ARTICLE TYPE

The Doubly-Bonded Ditungsten Anion [W₂Cp₂(μ-PPh₂)(NO)₂]⁻: An Entry to the Chemistry of Unsaturated Nitrosyl Complexes

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Complex [W₂Cp₂(μ-I)(μ-PPh₂)(NO)₂] was prepared by reacting [W₂Cp₂(μ-I)(μ-PPh₂)(CO)₂] with NO at 233 K followed by decarbonylation in refluxing toluene. It was reduced by Na(Hg) in acetonitrile to give Na[W₂Cp₂(μ-PPh₂)(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 (NH₄)PF₆ and [AuCl{P(p-tol)₃}] gave the
10 hydride [W₂Cp₂(μ-H)(μ-PPh₂)(NO)₂] and cluster [AuW₂Cp₂(μ-PPh₂)(NO)₂{P(p-tol)₃}] respectively, also featuring multiple W−W bonding (experimental W−W ca. 2.75 Å), and its reaction with S₈ yielded the electron-precise derivative Na[W₂Cp₂(μ-PPh₂)(μ-S)(NO)₂], which was methylated by Me₂SO₄ to give the thiolate complex [W₂Cp₂(μ-PPh₂)(μ-SMe)(NO)₂].

The chemistry of metal nitrosyl complexes is a mature field of
15 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
20 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
25 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,
30 these including as most relevant groups the doubly-bonded complexes [M₂L₂(μ-NO)₂] (Fe, Ru, Os; L = Cp or related ligand),[5] and [W₂L₂(μ-H)₂H₂],[6] along with a few other isolated examples.[7] As for complexes displaying triple intermetallic bonds we can only quote the diphosphine-bridged [Re₂Cl₅(μ-
35 dppm)(NO)],[8] and the carbyne-bridged cation [Mo₂Cp₂(μ-CPh)(μ-PCy₂)(μ-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
40 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
45 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-
50 deficient species. Here we report the successful preparation of the Na⁺ salt of the anion [W₂Cp₂(μ-PPh₂)(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
55 complexes [Fe₂L₂(μ-NO)₂]⁻, these yielding derivatives easily degrading to monoiron species.[11] As shown below, the W₂ anion and all derivatives are efficiently protected against degradation by the bridging PPh₂ ligand, thus anticipating a wide potential for this anion in the chemistry of binuclear nitrosyl complexes.
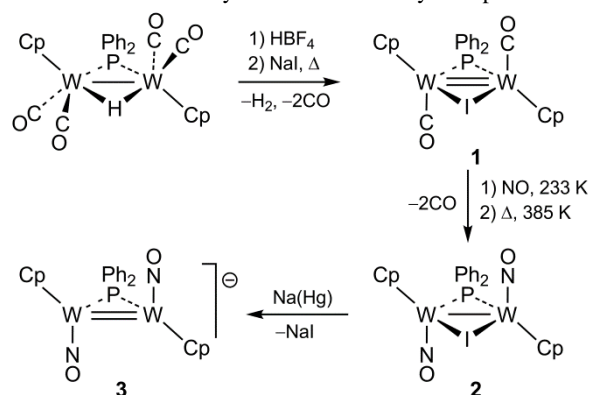
60 **Scheme 1**

The title anion can be prepared by a multistep procedure involving the isolable complexes [W₂Cp₂(μ-I)(μ-PPh₂)(CO)₂] (**1**) and [W₂Cp₂(μ-I)(μ-PPh₂)(NO)₂] (**2**) (Scheme 1).[12] Compound **1** is first prepared by following the method implemented previously
65 for its PCy₂-bridged analogue,[13] now involving dehydrogenation of [W₂Cp₂(μ-H)(μ-PPh₂)(CO)₄] with HBF₄·OEt₂ in CH₂Cl₂

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 N_2) 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*-[$W_2Cp_2(\mu-PPh_2)_2(NO)_2$] 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 [$W_2Cp_2(\mu-PPh_2)(NO)_2$]$^-$ (**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.
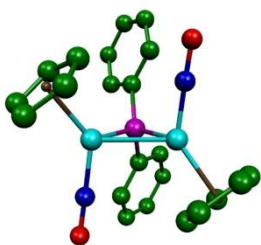

Figure 1. DFT-optimized structure of the anion **3**, with H atoms omitted. Selected bond lengths (Å) and angles (°): W−W = 2.580; W−P = 2.439; W−N = 1.782. W−W−N = 97.

HOMO−1 (−1.21)   HOMO−1 (−5.34)
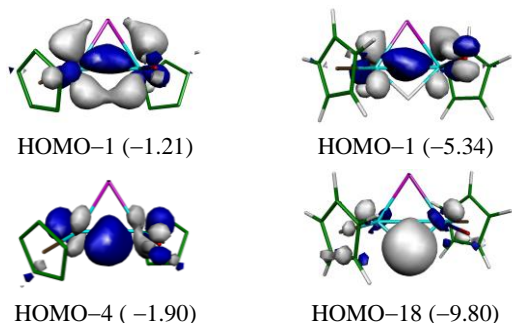
HOMO−4 (−1.90)   HOMO−18 (−9.80)

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 W_2P 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 [$W_2Cp_2(CO)_4$].[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 (NH_4)PF_6 yields a red solution thought to contain a solvate complex [$W_2Cp_2H(\mu-PPh_2)(NCMe)(NO)_2$] which, upon removal of solvent, yields the purple unsaturated hydride [$W_2Cp_2(\mu-H)(\mu-PPh_2)(NO)_2$] (**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 ($\delta_H = -10.79$ 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 [$Mo_2Cp_2(\mu-PCy_2)(\mu-Y)(NO)_2$] (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 W_2 σ interaction (HOMO−1), little perturbed with respect to that in **3**, and a closed tricentric W_2H 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 [$W_2Cp_2(CO)_6$].[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 ($\delta_H = -1.09$ ppm; $J_{HP} = 9$ Hz, $J_{HW} = 104$ Hz), to yield the electron-precise derivative [$W_2Cp_2H(\mu-PPh_2)(CO)(NO)_2$] (**5**). Further studies on the reactivity of **4** towards different organic and inorganic molecules are now in progress.
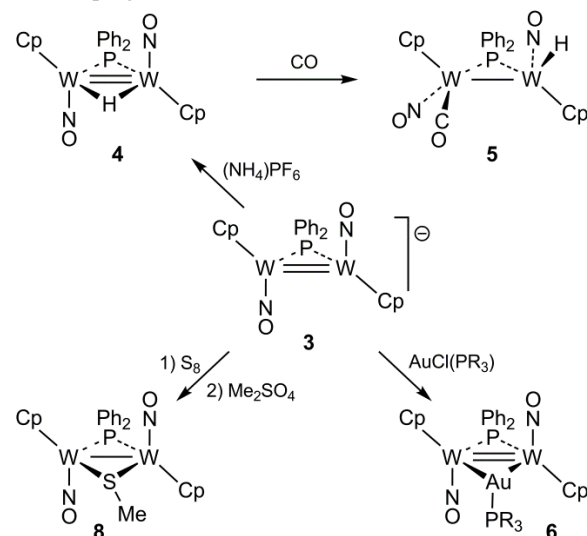
Scheme 2

The anion **3** reacts readily with [AuCl{P(*p*-tol)$_3$}] to give the corresponding heterometallic cluster [AuW$_2$Cp$_2$(μ-PPh$_2$)(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 W_2H and W_2Au interactions in these compounds as genuinely bonding with respect to the ditungsten centre. It can be anticipated than other unsaturated heterometallic clusters will be readily available from **3**.
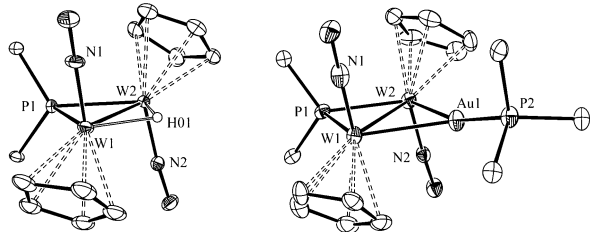

Figure 3. ORTEP diagrams (30% probability) of compounds **4** (left) and **6** (right)**,** with H atoms (except the H ligand) and Cy and *p*-tol groups (except their C^1 atoms) omitted. Selected bond distances (Å). Compound **4**: W1−H = 1.851; W2−H = 1.851. Compound **6**: W1−Au= 2.7098(7); W2−Au = 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 $Na[W_2Cp_2(\mu\text{-}PPh_2)(\mu\text{-}S)(NO)_2]$ (**7**), a complex which can be readily alkylated to give isolable thiolate-bridged derivatives, eg. $[W_2Cp_2(\mu\text{-}PPh_2)(\mu\text{-}SMe)(NO)_2]$ (**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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12 The ESI contains details of the synthesis, analytical, spectroscopic and crystallographic data of complexes **1** to **8**.

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17 We have adopted a "half-electron" counting convention for complexes displaying bridging hydrides or related groups as $Au(PR_3)$, so **4** and **6** are regarded as having M=M bonds (but see our DFT description of such bonds). Other authors recommend the adoption of a "half-arrow" convention (J. C. Green, M. L. H. Green and G. Parkin, *Chem. Commun.*, 2012, **48**, 11481 and references therein). Under such convention, however, the 32-electron hydride **4** should be assimilated to the 34-electron complexes $[W_2Cp_2(\mu\text{-}Y)(\mu\text{-}PCy_2)(NO)_2]$ (Y= I, PR_2, etc), a relationship which we consider of little use to interpret the strong differences separating the structure, spectroscopic properties, and reactivity of these molecules.

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