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Large pi-systems containing W-N=N-W groups

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Draft

Abstract

The compound $\text{Cl-W}(\text{Mes})_3\text{-N=N-W}(\text{Mes})_3\text{-Cl}$ can polymerize, giving large inorganic pi systems containing N_2 and $\text{W}(\text{Mes})_3$ where Mes=mesityl. Some of these compounds have been studied in the present paper using B3LYP functional. A description of the molecular orbitals from the pi system is given, explaining the role of the mesityl groups, the terminal chlorines and the d atomic orbitals from W in the whole conjugated system. Other data such as bond order, atomic partial charges or geometry are studied. These compounds are also compared with some hypothetical derivatives.

Keywords

Conjugated systems, W, N_2 , B3LYP.

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1 Introduction

The compounds with metal-dinitrogen bond have been known for many years. Some of them have been studied because of their magnetic properties, or with the aim of achieving N₂ fixation and reduction.¹ However, the compounds of W with dinitrogen have not been thoroughly studied yet.

The atoms of W in these compounds can be considered as W⁴⁺ thus its electronic configuration is d². Despite that, the molecule is clearly diamagnetic.² In contrast, the atoms of Mo can be considered as Mo³⁺. Its electronic configuration is d³ and the equivalent compounds with Mo-N₂ are paramagnetics, with a triplet state. Apart from that, the main goal of dinitrogen fixation by coordination with metals is the cleavage of the N₂ triple bond, and this is not achieved when the metal is W. So, this kind of compounds has very odd properties.

Solari *et al.*² have reported that Cl-W(Mes)₃-N=N-W(Mes)₃-Cl is able to polymerise, giving [Cl-W(Mes)₃-(N=N-W(Mes)₃)₂-Cl]⁻ and [Cl-W(Mes)₃-(N=N-W(Mes)₃)₃-Cl]²⁻ and so on. These compounds will be named as W₂, W₃ and W₄ hereafter. One of the most curious aspects of these compounds is the large pi unsaturated system, with 2, 3 or 4 atoms of W bonded to 1, 2 or 3 molecules of N₂. None of the other metals is known to be able to develop such linear unsaturated pi system, with dinitrogen as a bridge, and more than 2 nuclei of transition's metal. For all these reasons, it is interesting to study that kind of inorganic compounds.

The goals of the present study are as follows. Firstly, to study the electronic structure of W₂, W₃ and W₄, using DFT. Molecular orbitals, partial atomic charges and bond orders are also studied. After that, next goal would be to explain or to predict some special characteristics of these compounds and their possible derivatives such as stability or formation of derivatives.

One of the first attempts to study theoretically some compounds similars to W_2 was performed ³ using Self-consistent field (SCF) and configurations interaction (CI) on $VH_3-N=N-VH_3$ compounds. In that study (and others related in the same reference), a simple model was made, with molecular orbitals as a linear combination of d_{xy} , d_{yz} from both metals and p_x , p_y from both nitrogens. As a result, 4 doubly degenerate energy levels (1e, 2e, 3e and 4e) were obtained. The strength of the M-N and N-N bonds depends on the occupation of these orbitals. Normally, 1e and 2e are occupied (and these are mostly bonding), with 8 electrons, and 3e and 4e are unoccupied (and less bonding). Hence this model involves H instead of mesityl, the author wishes to investigate the real system, and tri or tetranuclear compounds as well.

In other studies, compounds like $Mo(N(R)Ar)_3-N=N-Mo(N(R)Ar)_3$ (where $R=C(CD_3)_2CH_3$, $Ar=3,5-C_6H_3Me_2$) are a triplet with S_6 symmetry.⁴ The symmetry can change from linear to a zig-zag transition state, leading to the split of N=N bond in two fragments by thermal excitation. Other similar compounds, with Mo and ligands such as $-N(tBu)Ar$, ($Ar=3,5-C_6H_3Me_2$)⁵ or mesityl⁶, decompose photochemically giving two ML_3-N fragments.

More studies has been performed in the same way, theoretical or experimental, about these kind of compounds, having as a metal Mo,^{7,8} Fe,^{9,10} Nb,¹¹⁻¹² or Co¹³ among several others. Besides these references, there are also some reviews about the state of the art in this topic,¹ which include other metals, but not W. It must be pointed out that all these studies are supposed to be performed with the aim of weakening the N-N bonds only in binuclear species. That is the opposite of the trend observed in $W-N=N-W$, which can polymerize without losing the N=N bond.

Finally, another study¹⁴ shows experimental evidences of a pi chain obtained after the photochemical cleavage of $Mo(Mes)_3-N=N-Mo(Mes)_3$, leading to $Mo(Mes)_3-N-Mo(Mes)_3-N=N-Mo(Mes)_3-N-Mo(Mes)_3$ which is unstable and decomposes. The

precursor could seem very similar to W_2 . However the former does not contain Cl, so the oxidation's number of Mo is +3 and the molecule is a triplet whereas in W_2 the W is bond to Cl, the oxidation's number is +4 and the molecule is a singlet.

To the best of the knowledge of the author no other study is performed about the Cl- $W(Mes)_3-N=N-W(Mes)_3-Cl$ molecule and their polymers.

2 Computational details

Some concerns have risen when the description of the molecule has been done. The decision of including all the atoms in the molecules leads to some restrictions. The symmetry group is C_{3h} . The data obtained by RX diffraction² shows that the geometry is almost C_{3h} but no exactly.

For the calculations, DFT¹⁵ has been used. The chosen functional has been B3LYP.¹⁶ Currently, this is one of the most used functionals in organic chemistry and in inorganic chemistry as well.¹⁷ The use of B3LYP, even though with transition's metals, is an acceptable choice given that the studied compounds have closed shells. However, with the aim of contrasting the results, another functionals such as PBE0¹⁸ and B3LYP with the Grimmes's correction¹⁹ for non-covalent interactions have been used as well in some cases.

The basis set has been chosen as follows. In first trials, some basis sets with Effective Core Potentials (ECP) have been used for W. Among the basis sets with moderate size, the best agreement with the experimental data for geometry has been achieved using SBKJC ECP basis set²⁰ in W. The basis set has been enlarged with one f gaussian set with $\zeta=0.43199$ taken from another basis set.²¹ For Cl and N, being they on the pi chain, the 6-311(d)²² basis set has been used. Finally, trying to keep the ensemble of basis in a reasonable size (note that W_2 has 126 atoms and W_4 has 252 atoms) the chosen basis set for C and H has been 6-31G.²³

In every molecule, the geometry has been defined according to the experimental data and the symmetry group. Some constraints for the optimization have been used. The optimization is performed until the variation in total energy is lower than 0.0001 hartrees in W_2 and 0.005 hartrees in W_3 and W_4 .

All the calculations are made with the Firefly 8.1.1 package,²⁴ which is partially based on the GAMESS (US) source code.²⁵ It is freely distributed and adapted for use with PCs.

3 Results and discussion

3.1 Geometry and electronic structure

For W_2 , the results of the geometry after optimization are summarized in table 1, which also contains experimental data about bond lengths. Overall, all the W-N or N-N bonds have a bond order of almost 1.5. For N-N bond lengths, the agreement of calculated data with experimental data is not very good. In order to improve these results, the geometry was optimized using the already cited functionals (B3LYP, PBE0), but also BP86 and B97-3.^{26,27} Apart from SBKJC, other basis sets with effective core potentials were tested, such as Stuttgart,²⁸ LANL2DZ²⁹ and Def2TZV.³⁰ In all these cases, the values for N-N bond length did not change significantly. To remove the constraints for geometry afforded slightly better results, which are reported in Table 1, using B3LYP and SBKJC. The experimental data are obtained using X-ray diffraction, thus these are obtained in solid state. Probably the lattice has a notable influence in geometry, and an *ab initio* calculation applied to an *in vacuo* molecule do not show the same effects. As a consequence, the results should be considered just in a semi quantitative way.

Table 1.

From Table 1, some trends can be noted. Firstly, with the polymerization the bond order of N-N remains almost constant. However, there is a W-N bond whose bond order becomes weaker with polymerization: 1.4 in W_2 , 0.9 in W_3 , 0.8 in W_4 . The longer the chain, the weaker this bond.

Usually, the relation between bond length and bond order (BO) in the dinitrogen systems is as follows:³¹ For the molecular dinitrogen N_2 , $BO=3$, the bond length is near 1.10 Å. For the $N=N$ double bond, $BO=2$, the bond length is close to 1.25 Å. In aromatic $N=N$ bonds, the bond order could be considered near 1.5 and the bond length is near 1.30 Å. Finally, for simple N-N bonds, with $BO=1$, the bond length is close to 1.42 Å. Then, the obtained BO (1.3 to 1.6) are slightly smaller than it would be expected for the calculated bond lengths (1.201 to 1.259 Å), and for the experimental data (1.18 to 1.26 Å). These bond lengths would require a BO nearer to 2.

3.2 Electronic structure

It would be interesting to look at the molecular orbitals involved in the pi bonds in W_2 . The first model for $M-N=N-M$ systems proposed by N. Re *et al.*³ was very simple. There are four atoms, with p_x , p_y for both N, and d_{xy} , d_{yz} from both M. There are eight involved atomic orbitals, so there are eight molecular orbitals: 1e, 2e, 3e and 4e, with 2, 3, 4 or 5 nodes across the chain. Two nodes are due to the d_{xy} and d_{yz} nodal plane. The current situation is, by far, more complex. In Figure 1, W_2 is shown. This sort of molecule is stable only if the mesityls are rotated as in the images. Otherwise, a methyl group of one mesityl is in touch with the methyl of another mesityl situated in the same W atom. Because of this rotation, the pi molecular orbitals along the chain are not completely conjugated with the pi systems of the mesityls. Then, there are molecular orbitals pi almost located in the mesityls, and other molecular orbitals pi placed in the linear chain, but not completely independent of the mesityls.

Figure 1. $\text{Cl-W(Mes)}_3\text{-N=N-W(Mes)}_3\text{-Cl}$, named W_2 in the main text. The black atoms are the chain (Cl-W-N-N-W-Cl). The C, H atoms are drawn with small radius for the sake of a best visibility of the chain.

Figure 2. In W_2 , the 232th molecular orbital. 232 and 233 are the HOMO. 232 shows clearly the overlap between the d from W and p from N. Cl does not participate in this molecular orbital. There is also some conjugation with pi bonds in two mesityls in each W. In 233 (not shown) the bonds between W and N are in a plane which would be perpendicular to the paper, and the conjugation is with the other mesityls, barely visible, which remains behind the W in the picture.

Figure 3. In W_2 , the 234th molecular orbital. 234 and 235 are the LUMO. There is an important contribution from the terminal Cl, whereas there is not an appreciable conjugation with the mesityls. This orbital is bonding between both N and antibonding between W and N whereas HOMO (Figure 2) is antibonding between both N and bonding between N and W.

The chlorine atoms participate in some but not all the pi molecular orbitals. Then, these molecular orbitals are formed mostly by d_{xy} of W and p_x of N, or d_{yz} of W and p_y of N, but in some cases p_x and p_y from chlorine allow to extend the unsaturated chain. The conjugation with mesityls (and in some cases with Cl) leads to a number of pi MO bigger than 8. However, in the studied orbitals, chlorine has not a clear pi bond with W.

Some peculiarities are found in this set of pi orbitals. There is not a "ground" pi molecular orbital completely bonding between W-N-N-W which would be like the MO 1e. In place of this molecular orbital there are three double degenerated orbitals e' which are a "typical" pi bond between N_2 , more or less coupled with some pi bonds of mesityls. If the same calculation is performed with H instead of mesityls, there is only one completely bonding 1e. So, the change of an "completely bonding" pi MO like "1e"

by some "partially bonding" pi MO is due to the conjugation with mesityls. The "d" atomic orbitals of W are not involved in those MO. Perhaps the conjugation reduces the energy of these MO, which becomes lower than the energy of the d from W.

The HOMO and LUMO (Figures 2 and 3) have e'' and e' symmetry, and they are similar to 2e and 3e from references.³ There is also another e'' which is similar to the last molecular orbital 4e from the cited reference.

The expected 4e double degenerated pi MO, completely antibonding, splits in two sets of double degenerated e'' pi MO. This is also an effect of the conjugation. If H is used instead of mesityls, only one double degenerated pi MO like 4e appears.

LUMO are mostly antibonding between W and N, and bonding between N_2 . In contrast HOMO are mostly bonding between W and N, and antibonding between N_2 . HOMO shows a node between N and W, where the bond order is weaker. Because of these differences between HOMO and LUMO with alternating bonding and antibonding zones, it is possible to make predictions about how the electronic occupation could modify the bond orders along the chain. This point will be discussed later.

Table 2.

Table 3.

Table 4.

For W_3 , there are 7 atoms in the chain (3W and 4N), so there should be 7 couples of pi MO. In W_4 (Figure 4) there are 6 N and 4 W, 10 couples of pi MO are possible. Again, there is not in any case a "ground" molecular orbital pi completely bonding but an ensemble of 9 MO with energies from -0.288 to -0.225 (Table 4).

Figure 4. $[\text{Cl-W}(\text{Mes})_3\text{-[N=N-W}(\text{Mes})_3\text{-Cl]}]^{2-}$, named W_4 in the main text. In black, the backbone of this compound, with two terminal Cl, four W and three N=N. Each W contains three mesityls, not completely visibles.

Figure 5. In W_4 , 452th MO. This MO is clearly bonding between each W and the nearer N. However, this is antibonding between each N-N pair. There is a strong conjugation with the six mesityls in the middle, but not the terminal ones. This OM is strikingly similar to the 232th in W_2 (Figure 2)

Figure 6. In W_4 , the 458th MO, which is the LUMO. There is not conjugation with mesytilenes. This MO is clary bonding between N-N and antibonding between W-N.

Figure 7. In W_4 , the 514th MO. 513 and 514 are arrays of d and p which are the pi MO with the highest energy, thus these are completely antibonding.

The composition of the pi MO for all these compounds can be summarized as follows: First, what should be a "ground" pi MO completely bonding becomes an ensemble of partially bonding pi MO because of the conjugation with the mesityls, without any participation of "d" from W. Second, there are the other pi MO, with d from the W. The MO near HOMO and LUMO can have some conjugation with Cl and mesityls. Finally, the higher energy is for the completely antibonding pi MO. Besides that, there are many other pi MO which are combinations of Mesityls.

Analysing the molecular orbitals, it is possible to explain the low tendency of this compounds of W to break the N=N bond, in contrast with other known compounds. In most of the studied compounds,^{6,7,14} the rupture of the N=N bond is related with the antibonding orbital a", which is usually unoccupied. However, due to the ligands, this orbital is energetically very close to the HOMO. With a thermal excitation this orbital can be filled. This leads to break the N=N bond. When thermal excitation is not enough, the excitation can be done photochemically, as explained in some references.¹⁴ The main idea is that the possibility of breaking the N=N bond depends basically on the gap HOMO-a", and the current study demonstrates that this gap depends strongly on the presence of Cl in the sides of the chain. The subjects of the present paper are molecules like Cl-W(Mes₃)-N=N-W(Mes₃)-Cl. The conditions for the synthesis are explained in some references.^{2,14} In almost the same experimental conditions, the use of MoCl₄ leads to molecules like Mo(R₃)-N=N-Mo(R₃) whereas the use of WCl₄ affords Cl-W(Mes₃)-N=N-W(Mes₃)-Cl. Therefore, the obtained compound of W has an oxidation number of +4 and contains chlorine whereas the obtained compound of Mo has an oxidation number of +3, without chlorine. The reasons why can be difficult to find, and these could involve lots of factors such as redox potentials, thermodynamics, kinetics, transition states, etc. These differences, then, can hardly be explained using only the quantum chemistry. However, given that W₂ has chlorine and

an oxidation number different than their Mo equivalent, and their stability is bigger, it is tempting to try to explain this differences in the stability of N=N bond.

The molecular orbital which is involved in the rupture of the N=N bond is a'' . This is shown in Figure 8. In W_2 , the gap from HOMO to a'' is bigger than 0.2 hartrees. On the other hand, in $Mo(R_3)-N=N-Mo(R_3)$, the MO a'' is very near the HOMO. The same calculation for W_2 with chlorine and their hypothetical congener $W(Mes)_3-N=N-W(Mes)_3$ without chlorine reveals what is the role of chlorine in that sort of compound. This results can be compared with the same calculations for $Mo(Mes)_3-N=N-Mo(Mes)_3$ and its hypothetical congener $Cl-Mo(Mes)_3-N=N-Mo(Mes)_3-Cl$. With chlorine, the oxidation number is +4, and without chlorine it is +3. In that case, the ground state is a triplet. The same calculation is performed for $Cl-W(Mes)_3-N=N-W(Mes)_3-Cl]^{2-}$, which is also a triplet. It is easy to see in all the studied examples that regardless of the metal, the multiplicity or the oxidation number, the energy of a'' rises strongly due to the overlap with chlorine. Tables 2, 3 and 4 summarise this results. The molecular orbital a'' is an antibonding orbital which is shown in figure 4. The antibonding interaction with p atomic orbitals from chlorine makes more energetic this a'' orbital, increasing the gap from HOMO. It makes very difficult to occupate this orbital, and the breaking seems not possible in that way. This effect can be checked also performing the same calculation for the molecules $F-W(Mes)_3-N=N-W(Mes)_3-F$ and $Br-W(Mes)_3-N=N-W(Mes)_3-Br$ from which there are not references, so these should be seen as hypothetical. The overlap with p atomic orbitals from these elements makes higher or lower the gap, as is shown in Table 5. The gap increases in the order $Br < Cl < F$.

Image 8. In W_2 , the 254th Molecular orbital. This is an a'' orbital and does not belong to the π system. However, as it is explained in the text, this MO plays a fundamental role in the reactivity of this compound. This MO is sigma antibonding between both N and it is empty. The presence of Cl makes more energetic this MO. Without the Cl, the energy of this MO decreases, and the possibility of being partially filled due a photochemical or thermal excitation is bigger, which can lead to a split of the $N=N$ bond.

Therefore, with chlorine (or another halogen) the state is a singlet. It is possible to achieve also a triplet with the gain of two electrons. In both cases the gap from e'' to a'' is near 0.200-0.290 and from e' to a'' is near 0.143-0.175 Hartree. The same occurs when the metal is Mo in place of W. Nevertheless, when the chlorine is not there, (the last two lines in Table 5) the gap from e'' to a'' decreases to a half or lower (0.102-0.110), and the gap e' to a'' decreases to a third (0.042-0.057). Then, the gap does not depend on the metal, or the multiplicity, but the presence of chlorine or another

halogen, which make σ^* more energetic. The higher the energy of σ^* , the lower the possibility of filling this molecular orbital due to a thermal or photochemical excitation.

Table 5.

Besides that, there is still another factor to consider in the stability of these compounds. The presence of 6, 9 or 12 mesityl groups should lead to some interactions between them. The optimization of W_2 adding the Grimme's correction for non covalent interactions gives almost the same geometry and bond orders. The total energy, however, decreases in 0.236 Hartree. This is only a rough estimation of the magnitude of the non-covalent interactions between the mesityl groups in the whole molecule, but it shows that these non covalent interactions between mesityl are not negligibles.

3.3 Ions

Looking carefully the HOMO and LUMO, it is clear that if these compounds gain or lose 2 electrons, a change in the occupation of HOMO and LUMO can change strongly the bond orders along the chain. For W_2 , to gain 2 electrons would increase N-N bond order and decrease N-W bond order. Curiously, to lose 2 electrons would give a similar effect. In both cases the molecule becomes a triplet state. This effect has been checked and table 6 shows these results.

Table 6.

The gain of 2 electrons gives a molecule with lower energy. The experimental procedure for the polymerization is described elsewhere ² and shows that the reaction begins with W_2 in suspension with Mg powder, which becomes Mg^{2+} . So, it is reasonable to expect that the reaction $W_2 + Mg \rightarrow W_2^{2-} + Mg^{2+}$ occurs and surely $[W_2]^{2-}$ is an intermediate of the reaction. The energy of the reaction depends on many effects such as the presence of the solvent (THF) or the surface of the solid Mg. However, such effects are out of the scope of the present study. Since B3LYP could not be the

best choice when there is an important change in the multiplicity of the molecule,³² these calculations are performed also using PBE0. These functional gives results very similar to these obtained with B3LYP.

Then, the oxidation $W_2^0 \rightarrow W_2^{2+}$ is extremely unlikely whereas the reduction $W_2^0 \rightarrow W_2^{2-}$ seems to be energetically allowed with $\Delta E = -0.045$ Hartrees.

4 Conclusions

The electronic structure of some special unsaturated systems (named W_2 , W_3 and W_4 in the text), which contains W, N_2 and mesityls, has been studied using DFT under some restrictions of symmetry. This compounds are relatively stables and do not show tendency to break the N=N bond. The calculations show that the bond order of N=N is close to 1.35, a bit small for the calculated bond length (1.26 Å). This bond order does not decrease when W_2 polymerises to W_3 or W_4 . The bond order for the N-W bond is near to 1.5.

For all the studied compounds, there are rich pi systems, by far more complicated than it should be expected. In this pi molecular orbitals there are d_{xz} , d_{yz} from the W and p_x , p_y from the N. However, there are also p_x , p_y from Cl, but only in a few molecular orbitals. Furthermore, there is a strong interaction with some linear combinations of pi bonds in mesityls. This allows, so, a plethora of pi molecular orbitals, and some of them are very localized along the W-N=N-W chain, and other ones very dispersed on the whole of the molecule. There is not a "ground" pi molecular orbital completely bonding along the W-N=N-W chain in any case.

These compounds are not able to break the N=N bond. Their homologues containing Mo can do this, with a photochemically induced excitation, and termally induced excitation in other cases. It is found that this is related with the fact that the sigma antibonding pi MO between both N is near the HOMO in the Mo compounds. For the

studied compounds with W instead of Mo, the presence of chlorine increases the energy of that antibonding MO, which hardly could be occupied.

It has been predicted that the bond order between N-N and W-N could be changed with the formation of ions, depending on the population of HOMO and LUMO. The gain of electrons allows a major stability, and the bond order of N=N bond rises, whereas the bond order for N-W decreases. The energy of the reaction $W_2 \rightarrow W_2^{2-}$, which possibly happens in presence of magnesium, has been estimated using different functionals such as B3LYP and PBE0, giving similar values *in vacuo*.

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Table 1: Relevant data for W_2 , W_3 , W_4 . In parenthesis, experimental data taken from Solari *et al.* [2]. In W_3 the bonding scheme is as follows: Cl-W(1)-N(1)-N(2)-W(2)-N(2)-N(1)-W(1)-Cl. In W_4 the bonding scheme is Cl-W(1)-N(1)-N(2)-W(2)-N(3)-N(3)-W(2)-N(2)-N(1)-W(1)-Cl. "Av." means "average data". Units of length are Angstroms and the units of the gap are Hartrees.

	W_2	W_3	W_4
Bond length	1.247	1.220 av. (1.272)	N(1)-N(2): 1.201 (1.212)
N-N	(1.180)		N(3)-N(3): 1.229 (1.264)
W-N	1.842 (1.846)	W(1)-N(1): 1.805 av. (1.794 av.) W(2)-N(2): 1.890 av. (1.871 av.)	W(1)-N(1): 1.812 (1.825) W(2)-N(2): 1.933 (1.931) W(2)-N(3): 1.873 (1.855)
W-Cl	2.402	2.460; 2.475	2.484 (2.494)
W-C	2.171	2.213 av.	2.218 av. (2.156 av.)
Bond order	1.365	1.525	N(1)-N(2): 1.622
N-N			N(3)-N(3): 1.567
W-N	1.410	W(1)-N(1): 1.438 av. W(2)-N(2): 0.940 av.	W(1)-N(1): 1.423 W(2)-N(2): 0.801 W(2)-N(3): 1.099
W-Cl	0.974	0.834 av.	0.760
W-C	1.000	0.944 av.	0.939
Charge W	+0.50	W(1): +0.28, W(2): +0.77	W(1): +0.39, W(2): +0.92
N	-0.29	N(1): -0.24, N(2): -0.45	N(1): -0.22, N(2): -0.47 N(3): -0.45
Cl	-0.33	-0.41	-0.48
Gap	0.1032	0.0894	0.0754

Table 2. MO for W_2 . Units of energy are Hartrees.

Molecular orbital	Energy	Description
252, 253 e'	0.036	$\pi^*(N-N)$, $\pi^*(N-W)$, $\pi^*(Mesityl)$
245, 246 e''	0.006	$\pi^*(N-N)$, $\pi^*(N-W)$
243, 244 e'	0.004	$\pi^*(Mesityl)$
234, 235 e'	-0.105	LUMO $\pi(N-N)$, $\pi^*(N-W-Cl)$
232, 233 e''	-0.208	HOMO $\pi^*(N-N)$, $\pi^*(N-W)$
220, 221 e''	-0.246	$\pi^*(N-N)$, $\pi^*(W-Cl)$, $\pi(W-N)$
218, 219 e'	-0.279	$\pi^*(Cl-W)$
178, 179 e'	-0.391	$\pi(N-N)$, $\pi(Mesityl)$
170, 171 e'	-0.397	$\pi(N-N)$, $\pi(Mesityl)$
149, 150 e'	-0.425	$\pi(N-N)$, $\pi(Mesityl)$

Table 3. MO for W_3 . Units of energy are Hartrees.

MO	Energy	Description
376, 377	0.140	$\pi^*(N-N)$, $\pi^*(W-N)$ utterly antibonding
354, 355	0.076	$\pi^*(N-N)$, $\pi^*(W-N)$
346, 347	-0.015	LUMO $\pi(N-N)$, $\pi^*(N-W)$, $\pi^*(Cl-W)$
344, 345	-0.105	HOMO $\pi^*(N-N)$, $\pi(N-W)$, $\pi^*(Cl-W)$
342, 343	-0.131	$\pi^*(N-N)$, $\pi(N-W)$, $\pi^*(Mesityl)$
324, 325	-0.176	$\pi^*(N-N)$, $\pi(N-W)$, $\pi^*(Cl-W)$, $\pi^*(Mesityl)$
271, 272	-0.302	$\pi(N-N)$, others
269, 270	-0.304	$\pi(N-N)$, others
262, 263	-0.312	$\pi(N-N)$
260, 261	-0.315	$\pi(N-N)$
237, 238	-0.342	$\pi(N-N)$, others
228, 229	-0.350	$\pi(N-N)$
217, 218	-0.359	$\pi(N-N)$
215, 216	-0.369	$\pi(N-N)$

Table 4. π MO for W_4 . Units of energy are Hartrees.

Molecular orbital	Energy	Description
513, 514 e''	0.228	$\pi^*(N-N)$, $\pi^*(W-N)$ utterly antibonding
495, 496 e'	0.194	$\pi^*(N-N)$, $\pi^*(W-N)$
492, 493 e''	0.173	$\pi^*(N-N)$, $\pi^*(W-Cl)$, $\pi(W-N)$
488, 489 e''	0.167	$\pi^*(N-N)$, $\pi^*(N-W)$, $\pi^*(Mesityl)$
486, 487 e'	0.161	$\pi^*(N-N)$, $\pi^*(N-W)$
481, 482 e''	0.147	Mix of π and π^* for N-N and N-W
460, 461 e''	0.084	Mix of π and π^* for N-N and N-W

458, 459 e'	0.060	LUMO π (N-N), π^* (N-W-Cl)
456, 457 e''	-0.015	HOMO π^* (N-N), π^* (N-W)
447, 448 e'	-0.084	π^* (N-N), π^* (W-Cl), π (W-N)
443, 444 e''	-0.088	π^* (Cl-W)
441, 442 e'	-0.089	π (N-N), π (Mesityl)
435, 436 e'	-0.094	π (N-N), π (Mesityl)
428, 429 e''	-0.112	π (N-N), π (Mesityl), π^* (W-Cl)
367, 368 e'	-0.225	π (N-N)
358, 359 e'	-0.238	π (N-N)
355, 356 e''	-0.245	π (N-N), π (Mesityl)
353, 354 e'	-0.245	π (N-N), π (Mesityl)
351, 352 e''	-0.247	π (N-N), π (Mesityl)
347, 348 e'	-0.250	π (N-N), π (Mesityl)
311, 312 e'	-0.280	π (N-N), π (Mesityl)
308, 307 e''	-0.284	π (N-N)
302, 303 e'	-0.288	π (N-N)

Table 5. Energy of some MO in W_2 and congeners.

	e''	e'	a''	Gap e''-a''	Gap e'-a''
$W_2N_2F_2(Mes)_6$	-0.201	-0.086	+0.089	0.290	0.175
$W_2N_2Cl_2(Mes)_6$	-0.208	-0.105	+0.047	0.255	0.152
$W_2N_2Br_2(Mes)_6$	-0.208	-0.109	+0.034	0.242	0.143
$W_2N_2Cl_2(Mes)_6^{2-}$	+0.029	+0.091	+0.235	0.206	0.144
$Mo_2N_2Cl_2(Mes)_6$	-0.203	-0.124	+0.027	0.230	0.151
$W_2N_2(Mes)_6$	-0.170	-0.102	-0.060	0.110	0.042
$Mo_2N_2(Mes)_6$	-0.164	-0.119	-0.062	0.102	0.057

Table 6. Characteristics of some ionic derivatives of W_2 .

	W_2^{2+}		W_2^0		W_2^{2-}	
	B3LYP	PBE0	B3LYP	PBE0	B3LYP	PBE0
Bond length N-N	1.163	1.162	1.259	1.256	1.222	1.217
W-N	2.129	2.104	1.862	1.841	1.920	1.902
W-Cl	2.300	2.279	2.419	2.387	2.594	2.547
W-C	2.098	2.073	2.153	2.134	2.180	2.154
Bond order N-N	2.305	2.330	1.357	1.368	1.569	1.594
W-N	0.514	0.548	1.423	1.468	1.161	1.184
W-Cl	1.230	1.297	0.934	0.999	0.605	0.669
W-C	1.146	1.133	1.018	0.999	0.979	0.963
Charge W	+0.45	+0.49	+0.51	+0.56	+0.40	+0.46
N	-0.24	-0.23	-0.30	-0.28	-0.30	-0.29
Cl	-0.12	-0.07	-0.34	-0.29	-0.58	-0.54
Gap	0.0213	0.0261	0.1032	0.1128	0.0280	0.0292
Relative energy	+5.5460	+0.5459	0.0000	0.0000	-0.0459	-0.0449

Figure 1. Cl-W(Mes)₃-N=N-W(Mes)₃-Cl, named W2 in the main text. The black atoms are the chain (Cl-W-N-N-W-Cl). The C, H atoms are drawn with small radius for the sake of a best visibility of the chain.

Figure 1

1164x1099mm (72 x 72 DPI)

Figure 2. In W2, the 232th molecular orbital. 232 and 233 are the HOMO. 232 shows clearly the overlap between the d from W and p from N. Cl does not participate in this molecular orbital. There is also some conjugation with pi bonds in two mesityls in each W. In 233 (not shown) the bonds between W and N are in a plane which would be perpendicular to the paper, and the conjugation is with the other mesityls, barely visible, which remains behind the W in the picture.

Figure 2
1164x1099mm (72 x 72 DPI)

Figure 3. In W2, the 234th molecular orbital. 234 and 235 are the LUMO. There is an important contribution from the terminal Cl, whereas there is not an appreciable conjugation with the mesityls. This orbital is bonding between both N and antibonding between W and N whereas HOMO (Figure 2) is antibonding between both N and bonding between N and W.

Figure 3
1164x1099mm (72 x 72 DPI)

Figure 4. $[\text{Cl}-\text{W}(\text{Mes})_3-[-\text{N}=\text{N}-\text{W}(\text{Mes})_3]_3-\text{Cl}]^{2-}$, named W4 in the main text. In black, the backbone of this compound, with two terminal Cl, four W and three N=N. Each W contains three mesityls, not completely visibles.

Figure 4

1541x941mm (72 x 72 DPI)

Figure 5. In W4, 452th MO. This MO is clearly bonding between each W and the nearer N. However, this is antibonding between each N-N pair. There is a strong conjugation with the six mesityls in the middle, but not the terminal ones. This OM is strikingly similar to the 232th in W2 (Figure 2)

Figure 5

1541x941mm (72 x 72 DPI)

Figure 6. In W4, the 458th MO, which is the LUMO. There is not conjugation with mesytilenes. This MO is clearly bonding between N-N and antibonding between W-N.

Figure 6

1541x941mm (72 x 72 DPI)

Figure 7. In W4, the 514th MO. 513 and 514 are arrays of d and p which are the pi MO with the highest energy, thus these are completely antibonding.

Figure 7
1541x941mm (72 x 72 DPI)

Figure 8. In W2, the 254th molecular orbital. This is an a'' orbital and does not belong to the π system. However, as it is explained in the text, this MO plays a fundamental role in the reactivity of this compound. This MO is sigma antibonding between both N and it is empty. The presence of Cl makes more energetic this MO. Without the Cl, the energy of this MO decreases, and the possibility of being partially filled due a photochemical or thermal excitation is bigger, which can lead to a split of the N=N bond.

Figure 8

953x980mm (72 x 72 DPI)