Supporting Information for:

On the Mechanism of Ni(II)-Promoted Michael-Type Hydroamination of Acrylonitrile and Its Substituted Derivatives

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<td>yellow</td>
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| collected reflections; $R_a$ | 45548; 0.0342 | 92637; 0.0099 | 61357; 0.0307 |
| unique reflections; $R_{int}$ | 45548; 0.0550 | 92637; 0.0250 | 61357; 0.0463 |
| $R_1$; $wR_2^b$ [$I > 2\sigma(I)$] | 0.0370; 0.0946 | 0.0316; 0.0821 | 0.0477; 0.1155 |
| $R_1$; $wR_2$ [all data] | 0.0481; 0.1008 | 0.0320; 0.0824 | 0.0518; 0.1178 |
| GOF                     | 1.044 | 1.124 | 1.108 |
| largest diff peak and hole | 0.646 and -0.375 | 0.387 and -0.272 | 1.524 and -0.427 |

a) $R_1=\Sigma(||F_o|-|F_c||)/\Sigma|F_o|$  
b) $wR_2=\{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)]\}^{1/2}$
### Table S2 Crystal Data, Collection, and Refinement Parameters for complexes 11 and 12

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<td>GOF</td>
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<td>largest diff peak and hole</td>
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\(a\) = \frac{\Sigma(|F_o|-|F_c|)}{\Sigma|F_o|}; \(b\) = \frac{\Sigma[w(F_o^2-F_c^2)^2]}{\Sigma[w(F_o^2)^2]^{1/2}}
Figure S1 Side view of the molecular diagram for complex 7. Thermal ellipsoids are shown at the 50% probability level. P-substituents and hydrogens are omitted for clarity.

Figure S2 Side view of the molecular diagram for complex 9. Thermal ellipsoids are shown at the 50% probability level. P-substituents and hydrogens are omitted for clarity.

Figure S3 Side view of the molecular diagram for complex 10. Thermal ellipsoids are shown at the 50% probability level. P-substituents and hydrogens are omitted for clarity.
Details of the diffraction studies

Crystals of compound 7 were obtained by slow evaporation of a concentrated THF solution at r.t. Crystals of compound 9 and 10 were obtained by slow evaporation of a concentrated dichloromethane solution at r.t. Crystals of compound 11 and 12 were obtained by slow evaporation of a concentrated acetone solution at r.t. The crystallographic data for all complexes were collected on a Bruker Venture Metaljet equipped with a Metal Jet source, an Helios MX Mirror Optics monochromator and a Bruker Photon 100 CMOS Detector. Cell refinement and data reduction were done using the ShelXL routine version July 2014. An empirical absorption correction, based on the multiple measurements of equivalent reflections, was applied. The space group was confirmed by ShelXT routine in the program OLEX2. The structures were solved by direct methods (ShelXT) and refined by full-matrix least-squares and difference Fourier techniques with OLEX2. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were set in calculated positions and refined as riding atoms with a common thermal parameter.
NMR Analysis

**Figure S4** Representation of complex [{2,6-(iPr₂PO)₂-4-(CO₂Me)C₆H₂}Ni(NCCH=CH₂)][OSO₂CF₃] (7)

**Figure S5** $^1$H NMR spectra (400 MHz) of complex 7 in CDCl₃
Figure S6 $^{13}$C{$^{1}$H} NMR spectra (101 MHz) of complex 7 in CDCl$_3$

Figure S7 $^{31}$P{$^{1}$H} NMR spectra (162 MHz) of complex 7 in CDCl$_3$
Figure S8 Representation of complex $\{2,6-(\text{Pr}_2\text{PO})_2-4-(\text{OMe})\text{C}_6\text{H}_2\}\text{Ni(NCCH=CH}_2\}]\text{[OSO}_2\text{CF}_3\}$ (8)

Figure S9 $^1$H NMR spectra (500 MHz) of complex 8 in C$_6$D$_6$
**Figure S10** $^{13}$C{$^{1}$H} NMR spectra (125 MHz) of complex 8 in C$_6$D$_6$

**Figure S11** $^{31}$P{$^{1}$H} NMR spectra (162 MHz) of complex 8 in C$_6$D$_6$
Figure S12 Representation of complex [{2,6-(iPr₂PO)₂-4- (CO₂Me)C₆H₂}Ni(NCCH=CHPh)][OSO₂CF₃] (9)

Figure S13 ¹H NMR spectra (400 MHz) of complex 9 in C₆D₆
**Figure S14** $^{13}$C{$^1$H} NMR spectra (MHz) of complex 9 in CDCl$_3$

**Figure S15** $^{31}$P{$^1$H} NMR spectra (MHz) of complex 9 in CDCl$_3$
Figure S16 Representation of complex [{2,6-(iPr$_2$PO)$_2$-4-(OMe)C$_6$H$_2$}Ni(NCCH=CHPh)][OSO$_2$CF$_3$], (NCCH=CHPh) (10)

Figure S17 $^1$H NMR spectra (400 MHz) of complex 10 in C$_6$D$_6$
Figure S18 \[^{13}\text{C}\{^1\text{H}\}\} NMR spectra (101 MHz) of complex 10 in CDCl\textsubscript{3}

Figure S19 \[^{31}\text{P}\{^1\text{H}\}\} NMR spectra (162 MHz) of complex 10 in CDCl\textsubscript{3}
**Figure S20** Representation of complex \([\{2,6-(iPr_2PO)_2C_6H_3\}Ni(NH_3)][OSO_2CF_3]\) (11)

**Figure S21** $^1$H NMR spectra (400 MHz) of complex 11 in C$_6$D$_6$
Figure S22 $^{13}$C{H} NMR spectra (101 MHz) of complex 11 in CDCl$_3$

Figure S23 $^{31}$P{H} NMR spectra (162 MHz) of complex 11 in C$_6$D$_6$
**Figure S24** Representation of complex \([\{2,6-(iPr_2PO)\}_2-4-(CO_2Me)_6H_2\}Ni(NH_3)][OSO_2CF_3]\) (12)

**Figure S25** $^1$H NMR spectra (500 MHz) of complex 12 in C$_6$D$_6$
Figure S26 $^{13}$C$\{^1\text{H}\}$ NMR spectra (125 MHz) of complex 12 in C$_6$D$_6$
Figure S27 $^{31}$P/$^1$H NMR spectra (202 MHz) of complex 12 in C$_6$D$_6$
Catalytic Tests

**Figure S28** Plot of the yield (TON) for the hydroamination of crotonitrile (14a) catalyzed by 3 and 4 for the mono-addition product over 2 h.
Figure S29 Plot of the yield (TON) for the hydroamination of methacrylonitrile (14b) catalyzed by 3 and 4 for the mono-addition product over 2 h.
Figure S30 Plot of the TOF (TON/time, h⁻¹) for the hydroamination of crotonitrile (14a) catalyzed by 3 and 4 for the mono-addition product over 2 h.
Figure S31 Plot of the TOF (TON/time, h\(^{-1}\)) for the hydroamination of methacrylonitrile (14b) catalyzed by 3 and 4 for the mono-addition product over 2 h
Figure S32 Plot of the yield (TON) for the hydroamination of crotonitrile (14a) catalyzed by 3 and 4 for the mono-addition product over 20 h.
Figure S33 Plot of the yield (TON) for the hydroamination of methacrylonitrile (14b) catalyzed by 3 and 4 for the mono-addition product over 20 h.
Figure S34 Plot of the TOF (TON/time, h\(^{-1}\)) for the hydroamination of crotonitrile (14a) catalyzed by 3 and 4 for the mono-addition product over 20 h
Figure S35 Plot of the TOF (TON/time, h⁻¹) for the hydroamination of methacrylonitrile (14b) catalyzed by 3 and 4 for the mono-addition product over 20 h.
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<th>TON(^a) (Yield, %)</th>
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a) TON and TOF are the average of three experiments under the same conditions.
Table S4 Results of the single addition product from the hydroamination reaction of crotonitrile (14a) catalyzed by complexes 3 and 4 over 20 h

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<th>CATALYST</th>
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<td>10 ± 2</td>
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<sup>a</sup> TON and TOF are the average of three experiments under the same conditions.
**Table S5** Formation of the double addition products from the hydroamination reaction of crotonitrile (14a) catalyzed by complexes 3 and 4 over 2 h

<table>
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<th>ENTRY</th>
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<th>TOF(^a) [h(^{-1})]</th>
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<td>1.73 ± 0.03</td>
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a) TON and TOF are the average of three experiments under the same conditions.
Table S6  Formation of the double addition products from the hydroamination reaction of crotonitrile (14a) catalyzed by complexes 3 and 4 over 20 h

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<th>SUBSTRATE</th>
<th>PRODUCT</th>
<th>CATALYST</th>
<th>TON(^a) (Yield, %)</th>
<th>TOF(^a) [h(^{-1})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>13a</td>
<td>15k</td>
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<td>0</td>
</tr>
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<tr>
<td>3</td>
<td>13c</td>
<td>15m</td>
<td>3</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>13d</td>
<td>15n</td>
<td>4</td>
<td>0</td>
<td>0</td>
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<td>15o</td>
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<tr>
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<td>13f</td>
<td>15p</td>
<td>4</td>
<td>0</td>
<td>0</td>
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<tr>
<td>7</td>
<td>13g</td>
<td>15q</td>
<td>3</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
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<td>13h</td>
<td>15r</td>
<td>4</td>
<td>0</td>
<td>0</td>
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<tr>
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<td>13i</td>
<td>15s</td>
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<tr>
<td>10</td>
<td>13j</td>
<td>15t</td>
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\(^a\) TON and TOF are the average of three experiments under the same conditions.
Table S7 Results of the single addition product from the hydroamination reaction of methacrylonitrile (14b) catalyzed by complexes 3 and 4 over 2 h

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<th>CATALYST</th>
<th>TON(^a)</th>
<th>TOF(^a)</th>
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</thead>
<tbody>
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<td></td>
<td></td>
<td></td>
<td>(Yield, %)</td>
<td>[h(^{-1})]</td>
</tr>
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<td>13a</td>
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<td>10,6 ± 0,7</td>
</tr>
<tr>
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<td>16b</td>
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<td>35 ± 1</td>
<td>17,5 ± 0,7</td>
</tr>
<tr>
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<td>13c</td>
<td>16c</td>
<td>3</td>
<td>5,2 ± 0,7</td>
<td>2,6 ± 0,4</td>
</tr>
<tr>
<td>4</td>
<td>13d</td>
<td>16d</td>
<td>4</td>
<td>7,8 ± 0,4</td>
<td>3,9 ± 0,2</td>
</tr>
<tr>
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<td>13e</td>
<td>16e</td>
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<td>3,2 ± 0,3</td>
<td>1,6 ± 0,2</td>
</tr>
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<td>6</td>
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<td>16f</td>
<td>4</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
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<td>13g</td>
<td>16g</td>
<td>3</td>
<td>7 ± 1</td>
<td>3,6 ± 0,5</td>
</tr>
<tr>
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<td>13h</td>
<td>16h</td>
<td>4</td>
<td>0,6 ± 0,1</td>
<td>0,30 ± 0,03</td>
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<td>13i</td>
<td>16i</td>
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<td>0</td>
</tr>
<tr>
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<td>13j</td>
<td>16j</td>
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<td>11,3 ± 0,3</td>
</tr>
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<td></td>
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<td>34,6 ± 0,7</td>
<td>17,3 ± 0,3</td>
</tr>
<tr>
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<td></td>
<td></td>
<td>4</td>
<td>12 ± 1</td>
<td>6,1 ± 0,5</td>
</tr>
<tr>
<td>13</td>
<td></td>
<td></td>
<td>3</td>
<td>14,6 ± 0,7</td>
<td>7,3 ± 0,4</td>
</tr>
<tr>
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<td></td>
<td>4</td>
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a) TON and TOF are the average of three experiments under the same conditions. * In this experiment, 5 mmol of amine was used instead of 1 mmol
Table S8 Results of the single addition product from the hydroamination reaction of methacrylonitrile (14b) catalyzed by complexes 3 and 4 over 20 h

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<th>PRODUCT</th>
<th>CATALYST</th>
<th>TON&lt;sup&gt;a&lt;/sup&gt; (Yield, %)</th>
<th>TOF&lt;sup&gt;a&lt;/sup&gt; [h&lt;sup&gt;-1&lt;/sup&gt;]</th>
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<tr>
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<td>16b</td>
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<td>28 ± 1</td>
<td>1,38 ± 0,05</td>
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<td>13c</td>
<td>16c</td>
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<td>12 ± 2</td>
<td>0,6 ± 0,1</td>
</tr>
<tr>
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<td>13d</td>
<td>16d</td>
<td>4</td>
<td>10 ± 1</td>
<td>0,5 ± 0,1</td>
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<tr>
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<td>16e</td>
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<td>3,3 ± 0,3</td>
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<td>16f</td>
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<td>3,4 ± 0,1</td>
<td>0,17 ± 0,01</td>
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<tr>
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<td>16g</td>
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<td>1,9 ± 0,2</td>
<td>0,09 ± 0,01</td>
</tr>
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<td>13h</td>
<td>16h</td>
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<td>0,11 ± 0,01</td>
</tr>
<tr>
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<td>16i</td>
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<td>0</td>
</tr>
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<td>13j</td>
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a) TON and TOF are the average of three experiments under the same conditions.
Table S9: Formation of the double addition products from the hydroamination reaction of methacrylonitrile (14b) catalyzed by complexes 3 and 4 over 2 h

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<th>TOF(^a) ([\text{h}^{-1}])</th>
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\(^a\) TON and TOF are the average of three experiments under the same conditions.
<table>
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<th>SUBSTRATE</th>
<th>PRODUCT</th>
<th>CATALYST</th>
<th>TON(^a) (Yield, %)</th>
<th>TOF(^a) [h(^{-1})]</th>
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<tr>
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<td>5 ± 1</td>
<td>0,2 ± 0,1</td>
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<td>0</td>
<td>0</td>
</tr>
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<td>16m</td>
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<td>0</td>
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<td>0</td>
<td>0</td>
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<td>0</td>
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<td>16q</td>
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a) TON and TOF are the average of three experiments under the same conditions.
**Table S11** Testing the formation of the hydroamination product in the presence of either 14a or 14b and in the absence of catalyst over 2 h

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<th>TON&lt;sup&gt;a&lt;/sup&gt; (Yield, %)</th>
<th>TOF&lt;sup&gt;a&lt;/sup&gt; [h&lt;sup&gt;-1&lt;/sup&gt;]</th>
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<sup>a</sup> TON and TOF are the average of three experiments under the same conditions.
References