

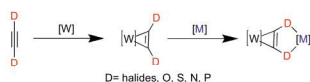


Iron-catalyzed, aerobic oxidation of a [W^{II}]-carbonyl- to a [W^{IV}]-oxo-complex in the presence of an α -P-substituted alkyne ligand

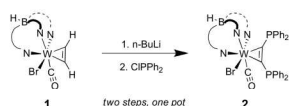
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Introduction

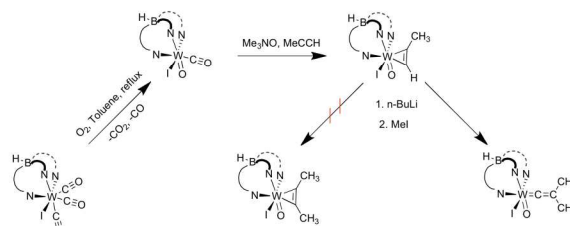
Compounds containing α -donor-substituted alkynes have been one of the main research topics of the Seidel group for some time.^[1] Their ability to coordinate one metal via the triple bond of the alkyne and another one via its donor functions render them a useful tool to generate polynuclear complexes with short metal-to-metal distances and accompanying interesting redox behaviour.



Whereas a large variety of such complexes are obtainable directly from the reaction of free or protected alkynes with a suitable precursor-complex, phosphine-substituted acetylenes like bis(diphenylphosphino)acetylene (dppa) can not be introduced in that way. Since coordination via the P-functions is much favored when compared to that via the triple bond, they need to be introduced after the alkyne is already attached to the metal. Deprotonation of an ethine-ligand, followed by addition of ClPPH₂ as an electrophile yields dppa-complex **2** in good yields on a multigram-scale^[2].



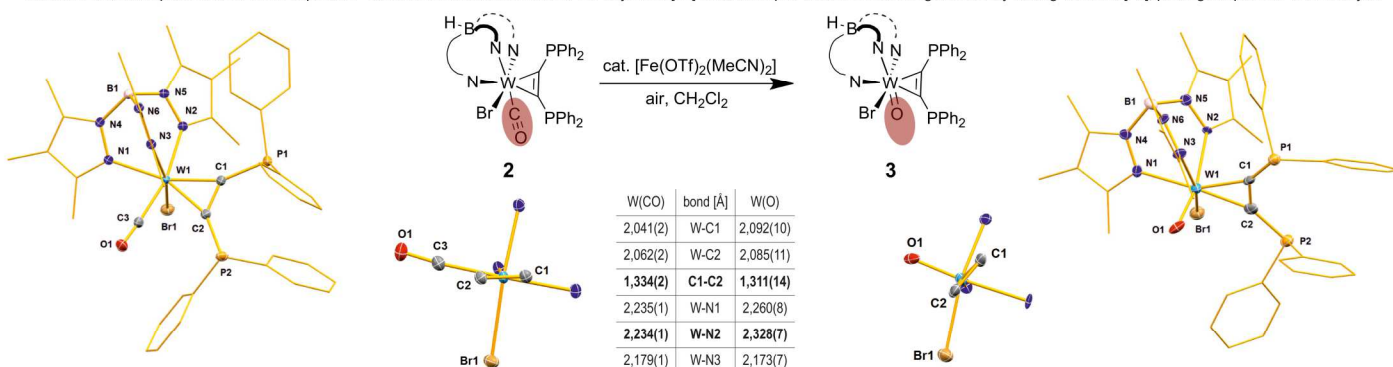
Alkyne complexes of tungsten bearing an oxo-ligand in their coordination sphere have been known for quite a while and their preparation and properties have been well examined.^[3,4] The established synthetic pathway to such moieties features an oxidation by aerobic oxygen at high temperatures, displacing and oxidizing carbonyl ligands to carbon dioxide in the process.^[4]



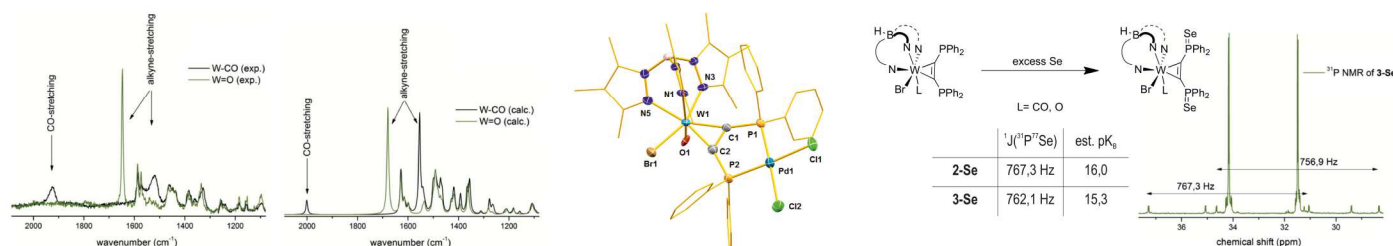
In these oxo-bearing compounds, electrophilic substitution of terminal alkyne-protons leads to rearrangement of the alkyne- to a vinylidene-ligand and not the substituted alkyne as in the case of the CO-analogues.^[4] Thus, tungsten-dppa complex **3** can not be obtained by known means. However, the compound would be of great interest with regards to its capabilities to act as a proton reservoir and its redox behaviour in the context of catalysis.

Results and Discussion

While trying to generate a dppa-bridged W-Fe-dinuclear complex from **2**, no reaction was observed after several days. However, after allowing some air to enter the reaction vessel, a slow decline of intensity was observed for the characteristic CO-band in the infrared spectrum. After workup, in addition to recovered starting material, a golden fraction was isolated that proved to be oxo-complex **3**. Surprisingly, a metal-centered oxidation had taken place instead of the expected P-oxidation that dominates after a few days if no [Fe] is added. Up to 60% of **3** could be generated by adding 15mol-% [Fe], proving the process to be catalytic.



XRD data was obtained of both the starting material and the resulting product. The most striking difference between the two lies in a pronounced structural trans-effect on the W-N2-bond due to the highly π -basic character of the oxo-ligand that allows strong donation to the metal. Another trend can be observed with regards to the coordinated alkyne, where a slightly elongated distance between the C-atoms and the tungsten is accompanied by a somewhat shortened triple bond. This indicates a weaker interaction between alkyne and metal, as does a shift in alignment of the alkyne with the other ligands. In **2**, the triple bond is in one plane with the W-CO-bond, donating into the d-orbital depleted by the π -backbonding to the CO, whereas it tends towards the Br-ligand in **3**. These structural differences correlate well with the Raman-data (see below).



Comparing the Raman spectra of **2** and **3**, a significantly increased required energy for the excitation of the alkyne-CC-stretching mode is observed. DFT-calculations (B3LYP) confirm the assignment of bands and show the same shift of 126 cm⁻¹ as the experimental spectrum. This correlates well with the shortened CC-bond and increased basicity of the P-atoms (see right).

Both **2** and **3** readily react with [(COD)PdCl₂] to give the dinuclear complexes. Their behaviour in Pd-catalyzed cross-coupling reactions will be studied in the near future. In that context, we hope to find the oxo-compound **3-PdCl₂** to be more robust than **2-PdCl₂** under harsh conditions and acting as a proton reservoir where required.

The basicity of a phosphine shows a linear correlation with and can be estimated from the ³¹P-⁷⁷Se-coupling constants of the corresponding P-selenides.^[5] In the case of **2** and **3**, the effect of the 2-electron-oxidation of the tungsten-backbone is overcome by the changed bonding situation between alkyne and metal. This leads to an increase in basicity of one order of magnitude in the W^{IV}-species.

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