One Pot Conversion of Benzophenone Imine into the Relevant 2-Aza-Allenium

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Synthesis and characterization of compounds: general experimental details.

Air/moisture sensitive compounds were manipulated under atmosphere of pre-purified argon using standard Schlenk techniques. The reaction vessels were oven dried at 140 °C prior to use, evacuated (10^{-2} \text{ mmHg}) and then filled with argon. WCl₆ (99.9%, Strem), imines (TCI Europe), NOBF₄ (95%, Sigma Aldrich) and deuterated solvents (98+%, Cortecnet) were commercial products stored under argon atmosphere as received. Once isolated, the metal products were conserved in sealed glass tubes under argon. Solvents (Sigma-Aldrich) were distilled from P₂O₁₀ before use. Infrared spectra were recorded at 298 K on a FT IR-Perkin Elmer Spectrometer, equipped with UATR sampling accessory. Magnetic susceptibilities (reported per W atom) were measured at 298 K on solid samples with a Magway MSB Mk1 magnetic susceptibility balance (Sherwood Scientific Ltd.). Diamagnetic corrections were introduced according to König.¹ NMR spectra were recorded on a Bruker Avance II DRX400 instrument equipped with BBFO broadband probe, at 298 K. The chemical shifts for ^1H and ^13C were referenced to the non-deuterated aliquot of the solvent. EPR spectra were recorded at 298 K on a Varian (Palo Alto, CA, USA) E112 spectrometer operating at X band, equipped with a Varian E257 temperature control unit and interfaced to IPC 610/P566C industrial grade Advantech computer, using acquisition board ² and software package especially designed for EPR experiments.³ Experimental EPR spectra were simulated by the WINSIM 32 program.⁴ GC-MS analyses were performed on a HP6890 instrument, interfaced with MSD-HP5973 detector and equipped with a Phenonex Zebron column. Carbon, hydrogen and nitrogen analyses were performed on Carlo Erba mod. 1106 instrument. The chloride content was determined by the Mohr method ⁵ on solutions prepared by dissolution of the solid in aqueous KOH at boiling temperature, followed by cooling down to room temperature and addition of HNO₃ up to neutralization.

Reaction of WCl₆ with benzophenone imine, Ph₂C=NH: synthesis and characterization of [Ph₂C=N=CPh₂][WCl₆], 1, and [Ph₂C=NH₂][WCl₆], 2.

A suspension of WCl₆ (370 mg, 0.933 mmol) in 1,2-dichloroethane (ca. 15 mL) was heated to ca. 80 °C, and then benzophenone imine (0.31 mL, 1.9 mmol) was added. The mixture was left stirring for 12 h, then it was cooled to room temperature and the volatile materials were removed in vacuo. A dark residue was obtained which was washed with pentane (20 mL) and dried in vacuo. NMR

analysis of the residue (in CD$_2$Cl$_2$) evidenced the presence of 1 and 2, with a slight prevalence of the latter. $^1$H NMR (CD$_2$Cl$_2$): $\delta$ = 11.99 (s, NH$_2$, 2); 7.98-7.94, 7.91-7.80, 7.65-7.37 ppm (m, Ph). $^{13}$C NMR (CD$_2$Cl$_2$): $\delta$ = 182.6 (C=N, 2); 157.0 (C=N=C, 1); 136.8, 135.3, 134.7, 133.2, 132.9, 132.4, 131.9, 131.8, 131.4, 130.6, 130.1, 129.8, 129.6, 129.5, 128.8, 128.4, 128.2, 127.3 ppm (Ph).

Crystallization from CH$_2$Cl$_2$/hexane at −30 °C afforded a crop of crystals of both 1 (orange) and 2 (dark red-brown), which were mechanically separated.

1. Yield: 208 mg, 30%. Anal. Calcd. for C$_{26}$H$_{20}$Cl$_6$NW: C, 42.03; H, 2.71; N, 1.89; Cl, 28.63. Found: C, 41.81; H, 2.93; N, 1.76; Cl, 28.31. IR (solid state, cm$^{-1}$): $\nu$ = 1860m, 1846m)sh, 1826m)sh cm$^{-1}$ (C=N=C).

7 Magnetic measurement: $\chi_M^{corr}$ = 3.54×10$^{-4}$ cgsu, $\mu_{eff}$ = 0.92 BM.

2. Yield: 189 mg, 35%. Anal. Calcd. for C$_{13}$H$_{12}$Cl$_6$NW: C, 26.98; H, 2.09; N, 2.42; Cl, 36.75. Found: C, 27.16; H, 1.96; N, 2.57; Cl, 36.40. IR (solid state, cm$^{-1}$): $\nu$ = 3056w (N−H), 1645m)s (C=N). Magnetic measurement: $\chi_M^{corr}$ = 3.74×10$^{-4}$ cgsu, $\mu_{eff}$ = 0.95 BM.

Reaction of NOBF$_4$ with benzophenone imine, Ph$_2$C=NH: identification of [Ph$_2$C=NH][BF$_4$], 3, and [Ph$_2$C=NH$_2$][BF$_4$].

A solution of benzophenone imine (0.10 mL, 0.60 mmol) in CH$_2$Cl$_2$ (10 mL) was treated with NOBF$_4$ (70 mg, 0.60 mmol). The resulting solution progressively turned violet; after 15 minutes reaction, an aliquot (0.05 mL) of the violet solution was withdrawn, conserved at 273 K and then analyzed by EPR at 293 K (see Figure SI1). The remaining solution was stirred for additional 18 h, then hexane was added to the final colourless solution (30 mL). The resulting pale yellow solid, corresponding to [Ph$_2$C=NH$_2$][BF$_4$], was dried in vacuo. Yield 113 mg, 70%. Anal. Calcd. for C$_{13}$H$_{12}$BF$_4$N: C, 58.03; H, 4.50; N, 5.21. Found: C, 58.20; H, 4.38; N, 5.10. IR (solid state, cm$^{-1}$): $\nu$ = 3322m, 3160m, 1651m)s (C=N), 1595m)s, 1455m)m, 1415w, 1382m, 1330w, 1311w, 1237m, 1187m)s, 1166w)m, 1024s, 999w, 824w)m, 668vs.

Reaction of WCl$_6$ with N-benzylidene-tert-butylamine, PhCH=NH$_2$.

A) Synthesis and characterization of [PhCH=NH$_2$Bu][WCl$_6$], 4.

To a suspension of WCl$_6$ (513 mg, 1.29 mmol) in hexane (ca. 10 mL), N-benzylidene-tert-butylamine (0.23 mL, 1.3 mmol) was added. The mixture was left stirring for 12 h at room temperature, then the resulting brown precipitate was isolated and dried in vacuo. Yield 348 mg, 48%. Anal. Calcd. for C$_{11}$H$_{16}$Cl$_6$NW: C, 23.64; H, 2.89; N, 2.51; Cl, 38.07. Found: C, 23.48; H, 3.01; N, 2.35; Cl, 37.90. IR (solid state, cm$^{-1}$): $\nu$ = 3252w (N−H), 2978w, 1650s (C=N), 1595m-s, 1455w-m, 1415w, 1382m, 1330w, 1311w, 1237m, 1187m-s, 1166w-m, 1024s, 999w, 824w-m.


745vs, 698w, 673s. Magnetic measurement: $\chi^\text{corr}_M = 2.90 \cdot 10^{-4}$ cgsu, $\mu^\text{eff} = 0.84$ BM. $^1$H NMR (CD$_3$CN): $\delta = 10.85$ (m, 1 H, $^3$J$_{HH} = 17.6$ Hz, NH); 8.77 (d, 1 H, $^3$J$_{HH} = 17.6$ Hz, CH); 8.10, 7.93, 7.75 (m, 5 H, Ph); 1.62 ppm (s, 9 H, CMe$_3$). $^{13}$C NMR (CD$_3$CN): $\delta = 168.6$ (C=N); 142.2 (ipso-Ph); 138.1, 132.6, 130.5 (Ph); 62.5 (CMe$_3$); 27.8 ppm (CMe$_3$).

B) Identification of PhC≡≡≡≡N and evidence for the formation of [PhC≡≡≡≡N]+. The reaction of WCl$_6$ (0.45 mmol) with N-benzylidene-tert-butylamine (0.45 mmol) was carried out in CD$_2$Cl$_2$ (2 mL), by following a procedure analogous to that described for the isolation of 4. The resulting red solution was separated from an abundant green-brown precipitate and analyzed by NMR. $^1$H NMR (CD$_2$Cl$_2$): $\delta = 10.50$ (br, NH); 8.90, 8.37 (s)br, CH); 7.93-7.26 (m, Ph); 4.50 (s); 1.75, 1.60 (s, CMe$_3$) ppm. $^{13}$C NMR (CD$_2$Cl$_2$): $\delta = 168.9$ (C=N); 146.8, 140.7, 137.5, 135.0, 132.5, 131.5, 130.8-127.8 (Ph); 121.4, 112.4, 110.9; 69.6, 65.0 (CMe$_3$); 36.1, 31.3 ppm (CMe$_3$). Then, the solution was dried in vacuo and the red residue was analyzed by IR spectroscopy. IR (solid state, cm$^{-1}$): $\nu = 2267$s, 2250w)sh, 2229w (C≡N), 1657s (C=N). NMR analysis of the precipitate revealed the presence of 4 as the prevalent species.

In a different experiment, WCl$_6$ (0.60 mmol) and N-benzylidene-tert-butylamine (0.60 mmol) were allowed to react in CDCl$_3$ (3 mL), for 18 h. The resulting mixture was treated with an aqueous solution of NaHCO$_3$ (6.3 mmol). After 48 h stirring, the orange organic phase was separated from a colourless solution and analyzed by $^1$H and $^{13}$C NMR spectroscopy, and GC-MS. PhCH=O, PhCH=NtBu and PhCN were detected in ca. 1:1:1 ratio.8,9

Gas-Chromatographic analyses. Samples for gas chromatographic analyses were prepared as follows: a mixture of WCl$_6$ (ca. 1 mmol) and the appropriate imine (ca. 2 mmol) in CH$_2$Cl$_2$ (10 mL) was stirred at room temperature for 48 h in a Schlenk tube tapped with a silicon stopper. Then an aliquot of the reaction atmosphere was withdrawn by a 1 mL syringe through the stopper, and injected into the GC instrument. The yields of N$_2$ formation were estimated based on analyses of gaseous standard mixtures containing known amounts of N$_2$. From WCl$_6$/benzophenone imine: 25%; from WCl$_6$/2,2,4,4-tetramethyl-3-pentanone imine: 7%; from WCl$_6$/N-benzylidene-tert-butylamine: not detected. A blank experiment carried out with benzophenone imine in the absence of WCl$_6$ led to the non detection of N$_2$.

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8 The treatment of the reaction mixture with a weakly basic water solution facilitates the release of the organic compounds from the highly oxophilic metal products, and allows the spectroscopic identification of the former. As blank experiments, we have made N-benzylidene-tert-butylamine (0.5 mmol) to interact with a mixture of WCl$_6$ (0.5 mmol), CDCl$_3$ (1.5 mL) and KHCO$_3$(aq) (ca. 10 mmol in 0.3 mL solution). The amines were generally identified by NMR as unique organic compounds in the resulting solutions.

X-ray crystallography.

The diffraction experiment was carried out on a Bruker APEX II diffractometer equipped with a CCD detector and using Mo-Kα radiation (Table SI1). Data were corrected for Lorentz polarization and absorption effects (empirical absorption correction SADABS \(^{10}\)). The structure was solved by direct methods and refined by full-matrix least-squares based on all data using \(F^2\) \(^{11}\). H-atoms were placed in calculated positions and treated isotropically using the 1.2 fold \(U_{iso}\) value of the parent atom. All non-hydrogen atoms were refined with anisotropic displacement parameters. The crystals of 1·CH\(_2\)Cl\(_2\) are non-merohedrally twinned. The TwinRotMat routine of PLATON \(^{12}\) was used to determine the twinning matrix and to write the reflection data file (.hkl) containing two twin components. Refinement was performed using the instruction HKLF 5 in SHELXL and one BASF parameter. Because of this twinning problem, the value of the weighted R factor is rather high as indicated by an ALERT A in the checkcif.

Table SI1. Crystal data and experimental details for 1·CH\(_2\)Cl\(_2\).

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<td>Largest diff. peak and hole, e Å(^3)</td>
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\(^{10}\) G. M. Sheldrick, *SADABS, Program for empirical absorption correction*, University of Göttingen, Göttingen, Germany, 1997.

\(^{11}\) G. M. Sheldrick, *SHELX97, Program for crystal structure determination*, University of Göttingen, Göttingen, Germany, 1997.

Figure S11. EPR spectrum of [Ph$_2$CNH][BF$_4$], 3: A) experimental (CH$_2$Cl$_2$, 293 K), B) calculated.

Line width = 0.17
Lorentzian = 45%
g$_{iso}$ = 2.0035

Hyperfine coupling constant

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**Electrochemical studies.** Electrochemical measurements were recorded on a Princeton Applied Research (PAR) 273A Potentiostat/Galvanostat, interfaced to a computer employing PAR M270 electrochemical software, and performed in CH$_2$Cl$_2$ solutions containing [N$_n$Bu$_4$][PF$_6$] (0.2 mol dm$^{-3}$) as the supporting electrolyte at room temperature (20±5 °C). HPLC grade CH$_2$Cl$_2$ (Sigma-Aldrich) was stored under argon over 3-Å molecular sieves. Electrochemical grade [N$_n$Bu$_4$][PF$_6$] was purchased from Fluka and used without further purification. Ferrocene (FeCp$_2$) was prepared according to literature.$^{13}$ Cyclic voltammetry was performed in a three-electrode cell, having a platinum-disc working electrode, a platinum-spiral counter electrode and a quasi-reference electrode of platinum. After recording a sufficient number of voltammograms, a small amount of ferrocene was added to the solution and a further voltammogram was recorded. Under the present experimental conditions, the one-electron oxidation of ferrocene occurs at $E^0 = +0.39$ V vs SCE.

Infrared (IR) and ultraviolet (UV-vis) spectroelectrochemical measurements were carried out using an optically transparent thin-layer electrochemical (OTTLE) cell equipped with CaF$_2$ windows, platinum mini-grid working and auxiliary electrodes and silver wire pseudo-reference electrode.$^{14}$ During the microelectrolysis procedures, the electrode potential was controlled by a Princeton Applied Research (PAR) 273A Potentiostat/Galvanostat, interfaced to a computer employing PAR M270 electrochemical software. Argon-saturated CH$_2$Cl$_2$ solutions of the compound under study, containing [N$_n$Bu$_4$][PF$_6$] 0.2 M as the supporting electrolyte, were used.

The *in situ* spectroelectrochemical experiments were performed by collecting IR/UV-vis spectra at constant time intervals during the oxidation, obtained by continuously increasing the initial working potential by a 1.0 mV/sec scan rate. IR spectra were recorded on a Perkin-Elmer FT-IR 1725X spectrophotometer and UV-vis spectra on a Perkin-Elmer Lambda EZ201 spectrophotometer.

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Figure S12. UV-vis spectra of Ph$_2$C=NH in CH$_2$Cl$_2$ solution, containing [N$^6$Bu$_4$][PF$_6$] (0.2 mol dm$^{-3}$) as the supporting electrolyte, recorded in an OTTLE cell as the potential is increased anodically from 0.0 to 2.0 V. The absorptions of the solvent and the supporting electrolyte have been subtracted.

Figure S13. (a) IR spectral changes recorded in an OTTLE cell as the potential of a CH$_2$Cl$_2$ solution of Ph$_2$C=NH is anodically increased from 0.0 to 2.0 V. [N$^6$Bu$_4$][PF$_6$] (0.2 mol dm$^{-3}$) as the supporting electrolyte. The absorptions of the solvent and the supporting electrolyte have been subtracted. (b) IR spectrum of [Ph$_2$C=NH$_2$][BF$_4$] in a CH$_2$Cl$_2$/[N$^6$Bu$_4$][PF$_6$] solution.
Figure S14. UV-vis spectra of PhCH=N'Bu in CH₂Cl₂ solution, containing [N₄Bu₄][PF₆] (0.2 mol dm⁻³) as the supporting electrolyte, recorded in an OTTLE cell as the potential is anodically increased from 0.0 to 2.0 V. The absorptions of the solvent and the supporting electrolyte have been subtracted.

Figure S15. (a) IR spectral changes recorded in an OTTLE cell as the potential of a CH₂Cl₂ solution of PhCH=N'Bu is anodically increased from 0.0 to 2.0 V. [N₄Bu₄][PF₆] (0.2 mol dm⁻³) as the supporting electrolyte. The absorptions of the solvent and the supporting electrolyte have been subtracted. (b) IR spectrum of [PhCH=N'Bu][BF₄] in a CH₂Cl₂/[N₄Bu₄][PF₆] solution.
Computational studies.

The computational geometry optimizations were carried out without symmetry constrains, using the hybrid-GGA EDF2 functional in combination with the 6-31G** basis set (ECP-based LANL2DZ basis set for elements beyond Kr). The “unrestricted” formalism was applied for compounds with unpaired electrons, and the lack of spin contamination was verified by comparing the computed $<S^2>$ values with the theoretical ones. The stationary points were characterized by IR simulations (harmonic approximation), from which zero-point vibrational energies and thermal corrections ($T = 298.15$ K) were obtained. Further optimization of selected geometries was carried out using the range-separated DFT functional $\omega$B97X, in combination with the split-valence polarized basis set of Ahlrichs and Weigend, with ECP on the metal centre. The C-PCM implicit solvation model ($\varepsilon = 9.08$) was added to $\omega$B97X calculations. The software used for C-PCM/$\omega$B97X calculations was Gaussian ’09, while EDF2 calculations were performed with Spartan ’08.

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21 Gaussian 09, Revision C.01, M. J. Frisch et al., Gaussian, Inc., Wallingford CT, 2010.

a') $\Delta G = -0.9$ kcal mol⁻¹

b') $\Delta G, -13.6$ kcal mol⁻¹. The geometry and spin density obtained for this step are in agreement with the oxidation of a chloride ligand to radical chlorine.

c') Oxidation of [WCl₄]⁻ by unreacted WCl₆ should afford the chloroimido complex WCl₄(NCl), $\Delta G = -39.4$ kcal mol⁻¹. The convergence to this stationary point can be ascribed to migration of Cl⁺, formally generated in step b', to the electron rich nitrogen atom.

d') The interaction of two WCl₄(NCl) molecules should result in a dinuclear species containing a bridging N₂ moiety, the N–N bond formation being accompanied by Cl migration to W ($\Delta G = +1.9$ kcal mol⁻¹).

e') The corresponding triplet state of the product, containing W(V) centres and N₂ as bridging ligand, is more stable by about 46 kcal mol⁻¹.

f') Decomposition of W⁶⁺Cl₅(µ-N₂)W⁶⁺Cl₅ to WCl₅ and N₂ is thermodynamically favourable ($\Delta G = -32.8$ kcal mol⁻¹), and further Gibbs free energy is liberated by the interaction of WCl₅ with chloride ($\Delta G = -42.5$ kcal mol⁻¹).
Figure S17. DFT-calculated structure of Ph₂C(Cl)NH-WCl₅ (C-PCM/wB97X calculations, dichloromethane as continuous medium). Selected computed bond lengths (Å) and angles (°): W–N 1.930; W–Cl (trans N) 2.352; W–Cl (cis N) 2.261, 2.322, 2.337, 2.343; N–H 1.026; C–N 1.472; C–Cl 1.829; N–W–Cl 83.9, 92.3, 93.4, 94.7, 172.1; N–C–Cl 102.8.

Figure S18. DFT-calculated structure of [WCl₅(NHCPh₂NHCPh₂)]Cl (EDF2 calculations). Hydrogen atoms on the phenyl rings have been omitted for clarity. Selected computed bond lengths (Å) and angles (°): W–N1 1.922; W–Cl (trans N1) 2.374; W–Cl (cis N) 2.284, 2.338, 2.346, 2.375; N1–H 1.074; N1–C 1.488; N2–C 1.503; N2–H 1.068; H–H 1.894, 2.003; N–W–Cl 88.6, 90.2, 93.7, 93.8, 176.5; N1–C–N2 103.1.
**Figure SI9.** DFT-calculated structure of WCl\(_5\)(NC\(_2\)Ph\(_2\)NHC\(_2\)Ph\(_2\)) (C-PCM/wB97X calculations, dichloromethane as continuous medium). Hydrogen atoms on the phenyl rings have been omitted for clarity. Selected computed bond lengths (Å) and angles (°): W–N1 1.726; W–Cl (trans N1) 2.491; W–Cl (cis N) 2.347, 2.360, 2.364, 2.394; N1–C 1.432; N2–C 1.499; N2–H 1.020; N–W–Cl 89.8, 93.9, 96.8, 96.9; N1–C–N2 108.4.

**Figure SI10.** DFT-calculated structure of WCl\(_5\)(NHC\(_2\)Ph\(_2\)NC\(_2\)Ph\(_2\)) (C-PCM/wB97X calculations, dichloromethane as continuous medium). Hydrogen atoms on the phenyl rings have been omitted for clarity. Selected computed bond lengths (Å) and angles (°): W–N1 1.916; W–Cl (trans N1) 2.362; W–Cl (cis N) 2.259, 2.336, 2.339, 2.353; N1–H 1.025; N1–C 1.498; N2–C 1.450; N–W–Cl 81.7, 94.3, 94.9, 95.0, 167.0; N1–C–N2 108.7.
Figure SI11. DFT-calculated structure of [Ph₂C=N=CH₂][WCl₄NH] (C-PCM/wB97X calculations, dichloromethane as continuous medium). Hydrogen atoms on the phenyl rings have been omitted for clarity. Selected computed bond lengths (Å) and angles (°): W–N 1.704; W–Cl (trans N) 2.539; W–Cl (cis N) 2.357, 2.361, 2.372, 2.389; N–H 1.020; N–C 1.268, 1.269; N–W–Cl 94.2, 94.2, 95.5, 95.8, 178.1; C–N–C 173.9.

Figure SI12. DFT-calculated structure of [WCl₄N]⁻ (C-PCM/wB97X calculations, dichloromethane as continuous medium). Selected computed bond lengths (Å) and angles (°): W–N 1.643; W–Cl 2.381, 2.386, 2.386, 2.390; N–W–Cl 99.8, 99.8, 100.3, 100.4.
Figure SI13. DFT-calculated structure of [WCl₃N]⁺ (C-PCM/wB97X calculations, dichloromethane as continuous medium). Selected computed bond lengths (Å) and angles (°): W–N 1.658; W–Cl (cis N) 2.409, 2.409, 2.409, 2.409; W–Cl (trans N) 2.765; N–W–Cl 95.7, 95.7, 95.7, 95.7, 180.0.

Figure SI14. DFT-calculated structure of WCl₄(NCl) (C-PCM/wB97X calculations, dichloromethane as continuous medium). Selected computed bond lengths (Å) and angles (°): W–N 1.693; W–Cl 2.325, 2.328, 2.330, 2.331; N–Cl 1.618; W–N–Cl 179.8; N–W–Cl 100.4, 100.4, 101.0, 101.1.
**Figure S115.** DFT-calculated structure of $W^\text{VI}{\text{Cl}}_5(\mu{-}\text{N}_2)W^\text{VI}{\text{Cl}}_5$ (C-PCM/wB97X calculations, dichloromethane as continuous medium). Selected computed bond lengths (Å) and angles (°): W–N 2.026, 2.026; W–Cl 2.282, 2.282, 2.283, 2.283, 2.286, 2.286, 2.325, 2.325, 2.325, 2.325, 2.325; N–N 1.136; W–N–N 178.3, 178.3; N–W–Cl 78.3, 78.3, 78.9, 78.9, 93.6, 93.6, 93.6, 93.6, 179.6, 179.6.

![DFT-calculated structure of $W^\text{VI}{\text{Cl}}_5(\mu{-}\text{N}_2)W^\text{VI}{\text{Cl}}_5$](image)

**Figure S116.** DFT-calculated structure of $W^\text{V}{\text{Cl}}_5(\mu{-}\text{N}_2)W^\text{V}{\text{Cl}}_5$ (C-PCM/wB97X calculations, dichloromethane as continuous medium). Selected computed bond lengths (Å) and angles (°): W–N 2.813, 2.919; W–Cl 2.235, 2.236, 2.263, 2.265, 2.266, 2.269, 2.327, 2.332, 2.332, 2.332; N–N 1.094; W–N–N 180.0, 180.0; N–W–Cl 71.2, 71.2, 71.5, 71.8, 88.2, 88.5, 89.4, 90.1, 179.6, 179.9.

![DFT-calculated structure of $W^\text{V}{\text{Cl}}_5(\mu{-}\text{N}_2)W^\text{V}{\text{Cl}}_5$](image)
**Figure SI17.** DFT-calculated structure of WCl₅(κ⁵-C,N-PhC≡N(tBu)) (C-PCM/wB97X calculations, dichloromethane as continuous medium). Selected computed bond lengths (Å) and angles (°): W−N 2.103; W−C 2.103; W−Cl 2.309, 2.325, 2.356, 2.378, 2.398; N=C 1.241; C=W−N 34.3; C−N−C(tBu) 138.2; N−C−C(Ph) 141.5.

**Figure SI18.** DFT-calculated structure of [PhC≡N(tBu)][WCl₅] (C-PCM/wB97X calculations, dichloromethane as continuous medium). Selected computed bond lengths (Å) and angles (°): W−Cl 2.322, 2.332, 2.325, 2.419, 2.428; C≡N 1.148; N−C(tBu) 1.463; C−C(Ph) 1.426.