Azide Complexes

The Molybdenum(V) and Tungsten(VI) Oxoazides $[MoO(N_3)_3]$, $[MoO(N_3)_3 \cdot 2 CH_3 CN]$, $[(bipy)MoO(N_3)_3]$, $[MoO(N_3)_5]^{2-}$, $[WO(N_3)_4]$, and $[WO(N_3)_4 \cdot CH_3 CN]$

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In memory of Howard S. Taylor

Abstract: A series of novel molybdenum(V) and tungsten(VI) oxoazides was prepared starting from $[MOF_4]$ (M = Mo, W)and Me_3SiN_3 . While $[WO(N_3)_4]$ was formed through fluorideazide exchange in the reaction of Me_3SiN_3 with WOF_4 in SO_2 solution, the reaction with $MoOF_4$ resulted in a reduction of Mo^{VI} to Mo^{V} and formation of $[MoO(N_3)_3]$. Carried out in acetonitrile solution, these reactions resulted in the isolation of the corresponding adducts $[MoO(N_3)_3 \cdot 2 CH_3 CN]$ and [WO- $(N_3)_4$ ·CH₃CN]. Subsequent reactions of $[MoO(N_3)_3]$ with 2,2'bipyridine and $[PPh_4][N_3]$ resulted in the formation and isolation of $[(bipy)MoO(N_3)_3]$ and $[PPh_4]_2[MoO(N_3)_5]$, respectively. Most molybdenum(V) and tungsten(VI) oxoazides were fully characterized by their vibrational spectra, impact, friction and thermal sensitivity data and, in the case of $[WO(N_3)_4:CH_3CN], [(bipy)MoO(N_3)_3], and [PPh_4]_2[MoO (N_3)_5$], by their X-ray crystal structures.

Polyazides are highly energetic compounds that have attracted considerable interest as potential high-energydensity materials (HEDM).^[1] Because of their highly endothermic nature, polyazido compounds are usually explosive and very shock sensitive, rendering the synthesis of molecules with a large number of azido groups difficult. The chemistry of high-oxidation-state metal polyazides is more challenging than the one of lower-oxidation-state metal polyazides, owing to the fact that the increased oxidation potential of the central metal atom results in an increased sensitivity and explosiveness.^[2] The stabilization of neutral polyazides by either anion or adduct formation has been well-established in recent years.^[3] Another less common approach for the stabilization of high-oxidation state metal azides is the introduction of oxygen atoms to reduce the oxidation potential of the central metal atom.^[4] The binary polyazides $Mo(N_3)_6$, $W(N_3)_6$, $[PPh_4][Mo(N_3)_7]$, and $[PPh_4][W(N_3)_7]$ have been described

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article are available on the WWW under http://dx.doi.org/10.1002/ anie.201505418. as very treacherous, extremely shock- and temperaturesensitive compounds that explode violently when warmed towards room temperature.^[5] The only structurally characterized polyazides of molybdenum and tungsten are $[W(N_3)_6]$ and $[NMo(N_3)_4]^{-.[5,6]}$ To the best of our knowledge, no molybdenum(V), molybdenum(VI), or tungsten(VI) oxopolyazides have been structurally characterized so far.

In analogy with our previously reported syntheses of $[Mo(N_3)_6]$, $[W(N_3)_6]$, $[MoO_2(N_3)_2]$, and $[WO_2(N_3)_2]$,^[5] the reaction of molybdenum or tungsten oxotetrafluoride with an excess of trimethylsilyl azide in acetonitrile solution at -20 °C resulted in a complete fluoride–azide exchange and the formation of dark maroon to black (M=Mo) or yellow-orange (M=W) solutions. When the volatile compounds (CH₃CN, Me₃SiF, and excess Me₃SiN₃) were pumped off from the WOF₄ reaction mixture, first at -20 °C and then at ambient temperature, the acetonitrile adduct [WO-(N₃)₄·CH₃CN] was isolated as an orange solid [Eq. (1)].

$$[WOF_4] + 4 Me_3SiN_3 \xrightarrow[-4Me_3SiF]{CH_3CN} [WO(N_3)_4 \cdot CH_3CN]$$
(1)

Single crystals of $[WO(N_3)_4$ ·CH₃CN] were grown from acetonitrile solution by slow evaporation of the solvent in vacuo. The compound was characterized by its X-ray crystal structure, vibrational and NMR spectra, as well as the observed reaction stoichiometry (see the Supporting Information). In the case of the $[MoOF_4]$ reaction, Mo^{VI} was reduced to Mo^V by Me₃SiN₃ under evolution of N₂ and very dark maroon-colored $[Mo(N_3)_3·2CH_3CN]$ was isolated when the volatile compounds were pumped off [Eq. (2)].

$$2 [MoOF_4] + 8 Me_3 SiN_3 \frac{CH_3 CN}{-8Me_3 SiF_5 - 3N_2} 2 [MoO(N_3)_3 \cdot 2 CH_3 CN]$$
(2)

Attempts of growing single crystals of the acetonitrile adduct $[MoO(N_3)_3 \cdot 2CH_3CN]$ that were suitable for X-ray crystal structure determination were unsuccessful. The compound was identified and characterized by the observed reaction stoichiometry, its vibrational spectra (Supporting Information), and its conversion into the adduct $[(bipy)MO-(N_3)_3]$ and the anion $[MO(N_3)_5]^{2-}$. The reaction of the metal oxotetrafluorides with trimethylsilyl azide in SO₂ solution at -20 °C resulted in the formation of the corresponding unsolvated oxoazides $[MoO(N_3)_3]$ and $[WO(N_3)_4]$, respectively. Both compounds are stable at ambient temperature but are treacherous and explode violently upon slight provocation (friction and impact). The composition of the compounds was

established by their vibrational spectra and the observed reaction stoichiometry (Supporting Information). The adduct $[(bipy)MoO(N_3)_3]$ was formed quantitatively when $[MoO(N_3)_3]$ was reacted with 2,2'-bipyridine (bipy) in acetonitrile solution [Eq. (3)]. It was isolated as a brown crystalline solid and characterized by its vibrational spectra and X-ray crystal structure.

$$[MoO(N_3)_3] + bipy \xrightarrow{CH_3CN} [(bipy)MoO(N_3)_3]$$
(3)

When a solution of $[(bipy)MoO(N_3)_3]$ in acetonitrile was kept in an evacuated thin-walled (0.5 mm wall thickness) FEP reactor for a period of several days, a dark heterogeneous mixture with some light-brown crystals was obtained once the solvent was removed. An X-ray crystal structure determination identified the crystalline material as $[((bipy)MoON_3)_2O_2]$ by X-ray crystal structure determination (Supporting Information). This doubly O-bridged molybdenum oxoazide was presumably formed through the hydrolysis of [(bipy)MoO- $(N_3)_3$ with moisture that had diffused into the reactor. No further attempts were made to characterize this compound or to identify other hydrolysis products. The metal oxoazides $[MoO(N_3)_3]$ and $[WO(N_3)_4]$ were quantitatively converted into salts containing the pentaazido anions $[MoO(N_3)_5]^{2-}$ and $[WO(N_3)_5]^-$, respectively, through reactions with $[PPh_4][N_3]$ in acetonitrile solution [Eq. (4) and (5)].

$$[MoO(N_3)_3] + 2 [PPh_4][N_3] \xrightarrow{CH_3CN} [PPh_4]_2 [MoO(N_3)_5]$$

$$\tag{4}$$

$$[WO(N_3)_4] + [PPh_4][N_3] \xrightarrow{CH_3CN} [PPh_4][WO(N_3)_5]$$
(5)

Both oxopentaazidometalate salts were isolated as orange-brown (Mo) or bright orange solids that were identified and characterized by the observed reaction stoichiometry and their vibrational and NMR spectra. The salt $[PPh_4]_2[Mo(N_3)_5]$ was also characterized by its X-ray crystal structure. Attempts to obtain single crystals of $[PPh_4][WO-(N_3)_5]$ were unsuccessful.

Details of the crystallographic data collection and refinement parameters for the structurally characterized compounds $[(bipy)MoO(N_3)_3]$, $[PPh_4]_2[MoO(N_3)_5]$, [((bipy)- $MoON_3)_2O_2$], and $[WO(N_3)_4 \cdot CH_3CN]$ are given in the Supporting Information. The bipyridine adduct [(bipy)MoO- $(N_3)_3$] crystallizes in the monoclinic space group $P2_1/n$ with four symmetry-related molecules per unit cell. While the solid-state structure consists of isolated and separated molecules, the closest intermolecular $N_{azide} \cdots N_{azide}$ distances are just 2.996(2) Å, which is about the sum of van der Waals radii (3.0 Å).^[7] The closest intermolecular Mo…N_{azide} and Mo…O distances are 3.839(2) Å and 5.154(2) Å, respectively. The structure of the $[(bipy)MoO(N_3)_3]$ molecule is derived from a pseudo octahedral geometry with the bipyridine ligand, the oxygen atom and one azido group in the equatorial positions and two azido groups occupying the axial positions (Figure 1 A). The average Mo-Nazide distance of 2.051(2) Å is about 0.01 Å shorter than that in the related molybdenum-(VI) dioxodiazide [(bipy)MoO₂(N₃)₂].^[8] The observed Mo–O distance of 1.691(1) Å in $[(bipy)MoO(N_3)_3]$ is 0.025 Å shorter than in $[(bipy)MoO_2(N_3)_2]^{[8]}$ but longer than in polymeric



Figure 1. Crystal structure of A) [(bipy)MoO(N₃)₃], B) [WO-(N₃)₄:CH₃CN], and C) the anion in $[PPh_4]_2[MoO(N_3)_5]$. Ellipsoids are set at 50% probability; hydrogen atoms have been omitted for clarity.

 $[MoOF_4]$ (1.64(1) Å),^[9] which contains F-bridges. The average N-N distances in the azido ligands of 1.143(3) Å for the terminal azide bonds and 1.212(2) Å for the internal bonds are typical for covalent azides. The tungsten oxoazide [WO- $(N_3)_4$ ·CH₃CN] crystallizes in the triclinic space group $P\overline{1}$ with two molecules per asymmetric unit (Z = 4, Z' = 2). The crystal structure of this metal oxoazide contains isolated molecules and the closest $N_{azide}{}^{\dots}N_{azide}$ distances (2.978(9) Å) are again comparable to the sum of van der Waals radii. The closest intermolecular W···N_{azide} and W···O distances are 3.997(4) Å and 4.267(4) Å, respectively. In both nonequivalent molecules of the unit cell, the coordination geometry around the central tungsten atom is derived from a distorted pseudo-octahedron with four azido groups in the equatorial positions (Figure 1B). The oxygen atom and the acetonitrile molecule occupy the axial positions. All four azido ligands are oriented away from the oxygen atom and pointing towards the acetonitrile ligand, resulting in a molecular structure resembling an umbrella. The W– N_{azide} distances range from 1.956-(4) Å to 2.019(4) Å with an average value of 1.989(4) Å that is shorter than the one observed for $([bipy)WO_2(N_3)_2]$ (2.049-(3) Å)^[8] but slightly longer than the one in $[W(N_3)_6]$ (1.978-(2) Å).^[5] The average W–O distance of 1.697(4) Å is 0.032 Å shorter than the one found in $[(bipy)WO_2(N_3)_2]^{[8]}$ and much shorter than in tetrameric and O-bridged [WOF₄] (2.11-(4) Å).^[10]

The salt $[PPh_4]_2[MoO(N_3)_5]$ crystallizes in the triclinic space group $P\overline{1}$ (Z=2). The solid-state structure consists of isolated and well-separated $[PPh_4]^+$ cations and $[MoO(N_3)_5]^{2-}$ anions. The closest intermolecular N···N and Mo···N distances are 4.471(2) Å and 6.480(2) Å, respectively. The closest intermolecular Mo···O distance is 9.985(1) Å. The structure of the $[MoO(N_3)_5]^{2-}$ anion is again derived from a distorted octahedron with the oxygen and one azido group occupying the axial positions and the remaining four N₃ ligands in the equatorial positions (Figure 1C). The average Mo-N_{azide}



distance of 2.112(2) Å is significantly longer than that of $[bipy(MoO(N_3)_3]$ (2.051(2) Å). The Mo–O distance of 1.684-(1) Å is somewhat shorter than the one in $[(bipy)MoO(N_3)_3]$.

Geometries were optimized at the B3LYP//DZVP2/ccpVDZ-PP and SVWN5//DZVP2/cc-pVDZ-PP levels^[11] of density functional theory for the metal oxoazide species $[MO(N_3)_3], [MO(N_3)_4]^-, [MO(N_3)_5]^{2-}, [MO(N_3)_4], and [MO (N_3)_5$]⁻, as well as the adducts [MO(N₃)₃·CH₃CN], [MO- $(N_3)_3 \cdot 2 CH_3 CN$, [MO(N₃)₄·CH₃CN], and [(bipy)MO(N₃)₃] (M = Mo, W). The obtained geometries and calculated vibrational frequencies and intensities are given in the Supporting Information. The local DFT functional was included as it often gives better geometries for transition metal compounds than do hybrid functionals such as B3LYP. Relative energies were calculated at the B3LYP/aug-cc-pVDZ(-PP), MP2/ ROMP2/aug-cc-pVDZ(-PP),^[12] and R/UCCSD(T)/aug-ccpVDZ(-PP)^[13] levels, the latter two at the SVWN5 geometries.^[14] The results are shown in Figure 2 for $[MO(N_3)_4]$ and in Figure 3 for $[MO(N_3)_3]$.



Figure 2. Optimized structures of the metal oxoazide species derived from closed shell $[MO(N_3)_4]$ (M = Mo, W) and relative energies $[kcal mol^{-1}]$ at the CCSD(T) level.

The calculated Mo–O bond distance in $[(bipy)MoO(N_3)_3]$ with the SVWN5 functional is 1.670 Å, 0.021 Å shorter than the experimental value. The averaged Mo–N bond distance is 2.000 Å, which is also shorter, by 0.051 Å compared to the experiment. For the external and internal azide bonds, the averaged N–N bond distances are predicted to be 1.166 Å and 1.220 Å, respectively, slightly longer than experiment. For $[WO(N_3)_4$ ·CH₃CN], the W–O bond and the averaged W–N bond distances are calculated to be 1.685 Å and 1.986 Å, which are also slightly shorter than the experimental values. In contrast, the predicted Mo–O bond distance in $[MoO-(N_3)_5]^{2-}$ with the SVWN5 functional is 1.710 Å, slightly longer than in the crystal by 0.026 Å. This difference could easily be



Figure 3. Optimized structures of the metal oxoazide species derived from $[MO(N_3)_3]$ (M = Mo, W) and reaction energies [kcal mol⁻¹] at the B3LYP, ROMP, and CCSD(T) levels.

due to the lack of counterions in the gas-phase calculations. The averaged Mo-N bond distance of 2.068 Å is still shorter than experiment. In case of the doublet states of oxidation state + V, the spin on the metal is somewhat delocalized onto the azide nitrogen atoms (Supporting Information). The electron affinities of $[MO(N_3)_4]$ were calculated at all three levels, as the ROMP2/MP2 and B3LYP levels did not agree well. The best results are at the CCSD(T) level and show that $[MoO(N_3)_4]$ is much easier to reduce than is $[WO(N_3)_4]$ by 0.67 eV, and the electron affinity (EA) of 4.13 eV for MoO- $(N_3)_4$ is comparable to that for $[MoF_6]$.^[15] The B3LYP EAs are higher than the CCSD(T) values and the ROMP2/MP2 values are lower than the CCSD(T) EAs. The binding energy of $N_3^$ to $[WO(N_3)_4]$ of 70 kcalmol⁻¹ is 6 kcalmol⁻¹ higher than the corresponding value for $[MoO(N_3)_4]$, showing that the former is a better Lewis acid. The N_3^- affinity for WO(N_3)₄ is comparable to the F^- affinity of $[WF_6]$.^[15] The addition of CH_3CN to $[Mo(N_3)_4]$ results in a pseudo-octahedral [Mo- $(N_3)_4$ ·CH₃CN]. The conformation shown in Figure 2 with CH₃CN occupying an axial position is prefered over the conformation with CH₃CN and three N₃ groups in equatorial positions by 8 kcal mol⁻¹ for W and 7 kcal mol⁻¹ for Mo.

The CH₃CN binding energy of 28 kcalmol⁻¹ for [WO-(N₃)₄] is 3 kcalmol⁻¹ larger than for [MOO(N₃)₄]. This pattern of the W compounds being better Lewis acids than the Mo compounds that are being more easily reduced is wellestablished in transition-metal oxide clusters and plays an important role in their catalytic acitivity.^[16] The addition of N₃⁻ to [WO(N₃)₃] is 3 kcalmol⁻¹ more exoergic than to [MoO(N₃)₃] and the value is larger than for the addition of N₃⁻ to [WO(N₃)₄]. This is consistent with the larger steric constraints for the latter. The addition of the second N₃⁻ ion is endothermic in the gas phase. To model this process, we performed single-point calculations using a self-consistent reaction field (SCRF) approach with CH₃CN as the solvent (ε = 35.7).^[17] The SCRF calculations were done with the COSMO approach and parameters at the ROMP2/aug-ccpVDZ level.^[18] The solvent-included calculations correspond to the free energy at 298 K obtained by adding the gas-phase and solvent-free energies. The free energies in CH₃CN for the addition of the first N_3^- ion are about half the exothermicity of the gas phase values but are still substantially exothermic. The addition of the second N_3^- ion in CH₃CN to form the dianion is also exothermic but the exothermicity is substantially smaller. Note that there are no counterions present in our SCRF model, which could further stabilize the formation of the dianion. The exothermicity for the addition of CH₃CN is essentially the same for $[MO(N_3)_3]$ and $[MO(N_3)_4]$. The addition of the second CH₃CN is less exothermic than that of the first CH₃CN.

The observed and calculated vibrational data of the investigated molybdenum and tungsten oxoazides are listed in the Supporting Information. The vibrational assignments are supported by the DFT calculations. The IR spectra of the compounds are dominated by bands that are due to the $v_{\rm as}(N_3)$ vibration modes at about 2000–2200 cm⁻¹. The v-(MoO) mode is observed at about 940-960 cm⁻¹ for the molybdenum compounds and at about 960–980 cm⁻¹ for the tungsten compounds. Furthermore, the strong bands of the $v_{as}(N_3)$ modes in the region 2000–2200 cm⁻¹ are the dominating features in the Raman spectra. The much weaker bands of the $v_s(N_3)$ modes are observed at about 1200–1350 cm⁻¹. They are characteristic for the presence of covalently bound azido groups. The M-N_{azide} stretching modes are observed at about 420-470 cm⁻¹. The presence of covalent azides was also confirmed by the ¹⁴N NMR spectra. Solutions of all compounds in SO₂, CD₃CN, or CDCl₃ exhibited resonances with chemical shifts of about -280 ppm, -140 ppm, and -200 ppm for N α , N β , and N γ , respectively, characteristic for covalent azido compounds.

The impact (IS) and friction sensitivities (FS) of the molybdenum(V) and tungsten(VI) oxoazides were determined using a BAM (Bundesanstalt für Materialforschung und-prüfung) impact and a BAM friction tester. The obtained sensitivity and stability data are summarized in Table 1. As can be expected, the metal polyazides $[MoO(N_3)_3]$ and $[WO(N_3)_4]$ are very sensitive to impact and friction. The acetonitrile adducts $[MoO(N_3)_3 \cdot 2 CH_3 CN]$ and $[WO(N_3)_4 \cdot CH_3 CN]$ show about the same sensitivities as the corresponding unsolvated compounds. Adduct formation

Table 1: Sensitivity data^[a] for the metal oxoazides.

Compound	T_{decomp} [°C]	FS [N]	IS [J]
RDX ^[b]	220	120	7.5
Pb(N ₃) ₂ ^[19]	300	0.1	2.5
[MoO(N ₃) ₃]	104 ^[c]	< 5	<1
$[MoO(N_3)_3 \cdot 2 CH_3 CN]$	145 ^[c,d]	< 5	<1
[(bipy)MoO(N ₃) ₃]	145	240	2
$[PPh_4]_2[MoO(N_3)_5]$	180 ^[e]	>360	>100
$[WO(N_3)_4]$	171 ^[c]	< 5	< 1
$[WO(N_3)_4 \cdot CH_3CN]$	170 ^[c]	< 5	<1
$[PPh_4][WO(N_3)_5]$	190	>360	12

[a] FS = friction sensitivity, IS = impact sensitivity. [b] 1,3,5-Trinitroperhydro-1,3,5-triazine, hexogen. [c] Explosion. [d] Broad endotherm at 85– 120°C. [e] Endotherm at 155°C (melting).

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The thermal stabilities of the oxoazides were determined through differential thermal analysis (DTA) scans with heating rates of 5°Cmin⁻¹. The resulting decomposition onset temperatures are included in Table 1. Only the bipyridine adduct $[(bipy)MoO(N_3)_3]$ as well as the salts $[PPh_4]_2$ - $[MoO(N_3)_5]$ and $[PPh_4][WO(N_3)_5]$ showed smooth decompositions. The compounds [MoO(N₃)₃], [MoO(N₃)₃·2 CH₃CN], $[WO(N_3)_4]$, and $[WO(N_3)_4 \cdot CH_3 CN]$ exploded violently upon heating at a rate of 5 °Cmin⁻¹. It is interesting to note that the molybdenum(V) azides are thermally less stable than the tungsten(IV) azides and that the solvate [MoO- $(N_3)_3$ ·2 CH₃CN] has a higher decomposition temperature than the unsolvated $[MoO(N_3)_3]$ while $[WO(N_3)_4 \cdot CH_3 CN]$ and $[WO(N_3)_4]$ decompose at similar temperatures. As can be expected, the salts $[PPh_4]_2[MoO(N_3)_5]$ and $[PPh_4][WO(N_3)_5]$ show the highest decomposition temperatures of 180 °C and 190 °C, respectively, among the azido compounds of this study.

In conclusion, a series of novel molybdenum(V) and tungsten(VI) oxoazides has been prepared and characterized. The reaction of $[WOF_4]$ with Me₃SiN₃ results in a complete fluoride-azide exchange and formation of $[WO(N_3)_4]$. The reaction of molybdenum oxotetrafluoride, $[MoOF_4]$, with Me₃SiN₃ results in the reduction of Mo^{VI} to Mo^V under N₂ evolution and formation of the novel molybdenum(V) azide $[MoO(N_3)_3]$. The solvent-free metal oxoazides could be isolated as explosive and highly sensitive solids when SO₂ was used as solvent. The solvated adducts [MoO-(N₃)₃·2 CH₃CN] and [WO(N₃)₄·CH₃CN] were obtained when the reactions of the metal oxofluorides with Me₃SiN₃ were carried-out in acetonitrile solution. The reactions of [MoO- $(N_3)_3$ with 2,2-bipyridine and $[PPh_4][N_3]$ resulted in the formation of $[(bipy)MoO(N_3)_3]$ and $[PPh_4]_2[MO(N_3)_5]$, respectively. The hydrolysis of $[(bipy)MoO(N_3)_3]$ resulted in the formation and isolation of $[((bipy)MoON_3)_2O_2]$. The molybdenum and tungsten oxoazides were characterized by their vibrational spectra, impact, friction and thermal sensitivity data, and, in the cases of $[WO(N_3)_4 \cdot CH_3 CN]$, $[(bipy)MoO(N_3)_3], [PPh_4]_2[MoO(N_3)_5], and$ [((bipy)- $MoON_3)_2O_2$, by their X-ray crystal structures. Most compounds of this work, the CH₃CN and N₃⁻ addition reactions of $[MO(N_3)_3]$ and $[MO(N_3)_4]$, as well as the reduction reactions of $[MO(N_3)_4]$ (M = Mo, W) were studied by computational methods.

Experimental Section

Caution! Polyazides are extremely shock-sensitive and can explode violently upon the slightest provocation. Because of the high energy content and the high detonation velocity of these azides, their explosions are particularly violent and can cause, even on a one mmol scale, significant damage. The use of appropriate safety precautions (safety shields, face shields, leather gloves, protective clothing, such as heavy leather welding suits and ear plugs) is mandatory. **Ignoring safety precautions can lead to serious injuries!**



Materials and apparatus: All reactions were carried out in Teflon-FEP ampules that were closed by stainless steel valves. Volatile materials were handled in a Pyrex glass vacuum line. Non-volatile materials were handled in the dry nitrogen atmosphere of a glove box. The starting materials [MoOF₄] and [WOF₄] were prepared from the corresponding hexafluorides and HF/SiO₂. PPh₄N₃ was prepared according to a previously reported procedure,^[20] and 2,2'-bipyridine (bipy) (Aldrich) was used without further purification. Trimethylsilyl azide (Aldrich) was purified by fractional condensation. Solvents were dried using standard methods and freshly distilled prior to use.

Crystal-structure determinations: The single-crystal X-ray diffraction data were collected on Bruker SMART or Bruker SMART APEX DUO diffractometers using Mo_{Ka} radiation The structures were solved by intrinsic phasing and refined on F^2 using the Bruker SHELXTL Software Package and ShelXle.^[21] ORTEP drawings were prepared using the ORTEP-3 for Windows V2.02 program.^[22] Further crystallographic details can be obtained from the Cambridge Crystallographic Data Centre (CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: (+44) 1223–336–033; e-mail: deposit@ccdc.cam.ac.uk) on quoting the deposition no. CCDC 1405935–1405937.

Computational methods: The geometries were optimized at the density functional theory (DFT)^[23] level with the LSDA (local spin density approximation) SVWN5^[24] and hybrid B3LYP^[25] exchangecorrelation functionals with the DFT-optimized DZVP2 basis set^[26] for H, C, N, and O atoms and the cc-pVDZ-PP^[27] basis set for Mo and W using the Gaussian09 program system.^[28] Vibrational frequencies were calculated to show that the structures were minima. The ROMP2 and CCSD(T) calculations were performed with the MOLPRO program system.^[29]

Further experimental details are given in the Supporting Information.

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