

## Electronic Supplementary Information

**Reaction of  $\text{N}\equiv\text{W}(\text{O}^t\text{Bu})_3$  with  $\sigma^3\lambda^5$ -phosphoranes. The [2+2] Cycloaddition Across the  $\text{W}\equiv\text{N}$  Triple Bond Resulting in First Representative of Inorganic Four-membered Metallacycle with Conjugated Endo- and Exocyclic Double Bonds.**

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## Experimental Section

**General Procedures.** All procedures were carried out under a dry argon atmosphere using standard Schlenk and glovebox techniques. Aromatic and aliphatic hydrocarbon solvents were dried and distilled from sodium benzophenone ketyl and stored over 4 Å molecular sieves before use. *tert*-Butyl alcohol was dried and distilled from CaO immediately before use. (Me<sub>3</sub>Si)<sub>2</sub>NP(NSiMe<sub>3</sub>)<sub>2</sub> (**I**), <sup>3</sup> and (Me<sub>3</sub>Si)<sub>2</sub>NPS(N<sup>t</sup>Bu) (**II**) <sup>4</sup> were prepared according to established procedures. N≡W(<sup>t</sup>BuO)<sub>3</sub> was prepared by reaction of N≡WCl<sub>3</sub> <sup>14</sup> with LiO<sup>t</sup>Bu in toluene. LiO<sup>t</sup>Bu was prepared from *tert*-butyl alcohol and lithium metal in hexane.

<sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P NMR spectra were recorded at 400, 100 and 162 MHz, respectively, using a Varian Mercury spectrometer (Palo Alto, CA). Benzene-*d*<sub>6</sub> and toluene-*d*<sub>8</sub> were used as internal standards for the proton (benzene-*d*<sub>6</sub> 7.16 ppm, toluene-*d*<sub>8</sub> 7.00 ppm) and carbon (benzene-*d*<sub>6</sub> 128.06 ppm, toluene-*d*<sub>8</sub> 137.50 ppm) NMR spectra, while 85 % H<sub>3</sub>PO<sub>4</sub> was used as an external standard for the <sup>31</sup>P NMR spectra.

### Preparation of [(Me<sub>3</sub>Si)<sub>2</sub>N-P(NSiMe<sub>3</sub>)<sub>2</sub>(O-<sup>t</sup>Bu)]{(<sup>t</sup>BuO)<sub>2</sub>W≡N} (**1**)

In a Schlenk flask (<sup>t</sup>BuO)<sub>3</sub>W≡N (0.41 g, 0.98 mmol) was dissolved in 2 mL of benzene, and the solution was cooled to 10 °C. A solution of (**I**) (0.36 g, 0.98 mmol) in 2 mL of benzene was slowly added dropwise. The mixture was stirred for 1.5 h at room temperature, produced a pale-yellow solution. Removal of solvent *in vacuo* resulted in a pale-yellow solid.

The residue was dissolved in 1 mL of hexane and kept at -30 °C for crystallization.

Yield: 0.54 g, (70%) of white crystals, mp 134 °C (with decomposition).

<sup>1</sup>H NMR (400 MHz, benzene-*d*<sub>6</sub>, 26 °C, ppm) δ = 0.35 (s, 9H, NSiMe<sub>3</sub>), 0.41 (s, 9H, NSiMe<sub>3</sub>), 0.55 (s, 18H, N(SiMe<sub>3</sub>)<sub>2</sub>), 1.42 (s, 9H, PO<sup>t</sup>Bu), 1.67 (s, 18H, O<sup>t</sup>Bu).

<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, benzene-*d*<sub>6</sub>, 26 °C, ppm) δ = 5.18 (d, <sup>3</sup>J<sub>PC</sub> = 2.0 Hz, N(SiMe<sub>3</sub>)<sub>2</sub>), 6.21 (d, <sup>3</sup>J<sub>PC</sub> = 2.0 Hz, NSiMe<sub>3</sub>), 6.94 (d, <sup>3</sup>J<sub>PC</sub> = 1.0 Hz, NSiMe<sub>3</sub>), 31.37 (d, <sup>3</sup>J<sub>PC</sub> = 4.0 Hz, POCMe<sub>3</sub>), 31.55 (s, OCMe<sub>3</sub>), 81.07 (s, OCMe<sub>3</sub>), 83.30 (d, <sup>2</sup>J<sub>PC</sub> = 9.0 Hz, POCMe<sub>3</sub>).

<sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, benzene-*d*<sub>6</sub>, 26 °C, ppm) δ = 8.10 (s, satellite <sup>2</sup>J<sub>WP</sub> = 8.1 Hz).

Anal. Calcd for C<sub>24</sub>H<sub>63</sub>N<sub>4</sub>O<sub>3</sub>PSi<sub>4</sub>W: C, 36.82; H, 8.11; N, 7.16. Found: C, 36.71; H, 7.99; N, 7.09.

### Preparation of [(Me<sub>3</sub>Si)<sub>2</sub>N-PS(N<sup>t</sup>Bu)]{(<sup>t</sup>BuO)<sub>3</sub>W=N} (**2**)

In a Schlenk flask, (<sup>t</sup>BuO)<sub>3</sub>W=N (0.36 g, 0.86 mmol) was dissolved in 2.0 mL of toluene, and the solution was cooled down to -25 °C. (0.25 g, 0.86 mmol) of (**II**) was dissolved in 1.5 mL of toluene thereafter slowly added dropwise. The mixture was stirred for 40 minutes at -25 °C, resulting in a deep-red solution. Maintaining the low temperature (-25 °C), the solvent was removed *in vacuo* (10<sup>-4</sup> mm Hg), yielding a dark red solid. The residue was dissolved in 1 mL of hexane and cooled down to -60 °C in order to induce further crystallization.

Yield: 0.37 g, 61% of red crystals.

<sup>1</sup>H NMR (400 MHz, toluene-*d*<sub>8</sub>, -25 °C, ppm) δ = 0.62 (br. s, 18H, SiMe<sub>3</sub>), 1.44 (s, 27H, O<sup>t</sup>Bu), 1.75 (s, 9H, N<sup>t</sup>Bu).

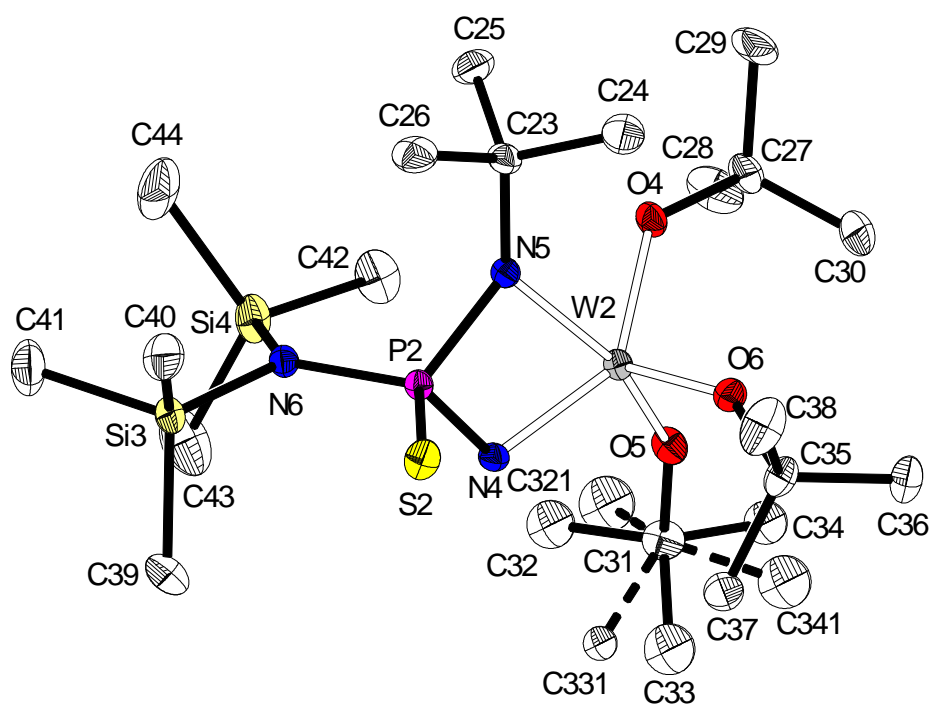
<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, toluene-*d*<sub>8</sub>, -25 °C, ppm) δ = 7.72 (br. s, SiMe<sub>3</sub>), 31.36 (s, OCMe<sub>3</sub>), 33.80 (d, <sup>3</sup>J<sub>PC</sub> = 8.0 Hz, NCMe<sub>3</sub>), 57.47 (d, <sup>2</sup>J<sub>PC</sub> = 5.0 Hz, NCMe<sub>3</sub>), 87.08 (s, OCMe<sub>3</sub>).

<sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, toluene-*d*<sub>8</sub>, -25 °C, ppm) δ = 29.02 (s).

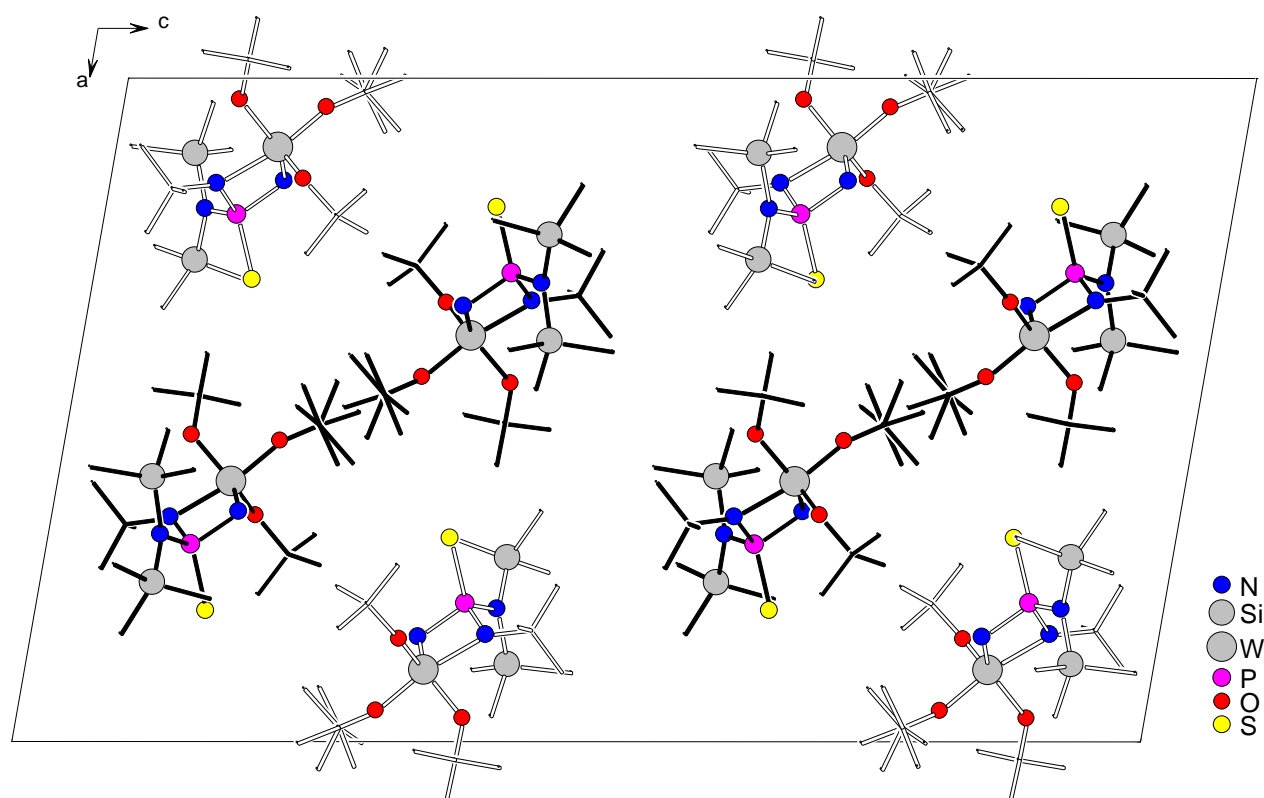
Anal. Calcd for C<sub>22</sub>H<sub>54</sub>N<sub>3</sub>O<sub>3</sub>PSSi<sub>2</sub>W: C, 37.13; H, 7.65; N, 5.90. Found: C, 37.21; H, 7.72; N, 5.78.

## Computational methods

Quantum-chemical calculations were performed for the molecules of Mo- and W-containing compounds in vacuum in the framework of density-functional theory (DFT). Becke'88 exchange with Perdew'86 correlation (BP86)<sup>19</sup> and with the hybrid three-parameter Becke Lee-Yang-Parr (B3LYP)<sup>20</sup> functionals as defined in TurboMole program system<sup>21</sup> together with Ahlrichs' triple-zeta split-valence basis set augmented by Coulomb fitting (def2-TZVPP/J)<sup>22</sup> using Zeroth Order Regular Approximation (ZORA) scalar relativistic Hamiltonian<sup>23</sup> were applied. The ORCA *ab initio*, DFT and semiempirical SCF-MO package<sup>24</sup> was used for all calculations. The geometries of molecules were fully optimized. For the geometries optimized within BP86 functional the vibrational frequencies were calculated using central finite difference approximation for derivatives evaluation with 0.005 Bohr increment for differentiation. Thermochemical properties at 213.15 and 298.15 K were derived using vibrational data in approximation of ideal gas and harmonic vibrations, as given by ORCA output.



**Figure S1.** The molecular structure of second independent molecule of (2). Thermal ellipsoids are drawn at the 25% probability level. Hydrogen atoms are omitted for clarity. The minor disorder components are shown with the broken bonds. Selected bond distances (Å) and angles (°) for (2): W2-N4 1.824(4), W2-N5 2.059(4), P2-N4 1.660(4), P2-N5 1.667(4), P2-N6 1.676(4), P2-S2 1.953(2), W2-O4 1.905(3), W2-O5 1.851(3), W2-O6 1.817(3), N4-W2-N5 73.9(2), W2-N4-P2 102.3(2), N4-P2-N5 89.5(2), W2-N5-P2 93.0(2).



**Figure S2.** The [010] projection of the crystal packing of structure (2). The molecules containing W1 atoms are shown with full bonds, while the ones that contain W2 atoms with empty bonds.