

Bioinspired Nucleophilic Attack on a Tungsten-Bound Acetylene: Formation of Cationic Carbyne and Alkenyl Complexes

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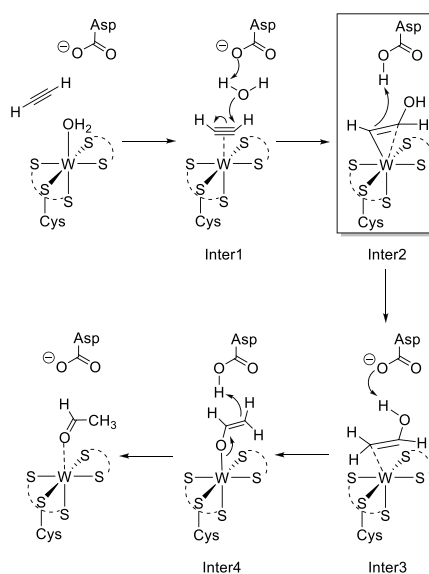
Supporting Information

ABSTRACT: Inspired by the proposed inner-sphere mechanism of the tungstoenzyme acetylene hydratase, we have designed tungsten acetylene complexes and investigated their reactivity. Here, we report the first intermolecular nucleophilic attack on a tungsten-bound acetylene (C_2H_2) in bioinspired complexes employing 6-methylpyridine-2-thiolate ligands. By using PMe_3 as a nucleophile, we isolated cationic carbyne and alkenyl complexes.

The anaerobic bacterium *Pelobacter acetylenicus* can grow on acetylene (C_2H_2) as a single carbon and energy source. Its utilization is performed by the tungstoenzyme acetylene hydratase (AH), which catalyzes the hydration of acetylene to acetaldehyde.^{1–4} The coordination sphere of the tungsten(IV) center in the active site consists of four sulfur atoms from two molybdopterin cofactors, a thiolate from cysteine, and a water molecule.⁵ Although several experimental^{5,6} and computational studies^{7–10} have been carried out to shed light on the reaction mechanism, it remains unclear where C_2H_2 is located during hydration. Because of lower energetic barriers, density functional theory calculations favor a mechanism where C_2H_2 replaces the coordinated water and subsequently undergoes nucleophilic attack by a hydroxide (Scheme 1).^{7–10} Apart from investigations on $[Et_4N]_2[W(O)(mnt)_2]$ ($mnt = \text{maleonitriledithiolate}$),^{11–13} synthetic approaches to elucidate the mechanism of AH have only included systems with tungsten-coordinated C_2H_2 .^{14,15} In a recent publication, the S,N -bidentate ligand pyridine-2-thiolate (PyS) was introduced to the tungsten(II) center to model the active site of AH as in Inter1 (Scheme 1).¹⁵ In contrast to previously reported structural model compounds,¹⁴ the coordination of a second C_2H_2 and subsequent insertion into the W–N bond occurred, showing that a second coordinated C_2H_2 is sufficiently activated to undergo a nucleophilic attack. A similar behavior was observed in molybdenum and tungsten complexes, where a nucleophilic attack on one of two coordinated hexafluorobut-2-yne moieties took place, yielding a η^2 -vinyl complex.^{16–20} Our aim is to facilitate an intermolecular nucleophilic attack by inhibiting the coordination of a second C_2H_2 and insertion as in the PyS system. Therefore, we anticipated the introduction of a methyl group next to the coordinating nitrogen atom in PyS (6-MePyS) so that the metal center is more shielded against the coordination of a second C_2H_2 .

For preparation of the redesigned tungsten complex $[W(CO)(C_2H_2)(6\text{-MePyS})_2]$ (**1**), which contains the desired 6-MePyS ligands and only one C_2H_2 , a previously developed procedure was modified.^{14,15,21} The reaction of

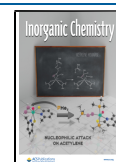
Scheme 1. Proposed Inner-Sphere Mechanism of the Hydration of C_2H_2 Performed by AH: Nucleophilic Attack of a Hydroxide on Coordinated C_2H_2 .⁸



$[WBr_2(CO)_3(NCMe)_2]$ with 2.1 equiv of $Na(6\text{-MePyS})$ in CH_2Cl_2 followed by stirring under a C_2H_2 atmosphere for 1 h allowed the isolation of **1** in 86% yield after silica gel filtration. The intermediately formed tricarbonyl complex $[W(CO)_3(6\text{-MePyS})_2]$ was characterized by single-crystal X-ray diffraction analysis (see the Supporting Information). Longer reaction times led to the insertion of a second C_2H_2 into the W–N

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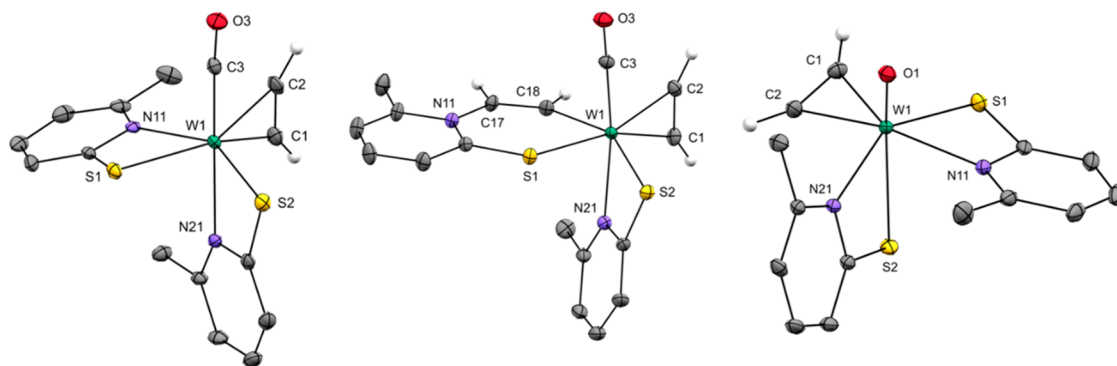
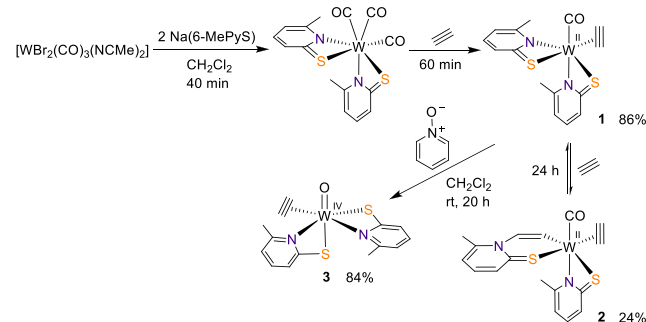


Figure 1. Molecular structures of **1** (left), **2** (middle), and **3** (right) with probability ellipsoids drawn at the 50% probability level.

bond forming $[\text{W}(\text{CO})(\text{C}_2\text{H}_2)(\text{HCCH-6-MePyS})(6\text{-MePyS})]$ (**2**), as previously observed in the unsubstituted analogue $[\text{W}(\text{CO})(\text{C}_2\text{H}_2)(\text{HCCH-PyS})(\text{PyS})]$.¹⁵ However, the additional methyl group significantly decreases intramolecular insertion because even after 24 h and repeated addition of C_2H_2 only partial conversion is observed. Furthermore, in the absence of additional C_2H_2 , **2** reacts reversibly to **1** under the elimination of acetylene or polyacetylene depending on the solvent. Nevertheless, we were able to isolate **2** and unambiguously confirm its structure by single-crystal X-ray diffraction analysis (Figure 1) and by spectroscopic means. In CD_2Cl_2 , the sterically hindered C_2H_2 protons of **1** resonate at 13.77 and 12.50 ppm and the carbon atoms at 205.73 and 204.14 ppm, suggesting that C_2H_2 acts as a four-electron donor.²² In ^1H NMR spectra of **2** recorded in CD_2Cl_2 , the $\eta^2\text{-C}_2\text{H}_2$ protons appear as singlets at 12.90 and 12.03 ppm. The protons of the inserted C_2H_2 couple with each other thus appear as doublets ($^3J = 10.9$ Hz) flanked with ^{183}W satellites at 7.61 and 6.89 ppm. IR spectra of **1** and **2** show strong $\text{C}\equiv\text{O}$ bands at 1891 and 1897 cm^{-1} , respectively. Single-crystal X-ray diffraction analyses of **1** and **2** revealed almost identical W–C1, W–C2, and C1–C2 bond distances (Figure 1) compared to the literature values of tungsten(II) acetylene complexes.^{23,24} The inserted C_2H_2 in **2** is strongly activated and therefore has more ethylene character with a C–C bond length of 1.349(3) Å compared to 1.310(3) Å in $\eta^2\text{-acetylene}$. Compared to the unsubstituted analogue $[\text{W}(\text{CO})(\text{C}_2\text{H}_2)(\text{PyS})_2]$ with W–N distances of 2.161 and 2.212 Å, **1** exhibits slightly longer bonds [2.197(3) and 2.259(4) Å].¹⁵ As was already observed in $[\text{MoO}_2(6\text{-MePyS})_2]$, the nitrogen atom in 6-MePyS is not able to bind to the metal center as tightly as it does in the unsubstituted version because of the methyl group in the ortho position.²⁵

Considering that the tungsten center in AH is in the oxidation state +IV, we oxidized **1** with pyridine *N*-oxide to obtain the tungsten(IV) complex $[\text{WO}(\text{C}_2\text{H}_2)(6\text{-MePyS})_2]$ (**3**) according to Scheme 2. After filtration to remove insoluble byproducts, **3** was crystallized in 84% yield. IR spectra show one strong band indicative of $\nu(\text{W}=\text{O})$ at 924 cm^{-1} .^{14,26–28} The ^1H NMR spectrum of **3** in CD_2Cl_2 shows two equally sharp singlets flanked with ^{183}W satellites for the C_2H_2 protons at 11.23 and 10.99 ppm. Thus, they are shifted upfield compared to **1**. The same trend is observed in the ^{13}C NMR spectrum, with resonances at 159.69 and 159.05 ppm being characteristic of a two- or three-electron-donor alkyne.²⁹ Single crystals suitable for X-ray diffraction analysis were grown from a CH_2Cl_2 /heptane solution. A molecular view of **3** is displayed in Figure 1. The C1–C2 bond [1.279(2) Å] is slightly shorter

Scheme 2. Synthesis of Complexes 1–3

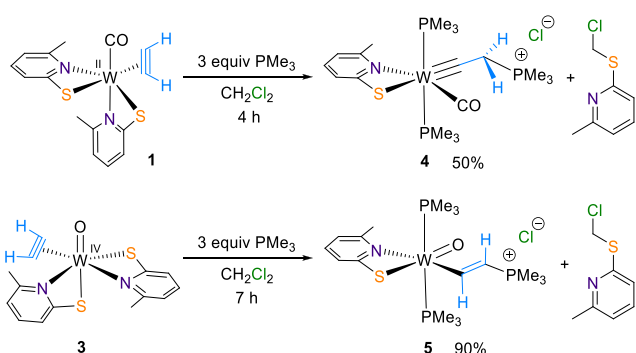


than that in **1** [1.306(7) Å], while the W–C bonds [W1–C1 of 2.022(5) Å for **1** vs 2.0693(15) Å for **3** and W1–C2 of 2.055(3) Å for **1** vs 2.1027(15) Å for **3**] are essentially longer.

With compounds **1** and **3** exhibiting related structures but different oxidation states of the metal center, a nucleophilic attack of PMe_3 on the coordinated C_2H_2 was investigated. Of particular interest to us was the potential formation of the intermediate Inter2 (Figure 1). Treatment of a CH_2Cl_2 solution of **1** with 3 equiv of PMe_3 led to an immediate color change from purple to orange-brown and full conversion of the starting material. An X-ray diffraction study on single crystals grown from a CH_2Cl_2 /heptane solution revealed the product to be an ion pair consisting of the tungsten carbyne complex $[\text{W}(\text{CO})(\text{CCH}_2\text{PMe}_3)(\text{PMe}_3)_2(6\text{-MePyS})]^+$ (**4**) and a chloride deriving from the solvent (Figure 2). Indeed, a nucleophilic attack of PMe_3 at the coordinated C_2H_2 under the formation of a P–C bond had occurred. However, the attack also leads to the cleavage of one 6-MePyS, which reacts with CH_2Cl_2 to form 2-((chloromethyl)thio)-6-methylpyridine (6-MePyS CH_2Cl) and Cl^- . The coordination surrounding of tungsten is completed by two PMe_3 ligands preserving the $18e^-$ character of the complex and explaining the need for 3 equiv of phosphine. After workup, pure **4** was obtained in 50% yield (Scheme 3).

The formation of **4** is also confirmed by ^1H NMR spectroscopy, where the CH_2 protons appear at 3.81 ppm as a doublet of triplets ($^2J_{\text{HP}} = 19.4$ Hz; $^4J_{\text{HP}} = 5.9$ Hz) and the methyl groups of the two tungsten-coordinated PMe_3 molecules at 1.44 ppm and those of the carbon-bound PMe_3 at 2.12 ppm. To confirm that the carbyne carbon atom as well as the adjacent methylene group indeed derive from the coordinated C_2H_2 , **1** was resynthesized using C_2D_2 to generate $[\text{W}(\text{CO})(\text{C}_2\text{D}_2)(6\text{-MePyS})_2]$ (**1D**). Upon reaction of **1D** with PMe_3 , the signal at 3.81 ppm is absent, confirming a reaction of

Scheme 3. Reaction of 1 and 3 with 3 equiv of PMe_3 in CH_2Cl_2 to Yield 4 and 5, Respectively



the coordinated C_2H_2 and no participation of CH_2Cl_2 .³⁰ While Cummins et al. reported the reaction of a molybdenum-bound (trimethylsilyl)acetylene with $\text{Li}[\text{BHET}_3]$ to a η^2 -vinyl complex and the subsequent formation of carbyne only after heating to 80°C for several hours, the η^2 -vinyl intermediate does not seem to be stable at all in our case.³¹ It is only observed in the ^1H NMR spectrum when a reaction of 1 is carried out with less than 3 equiv of PMe_3 directly in a J. Young NMR tube. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of 4 shows a triplet at 19.87 ppm for the carbon-bound PMe_3 and a doublet at -17.94 ppm being flanked with ^{183}W satellites ($^1J_{\text{WP}} = 277.8$ Hz) for the tungsten-bound PMe_3 . In the ^{13}C NMR spectrum, the methylene carbon resonates at 46.80 ppm (d, $^1J_{\text{CP}} = 49.5$ Hz). CO (q at 250.98 ppm) and $\text{W}\equiv\text{C}$ (dt at 249.22 ppm) carbon atoms give signals of a similar shift and coupling pattern and could only be distinguished by heteronuclear multiple-bond correlation (HMBC) between the carbyne carbon and methylene protons. The $\text{W}\equiv\text{C}$ resonance is similar to that of $[\text{W}(\text{CCH}_3)(\text{PMe}_3)_4\text{Cl}]$ (253.3 ppm)³² but shifted upfield compared to those of similar compounds like $[\text{W}(\text{CCH}_2\text{Ph})(\text{CO})_2(\text{dppe})\text{Cl}]$ (276.3 ppm),³³ $[\text{Tp}'(\text{CO})_2\text{WCCH}_2\text{W}(\text{CO})(\text{C}_2\text{Ph}_2)\text{Tp}]$ (312 ppm),³⁴ and $[\text{Mo}(\text{CCH}_2\text{B}(\text{C}_6\text{F}_5)_3)(\text{dppe})_2]$ (347.0 ppm).³⁵ The byproduct 6-MePySCH₂Cl was identified by ^1H NMR and mass spectroscopy. When the reaction was carried out in CD_2Cl_2 , the singlet for the methylene protons was absent. To a lesser extent, also bis((6-methylpyridin-2-yl)thio)methane $[(6\text{-MePyS})_2\text{CH}_2]$ was found, which was formed by the reaction of another 6-MePyS with the formerly generated 6-MePySCH₂Cl. The $\text{W}-\text{C}$ bond length of 1.793(4) Å in 4 confirms the triple-bond character, yet falls toward the shorter end of $\text{W}\equiv\text{C}$ distances in recently published carbyne complexes (ca. 1.76–1.86 Å).^{36–42} The $\text{W1}-\text{C1}-\text{C2}$ angle of $179.4(4)^\circ$ is almost perfectly linear, and the $\text{C1}-\text{C2}$ distance of 1.486(6) Å indicates a single bond.⁴³ The $\text{P1}-\text{C2}$ bond [1.795(4) Å] is slightly longer than the other three $\text{P1}-\text{C}$ bonds [1.761(5)–1.779(5) Å] but shorter than the remaining $\text{P}-\text{C}$ bonds [1.807(6)–1.827(4) Å]. The $\text{W}-\text{S}$ bond [2.6605(16) Å] is considerably longer than those in 1 [$\text{W1}-\text{S1}$ 2.5834(12) Å; $\text{W1}-\text{S2}$ 2.4073(12) Å], indicating a strong trans influence of the carbyne ligand.⁴⁴

Treatment of a CH_2Cl_2 solution of 3 with 3 equiv of PMe_3 led to an immediate color change from light yellow to dark green. After workup, the ethenyl complex $[\text{WO}(\text{CHCHPMe}_3)(\text{PMe}_3)_2(6\text{-MePyS})]\text{Cl}$ (5; Scheme 3) was isolated in 90% yield as a black-green crystalline powder. Its structure was unambiguously identified by single-crystal X-ray diffraction analysis (Figure 2). Again, a nucleophilic attack at the

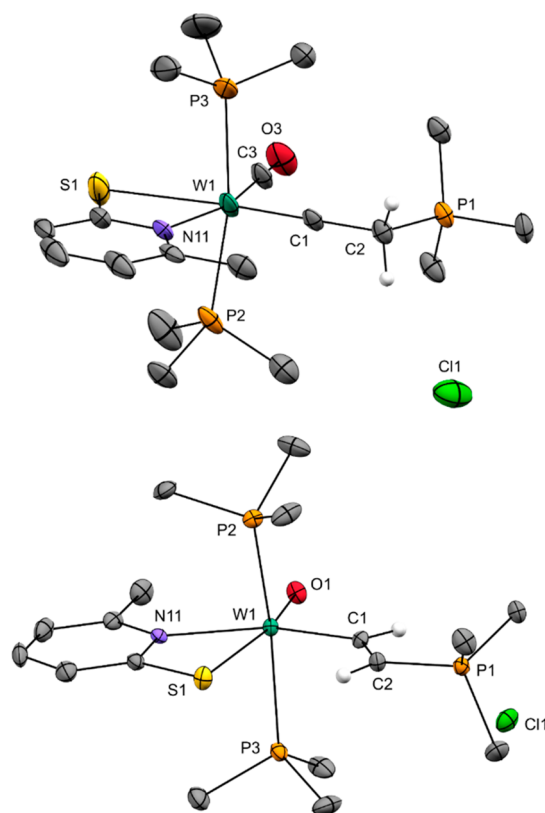


Figure 2. Molecular structures of 4 (top) and 5 (bottom) with probability ellipsoids drawn at the 30% (4) and 50% (5) probability levels, respectively.

coordinated C_2H_2 had occurred, forming a $\text{P}-\text{C}$ bond. In contrast to 4, however, 5 remains with a coordinated ethenyl ligand exhibiting a $\text{W}-\text{C}$ single bond. Similar reactions were already performed with chromium(0)-bound C_2H_2 ; however, treatment with PMe_3 predominantly led to an exchange with the coordinated C_2H_2 .⁴⁵ The ethenyl protons of 5 are clearly identified by ^1H NMR spectroscopy with resonances at 11.42 and 4.26 ppm and coupling to each other with $^3J = 17.5$ Hz. Upon reaction of $[\text{WO}(\text{C}_2\text{D}_2)(6\text{-MePyS})_2]$ (3D) with PMe_3 in CD_2Cl_2 , the ethenyl proton resonances are absent. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of 5 shows two rather broad singlets at 4.73 and -22.14 ppm, with the latter being flanked with ^{183}W satellites. The ethenyl carbon bound to the tungsten center resonates at 222.99 ppm and thus exhibits a significant downfield shift compared to the literature. The other gives a doublet at 96.83 ppm and is thus considerably shifted upfield compared to similar compounds.^{46,47} The $\text{W}-\text{C}$ distance of 2.068(3) Å is shorter than that in rare examples of tungsten ethenyl complexes like $[\text{WO}_2(\text{CHCH}_2)(\text{Tp}')]$ (2.136 Å)⁴⁶ and $[\text{W}(\text{Cp})(\text{CHCHC}(\text{CH}_3)_3)(\eta^2\text{-C}(\text{O})\text{NR}^1\text{R}^2)(\text{NO})]$ (2.161 Å),⁴⁷ while the $\text{C1}-\text{C2}$ distance of 1.363(4) Å is slightly longer compared to the aforementioned compounds (1.305 and 1.332 Å). The $\text{W1}-\text{C1}-\text{C2}$ [$135.8(2)^\circ$] and $\text{C1}-\text{C2}-\text{P1}$ [$123.4(2)^\circ$] angle confirm a slight deviation from sp^2 hybridization on the carbon atoms. In contrast to 4, the $\text{P1}-\text{C2}$ bond [1.745(3) Å] is slightly shorter than the other three $\text{P1}-\text{C}$ bonds [1.774(3)–1.796(3) Å].

In conclusion, we report the synthesis of tungsten acetylene complexes where intramolecular insertion of C_2H_2 into the $\text{W}-\text{N}$ bond is prevented by steric adjustment at the ancillary ligand. This allowed the investigation of an intermolecular

nucleophilic attack at the solely coordinated C_2H_2 using PMe_3 . Starting from the tungsten(II) complex **1**, a tungsten ethynyl complex is formed; hence, the four-electron-donor C_2H_2 converts to the four-electron-donor carbyne when assuming retention of the metal oxidation state. When the carbyne is considered to be a six-electron donor, oxidation to tungsten(IV) is formally taking place. Regarding the oxido ligand as a six-electron donor, the two-electron-donor C_2H_2 in the tungsten(IV) complex **3** converts to a two-electron-donor ethenyl moiety. In both cases, the reactions proceed under preservation of the $18e^-$ character of the complexes. One 6-MePyS ligand is cleaved under reaction with CH_2Cl_2 to form 6-MePySCH₂Cl and the counterion Cl^- for the cationic tungsten complexes; thus, the presence of CH_2Cl_2 is crucial. We assume that cleavage of the sulfur ligand relieves the charge at tungsten accumulated as a result of the nucleophilic attack. The attack of PMe_3 on the tungsten(IV)-bound C_2H_2 to form an ethenyl ligand resembles the step in which the Inter2 intermediate of the proposed mechanism of AH is formed.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.inorgchem.1c00643>.

Experimental details, syntheses, crystallographic data, and NMR spectra of all compounds (PDF)

Accession Codes

CCDC 2050311–2050316 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Author Contributions

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Notes

The authors declare no competing financial interest.

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