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# Activation of C=N Bonds by High Valent Group 6 Metal Chlorides, Including the Conversion of a α-Diimine into a Functionalized Imidazolium

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# Supporting Information

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**Figure SI-1**. DFT-optimized geometry of [**DAD**$^{Me}$][$WCl_6$] (C-PCM/ωB97X calculations) and spin density surface (isovalue = 0.01 a.u.). Hydrogen atoms on the Xyl moieties are omitted for clarity. Colour map: W, orange; Cl, green; N, blue; C, grey; H, white; spin density surface: yellow tones. Selected computed lengths (Å): C1-N1 1.265, C2-N2 1.258, C1-C2 1.494, W-Cl (average) 2.348, W---N1 5.302, W---N2 6.687.

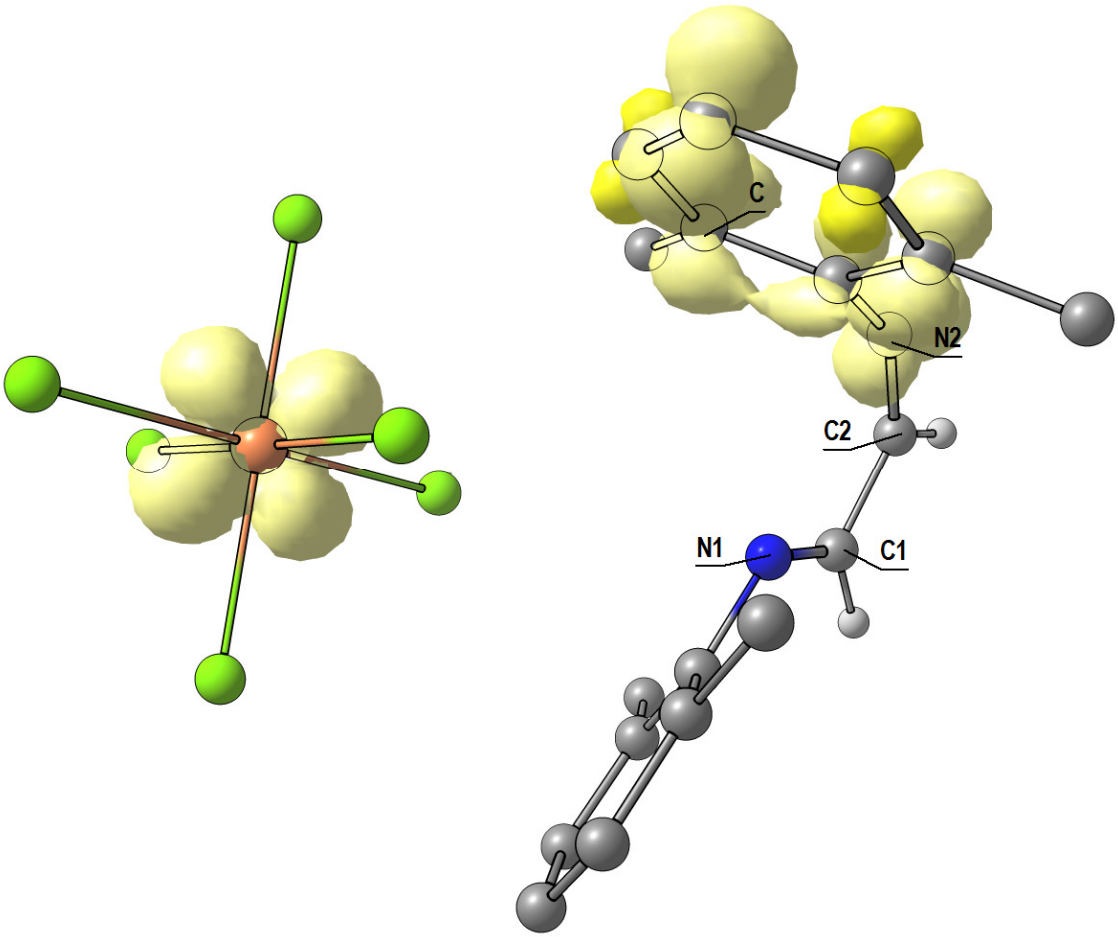

**Figure SI-2**. DFT-optimized geometry of [XylNCHCHN(Xyl)CH(NXyl)CHNXyl]$^{+\bullet}$ (C-PCM/ωB97X calculations) and spin density surface (isovalue = 0.01 a.u.). Hydrogen atoms on the Xyl moieties are omitted for clarity. Colour map: N, blue; C, grey; H, white; spin density surface: yellow tones. Selected computed lengths (Å): C1-N1 1.258, C2-N2 1.425, C2-N3 1.492, C3-N3 1.288, C4-N4 1.268, C1-C2 1.529, C3-C4 1.471.

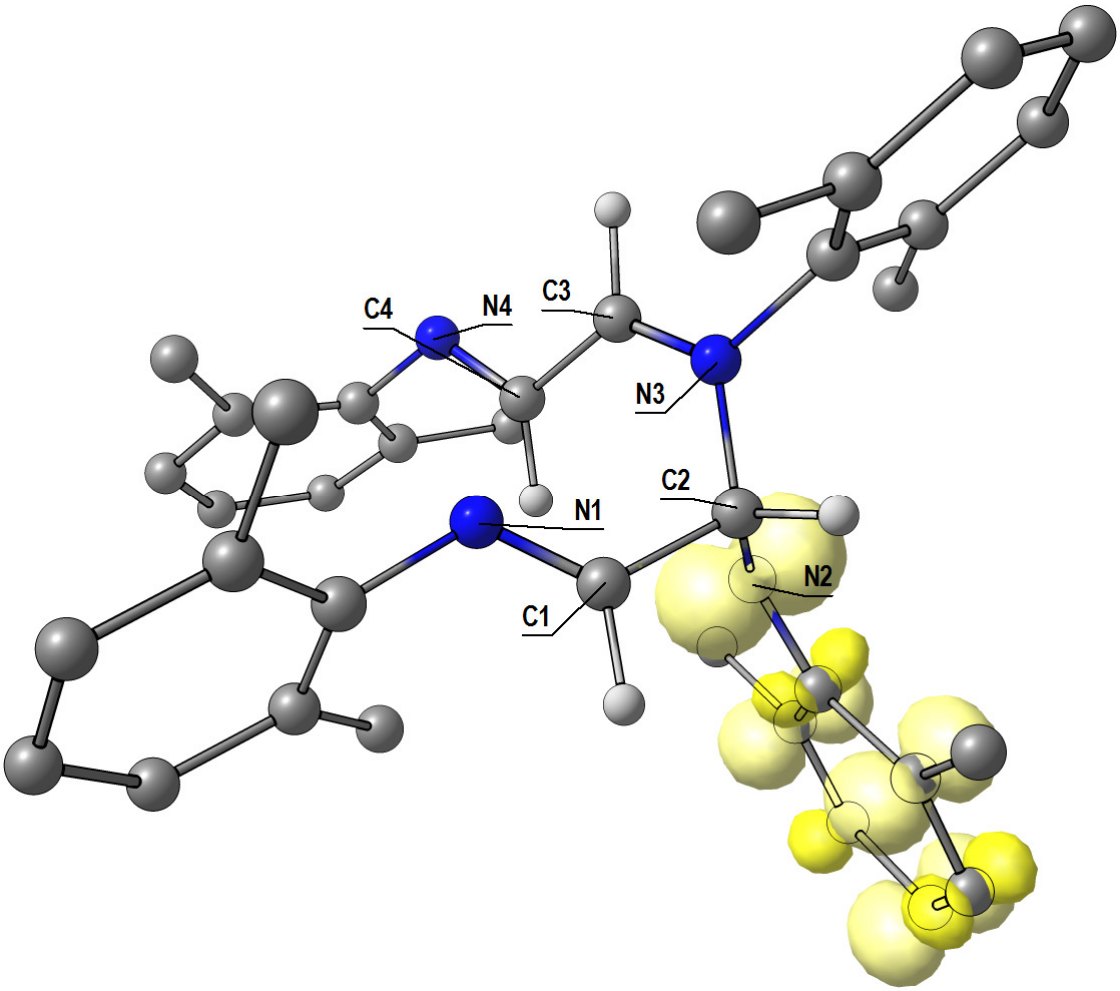

**Figure SI-3**. DFT-optimized geometry of $[XylNCHCHN(Xyl)CH(NXyl)CHNXyl]^{2+}$ (C-PCM/ωB97X calculations). Hydrogen atoms on the Xyl moieties are omitted for clarity. Colour map: N, blue; C, grey; H, white. Selected computed lengths (Å): C1-N1 1.253, C2-N2 1.429, C2-N3 1.481, C3-N3 1.293, C4-N4 1.269, C1-C2 1.541, C3-C4 1.467.

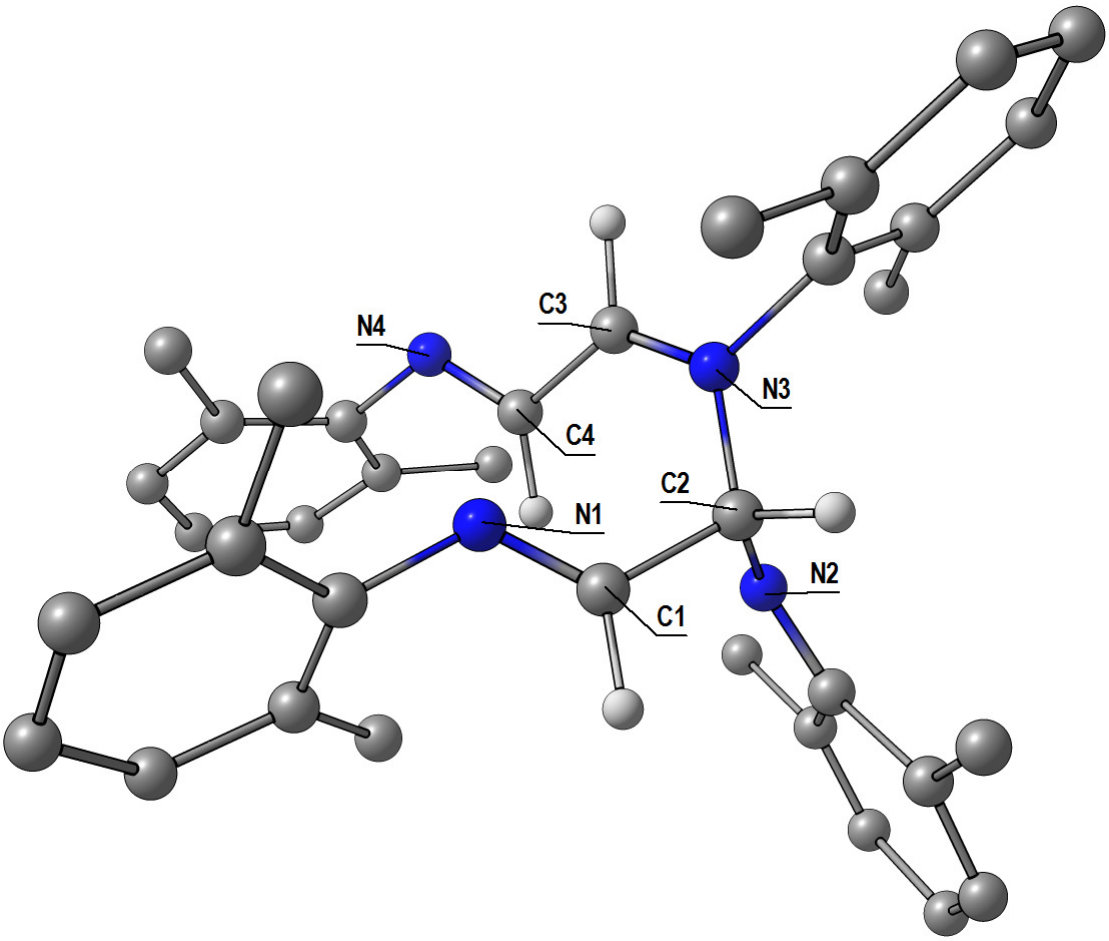

**Figure SI-4**. DFT-optimized geometry of $[WCl_5\{N(Ar)C(CHNXyl)NXylCHCHNXyl\}]^+$ (C-PCM/ωB97X calculations) and spin density surface (isovalue = 0.01 a.u.). Hydrogen atoms on the Xyl moieties are omitted for clarity. Colour map: W, orange; Cl, green; N, blue; C, grey; H, white; spin density surface: yellow tones. Selected computed lengths (Å): C1-N1 1.265, C2-N2 1.256, C2-N3 1.464, C3-N3 1.291, C4-N4 1.271, C1-C2 1.491, C3-C4 1.471, W-Cl (average) 2.294, W---N2 4.307.

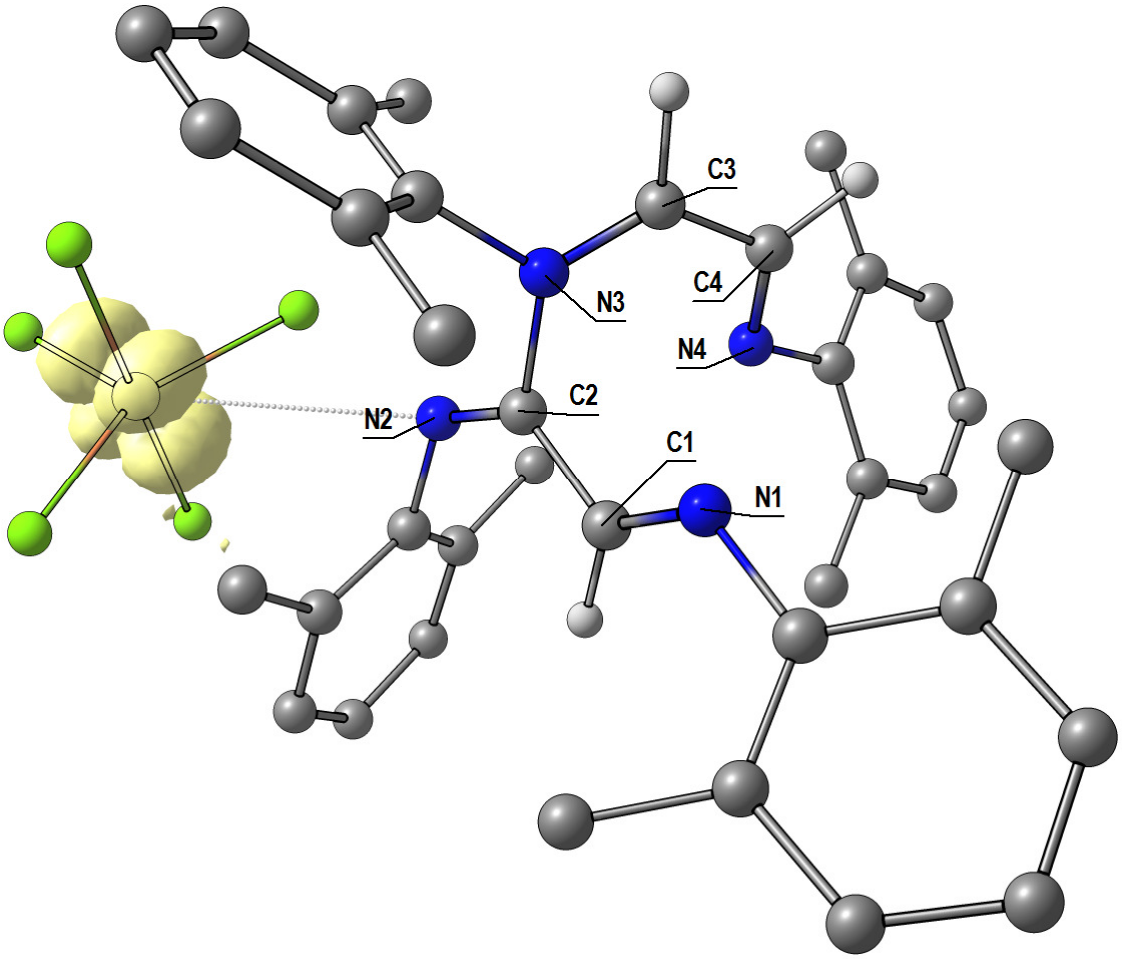

**Figure SI-5**. DFT-optimized geometry of $WCl_4$(NClXyl) and [XylNCHCHN(Xyl)C(Cl)CHNXyl]$^{+\bullet}$ (C-PCM/ωB97X calculations) and spin density surface (isovalue = 0.01 a.u.). Hydrogen atoms on the Xyl moieties are omitted for clarity. Colour map: W, orange; Cl, green; N, blue; C, grey; H, white; spin density surface: yellow tones. Selected computed lengths (Å): C1-N1 1.284, C2-Cl 1.689, C2-N3 1.355, C3-N3 1.354, C4-N4 1.296, C1-C2 1.449, C3-C4 1.430, W-Cl (average) 2.341, W-N2 1.693.

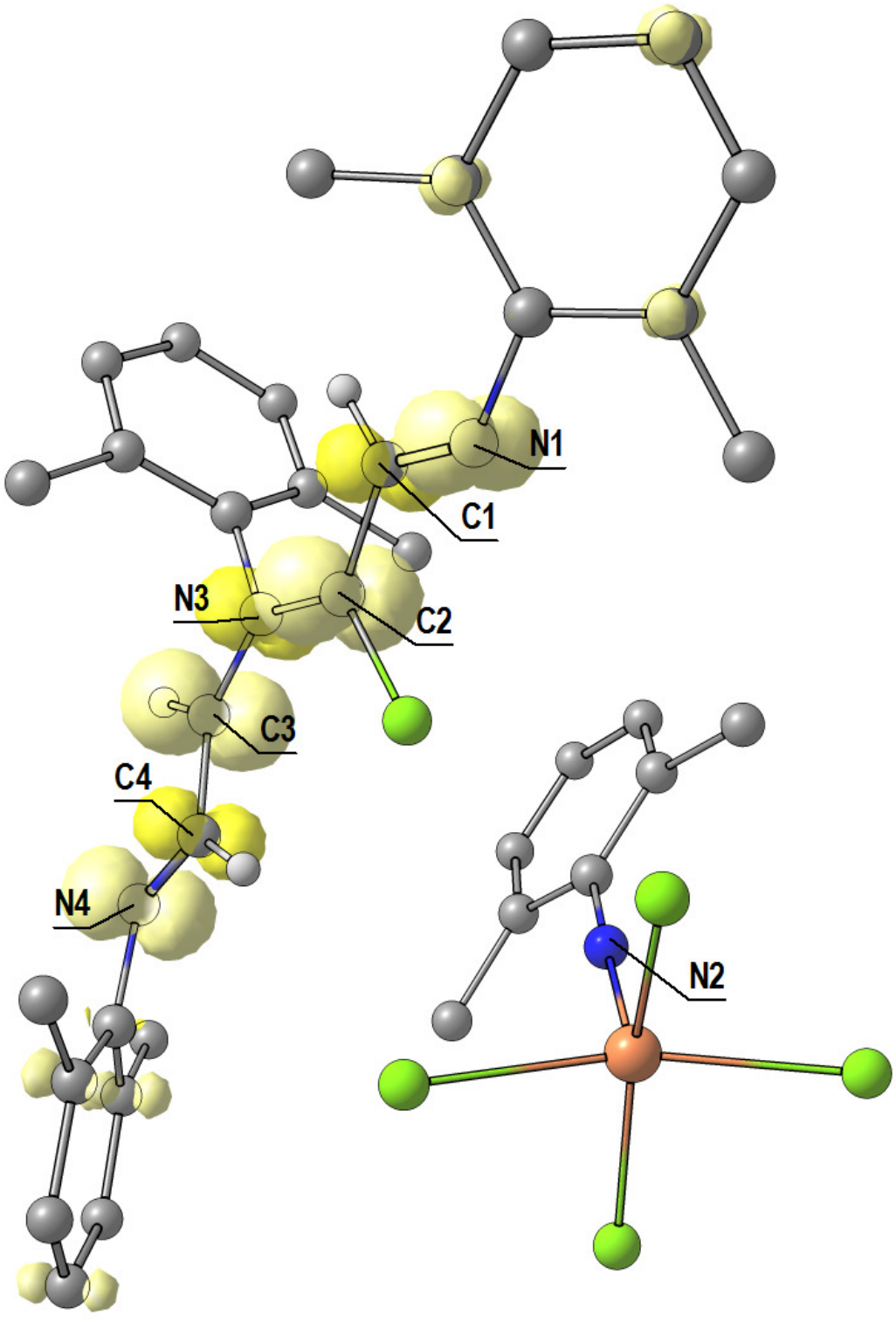

**Figure SI-6**. DFT-optimized geometry of $WCl_4$(NClXyl) and of the cation in **1** (C-PCM/ωB97X calculations) and spin density surface (isovalue = 0.01 a.u.). Hydrogen atoms on the Xyl moieties are omitted for clarity. Colour map: W, orange; Cl, green; N, blue; C, grey; H, white; spin density surface: yellow tones. Selected computed lengths (Å): C1-N1 1.267, C2-N3 1.343, C2-N4 1.344, C3-N3 1.379, C4-N4 1.376, C1-C2 1.471, C3-C4 1.360, W-Cl (average) 2.335, W-N2 1.881, N2-Cl 1.746.