# ORGANOMETALLICS

# Steric and Electronic Parameters of a Bulky yet Flexible N-Heterocyclic Carbene: 1,3-Bis(2,6-bis(1ethylpropyl)phenyl)imidazol-2-ylidene (IPent)

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# **Supporting Information**

ABSTRACT: The free N-heterocyclic carbene IPent (1; IPent = 1,3-bis(2,6-bis(1-ethylpropyl)phenyl)imidazol-2-ylidene) was prepared from the corresponding imidazolium chloride salt (2). The steric and electronic parameters of 1 were determined by synthesis of the gold(I) chloride complex [Au(IPent)Cl] (3) and the nickel-carbonyl complex [Ni- $(IPent)(CO)_3$  (4), respectively. 3 and 4 were fully characterized by NMR spectroscopy, elemental analysis, and X-ray diffraction studies on single crystals.

uring the last few decades, N-heterocyclic carbenes (NHCs) have become a well-established tool in organic and organometallic chemistry.<sup>1,2</sup> They can participate in a wide range of catalytic processes as ancillary ligands in transitionmetal catalysis<sup>1,3</sup> or as organocatalysts.<sup>4</sup> Due to their strong  $\sigma$ donor properties and usually large steric demand, NHC ligands are able to stabilize low-valent transition-metal complexes that can be used in many catalytic processes.3d,5 In this context, significant efforts have targeted the development and characterization of new NHC ligands. One of the structural parameters that can be modified to tune the ligand electronic and steric properties is the N-substituent of the imidazolium ring.<sup>1a</sup> Recently, bulky NHCs with "flexible sterics", i.e. ligands capable of adjusting their steric bulk as a function of incoming substrates such as IBiox5-12,6 CAAC (cyclic (alkyl)(amino)carbenes),<sup>7</sup> IBiox[(-)menthyl],<sup>8</sup> and IPr\*<sup>9</sup> (Figure 1), have drawn significant attention because of their spectacular reactivity.

Organ and co-workers have recently reported the excellent activity of palladium complexes containing the hindered yet flexible IPent ligand (1). This ligand is a bulkier analogue of IPr (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene), oneof the most common NHC ligands, and has been shown to significantly increase the activity of the [Pd-PEPPSI-NHC] systems in challenging cross-coupling reactions.<sup>10</sup> As part of our ongoing research into the development of new catalysts containing NHC ligands, we were interested in the isolation and characterization of free IPent. Herein, we report the synthesis and the steric and electronic characterization of this





Figure 1. Examples of NHC ligands with "flexible sterics".

bulky ligand (1). To synthesize the IPent $\cdot$ HCl salt<sup>11</sup> (2), the required aniline can be prepared following Steele's method.<sup>12</sup> This compound was converted to 2 following standard procedures for the synthesis of NHC·HX salts (Scheme 1, Supporting Information).<sup>13</sup>

The free carbene IPent (1) was easily generated by treatment of 2 with NaH and KO<sup>t</sup>Bu for 16 h (unoptimized reaction time) at room temperature in THF. 1 was isolated as a white solid in 65% yield (eq 1) and characterized by  ${}^{1}$ H and  ${}^{13}$ C{ ${}^{1}$ H} NMR spectroscopy and elemental analysis. The most salient spectroscopic feature of this compound is the presence of a singlet at 220.5 ppm corresponding to the carbenic carbon in the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum.<sup>14</sup>

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# Scheme 1. Synthetic Steps Leading to 2



To better understand the reactivity and use of NHCs in catalytic processes, the quantification of their steric and electronic properties is of fundamental importance. Therefore, we set out to evaluate these parameters for **1**. To determine the steric demand of NHC ligands, our group, in collaboration with Cavallo, have proposed the "percent buried volume" model. This value ( $%V_{bur}$ ) is defined as the percentage of the total volume of a sphere centered upon the metal atom that is occupied by the ligand.<sup>5c,15</sup> The gold(I) [Au(NHC)Cl] family of complexes is a useful metal-based model to quantify the steric properties of different ligands.<sup>5c</sup> Therefore, [Au(IPent)-Cl] (**3**) was synthesized by treatment of **1** with 1 equiv of [Au(DMS)Cl] (DMS = dimethyl sulfide) in THF (eq 2).



Complex 3 was fully characterized by <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectroscopy, elemental analysis, and X-ray diffraction analysis. The carbene peak in the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum appears at 174.2 ppm and compares well with signals for related [Au(NHC)Cl] complexes.<sup>16</sup> Crystals of 3 were grown by slow vapor diffusion of pentane into a saturated dichloromethane solution. Interestingly, two variants of complex 3 were found in the crystal lattice. These two low-energy conformers can be considered as indicative of the high degree of flexibility of the ligand (Figure 2).

Complex 3 presents the expected linear geometry with C– Au–Cl angles of 175.9(4)° (3a) and 177.2(3)° (3b). The Au–  $C_{carbene}$  distances found for the conformers are 1.979(10) Å (3a) and 1.968(11) Å (3b). The %V<sub>bur</sub> value of IPent for each



Figure 2. ORTEP representation of the conformer 3a showing thermal ellipsoids at the 50% probability level.

of the conformers of 3 was calculated using the SambVca<sup>17</sup> software. These values (49.0 (3a), 48.6 (3b)) show that IPent is a bulky ligand, presenting a steric demand significantly higher than that reported for IMes or IPr and closer to that for IPr\* (Table 1).

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NHC	Au-C1 (Å)	$%V_{\rm bur}{}^a$
IMes <sup>b</sup>	1.998(5)	36.5
$\operatorname{IPr}^{b}$	1.942(3)	44.5
IPr*c	1.987(7)	50.4
IPent	1.968(11), 1.979(10)	48.6, 49.0

<sup>*a*</sup>Parameters used for SambVca calculations: sphere radius, 3.50 Å; Au–C1, 2.00 Å; mesh spacing, 0.05; Bondi radius, 1.17. H atoms are excluded. <sup>*b*</sup>Taken from ref 16. <sup>*c*</sup>Taken from ref 9c.

To better characterize the bulkiness of IPent, the steric map of the square-planar standard model complex  $[Ir(IPent)Cl-(CO)_2]$  was first calculated (Figure 3).<sup>18</sup> This map shows a top



Figure 3. Steric mapping for the model complex  $[Ir(IPent)Cl(CO)_2]$  and [Pd-PEPPSI-IPent].

view of the complex and represents the space IPent occupies around the iridium atom, which is not homogeneously distributed. Two quadrants appear to be very bulky, while the two others show much lower steric hindrance. We hypothesized that this map would be a good qualitative model for the [Pd-PEPPSI-IPent] complex, which also presents a square-planar geometry. Therefore, we retrieved the crystal data from the CCDC database reported by Organ for this complex and calculated its steric map. We were pleased to observe similar steric occupations in both cases (Figure 3). This distribution might very well explain the high catalytic activity of the [Pd-PEPPSI-IPent] complex in cross-coupling reactions.<sup>10</sup> The less hindered quadrant could facilitate the entrance of substrates into the metal coordination sphere, whereas the bulkier direction might promote the reductive elimination of the coupling products, as has been previously postulated for [Pd(NHC)(cinnamyl)Cl] complexes.<sup>18a,b</sup>

Once the steric parameters of IPent were determined, we next looked at its electronic properties. One established method to determine the electronic parameters of two-electron ligands is by IR measurements of the carbonyl stretching frequencies  $(\nu)$  of the related  $[Ni(L)(CO)_3]$  complexes.<sup>19,20</sup> The A<sub>1</sub> carbonyl stretching frequency of CO ligands in these compounds is known as the Tolman electronic parameter

(TEP) and is directly correlated to the electron-donating ability of the ligand: a lower TEP corresponds to a more  $\sigma$ -donating ligand.<sup>19</sup> Therefore, the nickel derivative [Ni(IPent)(CO)<sub>3</sub>] (4) was synthesized (eq 3).



Treatment of a THF solution of 1 with a slight excess of  $[Ni(CO)_4]$  (see the Experimental Section for safety information) for 3 h led to the desired nickel complex 4, which was isolated as a beige microcrystalline solid in 92% yield (eq 3). The color of compound 4 hinted at its saturated character.<sup>20d</sup> This was also supported by its IR spectra in solution, where the positions of the carbonyl bands, 2049.3 (A<sub>1</sub>) and 1959.8 (E) cm<sup>-1</sup> in dichloromethane solution and 2053.1 (A<sub>1</sub>) and 1977.8 and 1970.7 (E) cm<sup>-1</sup> in hexane solution, are consistent with the existence of the tricarbonyl complex (Table 2). Thus, the TEP

# Table 2. Comparison of 4 with $[Ni(NHC)(CO)_3]$ Analogues<sup>*a*</sup>

NHC	Ni–C1 (Å)	$\text{TEP}_{\text{DCM}} (\text{cm}^{-1})$	$\text{TEP}_{\text{hex}} (\text{cm}^{-1})$	$%V_{\rm bur}{}^a$
$\mathrm{IMes}^{b}$	1.971(3)	2050.7	2054.0	34.0
$IPr^{b}$	1.979(2)	2051.5	2055.1	38.1
IPr*c	1.971(3)	2052.7	d	38.8
IPent	1.973(4)	2049.3	2053.1	39.4

<sup>*a*</sup>SambVca parameters: sphere radius, 3.50 Å; Ni–C1, 2.00 Å; mesh spacing, 0.05; Bondi radius, 1.17. H atoms are excluded. <sup>*b*</sup>Reference 20d. <sup>*c*</sup>For comparison, the published CIF file was retrieved<sup>23</sup> and the %  $V_{\text{bur}}$  recalculated using the parameters described in footnote *a*. <sup>*d*</sup>[Ni(IPr\*)(CO)<sub>3</sub>] is insoluble in hexane.

for this ligand, 2049.3 cm<sup>-1</sup> in DCM and 2053.1 cm<sup>-1</sup> in hexane, shows that IPent (1) is slightly more  $\sigma$ -donating than IMes, IPr and IPr\*. The TEP value obtained in DCM solution agrees with the value recently reported by Organ of 2049.6 cm<sup>-1</sup>,<sup>21</sup> which was calculated from the CO stretching frequencies of the [Ir(IPent)Cl(CO)<sub>2</sub>] complex by applying the correlation we previously established between the Ir and Ni systems.<sup>22</sup>

Complex 4 was also characterized by <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectroscopy and elemental analysis. The resonance due to the carbenic carbon appears at 196.8 ppm in the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum and confirms the coordination of the ligand to the nickel atom.<sup>20d</sup> 4 was structurally characterized by single-crystal diffraction studies. Crystals of 4 were grown by slow cooling of a saturated hexane solution to -40 °C (Figure 4).

The structure of 4 confirms the presence of three carbonyl groups coordinated to the metal center. 4 presents the expected tetrahedral geometry around the Ni atom with C–Ni–C angles between 108 and 111°.<sup>20d</sup> The percent buried volume for 4 was also calculated using SambVca and compared with those for other [Ni(NHC)(CO)<sub>3</sub>] complexes (see Table 2). Interestingly, IPent presents the largest %*V*<sub>bur</sub> value for this family of complexes, even larger than that calculated for IPr\*. The remarkable difference between the percent buried volume computed for the linear complex **3** (48.8) and for **4** (39.4) highlights the degree of flexibility of the IPent ligand.



Figure 4. ORTEP representation of  $[Ni(IPent)(CO)_3]$  (4) showing thermal ellipsoids at the 50% probability level.

In summary, the free IPent carbene (1) has been obtained from the corresponding imidazolium chloride salt (2) and its steric and electronic properties have been evaluated. The  $%V_{bur}$ value of IPent in [Au(IPent)Cl] (3) was calculated and compared to the reported values for other [Au(NHC)Cl] complexes. The steric mapping of a square-planar model complex containing 3 is also reported. The electronic properties of IPent were evaluated by means of IR measurements of [Ni(IPent)(CO)<sub>3</sub>] (4). These parameters show that IPent is a flexible ligand, bulkier and more  $\sigma$ -donating than IPr.

# EXPERIMENTAL SECTION

**Preparation of IPent (1).** In a glovebox, **2** (200 mg, 0.372 mmol), NaH (13.4 mg, 0.558 mmol), and the tip of a spatula of KO<sup>6</sup>Bu were dissolved in THF (15 mL). The mixture was stirred at room temperature for 16 h and filtered. Then, the solvent was removed in vacuo. The residue was redissolved in pentane and filtered through Celite. The solvent was removed in vacuo, affording a white solid. Yield: 120 mg (65%). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>): δ 7.32 (t, *J* = 7.8 Hz, 2H, CH<sub>Ar</sub>), 7.11 (d, *J* = 7.8 Hz, 4H, CH<sub>Ar</sub>), 6.73 (s, 2H, CH<sup>4,5</sup>), 2.67–2.53 (m, 4H, Et<sub>2</sub>CH), 1.46–1.76 (m, 16 H, CH<sub>3</sub>CH<sub>2</sub>), 0.93 (t, *J* = 7.6 Hz, 12H, CH<sub>3</sub>), 0.83 (t, *J* = 7.6 Hz, 12H, CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>): δ 220.5 (C<sub>carb</sub>), 143.3 (C<sub>Ar</sub>), 141.4 (C<sub>Ar</sub>), 128.2 (CH<sub>Ar</sub>), 123.8 (CH<sub>Ar</sub>), 122.2 (CH<sup>4,5</sup>), 42.0 (Ar-CHEt<sub>2</sub>), 29.2 (CH<sub>2</sub>CH<sub>3</sub>), 28.9 (CH<sub>2</sub>CH<sub>3</sub>), 12.5 (CH<sub>3</sub>), 11.9 (CH<sub>3</sub>). Anal. Calcd for C<sub>35</sub>H<sub>52</sub>N<sub>2</sub> (733.22): C, 83.94; H, 10.47; N, 5.59. Found: C, 83.85; H, 10.49; N, 5.69.

Preparation of [Au(IPent)Cl] (3). In a glovebox, [Au(DMS)Cl] (60.0 mg, 0.204 mmol) was added to a solution of 1 (102 mg, 0.204 mmol) in THF (10 mL). The mixture was kept in the dark and stirred at room temperature for 16 h. Then, the reaction mixture was filtered through silica outside the glovebox. The solvent was concentrated, and pentane (4 mL) was added to the solution. A white solid was obtained, which was washed with pentane and dried under vacuum. Yield: 121 mg (81%). <sup>1</sup>H NMR (400 MHz,  $CD_2Cl_2$ ):  $\delta$  7.55 (t, J = 7.8 Hz, 2H,  $(\dot{H}_{Ar})$ , 7.26 (d, J = 7.8 Hz, 4H,  $(\dot{H}_{Ar})$ , 7.11 (s, 2H,  $(\dot{H}^{4,5})$ , 2.24–2.08 (m, 4H, Et<sub>2</sub>CH), 1.45–1.85 (m, 16 H, CH<sub>3</sub>CH<sub>2</sub>), 0.93 (t, J = 7.6 Hz, 12H, CH<sub>3</sub>), 0.79 (t, J = 7.6 Hz, 12H, CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz,  $C_6D_6$ ):  $\delta$  174.2 (Au-C), 143.4 ( $C_{Ar}$ ), 136.8 ( $C_{Ar}$ ), 130.2 ( $CH_{Ar}$ ), 124.7 (CH<sub>Ar</sub>), 123.7 (CH<sup>4,5</sup>), 42.8 (Ar-CHEt<sub>2</sub>), 29.2 (CH<sub>2</sub>CH<sub>3</sub>), 28.1 (CH<sub>2</sub>CH<sub>3</sub>), 12.7 (CH<sub>3</sub>), 12.2 (CH<sub>3</sub>). Anal. Calcd for C<sub>35</sub>H<sub>52</sub>AuClN<sub>2</sub> (733.22): C, 57.33; H, 7.15; N, 3.82. Found: C, 57.29; H, 7.06; N, 3.85.

**Preparation of [Ni(CO)<sub>3</sub>(IPent)] (4).** In a glovebox,  $[Ni(CO)_4]$  (50.0  $\mu$ L, 0.381 mmol) was chilled to -40 °C and added *via* syringe to a THF (10 mL) solution of 1 (127 mg, 0.254 mmol) at -40 °C. (*Caution!*  $[Ni(CO)_4]$  is an extremely toxic substance and should be handled with appropriate safety measures.) All the glassware and syringes used in this synthetic procedure were washed with a PPh<sub>3</sub> solution in THF to neutralize any remaining  $[Ni(CO)_4]$ . After 3 h, the solvent was removed under vacuum. The residue was dissolved in pentane and filtered through Celite. The solvent was evaporated, affording a beige solid. Yield: 148 mg (76%). <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  7.27 (t, J =

7.8 Hz, 2H, CH<sub>Ar</sub>), 7.21 (d, J = 7.8 Hz, 4H, CH<sub>Ar</sub>), 6.62 (s, 2H, CH<sup>4,5</sup>), 2.46–2.38 (m, 4H, Et<sub>2</sub>CH), 1.97–1.83 (m, 4H, CH<sub>3</sub>CH<sub>2</sub>), 1.82–1.62 (m, 4 H, CH<sub>3</sub>CH<sub>2</sub>), 1.56–1.38 (m, 8H, CH<sub>3</sub>CH<sub>2</sub>), 1.08 (t, J = 7.6 Hz, 12H, CH<sub>3</sub>), 0.73 (t, J = 7.6 Hz, 12H, CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  197.9 (C=O), 196.8 (NCN), 144.1 (C<sub>Ar</sub>), 139.2 (C<sub>Ar</sub>), 129.3 (CH<sub>Ar</sub>), 125.5 (CH<sub>Ar</sub>), 123.9 (CH<sup>4,5</sup>), 41.7 (Ar-CHEt<sub>2</sub>), 28.2 (CH<sub>2</sub>CH<sub>3</sub>), 26.4 (CH<sub>2</sub>CH<sub>3</sub>), 12.6 (CH<sub>3</sub>), 11.3 (CH<sub>3</sub>). IR  $\nu_{CO}$  (hexane, cm<sup>-1</sup>): 2053.1 (s), 1977.9, 1970.7 (vs). IR  $\nu_{CO}$  (DCM, cm<sup>-1</sup>): 2049.3 (s), 1959.8 (vs). Anal. Calcd for C<sub>38</sub>H<sub>52</sub>N<sub>2</sub>NiO<sub>3</sub> (643.52): C, 70.92; H, 8.14; N, 4.35. Found: C, 70.80; H, 8.23; N, 4.41.

# ASSOCIATED CONTENT

#### **S** Supporting Information

Text, figures, and CIF files giving full characterization data, crystallographic data for 3 and 4, details of the synthesis of 2, and steric maps of 3 and 4. This material is available free of charge via the Internet at http://pubs.acs.org.

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# Notes

The authors declare no competing financial interest.

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