 1,3-dimesitylimidazolin-2-ylidene **4**.

### Scheme 1. Routes to Each of the Four Complex Types<sup>a</sup>



<sup>a</sup>Shown here for carbene **1** with similar conditions used for analogue **2**. (i)  $\text{KHMDS}$  or  ${}^n\text{BuLi}/\text{THF}$ ,  $-78$  to  $-40$  °C; (ii)  $[\text{IrCl}(\text{cod})_2]/\text{THF}$  and then  $\text{CO}(\text{g})$ ; (iii)  $\text{LiAlH}_4/\text{Et}_2\text{O}$   $-40$  °C; (iv)  $[\text{PdBr}_2\{\text{Pr}_2\text{-bimy}\}]_2/\text{THF}$ ; (v) elemental selenium in  $\text{THF}$ ,  $10$  °C.

Another IR-based probe is the hydride stretch of the alane derivative of the ligand in question. The stability of the compound (and other group XIII metal hydrides) is used as a comparator for the ligand being examined.<sup>19–21</sup> The IR stretching frequency of the hydride has also been used as a means of comparing ligand properties,<sup>22</sup> with a higher wavenumber value correlating with a less nucleophilic/less  $\sigma$ -donating ligand. However, the technique is not widespread and suffers from similar issues as those of TEP, requiring consistent measurement conditions and providing low precision values.

There are two more recently developed nuclear magnetic resonance (NMR)-based probes for assessing the electronic characteristics of NHCs and ligands in general. The first method, coined as the Huynh electronic parameter (HEP), uses  $^{13}\text{C}$  NMR spectroscopy to measure the  $\sigma$ -electron-donating ability of a ligand *trans* to a benzimidazolin-2-ylidene probe, when measured in  $\text{CDCl}_3$  and referenced to  $77.7$  ppm.<sup>23</sup> The second technique assesses the  $\pi$ -electron-accepting ability of the NHC in an NHC-selenium adduct by measuring the  $^{77}\text{Se}$  NMR chemical shift of the selenium nuclei. We have previously compared and contrasted these techniques, including considerations around obtaining reliable data<sup>24</sup> and noting limitations of the methods.<sup>25</sup>

With the development of new techniques and the increased availability of data, it is clear that both steric and electronic properties determine the behavior of NHCs<sup>13,14</sup> and ligands in general.<sup>26</sup> To predict how an NHC will behave—either as a support ligand or as an organocatalyst—both the steric and electronic properties of that NHC need to be understood.

1,2,3-Triazole-derived NHCs are becoming more widely studied<sup>27,28</sup> with the available data suggesting that they are strong electron donors.<sup>29–31</sup> This increased donation is not purely due to the presence of an additional nitrogen within the heterocycle as 1,2,4-triazole derivatives (such as NHC **3** in Figure 1) are far less electron-donating than their 1,2,3-triazole equivalents<sup>14</sup> and indeed are often less donating than similar imidazole derivatives.<sup>32,33</sup> This increased donation is likely because 1,2,3-triazole-derived NHCs are mesoionic; all sensible canonical forms possess charge separation resulting in a zwitterion. Mesoionic carbenes are one of several types of “abnormal” carbenes.<sup>34</sup>

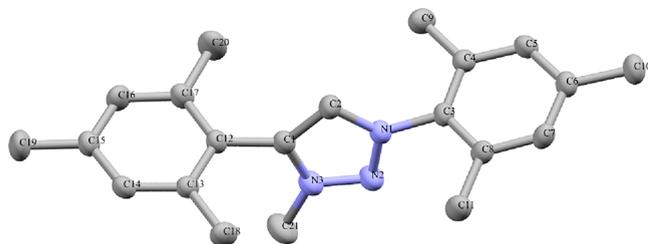
The aim of the work described was to investigate the properties of the mesoionic 1,4-dimesityl-3-methyl-1,2,3-triazolin-5-ylidene (**1**). This NHC was compared to the closely related 1,3-dimesityl-4-methylimidazolin-2-ylidene (**2**) in an attempt to isolate the effect of changing the core heterocycle from that of changing substituents. We undertook a comprehensive analysis of both the steric and electronic properties of the NHCs and their performance as organocatalysts.

## RESULTS AND DISCUSSION

**Preparation of the Complexes.** The azolium salt precursors of the NHCs **1** and **2** were prepared as previously reported,<sup>24,35</sup> and a range of complexes were prepared through deprotonation of the relevant azolium salt ( $\text{1}\cdot\text{HBF}_4$  or  $\text{2}\cdot\text{HBF}_4$ ) and treatment with the appropriate metal precursor (Scheme 1). The alanes were very unstable and decomposed

on exposure to air and under prolonged storage at room temperature. In contrast, the iridium, palladium, and selenium complexes were air-stable and able to be purified using column chromatography. The preparation of complexes **1** [Ir(CO)<sub>2</sub>Cl],<sup>36</sup> **2** [Ir(CO)<sub>2</sub>Cl],<sup>37</sup> **1** [Pd],<sup>24,30</sup> **2** [Pd],<sup>24</sup> **1**=Se,<sup>24</sup> and **2**=Se<sup>24</sup> has been previously reported, with standard characterization data matching that found in the literature.

**Preparation and Analysis of the Free Carbene 1.** The azolium salt **1**·HBF<sub>4</sub> was deprotonated with potassium *bis*(trimethylsilyl)amide (KHMDs) to generate the free NHC **1** [Scheme 1(i)] as a crystalline purple solid (SCXRD structure in Figure 2). This result confirmed that NHC **1** is



**Figure 2.** Molecular structure of carbene **1**. Atoms are shown with anisotropic atomic displacement parameters at 50% probability, and selected hydrogen atoms are omitted for clarity. Selected bond lengths (Å): C(2)–N(1): 1.372(3) and angles (°): N(1)–C(2)–C(1): 99.48(2).

stable and isolable as a free carbene, consistent with previous reports.<sup>29,31</sup> The <sup>13</sup>C NMR chemical shift of the carbenic center (196.64 ppm, C<sub>6</sub>D<sub>6</sub>) is one of the most upfield-shifted signals reported for an NHC,<sup>b</sup> consistent with the mesoionic nature of the carbene.<sup>13,38</sup>

The N–C–C angle of the isolated NHC **1** [99.48(2)°] is more acute than the equivalent N–C–N angle for the closely related NHC **4** [Figure 1 NHC **4**, 101.4(2)°].<sup>39</sup> Indeed, it is more acute than those of most reported imidazolin-2-ylidenes,<sup>13</sup> indicating that NHC **1** is more strongly  $\sigma$ -electron-donating than NHC **2**.

The carbene **1** was stable in C<sub>6</sub>D<sub>6</sub> solution for hours, with the purple–red color of the solution slowly fading over days. After 6 months, the solution had turned colorless; NMR spectroscopy suggested complete conversion to the 5-substituted triazole **1d** (see the Supporting Information). A proposed mechanism for the formation of the heterocycle **1d** is shown in Figure 3 and is consistent with that observed by Bertrand.<sup>31</sup> A signal attributable to the intermediate anionic carbenic triazole **1b** was observed at 197.55 ppm in the <sup>13</sup>C NMR spectrum of a solution of crude NHC **1** in C<sub>6</sub>D<sub>6</sub>. This

rearrangement occurred under ambient conditions over a much extended time period, compared to 12–48 h at 50 °C.<sup>27</sup>

### Discussion of the Steric Features of NHCs **1** and **2**.

The % *V*<sub>bur</sub> value is a metric used to compare the steric properties of a ligand. The value is calculated from an SCXRD structure and is defined as the percentage of a sphere filled by the ligand at a specified distance (usually 2.00 or 2.28 Å) from the metal center.<sup>9</sup> The catalytic performance of NHCs has been correlated<sup>10</sup> with the % *V*<sub>bur</sub>.

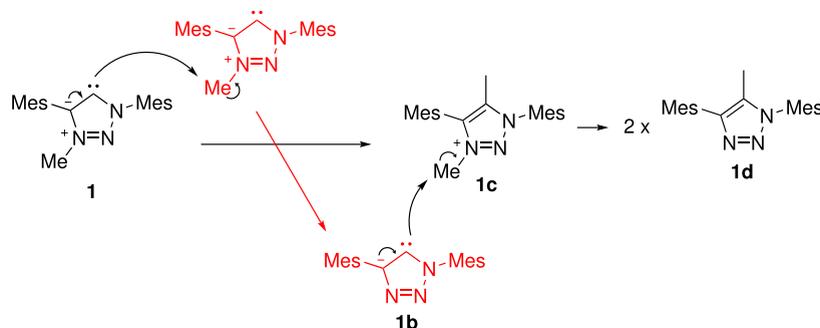
With SCXRD structures obtained for several of the complexes prepared in this work, the steric nature of the ligands **1** and **2** was considered. The % *V*<sub>bur</sub> was calculated for the NHCs **1** and **2** using both the palladium complexes (**1**[Pd] and **2**[Pd]) and the aluminum complexes (**1**[Al] and **2**[Al]). The % *V*<sub>bur</sub> values for the NHCs were calculated using typical values: a metal–carbon distance of 2.28 Å and no protons.<sup>40</sup> The % *V*<sub>bur</sub> values are comparable, with that of the normal carbene **2** ([Pd]: 29.1%, [Al]: 29.5%) being slightly larger than that of the mesoionic carbene **1** ([Al]: 26.7%, [Pd]: 27.3%). These % *V*<sub>bur</sub> values are between those of PEt<sub>3</sub> (27.1%) and PPh<sub>3</sub> (29.6%),<sup>9</sup> and the variations are within the range typical for % *V*<sub>bur</sub> calculated for a given ligand on different metal centers.<sup>c</sup>

The % *V*<sub>bur</sub> gives an indication of the steric bulk of the ligand. However, it does not provide any insights into the 3D configuration of the ligand.<sup>40</sup> For example, a ligand that blocks only one side of the metal complex could have the same % *V*<sub>bur</sub> value as that of a smaller ligand that blocks the entire face of the complex. For this reason, Cavallo proposed the use of steric maps to holistically compare the steric properties of ligands.<sup>11</sup> Steric maps were calculated for each of the carbenes **1** and **2** using the alane and HEP complexes (Figure 4). These data show that both ligands present almost identical steric demands, with NHC **1** being slightly less bulky, consistent with the % *V*<sub>bur</sub> values.

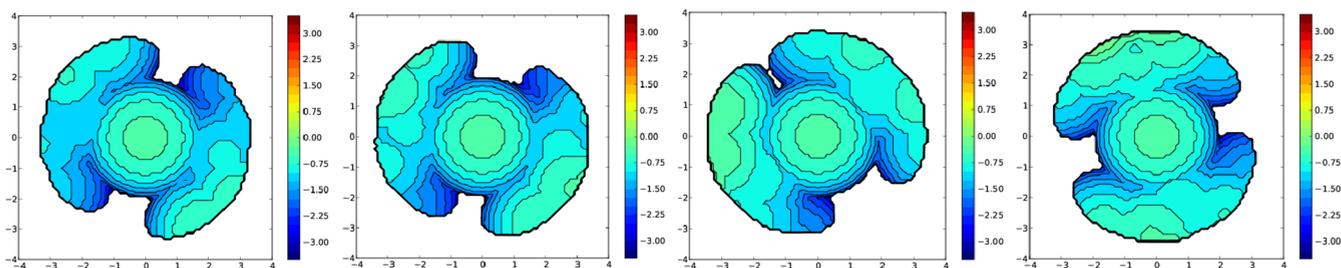
It is common for the steric and the electronic properties of ligands to be considered in isolation.<sup>11</sup> However, it is clear that these two properties can have complex interdependencies.<sup>40</sup> Some probe methodologies are strongly affected by the steric properties,<sup>25</sup> and care must be taken when assessing the data obtained using them.<sup>24</sup> The % *V*<sub>bur</sub> and steric maps both suggest that NHCs **1** and **2** are sufficiently similar such that the electronic probe results become free from steric interference.

## DISCUSSION OF THE ELECTRONIC PROBES USED

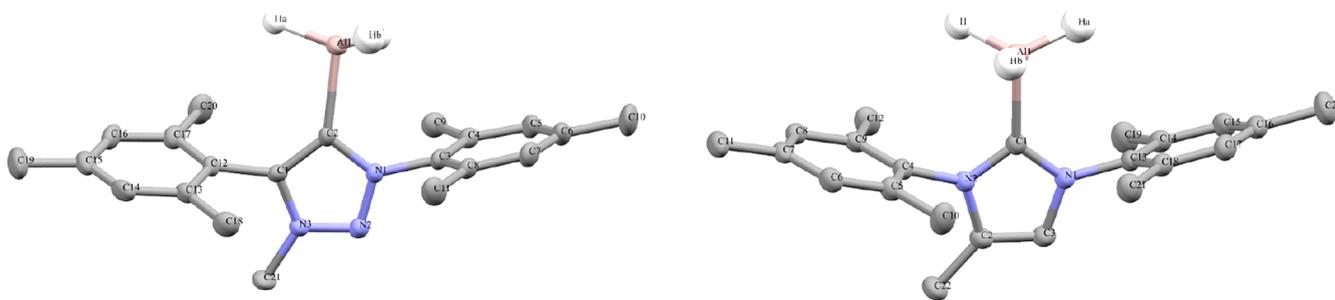
**IR Techniques.** The IR spectra of the TEP complexes (**1**[Ir(CO)<sub>2</sub>Cl] and **2**[Ir(CO)<sub>2</sub>Cl]) were obtained in dichloromethane (DCM), with data matching that reported,<sup>36,37</sup> given



**Figure 3.** Proposed mechanism for the transformation of NHC **1** into **1d**.



**Figure 4.** Steric maps for **1[Al]** (left most); **1[Pd]** (left middle); **2[Al]** (right middle); and **2[Pd]** (right most). Calculated using SambVca.<sup>41</sup> Settings: Bondi radii scaled by 1.17; sphere radius 3.5 Å; M–C: 2.28 Å; mesh spacing for numerical integration 0.10; H atoms not included.



**Figure 5.** Molecular structures of the alanes **1[Al]** (left) and **2[Al]** (right). Atoms are shown with anisotropic atomic displacement parameters at 50% probability, and selected hydrogen atoms are omitted for clarity. Hydride atoms were located in the difference map. Selected bond lengths (Å): **1[Al]** Al(1)–C(2): 2.047(5), C(2)–C(1): 1.375(6), C(2)–N(2): 1.369(6), Al(1)–H: 1.47(5), Al(1)–Ha: 1.45(5), Al(1)–Hb: 1.60(7); **2[Al]** Al(1)–C(1): 2.048(2), Al(1)–H: 1.51(2), Al(1)–Ha: 1.50(3), Al(1)–Hb: 1.55(2), C(1)–N(2): 1.349(2), C(1)–N(2): 1.360(2) and angles (°): **1[Al]** N(1)–C(2)–C(1): 102.3(4); **2[Al]** N(1)–C(1)–N(2): 104.2(1).

the reported uncertainties (**1[Ir(CO)<sub>2</sub>Cl]**: 1975.67, 2061.39  $\text{cm}^{-1}$ , TEP:<sup>d</sup> 2046.9  $\text{cm}^{-1}$  vs 2047.3  $\text{cm}^{-1}$ ;<sup>e</sup> **2[Ir(CO)<sub>2</sub>Cl]**: 1978.2, 2064.5  $\text{cm}^{-1}$ , TEP: 2049.3  $\text{cm}^{-1}$  vs 2049.0  $\text{cm}^{-1}$ ).

The literature values of the TEP for the complexes **1[Ir(CO)<sub>2</sub>Cl]**<sup>36</sup> and **2[Ir(CO)<sub>2</sub>Cl]**<sup>37</sup> are both based on complexes involving the same metal and halide and collected as solutions in the same solvent (DCM), satisfying the first two considerations discussed above. The values obtained in this work match those reported within 0.5  $\text{cm}^{-1}$  and suggest that carbene **1** is a stronger electron donor than carbene **2** by ca. 2  $\text{cm}^{-1}$ —small yet significant on the TEP scale. For example, the TEP value of 1,3-di-1-adamantylimidazolin-2-ylidene is reported as 1  $\text{cm}^{-1}$  lower than that of NHC **4**.<sup>14</sup> While distinguishing the two NHCs, the TEP values give limited information that NHC **1** is a stronger electron donor than **2**, without distinguishing the  $\sigma$ - or  $\pi$ -components of the electronic properties.

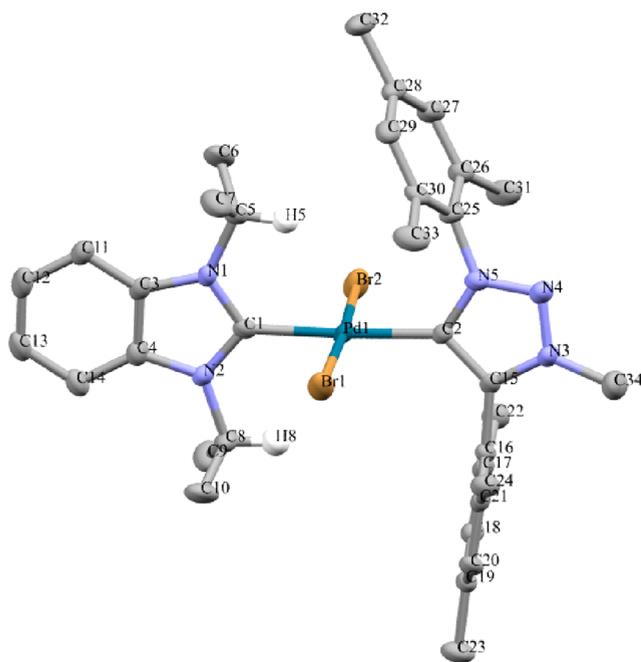
The IR absorbances of the hydrides of alane compounds have also been used to probe electronic properties.<sup>21,22</sup> The two alanes considered herein exhibited high melting points (**1[Al]**: 193–196 °C; **2[Al]**: 203–204 °C), consistent with alane complexes of other NHCs. Spectroscopic data of the isolated materials supported their identity, noting broad hydridic signals in the <sup>1</sup>H NMR spectra in the expected region<sup>20</sup> (**1[Al]**: 4.0 ppm; **2[Al]**: 3.8 ppm) and the absence of signals above 7 ppm attributable to a C<sub>2</sub> proton. The IR spectra contained sharp signals at 1719.7  $\text{cm}^{-1}$  (**1[Al]**) and 1743.7  $\text{cm}^{-1}$  (**2[Al]**). The IR absorbance for complex **2[Al]** is extremely close to that of the diprotio equivalent **4[Al]** (1743  $\text{cm}^{-1}$ ).<sup>19</sup> This outcome is unsurprising, given the similarity of the two species, with the addition of a weakly electron-donating methyl group four bonds from the aluminum center,<sup>8</sup> and suggests that both imidazolin-2-ylidene species are strong electron donors. The IR absorbance of alane **1[Al]**

(1719.7  $\text{cm}^{-1}$ ) is significantly lower than that of complex **2[Al]**, which indicates that NHC **1** is significantly more electron-donating, and nucleophilic, than NHC **2**,<sup>22</sup> although this probe is not quantitative. The NCN angle in alane **2[Al]** [Figure 5, right: 104.2(1)°] is slightly more obtuse than the analogous NCC angle in complex **1[Al]** [Figure 5, left: 102.3(4)°], which also suggests that NHC **2** is less  $\sigma$ -electron-donating than NHC **1**.<sup>13</sup>

**NMR-Based Probe Techniques.** The HEP has been used to investigate the electronic properties of a wide variety of NHCs. The preparation and characterization of the palladium complex **2[Pd]** have been previously reported,<sup>24</sup> while complex **1[Pd]** was prepared using the same method with spectroscopic data that matched that in the literature,<sup>30</sup> once the solvent referencing was considered. The SCXRD structure (Figure 6) shows the expected *trans*-**1[Pd]** complex. The Pd(1)–C(1) bond length [2.010(4) Å] is the same within uncertainty as that of complex **2[Pd]** [2.008(3) Å].<sup>24</sup> However, the carbenic carbon angle is slightly more acute (**1[Pd]**: 102.0(3)° compared to **2[Pd]**: 103.9(3)°), suggesting a larger HOMO–LUMO gap in the palladium complex, consistent with stronger  $\sigma$ -electron donation by ligand **1** than by ligand **2**.<sup>1</sup>

The HEP values for the two complexes (**1[Pd]**: 179.53 ppm, **2[Pd]**: 177.56 ppm) suggest that carbene **1** is significantly more  $\sigma$ -electron-donating than carbene **2**. Indeed, even in absolute terms, carbene **1** is one of the most  $\sigma$ -electron-donating NHCs reported and is only exceeded by three imidazolin-2-ylidenes—all with alkyl *N*-substituents.<sup>14,43</sup>

Ganter's selone probe provides another means of examining both the  $\pi$ -electron-accepting ability and the  $\sigma$ -electron-donating ability of NHCs.<sup>44,45</sup> We have previously reported the preparation and characterization of the selone complexes **1=Se** and **2=Se**,<sup>24</sup> with signals in the <sup>77</sup>Se NMR spectrum at



**Figure 6.** Molecular structure of complex **1**[Pd]. Atoms are shown with anisotropic atomic displacement parameters at 50% probability, and selected hydrogen atoms and one chloroform are omitted for clarity. Selected bond lengths (Å): Pd(1)–C(1): 2.010(4) and Pd(1)–C(2): 2.036(4) and Pd(1)⋯H(5): 2.654 angles (°): N(2)–C(1)–N(1): 106.8(3) and N(5)–C(2)–C(15): 102.0(3).

–9.5 and 30.1 ppm, respectively.<sup>14</sup> The <sup>77</sup>Se NMR chemical shift for selone **1**=Se is shifted significantly upfield, suggesting that carbene **1** is a very weak  $\pi$ -electron-accepting NHC<sup>44</sup> and is the weakest  $\pi$ -electron-accepting triazolium-derived NHC so far reported.<sup>14</sup> The <sup>13</sup>C–<sup>77</sup>Se coupling constant of the selone species is an indicator of the  $\sigma$ -electron-donating ability of the NHCs,<sup>45</sup> where a smaller coupling constant indicates a stronger  $\sigma$ -electron-donating NHC. The literature method required 48 h per spectrum,<sup>45</sup> and there has been minimal uptake of the technique. Through use of a cryoprobe NMR spectrometer, the coupling constants could be distinguished within a 2 h period. The results suggest that carbene **1** (<sup>13</sup>C–<sup>77</sup>Se: 218.6 Hz in **1**=Se) is a significantly stronger  $\sigma$ -electron-donating NHC than carbene **2** (<sup>13</sup>C–<sup>77</sup>Se: 228.5 Hz in **2**=Se).

The HEP and selone techniques both provide a measure of  $\sigma$ -electron-donating ability. The results of both of these NMR probe techniques suggest that NHC **1** is a significantly stronger  $\sigma$ -electron donor. As we have previously shown,<sup>25</sup> the two measures are only reliable when the steric properties of the probed ligands are relatively consistent. Since the %  $V_{\text{bur}}$  values for the NHCs **1** and **2** are comparable, it is reasonable to

assume that both probe values are reliable. As such, carbene **1** can be placed onto the same correlations as previously shown—see the Supporting Information for more details.

**Using  $pK_a$  Values as Thermodynamic Measures of Donating Ability.** We have previously reported the  $pK_a$  values of the azolium salts **1**-HI and **2**-HCl, determined in dimethyl sulfoxide (DMSO).<sup>35,46,i</sup> The  $pK_a$  difference of ca. 0.5 indicates that NHC **1** is more basic than NHC **2**. As discussed previously, the difference is significant, though larger changes can be obtained through different N-substitutions.<sup>46</sup> One possible explanation of this difference is that the  $pK_a$  value can be considered a measure of the electron donation of the NHC to a proton—which can only accept  $\sigma$ -electron density. This argument remains entirely consistent with that of the IR and NMR probes introduced above.

**Comparison of the NHCs **1** and **2** as Organocatalysts.** 1,2,3-Triazolium-5-ylidenes have seen some use as support ligands for organometallic catalysts<sup>47,48</sup> and are comparatively rarely used as organocatalysts.<sup>49–52</sup> The behavior of NHCs **1** and **2** was probed by comparing the in situ organocatalytic formation of  $\gamma$ -butyrolactone **7** (Scheme 2). The reaction proceeds through nucleophilic attack of the NHC on the *trans*-cinnamaldehyde **5** to form a Breslow intermediate<sup>53</sup> and reacts with *p*-bromobenzaldehyde **6**. Both NHCs **1** and **2** successfully catalyzed the reaction, going to completion within ca. 2 h and with similar conversion profiles—see the Supporting Information for more details.

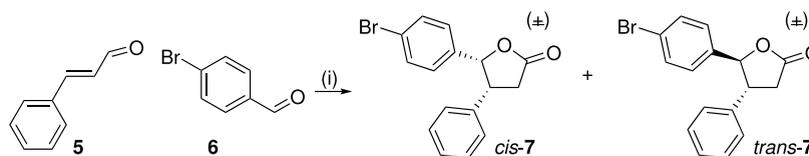
Since the two NHCs catalyze the reaction at approximately the same rate, this suggests that there is no significant difference in the rate-determining step of the mechanism. However, there is clearly a difference in the product-determining step of the reaction—see the Supporting Information for a brief discussion.

## SUMMARY

Consideration of all of the results mentioned above provides a consistent picture of the electronic properties of the mesoionic NHC **1** and allows for comparison to those of the “normal” NHC **2**. The salient data for NHCs **1** and **2** are compiled in Table 1. Taken all together, the following can be stated:

1. The NHCs **1** and **2** have very similar steric properties—similar enough to be deemed consistent (%  $V_{\text{bur}}$  and steric maps).
2. NHC **1** is a stronger electron donor than its analogue NHC **2** (TEP, alane,  $pK_a$ ).
3. NHC **1** is a stronger  $\sigma$ -electron donor than NHC **2**; indeed, it is stronger than any 1,3-dimesitylimidazolium-2-ylidene reported<sup>14,24</sup> and is only exceeded by less bulky 1,3-diisopropyl- and 1,3-dimethylimidazolium-2-ylidenes<sup>14,43</sup> (HEP and <sup>13</sup>C–<sup>77</sup>Se coupling constant).

**Scheme 2.** NHC-Catalyzed Reaction of *trans*-Cinnamaldehyde (**5**) with *p*-Bromobenzaldehyde (**6**) to Form the *cis*- and *trans*-Isomers of the  $\gamma$ -Butyrolactone (**7**)<sup>2</sup>



<sup>2</sup>(i) 10 mol % precatalyst (**1**-HBF<sub>4</sub> or **2**-HBF<sub>4</sub>), 10 mol % KHMDs, THF, 25 °C

**Table 1. Compiled Electronic and Steric Properties of NHCs 2 and 1 in This Work Unless Noted<sup>a</sup>**

	NHC 1	NHC 2
NHC interior angle	99.48(2) <sup>o</sup>	101.4(2) <sup>o,b</sup>
TEP/cm <sup>-1</sup>	2046.9	2049.3
alane/cm <sup>-1</sup>	1719.7	1743.7
alane interior angle	102.3(4) <sup>o</sup>	104.2(1) <sup>o</sup>
HEP/ppm	179.53	177.56
<sup>77</sup> Se <sup>c</sup> /ppm	-9.5	30.06
<sup>13</sup> C- <sup>77</sup> Se/Hz	218.6	228.5
% V <sub>bur</sub>	26.7-27.4	29.1-29.5
pK <sub>a</sub> <sup>d</sup>	22.26 ± 0.09	22.75 ± 0.14

<sup>a</sup>See Figure 4 for steric maps. <sup>b</sup>Data taken from ref 39. <sup>c</sup>Data reported in ref 24. <sup>d</sup>Of the corresponding azolium salt, data from refs 35 and 46.

- NHC 1 is significantly less  $\pi$ -electron-accepting than NHC 2. The <sup>77</sup>Se NMR chemical shift for selone 1=Se is one of the highest fields of all selones reported, exceeded only by seven reported NHCs.<sup>14,25</sup> It is worth repeating that NHCs 1 and 2 are unique in that their steric properties are highly consistent, such that the <sup>77</sup>Se data are reliable for electronic comparisons. The reported values for sterically bulky NHCs, such as 1,3-diamantylimidazolin-2-ylidene, are potentially not representative of the true  $\pi$ -electron-accepting abilities of the NHCs.<sup>25</sup>
- The relative <sup>13</sup>C-<sup>77</sup>Se NMR coupling constant indicates that NHC 1 has a significantly lower-energy HOMO than NHC 2.<sup>45</sup> The <sup>77</sup>Se NMR chemical shift implies that NHC 1 has a moderately higher-energy LUMO than NHC 2.<sup>45,j</sup> This suggests that NHC 1 has a smaller HOMO-LUMO gap and thus is expected to exhibit more triplet-carbene character than NHC 2.
- The rate of formation of lactone 7 is indistinguishable between the two NHCs, yet the stereochemical outcome of the organocatalytic formation of compound 7 is affected by the *electronic properties* of the NHCs.

## CONCLUSIONS

This work provides the first comprehensive analysis of a mesoionic carbene, with a comparison to a sterically paired normal carbene. The 1,2,3-triazolin-derived NHC 1 was shown to be sterically matched with the imidazolin-derived NHC 2. The mesoionic NHC 1 was shown to be a stronger electron donor than NHC 2, a stronger  $\sigma$ -electron donor, and one of the least  $\pi$ -electron-accepting NHCs reported to date. Comparison of the organocatalytic formation of  $\gamma$ -butyrolactone showed that both NHCs catalyze the reaction at approximately the same rate yet with different *cis/trans* ratios, which provides the first report of strong evidence that stereochemical outcome of this reaction can be controlled by the electronic properties of an NHC organocatalyst. This finding hints at a variety of applications controlling organocatalytic reactions with NHC electronics, including stereochemical control using switchable NHCs and in heterogeneous applications.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.2c04682>.

Experimental procedures and characterization data for all new compounds and brief discussion about the mechanism of the organocatalysis (PDF)  
 Crystallographic data for complex 1 (CIF)  
 Crystallographic data for complex 1 aluminum (CIF)  
 Crystallographic data for complex 1 palladium (CIF)  
 Crystallographic data for complex 1 aluminum (CIF)

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### Notes

The authors declare no competing financial interest.

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## ADDITIONAL NOTES

<sup>a</sup>This uncertainty is particularly large, given that the range of reported TEP values of NHCs is 37 cm<sup>-1</sup> and that of 4,5-substituted imidazolin-2-ylidenes is 8 cm<sup>-1</sup>.<sup>14</sup>

<sup>b</sup>The chemical shift of the carbenic carbon of NHC 1 is further upfield than that of similar 1,2,3-triazolin-5-ylidenes reported at  $\delta = 202.1$  and 198.3.<sup>31</sup>

<sup>c</sup>For example, NHC 4 has been calculated between 25.8% (Table 19, entry 10)<sup>9</sup> and 33.1% (Table 19, entry 9). It is worth noting the % V<sub>bur</sub> calculated for 4[AuBr<sub>3</sub>] is erroneously reported as 39.2% (Table 19, entry 2)<sup>9</sup> instead of 29.2%. 4[BaN(SiMe<sub>3</sub>)<sub>2</sub>] (entry 9) was recalculated using SambVca 2.1.<sup>41</sup>

<sup>d</sup>Calculated using TEP = 0.8475 [ $\bar{\nu}_{av} + 336.2$ ] cm<sup>-1</sup>.<sup>14,42</sup>

<sup>e</sup>Recalculated from the reported values<sup>36</sup> of 1976 and 2062 cm<sup>-1</sup>.

<sup>f</sup>Recalculated from the reported values<sup>37</sup> of 1978.0 and 2064.4 cm<sup>-1</sup>.

<sup>g</sup>For example, the diprotio and dimethyl variants of 2,3-diisopropylimidazolin-2-alane are reported as 1719 and 1718 cm<sup>-1</sup>, respectively.<sup>20</sup>

<sup>h</sup>The spectra for both 1=Se and 2=Se were referenced to 0.022 M (PhSe)<sub>2</sub> in CDCl<sub>3</sub> at 463 ppm; this is important as

both the reference concentration and solvent choice can affect the observed chemical shift.<sup>44</sup>

<sup>1</sup>DMSO is a dissociating solvent, and it has been shown that under the conditions used, the pK<sub>a</sub> value was independent of the anion of the azolium salt.<sup>46</sup>

<sup>1</sup>On the spread that we have determined for imidazolin-2-ylidene-derived NHCs,<sup>24</sup> the span for <sup>77</sup>Se NMR chemical shifts is ca. 140 ppm, and <sup>13</sup>C–<sup>77</sup>Se NMR coupling is ca. 18 Hz.

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