Supporting Information for the article

Revealing the Unusual Role of Bases in Activation/Deactivation of Catalytic Systems: O-NHC Coupling in M/NHC Catalysis

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S1. Additional data, tables, schemes
Table S1. Reaction of M-NHC complexes with oxygen bases

<table>
<thead>
<tr>
<th>N</th>
<th>Starting M-NHC complex</th>
<th>Solvent (ml)</th>
<th>Base (mol : mol of M-NHC)</th>
<th>Reaction temperature, °C</th>
<th>Reaction time, h</th>
<th>Products (HPLC or GC)</th>
<th>Isolated yield of azolone 7, %</th>
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<td>N</td>
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<td>Solvent (ml)</td>
<td>Base (mol : mol of M-NHC)</td>
<td>Reaction temperature, °C</td>
<td>Reaction time, h</td>
<td>Products</td>
<td>(HPLC or GC)/isolated yield of azolone 7, %</td>
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⁴A mixture of the complex 2-6 (0.3 mmol), solvent (5 mL) and base (0.9-3 mmol) was vigorously stirred in a teflon screw cap tube at 100 °C within 1-48 h, then neutralized with 20% HCl aqueous solution to pH ~9 under argon atmosphere. The resulted mixture was centrifuged and analyzed by HPLC and GC-MS. If necessary, the products 7 were isolated as described in the Experimental Section of the manuscript. ³M aqueous solution.
Figure S1. Variable temperature study for the formation of azolone 7a in the reaction between the compound 2a (0.1 mmol) and t-BuOK (1 mmol) in 1,4-dioxane at 40 °C, 70 °C, and 100 °C.
Table S2. Stability of azolones 7 in the presence of KOH and t-BuOK

![Diagram of azolones 7 with arrows indicating the reaction with base to form decomposition products.]

| N  | Starting azolone 7 | Solvent (ml) | Base (mol: mol of azolone 7) | Reaction temperature, °C | Reaction time, h | Conversion of azolone 7, %
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<td>1</td>
<td>7a</td>
<td>pyridine (0.4) + H₂O (0.1)</td>
<td>KOH b (10 : 1)</td>
<td>100</td>
<td>24</td>
<td>~0</td>
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<tr>
<td>2</td>
<td>7a</td>
<td>pyridine (0.5)</td>
<td>t-BuOK (10 : 1)</td>
<td>100</td>
<td>24</td>
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<tr>
<td>3</td>
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<td>pyridine (0.4) + H₂O (0.1)</td>
<td>KOH b (10 : 1)</td>
<td>100</td>
<td>24</td>
<td>~0</td>
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<td>pyridine (0.4) + H₂O (0.1)</td>
<td>KOH b (10 : 1)</td>
<td>100</td>
<td>24</td>
<td>4</td>
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<td>KOH b (10 : 1)</td>
<td>100</td>
<td>90</td>
<td>10</td>
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<td>pyridine (0.4) + H₂O (0.1)</td>
<td>KOH b (10 : 1)</td>
<td>100</td>
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A mixture of the compounds 7 (30 µmol), solvent and base (0.3 mmol) was vigorously stirred in a teflon screw cap tube at the corresponding temperature within 24-90 h, then analyzed by HPLC and GC-MS. b3M aqueous solution of KOH. cDetermined by HPLC and GC-MS.
Scheme S1. Reactions of benzimidazolium salts 1 with strong oxygen bases.¹

1,3-Dialkylated azolium salts are hydrolyzed by strong bases like KOH to give \( N,N\)-dialkylbenzene-1,2-diamines 8.¹ Hydrolysis usually accompanied by the disproportionation of “pseudobases” 17 and 18 to give azolones 7 and azolines 19.¹ The azolines 19, apparently, are unstable in the conditions of the Table S1. However, trace amounts of compounds with m/z corresponding to the [M⁺] of azolines 19 were observed in GC-MS spectra of the reaction mixtures. Analogous reactions proceed under the action of alcoholates. Indeed, the HPLC yield of azolone 7a in the reaction mixture after heating compound 1a with \( t\)-BuOK in 1,4-dioxane at 100 °C within 20 h amounted ~ 10% (see Experimental Section for details).

Scheme S2. Plausible stoichiometry’s for the reactions of complexes 2-6 with KOH and t-BuOK

Reactions of Type 1

\[
\begin{align*}
\text{R} \quad \text{N} & \quad \text{X} \quad \text{N} \quad \text{R'} \\
\text{M} \quad \text{X} & \quad \text{N} \quad \text{R'} \\
\text{2,5} & \quad + \quad 2\text{KOH} & \quad \rightarrow & \quad \text{R} \quad \text{N} & \quad \text{O} \\
& & & & \quad \quad \text{M}(0) & \quad \text{P} \\
& & & & \quad + \quad 2\text{KX} & \quad + \quad \text{H}_2\text{O}
\end{align*}
\]

\[
\begin{align*}
\text{R} \quad \text{N} & \quad \text{X} \quad \text{N} \quad \text{R'} \\
\text{M} \quad \text{X} & \quad \text{N} \quad \text{R'} \\
\text{2,5} & \quad + \quad 2\text{t-BuOK} & \quad \rightarrow & \quad \text{R} \quad \text{N} & \quad \text{O} \\
& & & & \quad \quad \text{M}(0) & \quad \text{P} \\
& & & & \quad + \quad 2\text{KX} & \quad + \quad \text{t-BuOH}
\end{align*}
\]

\[
\begin{align*}
\text{R} \quad \text{N} & \quad \text{X} \quad \text{N} \quad \text{R'} \\
\text{M} \quad \text{X} & \quad \text{N} \quad \text{R'} \\
\text{2,5} & \quad + \quad \text{K}_2\text{CO}_3 & \quad \rightarrow & \quad \text{R} \quad \text{N} & \quad \text{O} \\
& & & & \quad \quad \text{M}(0) & \quad \text{P} \\
& & & & \quad + \quad 2\text{KX} & \quad + \quad \text{CO}_2
\end{align*}
\]

\[M = \text{Pd, Pt}; \quad \text{X} = \text{Cl, Br, I}\]

Reactions of Type 2

\[
\begin{align*}
\text{R} \quad \text{N} & \quad \text{X} \quad \text{N} \quad \text{R'} \\
\text{M} \quad \text{X} & \quad \text{N} \quad \text{R'} \\
\text{3} & \quad + \quad 4\text{t-BuOK} & \quad \rightarrow & \quad \text{R} \quad \text{N} & \quad \text{O} \\
& & & & \quad \quad \text{M}(0) & \quad \text{P} \\
& & & & \quad + \quad 2\text{Pd}^0 & \quad + \quad 4\text{KBr} & \quad + \quad 2\text{t-BuOH}
\end{align*}
\]

\[
\begin{align*}
\text{R} \quad \text{N} & \quad \text{X} \quad \text{N} \quad \text{R'} \\
\text{M} \quad \text{X} & \quad \text{N} \quad \text{R'} \\
\text{3} & \quad + \quad 4\text{KOH} & \quad \rightarrow & \quad \text{R} \quad \text{N} & \quad \text{O} \\
& & & & \quad \quad \text{M}(0) & \quad \text{P} \\
& & & & \quad + \quad 2\text{Pd}^0 & \quad + \quad 4\text{KBr} & \quad + \quad 2\text{H}_2\text{O}
\end{align*}
\]

\[M = \text{Pd, Ni}; \quad \text{X} = \text{Cl, Br, I}\]

Reactions of Type 3

\[
\begin{align*}
\text{R} \quad \text{N} & \quad \text{X} \quad \text{N} \quad \text{R'} \\
\text{M} \quad \text{X} & \quad \text{N} \quad \text{R'} \\
\text{4,6} & \quad + \quad 2\text{KOH} & \quad \rightarrow & \quad \text{R} \quad \text{N} & \quad \text{O} \\
& & & & \quad \quad \text{M}(0) & \quad \text{NHC} \\
& & & & \quad + \quad 2\text{KX} & \quad + \quad \text{H}_2\text{O}
\end{align*}
\]

\[
\begin{align*}
\text{R} \quad \text{N} & \quad \text{X} \quad \text{N} \quad \text{R'} \\
\text{M} \quad \text{X} & \quad \text{N} \quad \text{R'} \\
\text{4,6} & \quad + \quad 2\text{t-BuOK} & \quad \rightarrow & \quad \text{R} \quad \text{N} & \quad \text{O} \\
& & & & \quad \quad \text{M}(0) & \quad \text{NHC} \\
& & & & \quad + \quad 2\text{KX} & \quad + \quad \text{t-BuOH}
\end{align*}
\]

\[M = \text{Pd, Ni}; \quad \text{X} = \text{Cl, Br, I}\]

For clarity, only 2-methylpropene and t-BuOH are shown as the products derived from t-BuOK, while another products like di-t-butyl ether may also be formed. For other alkaline metal bases (Na, Cs), stoichiometry’s are similar.
S2. ESI-MS monitoring of Azolones formation
Figure S2. Real-time abundance of 7a (in ionic [M + K]^+ form) in the reaction between the complex 2a and KOH_aq in THF at 100 °C. Solution of KOH in H_2O was added after 1.0 min. Insert shows the ESI-(+)MS spectrum of the reaction mixture, expanded to the [M + K]^+ region.
Figure S3. Real-time abundance of 7a (in ionic [M + K]^+ form) in the reaction between the complex 4a and KOH\textsubscript{aq} in THF at 100 °C. Solution of KOH in H\textsubscript{2}O was added after 1.0 min.
Figure S4. Real-time abundances (in ionic [M + K]^+ form) of 7a (purple line) and intermediate hydroxy-complexes (blue and yellow lines) in the reaction between the complex 4a and KOH in THF at 100 °C. Solution of KOH in H₂O was added after 1.0 min.
Figure S5. Collision induced dissociation tandem mass spectrometry experiment demonstrating the formation of **7a** (in ionic [M + K]$^+$ form) from the intermediate hydroxy-complex **9** (in a [C$_{18}$H$_{22}$N$_4$O$_2$Pd + K]$^+$ form) during the reaction between the complex **4a** and KOH$_{aq}$ in THF at 100 °C.
Figure S6. Real-time abundance of 7a (in ionic [M + K]^+ form) in the reaction between the complex 2a and tert-BuOK in THF at 100 ºC. Suspension of tert-BuOK in THF was added after 1.0 min.
Figure S7. Real-time abundance of 7b (in ionic [M + K]+ form) in the reaction between the complex 2b and KOH$_{aq}$ in THF at 100 ºC. Solution of KOH in H$_2$O was added after 1.0 min. Insert shows ESI-(+)MS spectrum of the reaction mixture, expanded to the [M + K]$^+$ region.
Figure S8. Real-time abundance of 7l (in ionic [M + K]$^+$ form) in the reaction between the complex 2o and KOH$_{aq}$ in THF at 100 ºC. Solution of KOH in H$_2$O was added after 1.0 min. Insert shows ESI-(+)MS spectrum of the reaction mixture, expanded to the [M + K]$^+$ region. At the beginning of the reaction one of the products (apparently, potassium bromide) rapidly covered the shield in the MS interface that significantly dropped all the signals down in intensity because of changes in field potentials.
Figure S9. Real-time abundance of 7o (in ionic [M + K]$^+$ form) in the reaction between the complex 2r and KOH$_{aq}$ in THF at 100 ºC. Solution of KOH in H$_2$O was added after 1.0 min. Insert shows ESI-(+)MS spectrum of the reaction mixture, expanded to the [M + K]$^+$ region.
Figure S10. Real-time abundances of 7a-[\(^{18}\)O] and 7a-[\(^{16}\)O] (in ionic [M + K]\(^+\) forms) in the reaction between the complex 2a and K\(^{18}\)OH\(_{aq}\) in THF at 100 °C. Solution of KOH in H\(_2^{18}\)O was added after 1.0 min. Insert shows ESI-(+)-MS spectrum of the reaction mixture, expanded to the [(18O)-M + K]\(^+\) region.
Figure S11. Real-time abundances of ions (in [M + Na]$^+$ and [M + K]$^+$ forms) confirming no isotope exchange between 7a-[16O] and KOH solution in H$_2^{18}$O.

In the first time region (up to ~ 0.8 min), a solution of non-labeled 7a-[16O] in THF was squeezed into the MS instrument. After the addition of a potassium hydroxide solution in H$_2^{18}$O (at ~0.8 min), an [M + K]$^+$ ion of the non-labeled 7a-[16O] jumped in the intensity, but no 7a-[18O] isotopomer was formed according to the ion traces in the second time region (0.8-12 min). After the addition of a small amount (40 ng; added as solution see Exp. part) of 2a (at 12 min), only a slight increase in the intensity of both 7a isotopomers was detected. Only after the addition of the significant amount (160 ng; added as solution see Exp. part) of 2a (17 min), a stable increase of the intensity of the 7a-[18O] isotopomer signal (purple line) was observed. These results corroborate the formation of the 7a-[18O] isotopomer from the reaction between the complex 2a and $^{18}$OH rather than through the isotope exchange between 7a-[16O] and KOH-H$_2^{18}$O solution.
S3. FE-SEM/EDS data
**Figure S12.** FE-SEM image and EDS spectrum of Pd black isolated from the reaction mixture after heating compound 2a with KOH in pyridine at 100 °C within 24 h.

**Figure S13.** TEM image and EDS spectrum of Pt black isolated from the reaction mixture after heating compound 5a with t-BuOK in 1,4-dioxane at 100 °C within 20 h.
S4. Raman spectra
Figure S14. Raman spectra of palladium black isolated from the reaction mixtures: 1 - heating compound 2a with 3M aqueous KOH solution in pyridine within 24 h; 2 – heating 2a with t-BuOK in 1,4-dioxane at 100 °C within 3 h; 3 – heating 4a with 3M aqueous KOH solution in pyridine within 24 h.

The metal precipitates isolated from the reaction mixtures were identified as Pd(0) nanoparticles (Figure S12). The absence of strong enough Raman signals from the obtained samples of palladium black confirmed the absence of any Pd oxides or complexes in the analytic sample.
Figure S15. Raman spectrum of Ni(OH)$_2$ isolated from the reaction mixture after heating compound 6a with 3M aqueous KOH solution in 1,4-dioxane at 100 °C within 20 h. The Raman spectrum is analogous to the literature data for the disordered β-Ni(OH)$_2$.\cite{1,2} The 3680 cm$^{-1}$ peak is associated with the stretching of the free OH$^-$ groups of the outer part of the crystallites of Ni(OH)$_2$. The 3570 cm$^{-1}$ intense peak is assigned to the free OH$^-$, while the 3580 cm$^{-1}$ shoulder to the linked OH$^-$ groups in the crystalline bulk [2].

Figure S16. Raman spectrum of nickel black isolated from the reaction mixture after heating compound 6a with t-BuOK in 1,4-dioxane at 100 °C within 20 h. The absence of strong enough Raman signals in the range of 30 – 4000 cm\(^{-1}\) corroborates the absence of any notable amounts of Ni oxides, hydroxides or complexes in the analytic sample.
S5. NMR spectra, ESI-MS and GC-MS data
Figure S17. $^1$H NMR spectrum of compound 1e (DMSO-$d_6$, 500 MHz).
Figure S18. $^{13}$C NMR spectrum of compound 1e (DMSO-$d_6$, 500 MHz).
Figure S19. ESI-(+)MS spectrum of compound 1e in CH$_3$CN solution, expanded to the [M]$^+$ region.
Figure S20. $^1$H NMR spectrum of compound 2b (CDCl$_3$, 500 MHz).
Figure S21. $^{13}$C NMR spectrum of compound 2b (CDCl$_3$, 125 MHz).
Figure S22. $^1$H NMR spectrum of compound 2e (CDCl$_3$, 500 MHz).
Figure S23. $^{13}$C NMR spectrum of compound 2e (CDCl$_3$, 125 MHz).
Figure S24. $^1$H NMR spectrum of compound 2g (CDCl$_3$, 500 MHz).
Figure S25. $^{13}$C NMR spectrum of compound 2g (CDCl$_3$, 125 MHz).
Figure S26. $^1$H NMR spectrum of compound 7a (CDCl$_3$, 500 MHz).
Figure S27. $^{13}$C NMR spectrum of compound 7a (CDCl$_3$, 125 MHz).
Figure S28. ESI-(+)-MS spectrum of compound 7a in CH$_3$CN solution, expanded to the [M + H]$^+$ region.
Figure S29. $^1$H NMR spectrum of compound 7a-$^{18}$O (CDCl$_3$, 500 MHz).
Figure S30. $^{13}$C NMR spectrum of compound 7a-$^{18}$O (CDCl$_3$, 125 MHz).
Figure S31. ESI-(+)MS spectrum of 1,3-dimethyl-1,3-dihydro-2H-benzimidazol-2-one-18O (7a-18O) in CH3CN solution expanded to the [M + H]+ region.
Figure S32. $^1$H NMR spectrum of compound 7b (CDCl$_3$, 500 MHz).
Figure S33. $^{13}$C NMR spectrum of compound 7b (CDCl$_3$, 125 MHz).
Figure S34. ESI-(+)MS spectrum of compound 7b in CH$_3$CN solution expanded to the [M + H]$^+$ region.
Figure S35. $^1$H NMR spectrum of compound 7c (CDCl$_3$, 400 MHz).
Figure S36. $^{13}$C NMR spectrum of compound 7c (CDCl$_3$, 100 MHz).
Figure S37. ESI- (+) MS spectrum of compound 7c in CH$_3$CN solution expanded to the [M + H]$^+$ region.
Figure S38. $^1$H NMR spectrum of compound 7d (CDCl$_3$, 500 MHz).
Figure S39. $^{13}$C NMR spectrum of compound 7d (CDCl$_3$, 125 MHz).
Figure S40. ESI-(+)MS spectrum of compound 7d in CH$_3$CN solution expanded to the [M + H]$^+$ region.
Figure S41. $^1$H NMR spectrum of compound 7e (CDCl₃, 500 MHz).
Figure S42. $^{13}$C NMR spectrum of compound 7e (CDCl$_3$, 125 MHz).
Figure S43. ESI-(+)-MS spectrum of compound 7e in CH$_3$CN solution expanded to the [M + H]$^+$ region.
Figure S44. $^1$H NMR spectrum of compound 7f (CDCl$_3$, 500 MHz).
Figure S45. $^{13}$C NMR spectrum of compound 7f (CDCl$_3$, 125 MHz).
Figure S46. ESI-(+)-MS spectrum of compound 7f in CH$_3$CN solution expanded to the [M + H]$^+$ region.
Figure S47. $^1$H NMR spectrum of compound 7g (CDCl$_3$, 500 MHz).
Figure S48. $^{13}$C NMR spectrum of compound 7g (CDCl$_3$, 125 MHz).
Figure S49. ESI-(+)MS spectrum of compound 7g in CH₃CN solution expanded to the [M + H]^+ region.
Figure S50. $^1$H NMR spectrum of compound 7h (CDCl$_3$, 500 MHz).
Figure S51. $^{13}$C NMR spectrum of compound 7h (CDCl$_3$, 125 MHz).
Figure S52. ESI-(+)-MS spectrum of compound 7h in CH$_3$CN solution expanded to the [M + H]$^+$ region.
Figure S53. $^1$H NMR spectrum of compound 7i (CDCl$_3$, 500 MHz).
Figure S54. $^{13}$C NMR spectrum of compound 7i (CDCl$_3$, 125 MHz).
Figure S55. ESI-(+)-MS spectrum of compound 7i in CH$_3$CN solution expanded to the [M + H]$^+$ region.
Figure S56. $^1$H NMR spectrum of compound 7j (CDCl$_3$, 500 MHz).
Figure S57. $^{13}$C NMR spectrum of compound 7j (CDCl$_3$, 125 MHz).
Figure S58. ESI-(+MS spectrum of compound 7j in CH$_3$CN solution expanded to the [M + H]$^+$ region.
Figure S59. ESI(+)MS spectrum of compound 7n in CH₃CN solution, expanded to the [M + H]⁺ region.
Figure S60. $^1$H NMR spectrum of dihydrochloride of compound 8a×2HCl (DMSO-$d_6$, 500 MHz).
Figure S6. $^{13}$C NMR spectrum of dihydrochloride of compound $8\times 2\text{HCl}$ (DMSO-$d_6$, 125 MHz)
Figure S62. $^1$H NMR spectrum of compound 8a (C$_6$D$_6$, 500 MHz)
Figure S63. $^{13}\text{C}$ NMR spectrum of compound 8a (C$_6$D$_6$, 125 MHz)
Figure S64. ESI-(+)MS spectrum of the dihydrochloride of compound 8ax2HCl in CH$_3$CN solution expanded to the [M – HCl – Cl]$^+$ region.
Figure S65. $^1$H NMR spectrum of dihydrochloride of compound 8b×2HCl (DMSO-$d_6$, 500 MHz).
Figure S66. ESI-(+)MS spectrum of the dihydrochloride of compound 8b×2HCl in CH$_3$CN solution expanded to the [M – HCl – Cl]$^+$ region.
Figure S67. $^1$H NMR spectrum of compound 8b (C$_6$D$_6$, 500 MHz)
Figure S68. $^{13}$C NMR spectrum of compound 8b ($\text{C}_6\text{D}_6$, 125 MHz)
Figure S69. $^1$H NMR spectrum of di perchlorate of compound 8c×2HClO$_4$ (DMSO-$d_6$, 500 MHz).
Figure S70. $^{13}$C NMR spectrum of di perchlorate of compound 8c×2HClO₄ (DMSO-$d_6$, 125 MHz)
Figure S71. ESI-(+)MS spectrum of the dihydrochloride of compound 8c·2HClO₄ in CH₃CN solution expanded to the [M – HClO₄ – ClO₄]⁺ region.
**GC-MS data**

GC-MS measurements were carried out using an Agilent 7890A GC system, equipped with an Agilent 5975C mass-selective detector (electron impact, 70 eV) and a HP-5MS column (30 m×0.25 mm × 0.25 μm film) using He as carrier gas at a flow of 1.0 mL/min. The following temperature program was used in all GC-MS measurements: initial temperature 45 °C, hold for 2 min, then 20 °C·min⁻¹ to 85 °C and hold for 5 min, then 25 °C·min⁻¹ to 185 °C and hold for 1 min, then 10 °C·min⁻¹ to 280 °C and hold for 6.5 min. Injector temperature: 290 °C, initial pressure 1.5128 psi. Injection volume: 0.5 μL using the splitless injection mode (splitless time: 0.75 min).
Figure S72. GC-MS chromatogram (TIC) of the authentic sample of azolone 7l (left) and the reaction mixture (right) after heating compound 2o with KOH\textsubscript{(aq)} in 1,4-dioxane (entry 37 in the Table S1).
Figure S73. GC-MS chromatogram (TIC) of the authentic sample of azolone 7n (top) and the reaction mixture after heating compound 2q with KOH\textsubscript{(aq)} in 1,4-dioxane (entry 41 in the Table S1) (bottom).
Figure S74. GC-MS chromatogram (TIC) of the authentic sample of diamine 8b (top) and the reaction mixture after heating compound 4b with t-BuOK in 1,4-dioxane (entry 46 in Table S1) (bottom).
Figure S75. GC-MS chromatogram (TIC) of the authentic sample of diamine 8c (top) and the reaction mixture after heating compound 6b with t-BuOK in 1,4-dioxane (entry 52 in Table S1) (bottom).
Figure S76. GC-MS chromatogram (TIC) of the compound 7a obtained by the reaction of 2a with K\textsuperscript{18}OH (top) and K\textsuperscript{16}OH (bottom) in aqueous pyridine.