Supplementary Data

The insertion reaction of acetonitrile on aryl nickel complexes stabilized by bidentate $N, N'$-chelating ligands.

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Figure 1S. MS (FAB+) of compounds 7c and 7c'.

Figure 2S. $^1$H NMR spectra of complexes 5a (500 MHz), 7a and 7c (250 MHz).

Figure 3S. MS (Cl, NH$_3$) of imine NH=C(Mes)Me.

Scheme 1S. Altenative mechanisms proposed for the evolution of the Mesityl-nitrile cationic species.

Tables 1 and 2. $^1$H NMR spectra of all compounds.
Figure 1S. MS (FAB+) of compounds 7c and 7c’
Figure 2S. Proton NMR spectra of complexes 5a (500 MHz), 7a and 7c (250 MHz).
Figure 3S. MS (Cl, NH$_3$) of imine NH=C(Mes)Me.
Scheme 1. Alternative mechanisms proposed for the evolution of the Mesityl-nitrile cationic species.
Table 1

<table>
<thead>
<tr>
<th>Compound</th>
<th>1H NMR Data of the [MBr(Mes)PIM] and [M(3,5-lut)(Mes)PIM] complexes</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>4b</strong> (cis)</td>
<td>9.13 (d, J 5.5, 1H, H1) 8.88 (t, J 8.2, 1H, H3) 2.42 (s, o-CH₃) 8.12 (d, J 8.0, 1H, H4) 2.02* (s, p-CH₃) 7.87 (dd, J 5, 1.5, 1H, H2) 7.28 (tt, J 7.5, 1.5, 1H, H9) 7.22 (tt, J 7.5, 1.5, 2H, H8,8') 6.80 (d, J 7.0, 2H, H7,7')</td>
</tr>
<tr>
<td><strong>4b</strong> (trans)</td>
<td>8.21 (td, J 7.5, 2, 1H, H3) 8.69 (t, J 5.5, 1H, H1) 5.23 (s, m-H) 8.04 (d, 1H, H4) 2.57 (s, o-CH₃) 7.70 (d, J 7.5, 2H, H7,7') 2.02* (s, p-CH₃)</td>
</tr>
<tr>
<td><strong>3b</strong> (cis)</td>
<td>9.31 (d, J 5.5, 1H, H1) 8.62 (s, m-H) 4.13 (s, m-H) 6.36 (s, m-H) 8.18 (td, J 7.5, 1.5, 1H, H3) 2.87 (s, o-CH₃) 7.96 (d, J 7.5, 1H, H4) 2.17 (s, p-CH₃) 7.82 (t, J 7.5, 1H, H2) 7.38-7.24* (m, 3H, H8,8',9)</td>
</tr>
<tr>
<td><strong>3b</strong> (trans)</td>
<td>8.12 (td, J 7.5, 2, 1H, H3) 8.58 (s, m-H) 5.19 (s, m-H) 6.43 (s, m-H) 7.85 (d, J 7.5, 1H, H4) 2.96 (s, o-CH₃) 7.67 (d, J 7.5, 2H, H7,7') 2.04 (s, p-CH₃) 7.44 (t, J 7, 1H, H2) 7.40 (d, J 7.5, 2H, H8,8') 7.38-7.24* (m, 1H, H9) 7.15 (d, J 5.5, 1H, H1)</td>
</tr>
<tr>
<td><strong>2b</strong> (cis)</td>
<td>9.19 (d, J 5.2, 1H, H1) 8.75 (s, m-H) 5.21 (s, m-H) 6.36 (s, m-H) 9.31 (d, J 8.2, 1H, H1) 8.62 (s, m-H) 4.13 (s, m-H) 6.36 (s, m-H) 8.18 (td, J 7.5, 1.5, 1H, H3) 2.87 (s, o-CH₃) 7.96 (d, J 7.5, 1H, H4) 2.17 (s, p-CH₃) 7.82 (t, J 7.5, 1H, H2) 7.38-7.24* (m, 3H, H8,8',9)</td>
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<tr>
<td><strong>2b</strong> (trans)</td>
<td>8.12 (td, J 7.5, 2, 1H, H3) 8.58 (s, m-H) 5.19 (s, m-H) 6.43 (s, m-H) 8.19 (td, J 7.5, 1.5, 1H, H3) 2.87 (s, o-CH₃) 7.96 (d, J 7.5, 1H, H4) 2.17 (s, p-CH₃) 7.82 (t, J 7.5, 1H, H2) 7.38-7.24* (m, 3H, H8,8',9)</td>
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<td><strong>3b</strong></td>
<td>9.13 (d, J 5.5, 1H, H1) 8.88 (t, J 8.2, 1H, H3) 2.42 (s, o-CH₃) 8.12 (d, J 8.0, 1H, H4) 2.02* (s, p-CH₃) 7.87 (dd, J 5, 1.5, 1H, H2) 7.28 (tt, J 7.5, 1.5, 1H, H9) 7.22 (tt, J 7.5, 1.5, 2H, H8,8') 6.80 (d, J 7.0, 2H, H7,7')</td>
</tr>
<tr>
<td><strong>3b</strong></td>
<td>8.21 (td, J 7.5, 2, 1H, H3) 8.69 (t, J 5.5, 1H, H1) 5.23 (s, m-H) 8.04 (d, 1H, H4) 2.57 (s, o-CH₃) 7.70 (d, J 7.5, 2H, H7,7') 2.02* (s, p-CH₃)</td>
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</table>

**Note:** Values in Hz, spectral data obtained in CDCl₃ or MeOD.
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<th>Peak</th>
<th>Position</th>
<th>Multiplicity</th>
<th>J (Hz)</th>
<th>Chemical Shift (ppm)</th>
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<td>7.33</td>
<td>tt</td>
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<td>1H</td>
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<td>7.24</td>
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<td>1H</td>
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<td>p-H</td>
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<td>2.42 (cis)</td>
<td>2.12</td>
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<td>1H</td>
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<tr>
<td>2.20</td>
<td>s</td>
<td></td>
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<td>p-H</td>
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Recorded at 500 MHz in acetone-d6, unless noted otherwise. Numbers of the peaks with asterisks are not determined precisely due to overlapping with other signals. Numbering is given in the diagram at the top of the table. (200 MHz, CDCl3)
For the Neutral and Ionic complexes, Trans : Trans configuration between the mesityl and the iminic nitrogen, Cis : Cis configuration between the mesityl and the iminic nitrogen.

(250 MHz, DMSO-d$_6$); (400 MHz, CDCl$_3$)
Table 2

<table>
<thead>
<tr>
<th>NN</th>
<th>L(3,5-lutidine or imine)</th>
<th>R(Mes)</th>
<th>E-(NH=C(R)(Mes))NN</th>
<th>Aromatic H</th>
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<tbody>
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<td>DAD</td>
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<td>7.25-7.45 (m, 10H)</td>
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<tr>
<td>2,2'-bipy</td>
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<td></td>
<td>8.75 (d, J 7.4, 4H, H2,2',8,8')</td>
</tr>
<tr>
<td>o-phen</td>
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<td></td>
<td>7.40-7.28 (m, 6H)</td>
</tr>
<tr>
<td>Ni(Mes){E-(NH=C(Mes))NN}BF4</td>
<td>7.57 (d, J 6.2, 2H, H2)</td>
<td>5.63s</td>
<td>2.27s</td>
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<tr>
<td>(H-w's)</td>
<td></td>
<td>4.70s</td>
<td>2.25s</td>
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<tr>
<td>(H-o's)</td>
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<td>4.29s</td>
<td>5.37s, 1.91s, 2.16s</td>
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<tr>
<td>(H-d's)</td>
<td></td>
<td>6.33 (s, m-H)</td>
<td>7.21-7.38 (m, 6H)</td>
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<tr>
<td>(H-H's)</td>
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<td>6.68 (bs, 2H, H2,2')</td>
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<tr>
<td>(H-p's)</td>
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<td>7.29 (d, J 6, 2H, H1)</td>
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<tr>
<td>(H-q's)</td>
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<td>7.14 (t, 2H, H2)</td>
<td>7.09 (d, J 6, 2H, H2)</td>
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<td>(H-r's)</td>
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<td>7.49 (d, J 6, 2H, H3)</td>
<td>7.29 (t, J 6, 2H, H7)</td>
<td></td>
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<tr>
<td>(H-s's)</td>
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<td>7.27 (t, J 6, 2H, H2)</td>
<td>7.40-7.38 (m, 6H)</td>
<td></td>
</tr>
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<td>(H-t's)</td>
<td></td>
<td>3.10 (s, o-CH3)</td>
<td>7.9-7.8 (m, 4H, H5,4,3)</td>
<td></td>
</tr>
<tr>
<td>(H-u's)</td>
<td></td>
<td>2.23 (s, p-CH3)</td>
<td>7.50 (t, J 6, 2H, H7)</td>
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<tr>
<td>(H-v's)</td>
<td></td>
<td>7.14 (t, 2H, H2)</td>
<td>7.49 (d, J 6, 2H, H3)</td>
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<tr>
<td>(H-w's)</td>
<td></td>
<td>7.09 (d, J 6, 2H, H2)</td>
<td>7.29 (t, J 6, 2H, H7)</td>
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<td>(H-x's)</td>
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<td>3.10 (s, o-CH3)</td>
<td>7.9-7.8 (m, 4H, H5,4,3)</td>
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<tr>
<td>(H-y's)</td>
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<td>2.23 (s, p-CH3)</td>
<td>7.50 (t, J 6, 2H, H7)</td>
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<td>7.14 (t, 2H, H2)</td>
<td>7.49 (d, J 6, 2H, H3)</td>
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</tr>
</tbody>
</table>
(H-\textsuperscript{d}s, \textsuperscript{s}) 8.29
(H\textsuperscript{-w}s, \textsuperscript{s}) 18.8
(H\textsuperscript{-w}s, \textsuperscript{s}) 15.86

7.82 (m, 1H, H\textsuperscript{7})
7.46 (m, 1H, H\textsuperscript{2})
4.51s 5.34s 2.10s 2.17s
6.40 (s, \textsuperscript{-H})
7.36-7.17 (several m, 6H)
2.40 (s, \textsuperscript{-CH\textsubscript{3}})

6.65 (d, J\textsuperscript{7.5}, 2H, H\textsuperscript{2,2'})
2.15 (s, \textsuperscript{p-CH\textsubscript{3}})
2.06 (s, \textsuperscript{m-CH\textsubscript{3}})

5.73 (s, \textsuperscript{-H})
7.78 (s, \textsuperscript{o-CH\textsubscript{2}C=CH\textsubscript{2}})
6.88 (m, 2H, H\textsuperscript{8,8'})
2.47 (s, \textsuperscript{o-CH\textsubscript{2}C=CH\textsubscript{2}})
7.14 (s, \textsuperscript{p-CH\textsubscript{2}C=CH\textsubscript{2}})

7.32-7.16 (m, 6H)
4.51s 4.74s 2.32s
6.34 (s, \textsuperscript{-H})
7.78 (s, \textsuperscript{o-CH\textsubscript{2}C=CH\textsubscript{2}})
6.88 (m, 2H, H\textsuperscript{8,8'})
2.47 (s, \textsuperscript{o-CH\textsubscript{2}C=CH\textsubscript{2}})

7.70-7.25 (m, 8H)
4.48s 4.97s 2.13s 2.15s
6.40 (s, \textsuperscript{-H})
9.16 (s, NH)
6.78 (m, 2H, H\textsuperscript{2,2'})
2.89 (s, \textsuperscript{o-CH\textsubscript{2}C=CH\textsubscript{2}})
6.66 (s, \textsuperscript{m-CH\textsubscript{3}})

6.73 (s, \textsuperscript{m-CH\textsubscript{3}})
2.41 (s, 3H, \textsuperscript{o-CH\textsubscript{3}})
2.46 (s, 3H, \textsuperscript{o-CH\textsubscript{3}})
1.54 (s, \textsuperscript{p-CH\textsubscript{3}})

8.50 (d, 1H)
6.81 (s, \textsuperscript{-H})
9.45 (s, NH)
8.41 (d, 1H)
3.18 (s, \textsuperscript{o-CH\textsubscript{2}C=CH\textsubscript{2}})
6.63 (s, \textsuperscript{m-CH\textsubscript{3}})
1.2

2.02 (8', o-CH)
2.22 (8', d-CH)
3.14 (d, 8', s-CH)
6.67 (6', s, CH)
9.57 (s, NH)
2.17 (8', d-CH)
2.26 (8', o-CH)
6.52 (6', s, CH)
7.50 (6', m, H)
9.68 (8', s, NH)
5.89 (8', o-CH)
2.21 (8', d-CH)
3.60 (8', s-CH)
3.82 (s, CH)

7.29 (d, 5', 4')
2.22 (8', p-CH)
8.25 (dd, 1H)
2.02 (o-CH)
7.86 (dd, 1H)
7.78 (dd, 1H)

6.88 (s, m-H)
9.83 (s, NH)
8.88 (dd, 1H)
3.14 (s, o-CH)
2.24 (s, p-CH)
N=C=C
8.31 (d, 2H, H 5,4)
2.22 (8', p-CH)
8.20 (dd, 1H)
2.21 (s, p-CH)
7.42 (d, 2H)

7.70-7.40 (m, 3H)
2.81 (s, o-CH)
7.50 (m, 5H Ph)
2.60 (s, p-CH)
6.52 (s, m-H)
2.26 (s, p-CH)
2.17 (s, p-CH)

9.00 (dd, 1H)
6.84 (s, m-H)
9.57 (s, NH)
8.79 (dd, 1H)
3.14 (s, p-CH)
2.24 (s, p-CH)
N=C=C
8.31 (d, 2H, H 5,4)
2.22 (8', p-CH)
8.20 (dd, 1H)
2.02 (o-CH)
7.86 (dd, 1H)
7.78 (dd, 1H)

7.22
3.60 (8', s-CH)

Recorded at 500 MHz in CDCl₃, unless noted otherwise. J in Hz.
(c) Recorded at 250 MHz in CDCl₃. (b) Recorded at 250 MHz in acetone-d₆.