The Effect of Pyridine-2-thiolate Ligands on the Reactivity of
Tungsten Complexes toward Oxidation and Acetylene Insertion

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ABSTRACT: Intending to deepen our understanding of tungsten acetylene (C₂H₂) chemistry, with regard to the tungstoenzyme acetylene hydratase, here we explore the structure and reactivity of a series of tungsten acetylene complexes, stabilized with pyridine-2-thiolate ligands featuring tungsten in both +II and +IV oxidation states. By varying the substitution of the pyridine-2-thiolate moiety with respect to steric and electronic properties, we examined the details and limits of the previously reported intramolecular nucleophilic attack on acetylene followed by the formation of acetylene inserted complexes. Here, we demonstrate that only the combination of high steric demand and electron-withdrawing features prevents acetylene insertion. Nevertheless, although variable synthetic approaches are necessary for their synthesis, tungsten acetylene complexes can be stabilized predictably with a variety of pyridine-2-thiolate ligands.

INTRODUCTION

Tungsten is the metal of choice for several challenging enzymatic reactions. ¹ Besides being in the active site of the metalloenzymes that catalyze redox reactions, it is also essential for the function of acetylene hydratase (AH). This is a unique example of a tungstoenzyme catalyzing the nonredox hydration of acetylene to acetaldehyde.¹−³ This reaction is the first metabolic step of the mesophilic bacterium Pelobacter acetylenicus, which consumes acetylene as its only carbon and energy source.² The only other known enzyme that accepts acetylene as a substrate is nitrogenase, which reduces acetylene to ethylene.⁶ The mechanism of the catalysis of AH remains elusive, as there are no reported crystal structures of the enzyme containing substrate or any inhibitor. Since one of the mechanistic ideas of AH suggests coordination of acetylene to the tungsten(IV) center,⁷−¹² we aim to synthesize and understand tungsten acetylene adducts with ligands similar to those in tungstoenzymes.¹³,¹⁴

The first tungsten(II) acetylene species bearing dithiocarbamate ligands was reported in 1978,¹⁵ thereafter, only a few other W–C₂H₂ adducts have been synthesized.¹⁶−²⁶ For example, Templeton et al. reported a tungsten(IV) oxo acetylene complex containing an N-donor boron-based scorpionate ligand.²⁰ In our group, the use of bioinspired S,N-bidentate ligands, such as SPhoz (2-(4′,4′-dimethylxazo-line-2′-yl)thiophenolate),²¹ PyS (pyridine-2-thiolate),²² and 6-MePyS (6-methylpyridine-2-thiolate),²⁶ allows the preparation of W(II) and W(IV) complexes and ensures a sulfur-rich environment, more closely resembling the one in the native enzyme. Additionally, complexes bearing those S,N-bidentate ligands allowed for important insight into the nature of the W–C₂H₂ chemistry. For instance, [WO(C₂H₂)(SPhoz)₂] is capable of reversible binding of C₂H₂ with the release of acetylene being triggered by irradiation.²¹ In addition, coordination and subsequent insertion of a second molecule of C₂H₂ into the tungsten–nitrogen bond take place in [W(CO)(C₂H₂)(PyS)₂] showing that the alkyne is activated toward the reaction with nucleophiles. The acetylene insertion was studied using C₂D₂ and revealed coordination of the second acetylene before insertion.²⁴ This represents the first example of a nucleophilic attack on a W-coordinated C₂H₂. Similar behavior has previously been observed for tungsten complexes but only with substituted alkynes.²⁷−³⁴ To sterically prevent the insertion from taking place, and to favor the attack from an external nucleophile, we introduced a methyl group in position 6 of the PyS ligand. The resulting complex [W(CO)(C₂H₂)(6-MePyS)₂] also reacts with the second molecule of acetylene, but insertion occurs only partially. Moreover, nucleophilic attack of PMe₃ on coordinated

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acetylene was observed for W(II) and W(IV) complexes bearing 6-MePyS ligands leading to carbyne and vinyl complexes, respectively.26

Herein, we explore the influence of different pyridine-2-thiolate ligands, namely, 4-methylpyridine-2-thiolate (4-MePyS), 3-chloropyridine-2-thiolate (3-ClPyS), and 5-nitro-6-methylpyridine-2-thiolate (5-NO2-6-MePyS) (Figure 1), on the oxidation and acetylene insertion reactivity.

RESULTS AND DISCUSSION

Choice of Ligands. Ligand design is based on PyS and 6-MePyS which previously allowed the preparation of tungsten acetylene complexes of the types [W(CO)(C2H2)(SN)2] and [WO(C2H2)(SN)2], (SN= bidentate pyridine-2-thiolate moiety).24,26 To investigate the insertion reaction, various substituents at the pyridine heterocycle were introduced as displayed in Figure 1. Since the electronic effects of substituents in positions 2, 4, or 6 in pyridine are known to be similar,35 we chose 4-MePyS for comparison with 6-MePyS to elucidate whether the insertion is prevented for electronic or steric reasons.36,37 The introduction of a nitro group in position 5 in 6-MePyS increases the electron-withdrawing properties, rendering the nitrogen donor less nucleophilic. A similar approach was used by introducing a chloro substituent at the PyS moiety. With both ligands, a reduced reactivity toward insertion is expected. The initial attempts to introduce the Cl to position 6 of the PyS moiety were not successful, so 3-ClPyS was prepared instead. Moreover, coordination of the known ligands 6-tert-butylpyridine-2-thiolate (6-‘BuPyS)38 and 6-trifluoromethylpyridine-2-thiolate (6-CF3PyS) to the tungsten(II) precursor [WBr3(CO)3(MeCN)2] was attempted, but it turned out to be unsuccessful due to steric hindrance of the large groups in position 6.

Introduction of the Ligand. Following the synthetic procedure for complexes employing the ligands PyS and 6-MePyS,24,26 the reaction of the tungsten precursor [WBr3(CO)3(MeCN)2] with 2.1−2.2 equiv of each ligand gives the tricarbonyl complex of the general formula [W(CO)3(SN)2] (Scheme 1). After filtration, complexes [W(CO)3(4-MePyS)2] (1a) and [W(CO)3(3-ClPyS)2] (1b) were isolated, crystallized, and characterized (see Supporting Information (SI)). In contrast, isolation and characterization of the tricarbonyl complex bearing two 5-NO2-6-MePyS ligands were not possible due to decomposition under the experimental conditions. 1H NMR spectra of 1a and 1b show the presence of only one ligand set due to fluxionality of the tricarbonyl moiety at room temperature, which is in accordance with the literature.39 Also, IR values related to CO stretching (2011, 1881 cm⁻¹ for 1a; 2014, 1932, 1906 cm⁻¹ for 1b) are in the same range as those known for W(II) tricarbonyl complexes.40

Figure 1. Pyridine-2-thiolates employed for the preparation of W complexes: (a) previously explored in W acetylene chemistry;24,26 (b) no coordination to W observed.
However, on the way to tungsten o xo acetylene complexes, the isolation and purification of tricarbonyl compounds turned out to be an unnecessary step. Indeed, in most of the cases, we chose an in situ approach in which the initial reaction of \([\text{WBr}_2(\text{CO})_3(\text{MeCN})_2]\) with the ligand salt is immediately followed by the treatment with acetylene.

**Reaction with Acetylene.** The reaction solutions of tricarbonyl complexes were purged with acetylene and subsequently stirred, after which the products were isolated as described in the SI. Exposing a toluene solution of \(1\) to an acetylene atmosphere (1 atm) leads to the formation of \([\text{W}(\text{CO})(\text{C}_2\text{H}_2)(4\text{-MePyS})](\text{CHCH-4-MePyS}))\) (3a) where one molecule of acetylene has inserted into the \(W-N\) bond and a second \(C_2H_2\) is coordinated. This is similar to what has recently been found for \([\text{W}(\text{CO})_2(\text{PyS})_2]\), 38 while only partial insertion occurred when position 6 was blocked by a methyl group as with 6-MePyS.26 The electronic effects of substituents in positions 2, 4, or 6 in pyridine are known to be similar35 (5.2),37 complexes bearing their respective thiolate ligand form additional methyl group is a stronger base than the parent Py pyridine heterocycles indicate that 4-MePy (6.0) with an nitro-group. The prevention of insertion is relevant for the synergistic effect of the steric demand of the methyl group in the 6-position and the electron-withdrawing properties of the nitro-group. The prevention of insertion is relevant for the oxidation to the biological oxidation state +IV, as all our attempts to oxidize inserted products were futile.

For the synthesis of \([\text{W}(\text{CO})(\text{C}_2\text{H}_2)(4\text{-MePyS})_2]\) (2a), we had to apply another synthetic procedure because of the aforementioned favored insertion in 4-MePyS. Similar to the preparation of \([\text{W}(\text{CO})(\text{C}_2\text{H}_2)(\text{PyS})_2]\),24 a metal precursor composed of a mixture of \([\text{WBr}_2(\text{CO})(\text{C}_2\text{H}_2)(\text{MeCN})_2]\) and \([\text{WBr}_2(\text{CO})(\text{C}_2\text{H}_2)(\text{MeCN})_2]\) was reacted with \(\text{Na}(4\text{-MePyS})\) in dichloromethane for 2 h. Complex 2a was obtained after purification using silica gel and recrystallization from dichloromethane/heptane as dark green crystals in a 19% yield.

**Oxidation to Tungsten(IV) Complexes.** Compounds 2a–d can be oxidized to complexes of the type \([\text{WO}(\text{C}_2\text{H}_2)-(\text{SN})_2]\) (4a–d) by a slight excess of pyridine-N-oxide (PyNO) as an oxygen source in dichloromethane (Scheme 1). The required reaction time for full conversion is highly dependent on the pyridine-2-thiolate ligand and ranges from 10 min in the case of the nitro-substituted 2c to several hours starting from 2a, 2b, and 2d. All o xo acetylene complexes can be isolated in high yields (4a 68%, 4b 87%, 4c 75%, and 4d 91%) as yellow powders. Furthermore, complex 4b can also be obtained directly from the reaction of PyNO with 3b due to the observed reversibility of the insertion in the latter. Compound 2c bearing 5-NO\(_2\)-6-MePyS is, in comparison to the other W(II) systems, oxidized significantly faster. This can be explained by a decrease in \(\pi\)-back-donation of tungsten to CO weakening the tungsten carbonyl bond, thereby facilitating the release of CO and oxidation of the metal center. This is supported by IR and X-ray data upon comparison of complex 2c (\(\nu (\text{CO})\) 1919 cm\(^{-1}\), \(\nu (\text{CO})\) 1969 Å) with its analogue lacking the nitro group \([\text{W}(\text{CO})(\text{C}_2\text{H}_2)(6\text{-MePyS})_2]\) (\(\nu (\text{CO})\) 1891 cm\(^{-1}\), \(\nu (\text{CO})\) 1958 Å).26

**Spectroscopic Data.** Coordination of acetylene was confirmed by \(^1\)H and \(^13\)C NMR spectroscopy. In the case of type 2 complexes, acetylenic protons resonate as two singlets in the region 12–14 ppm due to the asymmetry of coordination (Table 1). Complexes 2a and 2b are found as a mixture of two isomers in solution, while complex 2c appears in isomerically pure form. For type 3 complexes, \(^1\)H NMR spectra show the presence of side-on coordinated (\(\eta^1\text{-C}_2\text{H}_2\)) and an inserted acetylene (\(\eta^2\text{-C}_2\text{H}_2\)). Side-on coordinated acetylene resonates in the same region as those in type 2, while the \(\eta^2\text{-C}_2\text{H}_2\) resonates in the form of two doublets in the aromatic region. Both inserted complexes 3a and 3b are isomerically pure. Due to \(\text{C}_2\text{H}_2\) release from 3b and its low solubility, it was not possible to record a meaningful \(^13\)C NMR spectrum.

**Table 1. Spectroscopic Data for Tungsten Acetylene Complexes**

| compound | \(^1\)H NMR of \(\eta^2\) C\(_2\)H\(_2\) \(\text{ppm}\) | \(^13\)C NMR of \(\eta^2\) C\(_2\)H\(_2\) \(\text{ppm}\) | IR (CO) \(\text{cm}^{-1}\) | IR (W=O) \(\text{cm}^{-1}\) |
|----------|------------------|------------------|-----------------|-----------------|
| 2a       | 13.62, 12.31     | 207.2, 206.4     | 1907            |                 |
| 2b       | 12.80, 12.49     | 209.4, 207.9     | 1896            |                 |
| 2c       | 14.10, 12.83     | 209.8, 207.4     | 1919            |                 |
| 3a       | 12.91, 11.99     | 198.4, 193.1     | 1907            |                 |
| 3b       | 12.96, 12.01     | Not available    | 1903            |                 |
| 3c       | 10.95, 10.94     | 158.1, 154.7     | 945             |                 |
| 3d       | 11.08, 11.00     | 157.1, 154.8     | 936             |                 |
| 3c       | 11.44, 11.15     | 160.2, 158.2     | 937             |                 |
| 4d       | 10.99            | 158.0, 155.0     | 937             |                 |

\(^4\)In \(\text{CD}_2\text{Cl}_2\) data of major isomer.
In the case of tungsten(IV) oxo species (type 4), acetylenic proton resonances are upfield-shifted compared to their W(II) analogues and flanked by $^{183}$W satellites. For complexes 4a–c, the acetylenic protons appear in the form of two singlets. Differently, complex 4d shows only one singlet for both C$_2$H$_2$ protons, presumably due to the dynamic behavior of coordinated acetylene. All type 4 complexes, except 4c, show an additional set of signals related to the presence of a second isomer in solution. As expected, signals are downfield-shifted when 5-NO$_2$-6-MePyS is bound to the tungsten center. Even though most of the complexes exhibit two isomers in solution, only one could be crystallized (vide infra). Upon dissolving single crystals, the same ratio of the two isomers is observed pointing toward an equilibrium in solution.

The reactivity and synthetic approaches for obtaining complexes 2, 3, and 4 vary significantly depending on the ligand, which is however hardly reflected when comparing NMR and IR data of the respective complexes. Thus, the acetylenic proton shifts in the tungsten(II) acetylene complexes 2a–c are very similar. This can possibly be ascribed to the long distance from the ligand substituents to the acetylenic protons. It suggests that the reactivity differences are primarily influenced by steric effects.

**Molecular Structures.** The crystal structures of complexes 1a–b, 2a–c, 3a–b, and 4a–d were determined by single-crystal X-ray diffraction analysis. Molecular views of types 2, 3, and 4 are given in Figures 2–4. Selected bond lengths of complexes 1–4 are presented in Table 2. Full crystallographic details such as structure refinement data as well as
In complex atoms of the pyridine-2-thiolate ligand. Moreover, the CO compounds. The carbonyl ligand in while bonded to.

The planes of the nitro groups enclose angles which is always located cis to the carbonyl or oxo groups. A significant loss of triple bond character and linearity is observed in all η²-bound acetylene molecules, which shows that the actual bonding situation is between the η²-adduct and metallacyclop propane resonance structures.

Monoacetylene carbonyl complexes (2a−c) show similar structural properties in terms of bond lengths and angles. Compounds 2a and 2b crystallized in S,S-trans configuration, while 2c crystallized as a S,S-cis isomer, as reported for similar compounds. The carbonyl ligand in 2a−c is trans to the N atoms of the pyridine-2-thiolate ligand. Moreover, the CO shows the common parallel arrangement with coordinated C$_2$H$_2$. In complex 2a, the carbonyl ligand and the acetylene ligand are disordered over two orientations. The complex lies on a twofold rotation axis parallel to the η²-C$_2$H$_2$ bond, being the only one not prone to acetylene release. On the contrary, for all the other complexes with longer C−C bonds (Table 2), at least a partial release of inserted acetylene was observed.

### Table 2. Selected Bond Lengths for Tungsten Acetylene Complexes

| Complex | C≡C | W−C$_2$H$_2$ | WCH═CH | W−CHCHN | C≡O$^a$ | W−CO | W═O | ref |
|---------|-----|--------------|---------|--------|--------|-------|------|-----|
| 2a      | 1.302(12) | 2.090(13) | 2.078(7) |        | 1.142(16) | 1.884(16) |       |     |
| 2b      | 1.286(6) | 2.020(4) | 2.048(5) |        | 1.148(5) | 1.962(4) |       |     |
| 2c      | 1.313(3) | 2.023(2) | 2.044(2) |        | 1.151(3) | 1.969(2) |       |     |
| [W(CO)](C$_2$H$_2$)(PyS)$_2]_2$ | 1.316(3) | 2.022(2) | 2.045(2) |        | 1.159(3) | 1.973(2) |       |     |
| [W(CO)](C$_2$H$_2$)(6-MePyS)$_2]_2$ | 1.306(7) | 2.022(5) | 2.055(3) |        | 1.167(6) | 1.958(5) |       |     |
| 3a      | 1.308(3) | 2.031(2) | 2.0505(19) |        | 1.331(3) | 2.104(2) | 1.157(3) | 1.987(2) |     |
| 3b      | 1.314(10) | 2.048(5) | 2.071(3) |        | 1.311(8) | 2.101(6) | 1.181(9) | 1.963(8) |     |
| [W(CO)](C$_2$H$_2$)(CHCH-PyS)(PyS)] | 1.3148(19) | 2.033(13) | 2.0582(13) | 1.3421(18) | 2.0964(13) | 1.161(15) | 1.9781(12) | 24  |
| [W(CO)](C$_2$H$_2$)(CHCH-6-MePyS)(6-MePyS)] | 1.310(3) | 2.047(2) | 2.065(2) |        | 1.349(3) | 2.103(2) | 1.168(3) | 1.974(2) | 26  |
| [W(CO)](C$_2$H$_2$)(CHCH-PnS)(PnS)] | 1.315(7) | 2.036(4) | 2.060(4) |        | 1.358(6) | 2.079(4) | 1.156(6) | 1.993(5) | 24  |
| 4a      | 1.280(3) | 2.095(2) | 2.093(2) |        | 1.280(3) | 2.095(2) | 1.7204(17) |       |     |
| 4b      | 1.274(5) | 2.083(3) | 2.094(4) |        | 1.274(5) | 2.083(3) | 1.701(3) |       |     |
| 4c      | 1.258(5) | 2.068(3) | 2.084(3) |        | 1.258(5) | 2.068(3) | 1.710(2) |       |     |
| 4d      | 1.260(4) | 2.073(2) | 2.087(3) |        | 1.260(4) | 2.073(2) | 1.712(2) |       |     |
| [WO(C$_2$H$_2$)(6-MePyS)$_2]_2$ | 1.279(2) | 2.0693(15) | 2.0672(7) |        | 1.279(2) | 2.0693(15) | 1.7153(13) | 26  |

$^a$Bond lengths are given in Å. Bond lengths of the unbound gases: C$_2$H$_2$, C≡C: 1.186(4) Å; $^4$C≡O, 1.12822(7) Å.}

experimental details are provided within the SI. All compounds feature distorted octahedral environments around the W atom. The center of the η²-C≡C bond occupies the sixth position, which is always located cis to the carbonyl or oxo groups. The carbonyl ligand in 4a−c is trans to the N atoms of the pyridine-2-thiolate ligand. Moreover, the CO shows the common parallel arrangement with coordinated C$_2$H$_2$. In complex 2a, the carbonyl ligand and the acetylene ligand are disordered over two orientations. The complex lies on a twofold rotation axis parallel to the η²-C$_2$H$_2$ bond, being the only one not prone to acetylene release. On the contrary, for all the other complexes with shorter C−C bonds (Table 2), at least a partial release of inserted acetylene was observed.

Complexes 4a, 4b, and 4d crystallized as S,S-trans isomers. The W−N distances trans to the oxo ligand are significantly longer (4a: W−N11 2.3464(18) Å, 4b: 2.306(4) Å, 4d: 2.314(2) Å) than W−N distances trans to the η²-acetylene ligand (4a: W−N11 2.219(2) Å, 4b: 2.242(4) Å, 4d: 2.221(2) Å). Moreover, the η²-C$_2$H$_2$ shows the typical orthogonal arrangement with the oxo ligand.

Similar to [WO(C$_2$H$_2$)(6-MePyS)$_2]_2$, complex 4c crystallizes as an S,S-cis isomer. The thiolate group opposite the oxo ligand has a distinctly larger W−N distance (W−N11 2.279(3) Å) than the other one (W−N1 2.245(3) Å). The W−N distance of the ligand opposite the η²-acetylene (W−N11 2.279(3) Å) is also distinctly longer than the other one (W−N1 2.225(2) Å). The η²-acetylene ligand (C1−C2 1.258(5) Å, W1−C2 1.978(3) Å) is almost normal to the W=O bond (C1−C2−W1−O1 88.2(2)°). C2−C1−W1−N1 177.9(2)° and eclipsed to W1−N21 (C1−C2−W1−N21 177.9(2)°, C2−C1−W1−N21 2.3(2)°).
Steric hindrance in position 6 leads exclusively to the formation of the S,S-cis isomer. The configuration in which both sulfur atoms are trans to each other is more likely to occur within complexes without steric interference in position 6, except for \([\text{W} (\text{CO}) (\text{C}_2\text{H}_2) (\text{PyS})_2]\) which crystallized as S,S-cis isomer. This trend is also reflected in the tricarbonyl complexes as presented in Table 3 (for crystallographic details, see SI Figures S1–2, Tables S1,S6–7). Moreover, all inserted complexes exhibit exclusively the S,S-cis configuration.

The geometry of type 2 complexes is likely influencing the reactivity toward acetylene, especially since the second molecule of \(\text{C}_2\text{H}_2\) seems to coordinate to the W(II) center prior to insertion.24 The latter occurs more easily when the metal center is not shielded by methyl groups in position 6. Moreover, carbonyl acetylene complexes bearing 6-MePyS2c and 5-NO\(_2\)-6-MePyS (2e) ligands exist as a single isomer in solution (S,S-cis), and this orientation may be too rigid to undergo the coplanar rearrangement necessary for the migratory insertion. In contrast, other pyridine-2-thiolate based complexes with no substituent at position 6 show the migratory insertion. In contrast, other pyridine-2-thiolate complexes as presented in Table 3 (for crystallographic details, see SI Figures S1–2, Tables S1,S6–7). Moreover, all inserted complexes exhibit exclusively the S,S-cis configuration.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.1c00472.

Full X-ray data, NMR spectra, and experimental procedures (PDF)

**Accession Codes**

CCDC 2103131—2103141 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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**Notes**

The authors declare no competing financial interest.

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