



The Doubly-Bonded Ditungsten Anion $[W_2Cp_2(\mu-PPh_2)(NO)_2]^-$: An Entry to the Chemistry of Unsaturated Nitrosyl Complexes

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The Doubly-Bonded Ditungsten Anion $[\text{W}_2\text{Cp}_2(\mu\text{-PPh}_2)(\text{NO})_2]^-$: An Entry to the Chemistry of Unsaturated Nitrosyl ComplexesM. Angeles Alvarez,^a M. Esther García,^a Daniel García-Vivó,^a Miguel A. Ruiz,^{*a} and Adrián Toyos^a

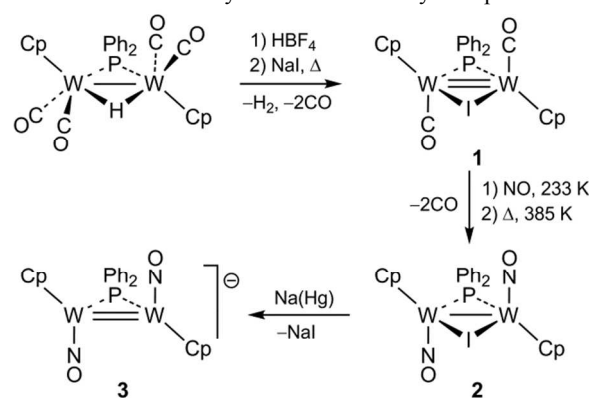
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Complex $[\text{W}_2\text{Cp}_2(\mu\text{-I})(\mu\text{-PPh}_2)(\text{NO})_2]$ was prepared by reacting $[\text{W}_2\text{Cp}_2(\mu\text{-I})(\mu\text{-PPh}_2)(\text{CO})_2]$ with NO at 233 K followed by decarbonylation in refluxing toluene. It was reduced by Na(Hg) in acetonitrile to give $\text{Na}[\text{W}_2\text{Cp}_2(\mu\text{-PPh}_2)(\text{NO})_2]$, the first anionic nitrosyl complex featuring a metal–metal multiple bond (computed W–W = 2.580 Å). Reactions of the latter anion with $(\text{NH}_4)\text{PF}_6$ and $[\text{AuCl}\{\text{P}(p\text{-tol})_3\}]$ gave the hydride $[\text{W}_2\text{Cp}_2(\mu\text{-H})(\mu\text{-PPh}_2)(\text{NO})_2]$ and cluster $[\text{AuW}_2\text{Cp}_2(\mu\text{-PPh}_2)(\text{NO})_2\{\text{P}(p\text{-tol})_3\}]$ respectively, also featuring multiple W–W bonding (experimental W–W ca. 2.75 Å), and its reaction with S_8 yielded the electron-precise derivative $\text{Na}[\text{W}_2\text{Cp}_2(\mu\text{-PPh}_2)(\mu\text{-S})(\text{NO})_2]$, which was methylated by Me_2SO_4 to give the thiolate complex $[\text{W}_2\text{Cp}_2(\mu\text{-PPh}_2)(\mu\text{-SMe})(\text{NO})_2]$.

The chemistry of metal nitrosyl complexes is a mature field of research where different approaches to the study of metal–NO interactions converge. The latter are of academic interest because of the outstanding versatility of the NO ligand, which enables the formation of many different coordination and organometallic complexes,¹ but also because nitric oxide has relevant activity in living organisms associated to its interaction with metal centers.^{1,2} Further interest in these complexes stems from the fact that nitric oxide is a major atmospheric pollutant requiring catalytic abatement, a process also based on the interaction of NO with metal atoms.^{1,3,4} Most of the work in this field, however, has been carried out so far on mononuclear complexes, while the chemistry of binuclear and polynuclear nitrosyl complexes remains comparatively much less explored. This is particularly so in the case of binuclear nitrosyls having metal–metal multiple bonds, of which only a few examples have been reported so far, these including as most relevant groups the doubly-bonded complexes $[\text{M}_2\text{L}_2(\mu\text{-NO})_2]$ (Fe, Ru, Os; L = Cp or related ligand),⁵ and $[\text{W}_2\text{L}_2(\mu\text{-H})_2\text{H}_2]$,⁶ along with a few other isolated examples.⁷ As for complexes displaying triple intermetallic bonds we can only quote the diphosphine-bridged $[\text{Re}_2\text{Cl}_5(\mu\text{-dppm})(\text{NO})]$,⁸ and the carbyne-bridged cation $[\text{Mo}_2\text{Cp}_2(\mu\text{-CPh})(\mu\text{-PCy}_2)(\mu\text{-NO})]^+$.⁹ Moreover the chemistry of all these binuclear substrates has been little explored either because of ready degradation of many of them to mononuclear species, or due to synthetic difficulties. Yet the idea of studying the chemistry of nitrosyl ligands at unsaturated dimetal centres remains an attractive one since the inherent reactivity associated with metal–metal multiple bonds may facilitate or induce unusual transformations in the coordinated ligands, as shown previously by us and others using highly unsaturated binuclear carbonyl complexes stabilized by bridging ligands, particularly P-donor ligands.¹⁰ Thus we decided to use related strategies to approach

the synthesis of unsaturated binuclear nitrosyls stabilized towards degradation to mononuclear species, so as to allow for a complete study of the chemistry and potential uses of these electron-deficient species. Here we report the successful preparation of the Na^+ salt of the anion $[\text{W}_2\text{Cp}_2(\mu\text{-PPh}_2)(\text{NO})_2]^-$, the first anionic nitrosyl complex featuring a metal–metal double bond, and an initial exploration of its reactivity. Previous examples of unsaturated anionic nitrosyls are restricted to the 33e diiron complexes $[\text{Fe}_2\text{L}_2(\mu\text{-NO})_2]^-$, these yielding derivatives easily degrading to monoiron species.¹¹ As shown below, the W_2 anion and all derivatives are efficiently protected against degradation by the bridging PPh_2 ligand, thus anticipating a wide potential for this anion in the chemistry of binuclear nitrosyl complexes.



Scheme 1

The title anion can be prepared by a multistep procedure involving the isolable complexes $[\text{W}_2\text{Cp}_2(\mu\text{-I})(\mu\text{-PPh}_2)(\text{CO})_2]$ (**1**) and $[\text{W}_2\text{Cp}_2(\mu\text{-I})(\mu\text{-PPh}_2)(\text{NO})_2]$ (**2**) (Scheme 1).¹² Compound **1** is first prepared by following the method implemented previously for its PCy_2 -bridged analogue,¹³ now involving dehydrogenation of $[\text{W}_2\text{Cp}_2(\mu\text{-H})(\mu\text{-PPh}_2)(\text{CO})_4]$ with $\text{HBF}_4\cdot\text{OEt}_2$ in CH_2Cl_2

solution, followed by reaction of the resulting cation with excess NaI in refluxing 1,2-dichloroethane. Compound **1** is then reacted with NO (5% in N₂) at 233 K to give a carbonyl intermediate (not isolated) which is further decarbonylated in refluxing toluene to yield **2**. Spectroscopic data for **2** are comparable to those reported for *trans*-[W₂Cp₂(μ-PPh₂)₂(NO)₂] and related species,¹⁴ and support its formulation as a *trans*-dinitrosyl complex. Compound **2** is finally reduced in acetonitrile with Na amalgam to give a brown solution containing the Na⁺ salt of anion [W₂Cp₂(μ-PPh₂)(NO)₂][−] (**3**) as the unique product, ready for further use. Unfortunately, all attempts to isolate the Na⁺ or other salts of this unsaturated anion have been unsuccessful so far. It should be also noted that the choice of solvent for this reaction is critical, for the use of tetrahydrofuran leads to mixtures of different anionic species, yet under study.

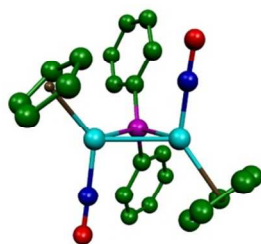


Figure 1. DFT-optimized structure of the anion **3**, with H atoms omitted. Selected bond lengths (Å) and angles (°): W–W = 2.580; W–P = 2.439; W–N = 1.782. W–W–N = 97.

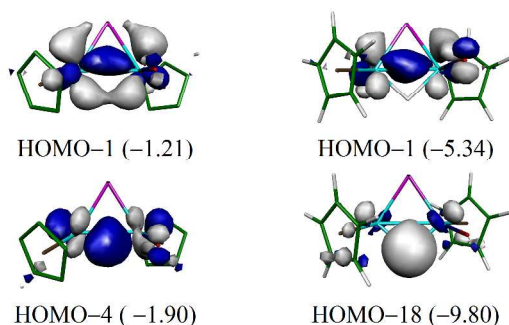
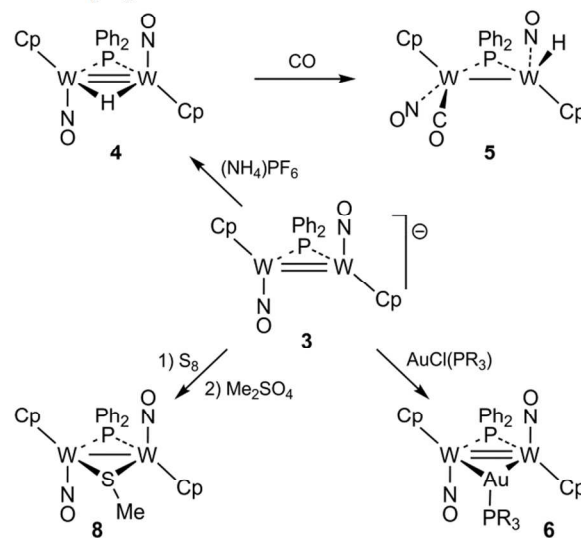


Figure 2. Selected DFT-computed MOs for **3** (left) and **4** (right), with energies (eV) indicated between brackets.

Complex **3** gives rise to a broad N–O stretch at 1463 cm^{−1}, some 100 cm^{−1} below those of **2**, which is suggestive of retention of terminal NO ligands. Indeed, the gas-phase DFT-computed structure of the anion with terminal nitrosyls is a true minimum in the corresponding potential energy surface (Figure 1), and it is some 66 kJ/mol more stable than an hypothetical isomer **3B** with bridging NO ligands.¹⁵ According to the 18e rule, a metal–metal double bond should be formulated for **3**, which is consistent with our DFT calculations. Even if there is significant orbital mixing, the double bond in **3** still can be visualized as resulting from the expected σ component (HOMO-4) and a π component with maximum density located in the W₂P plane (HOMO-1, Figure 2), whereas the corresponding antibonding combination is the LUMO of the molecule. All of this in turn is consistent with the short W–W length of 2.580 Å and with the high electron density of 0.642 eÅ^{−3} at the intermetallic bond critical point, a value close to the figure of 0.652 eÅ^{−3} computed at the same level of theory for the triply-bonded [W₂Cp₂(CO)₄].¹⁶

The chemical behaviour of **3** reveals a considerable metal-based nucleophilicity which makes it an useful synthetic precursor for other unsaturated nitrosyl complexes (Scheme 2). Thus, reaction with (NH₄)PF₆ yields a red solution thought to contain a solvate complex [W₂Cp₂H(μ-PPh₂)(NCMe)(NO)₂] which, upon removal of solvent, yields the purple unsaturated hydride [W₂Cp₂(μ-H)(μ-PPh₂)(NO)₂] (**4**) in ca. 65% yield. Compound **4** also is a 32-electron complex for which an intermetallic double bond should be formulated according to the 18e rule.¹⁷ An X-ray study of **4** (Figure 3)¹² confirmed the presence of the hydride ligand (δ_H = −10.79 ppm; J_{HW} = 145 Hz) bridging a ditungsten centre which displays a short intermetallic length of 2.7699(7) Å, still significantly shorter than the distances of ca. 2.90 Å recently measured for related, but electron-precise, complexes of the type [Mo₂Cp₂(μ-PCy₂)(μ-Y)(NO)₂] (Y = 3e-donor group).¹⁸ The DFT-computed MOs of **4** allow for a more precise description of the double bond in **4** as being composed of a bicentric W₂ σ interaction (HOMO-1), little perturbed with respect to that in **3**, and a closed tricentric W₂H interaction represented by the strongly stabilized HOMO-18 orbital, which is derived from interaction of the π bonding orbital of the parent anion (HOMO-1) with the proton (Figure 2).¹⁵ Because of the short intermetallic length in **4** (calcd 2.724 Å), the latter interaction should be considered of bonding character with respect to the intermetallic interaction, which is consistent with the large electron density of 0.500 eÅ^{−3} retained at the corresponding bond critical point, still much higher than the figure of 0.204 eÅ^{−3} computed for the singly-bonded [W₂Cp₂(CO)₆].¹⁵ The electronic unsaturation of **4** was chemically tested through its fast reaction with CO (1 atm), which involves coordination of a CO molecule and displacement of the hydride ligand to a terminal position *trans* to P (δ_H = −1.09 ppm; J_{HP} = 9 Hz, J_{HW} = 104 Hz), to yield the electron-precise derivative [W₂Cp₂H(μ-PPh₂)(CO)(NO)₂] (**5**). Further studies on the reactivity of **4** towards different organic and inorganic molecules are now in progress.



Scheme 2

The anion **3** reacts readily with [AuCl{P(*p*-tol)₃}] to give the corresponding heterometallic cluster [AuW₂Cp₂(μ-PPh₂)(NO)₂{P(*p*-tol)₃}] (**6**), which is isolobal-related to the

hydride **4**. Accordingly, the structure of **6** (Figure 3) is strongly related to that of **4** and the W–W length remains very short (2.7376(7) Å), actually shorter than that in **4**, in spite of the much larger size of the gold atom. This also supports our interpretation of the tricentric W₂H and W₂Au interactions in these compounds as genuinely bonding with respect to the ditungsten centre. It can be anticipated that other unsaturated heterometallic clusters will be readily available from **3**.

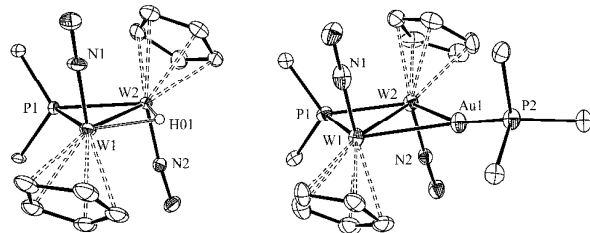


Figure 3. ORTEP diagrams (30% probability) of compounds **4** (left) and **6** (right), with H atoms (except the H ligand) and Cy and *p*-tol groups (except their C¹ atoms) omitted. Selected bond distances (Å). Compound **4**: W1–H = 1.851; W2–H = 1.851. Compound **6**: W1–Au = 2.7098(7); W2–Au = 2.7286(7).

The unsaturated nature of anion **3** allows for further functionalisation of the ditungsten centre via electron-precise anionic derivatives. This is illustrated through the reaction of **3** with elemental sulphur, which yields the electron-precise sulphide-bridged anion Na[W₂Cp₂(μ-PPh₂)(μ-S)(NO)₂] (**7**), a complex which can be readily alkylated to give isolable thiolate-bridged derivatives, eg. [W₂Cp₂(μ-PPh₂)(μ-SMe)(NO)₂] (**8**).¹² Analogous reactions are observed with other group 16 elements, currently under study.

In summary, we have implemented an efficient synthetic route to the unsaturated anion **3**, the first anionic nitrosyl complex featuring a metal–metal double bond. This complex displays considerable metal-based nucleophilicity which enables the addition of different electrophiles at this site, whereby a wide range of ditungsten nitrosyl derivatives can be obtained, either unsaturated or electron-precise ones, thus opening new opportunities to further explore the activation of nitric oxide at unsaturated di- and polynuclear complexes, and further work in that direction is now in progress.

Notes and references

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† Electronic Supplementary Information (ESI) available: A PDF file containing preparative and spectroscopic data for new compounds, and details of DFT calculations. CCDC 1476913–1476914 contain the crystallographic data for compounds **4** and **6**. See DOI: 10.1039/b000000x/

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M. Angeles Alvarez, M. Esther García, Daniel García-Vivó, Miguel A. Ruiz,* and Adrián Toyos

Text for Table of Contents

The title complex, which is the first anionic nitrosyl complex featuring a metal-metal multiple bond, displays substantial metal-based nucleophilicity, thus providing synthetic access to different unsaturated hydride and heterometallic nitrosyl derivatives, as well as a variety of electron-precise molecules.

Graphic for Table of Contents

