Inorganic Chemistry

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Reactions of the Unsaturated Ditungsten Complexes $[W_2Cp_2(\mu\text{-}PPh_2)_2(CO)_x]$ (x = 1, 2) with Nitric Oxide: Stereoselective Carbonyl Displacement and Oxygen-Transfer Reactions of a Nitrite Ligand

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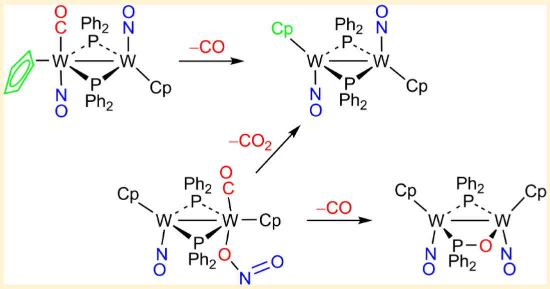
Supporting Information



ABSTRACT: The dicarbonyl complex *trans*-$[W_2Cp_2(\mu\text{-}PPh_2)_2(CO)_2]$ (Cp = η^5-C_5H_5) reacted rapidly with NO (5% in N_2) at 273 K to give selectively *cis*-$[W_2Cp_2(\mu\text{-}PPh_2)_2(NO)_2]$. In contrast, the analogous reactions of monocarbonyl $[W_2Cp_2(\mu\text{-}PPh_2)_2(\mu\text{-}CO)]$ yielded either *trans*-$[W_2Cp_2(\mu\text{-}PPh_2)_2(NO)_2]$ or the nitrito complex $[W_2Cp_2(\mu\text{-}PPh_2)_2(ONO)(CO)(NO)]$ (W−W = 2.9797(4) Å), depending on experimental conditions, with the latter presumably arising from reaction with trace amounts of oxygen in the medium. The stereoselectivity of the above reactions can be rationalized by assuming the participation of 33-electron $[W_2Cp_2(\mu\text{-}PPh_2)_2(CO)(NO)]$ intermediates which rapidly add a second molecule of NO *via* η^2-C_5H_5 intermediates to eventually yield the corresponding dinitrosyls with inversion of the stereochemistry at the dimetal center, as supported by density functional theory (DFT) calculations. The nitrito complex was thermally unstable and evolved through oxygen transfer either to the carbonyl ligand, to yield the above dinitrosyls with release of CO_2, or to the phosphide ligand, to give the phosphinito derivative *cis*-$[W_2Cp_2(\mu\text{-}OPPh_2)(\mu\text{-}PPh_2)(NO)_2]$, depending on experimental conditions. According to DFT calculations, the first process would involve transient dissociation/recombination of the nitrite ligand followed by coupling to carbonyl to give an intermediate with a chelate W{*C,N*-C(O)ON(O)} ring. Indeed, the nitrite ligand could be easily removed upon reaction of the nitrito complex with Na(BAr′$_4$), but immediate decomposition also took place to render the electron-precise dicarbonyl $[W_2Cp_2(\mu\text{-}PPh_2)_2(CO)_2(NO)]BAr'_4$ (W−W = 2.9663(3) Å) as the unique product (Ar′ = 3,5-$C_6H_3(CF_3)_2$). Attempts to decarbonylate the latter complex photochemically yielded instead the oxo derivatives *cis*- and *trans*-$[W_2Cp_2(\mu\text{-}PPh_2)_2(O)(NO)]BAr'_4$ as the only isolable products (W−W = 2.980(2) and 3.0077(3) Å, respectively).

■ INTRODUCTION

Nitric oxide is a major atmospheric pollutant requiring catalytic abatement,[1,2] but also a fascinating ligand able to coordinate to transition-metal atoms (M) in many different ways to form an enormous variety of coordination and organometallic complexes,[3] and moreover a molecule with relevant activity in living organisms, a role strongly related with its interaction with metal complexes.[3,4] Dissociation of the M−NO bond is particularly relevant for the *in situ* liberation of this biologically active molecule. In contrast, the activation and eventual cleavage of the strong N−O bond is the matter of interest when facing possible applications related to the catalytic abatement of this molecule. Most of the work in the latter area has been concentrated so far in the use of heterogeneous catalysts, which indeed can be quite efficient. However, after decades of extensive research, the search for more efficient, cheaper, durable, and environmentally friendly catalysts continues.[5] Binuclear complexes having metal−metal multiple bonds have highly reactive dimetal sites with significant and tunable electronic and coordinative unsaturation, and thus can be considered as the simplest (if crude) molecular models of metal surfaces, but relatively little work has been carried out so far to explore their potential in the activation of nitrogen oxides.

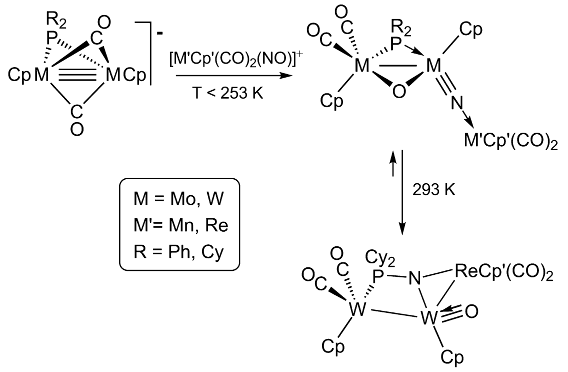
Among organometallic species, only a few complexes with metal−metal multiple bonds have been reacted with NO so far. The 32-electron dihydride complexes $[W_2L_2(\mu\text{-}H)_2(CO)_4]$ (L = η^5-C_5H_5 or Cp, C_5Me_5 or Cp*) and $[Mn_2(\mu\text{-}H)_2(CO)_6(\mu\text{-}L'_2)]$ (L'_2 = $Ph_2PCH_2PPh_2$, $(OEt)_2POP(OEt)_2$) reacted rapidly with NO, but just to give nitrosyl derivatives after displacement of H_2 and CO.[6,7] In contrast, an unusual nitrosyl dimerization takes place in the reaction of NO with the isoelectronic hydrides $[Ru_2(\mu\text{-}H)(\mu\text{-}P^tBu_2)(CO)_4(\mu\text{-}Ph_2PXPPh_2)]$ (X = CR_2, NR) to give hyponitrite derivatives which eventually release N_2O upon protonation and heating.[8] In the absence of bridging ligands, a metal−metal triple bond is likely to be fully cleaved by NO (rather than the opposite), as shown by reactions of the latter with tetracarbonyls $[M_2Cp^*_2(CO)_4]$ (M = Cr, Mo) to give the corresponding mononuclear nitrosyls $[MCp^*(CO)_2(NO)]$.[9] We have recently studied reactions of

Received: March 3, 2014
Published: April 16, 2014

dx.doi.org/10.1021/ic500498k | *Inorg. Chem.* 2014, 53, 4739−4750

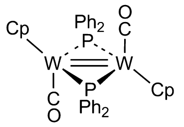
NO with the 30-electron hydrocarbyl-bridged complexes $[Mo_2Cp_2(\mu\text{-}PCy_2)(\mu\text{-}R)(CO)_2]$ (R = Me, CH_2Ph, Ph). In that case, the presence of the bridging dicyclohexylphosphido ligand expectedly suppressed the cleavage of the dimetal unit, but no activation of nitric oxide was observed, just carbonyl displacement to give different dinitrosyl derivatives.[10] Interestingly, however, we also found that the isoelectronic anions $[M_2Cp_2(\mu\text{-}PR_2)(\mu\text{-}CO)_2]^-$ (R = Ph, M= Mo;[11] R = Cy, M = Mo, W)[12] are able to cleave the N−O bond of a *metal-bound* nitrosyl at quite low temperatures to give the corresponding oxo nitride derivatives, with the latter being involved (when M = W and M′ = Re) in a very unusual P−N bond formation and cleavage equilibrium (Scheme 1). Finally, some complexes having quintuple Cr−Cr bonds have been shown recently to cleave N_2O,[13] or to induce disproportionation of NO into coordinated NO_2 and N_2O,[14] in both cases with full cleavage of the intermetallic bond.

Scheme 1



Aimed by the above precedents, we decided to further explore the potential of unsaturated cyclopentadienyl complexes for N−O bond activation by examining reactions of the diphenylphosphido-bridged ditungsten compounds $[W_2Cp_2(\mu\text{-}PPh_2)_2(CO)_2]$ (**1**) and $[W_2Cp_2(\mu\text{-}PPh_2)_2(\mu\text{-}CO)]$ (**2**) (Chart 1)[15] with nitric oxide, which is the subject of the present Article. As it will be shown, although N−O bond cleavage processes were not detected, a strong activation toward oxidation was observed, to yield a nitrito derivative eventually evolving through intramolecular oxygen-transfer to either carbonyl or phosphido ligands, then giving nitrosyl derivatives. Moreover, a strong steroselectivity in CO displacement by NO was observed in these reactions, a process enabled by an unusual and reversible η^5/η^2 haptotropic shift of the cyclopentadienyl ligand, according to DFT calculations.

Chart 1



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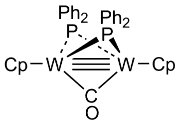

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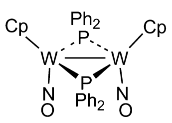
■ RESULTS AND DISCUSSION

Reactions of Compounds 1 and 2 with NO. The dicarbonyl complex **1** reacts rapidly with NO (5% in N_2) at 273 K to give selectively the *cis*-dinitrosyl derivative *cis*-$[W_2Cp_2(\mu\text{-}PPh_2)_2(NO)_2]$ (**3**) in high yield (Chart 2). This complex is analogous to the pentamethylcyclopentadienyl complexes *cis*-$[M_2Cp^*_2(\mu\text{-}PPhR)_2(NO)_2]$ (M = Mo, W; R = Ph, H) prepared previously by Legzdins et al. in modest yield (ca. 15%) from the reactions of $[MCp^*Cl_2(NO)]$ with LiPPhR (Mo−Mo = 3.099(2) Å when R = H).[16]

Chart 2



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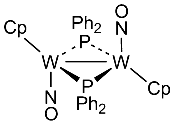

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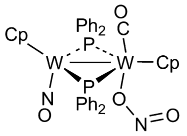


5

In contrast, reactions of the monocarbonyl complex **2** with NO (5% in N_2) were somewhat slower and, above all, more difficult to reproduce, since they could yield either the *trans*-dinitrosyl derivative *trans*-$[W_2Cp_2(\mu\text{-}PPh_2)_2(NO)_2]$ (**4**) or the nitrito complex $[W_2Cp_2(\mu\text{-}PPh_2)_2(ONO)(CO)(NO)]$ (**5**) as major products, or a mixture of both, depending on experimental conditions (Chart 2). Best yields of dinitrosyl **4** were obtained when gently bubbling NO through dichloromethane solutions of the triply bonded complex at 273 K, while best yields of the nitrito **5** were obtained with a strong bubbling of the gas at 223 K. Compound **5** in turn is thermally unstable above ca. 283 K, and it evolves to different products depending on experimental conditions, a matter to be discussed later on.

The appearance of the nitrito ligand in **5** might be due to disproportionation of NO during reaction (3NO → N_2O + NO_2), as postulated for the reactions of the quintuply bonded dichromium complex mentioned above,[14] or to the presence of trace amounts of O_2 in the reaction medium that would rapidly oxidize either the free or metal-bound molecule ($NO + {}^1/_2O_2 \rightarrow NO_2$). A separate reaction of **2** with NO carried out at 223 K in a closed vessel after condensing the gas at ca. 77 K gave a solution of **5** with only trace amounts of N_2O dissolved, as determined from the very weak intensity of its characteristic IR band at ca. 2223 cm^{-1}. This excludes NO disproportion as the main source of the nitrito ligand in our case, which then is attributed to the presence of trace amounts of O_2 (or NO_2) in the gas mixture, a proposal consistent with the increased yield of **5** observed when thoroughly bubbling the gas through the cold solution. On purpose reaction of **2** with a mixture of air and NO (therefore containing large amounts of NO_2), however, led to extensive decomposition and formation of oxo complexes comparable to compounds **8** and **9** (presumably the corresponding nitrite salts, see below), as revealed by another separate experiment.

Solution Structure of Dinitrosyl Complexes 3 and 4. The ^{31}P NMR spectra of isomers **3** and **4** display a resonance at ca. 120 ppm, strongly coupled to two equivalent W atoms (J_{PW} ca. 340 Hz) in each case (Table 1). In agreement with this, their NMR spectra exhibit a single resonance for the Cp ligands. Both complexes give rise to two N−O stretching bands at around 1600 cm^{-1}, corresponding to terminal N−O stretches, and their relative intensity allows their unequivocal

Table 1. Selected IR[a] and $^{31}P\{^1H\}$ NMR Data[b] for New Compounds

compd	ν(NO)	δ_P (J_{PW})
cis-$[W_2Cp_2(\mu\text{-}PPh_2)_2(NO)_2]$ (**3**)	1625 (vs), 1584 (w)	119.6 (337)
trans-$[W_2Cp_2(\mu\text{-}PPh_2)_2(NO)_2]$ (**4**)	1581 (m), 1552 (vs)	122.2 (342)
$[W_2Cp_2(\mu\text{-}PPh_2)_2(ONO)(CO)(NO)]$ (**5**)	1901 (s),[c] 1623 (vs)	76.1 (315, 295)[d]
cis-$[W_2Cp_2(\mu\text{-}OPPh_2)(\mu\text{-}PPh_2)(NO)_2]$ (**6**)	1618 (vs), 1582 (m)	145.5 (301, 289)[e] 62.1 (381)[e]
$[W_2Cp_2(\mu\text{-}PPh_2)_2(CO)_2(NO)]BAr'_4$ (**7**)	2036 (w),[c] 1973 (vs),[c] 1639 (m)	35.6 (305, 224)
cis-$[W_2Cp_2(\mu\text{-}PPh_2)_2(O)(NO)]BAr'_4$ (**8**)	1690 (vs)	111.4 (347, 320)
cis-$[W_2Cp_2(\mu\text{-}PPh_2)_2(O)(NO)]BF_4$ (**8′**)	1682 (vs)	109.6 (346, 320)
trans-$[W_2Cp_2(\mu\text{-}PPh_2)_2(O)(NO)]BAr'_4$ (**9**)	1649 (vs)	117.8 (344, 317)

[a] Recorded in dichloromethane solution, with N−O stretching bands [ν(NO)] in cm^{-1}. [b] Recorded in CD_2Cl_2 at 121.50 MHz and 298 K, with $^{31}P-^{183}W$ coupling constants (J_{PW}) in Hz. [c] C−O stretching band. [d] Averaged spectrum, mainly corresponding to the nitrito isomer; for low-temperature data of nitrito and nitro isomers see the Experimental Section. [e] Doublet resonance, J_{PP} = 20 Hz.

identification as *cis* (strong and weak, in order of decreasing frequencies) and *trans* (weak and strong) dinitrosyl isomers, respectively, by following the same trends established for $M_2(CO)_2$ oscillators.[3,17,18] For comparison, the *cis*-dinitrosyl complex $[W_2Cp^*_2(\mu\text{-}PPh_2)_2(NO)_2]$ displayed N−O stretches at 1604 (vs) and 1557 (w) cm^{-1},[16] while the *trans*-dinitrosyl acyl complex $[Mo_2Cp_2(\mu\text{-}PCy_2)\{\mu\text{-}C(O)Me\}(NO)_2]$ displayed bands at 1610 (w) and 1578 (vs) cm^{-1}.[10]

Further support for the structural identification of isomers **3** and **4** was obtained through density functional calculations (DFT) of these molecules (Figure 1; see the Experimental Section and Supporting Information for details),[19] that yielded energy minima with geometrical parameters comparable to those of related complexes of type $[M_2Cp_2(\mu\text{-}X)(\mu\text{-}Y)(NO)_2]$ (M = Mo, W; X, Y = 3-electron ligand) structurally characterized previously through diffraction methods (most of them with a *trans* geometry).[10,16,20] The computed intermetallic distance for both molecules is around 3.10 Å, which is consistent with the single intermetallic bond to be formulated for these isomers according to the EAN formalism (cf. 2.91−3.10 Å experimentally determined in the mentioned complexes). Apart from their different conformation, other geometrical parameters of these isomers were comparable to each other. A slight distortion of the Cp ligands can be appreciated in both cases, with the carbon atoms placed *trans* to the NO groups displaying W−C distances ca. 0.1 Å longer, an effect that can be identified with the strong *trans* influence of the nitrosyl ligand. Finally, we note that the *trans* isomer **4** was computed to be substantially more stable (by 60 kJ/mol in the gas phase) than the *cis* isomer **3**. Yet, no isomerization of **3** into **4** was observed in solution, even in refluxing toluene, as shown by separate experiments.

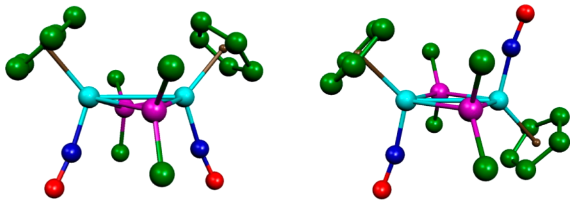


Figure 1. DFT-optimized structures of isomers **3** (left) and **4** (right), with H atoms and Ph groups (except their C^1 atoms) omitted for clarity. Selected bond lengths (Å) for **3**: W−W = 3.110; W−N = 1.794; N−O = 1.199; W−P = 2.447, 2.455; W−Cp(centroid) = 2.079; W−W−N = ca. 108°. Selected bond lengths for **4**: W−W = 3.095; W−N = 1.789; N−O = 1.211; W−P = 2.443, 2.444; W−Cp(centroid) = 2.079; W−W−N = ca. 101°.

Solid-State and Solution Structure of Compound 5. The structure of **5** (Figure 2 and Table 2) is built up from WCp fragments bridged by two diphenylphosphido ligands defining a flat W_2P_2 central skeleton. The metal atoms complete their coordination spheres with a terminal nitrosyl (at W1) and transoid carbonyl and nitrito ligands (at W2), the carbonyl and nitrosyl ligands being placed at opposite sides of the W_2P_2 plane. A metal−metal single bond should be formulated for this 34-electron complex, which is in agreement with the intermetallic length of 2.9797(4) Å, within the range of observed distances for the electron-precise $[M_2Cp_2(\mu\text{-}X)(\mu\text{-}Y)(NO)_2]$ complexes mentioned above.

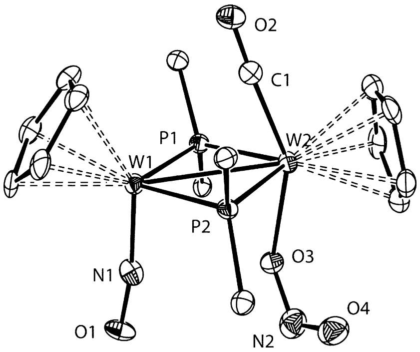


Figure 2. ORTEP diagram (30% probability) of compound **5** with H atoms and Ph groups (except their C^1 atoms) omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Compound 5

W1−W2	2.9797(4)	W1−P1−W2	75.32(4)
W1−P1	2.4517(14)	W1−P2−W2	75.52(4)
W1−P2	2.4424(15)	W1−N1−O1	171.2(5)
W2−P1	2.4251(15)	W2−C1−O2	176.9(6)
W2−P2	2.4233(14)	W2−O3−N2	133.7(5)
W1−N1	1.795(6)	O3−N2−O4	115.7(7)
W2−C1	1.973(7)	C1−W2−P1	81.6(2)
W2−O3	2.183(5)	C1−W2−P2	80.6(2)
N1−O1	1.209(7)	C1−W2−O3	150.8(2)
C1−O2	1.167(8)	C1−W2−W1	73.7(2)
O3−N2	1.283(8)	O3−W2−W1	77.7(1)
N2−O4	1.198(9)	N1−W1−W2	98.4(2)

The most remarkable feature in the structure of **5** is the presence of an O-bound nitrite anion and its extreme transoid positioning relative to the carbonyl ligand, with a very large O−W−C angle of ca. 151°, to be compared with the values of around 120° usually observed for transoid ligands in four-legged piano stool structures of the group 6 metals. This unusual geometrical arrangement is expected to cause a strong weakening in the W−O(nitrito) bond, due to the large *trans* influence of the carbonyl ligand. Indeed, the nitrito ligand of **5** is easily decoordinated, as will be discussed later on. Moreover, the W2−O3 length of 2.183(5) Å must be considered as relatively elongated. Unfortunately, only a few nitrito complexes that can be used for comparison have been characterized structurally so far. Even if nitrito complexes are well-known in classical coordination chemistry, they are a rarity in the family of metal−metal bonded compounds or in that of the cyclopentadienyl complexes, with the Mo cluster $(PPh_4)_2[Mo_6(\mu_3\text{-Cl})_6(ONO)_6]$,[21] and the chromium complex $[CrCp(NO)_2(ONO)]$,[22] apparently being the unique compounds structurally characterized so far within these families.[23] In any case, the W−O length in **5** indeed is significantly longer than the values of ca. 2.11 Å measured in the mentioned Mo_6 cluster, and substantially longer than the values determined in related W_2 complexes having anionic O-donors not involved in *trans* competition with carbonyl ligands (cf. 2.07 Å in the catechodiolate complex $[W_2Cp_2(\mu\text{-PPh}_2)_2(O,O'\text{-}O_2C_6H_4)(CO)]$).[24]

Spectroscopic data in solution for **5** are consistent with the retention of the structure present in the crystal lattice. First we note that the nitrite ligand remains bound to the metal in solution, as indicated by a very low electrical conductivity of less than 5 S cm^2 mol^{-1} in acetone solution, while the carbonyl ligand gives rise to an IR band at 1901 cm^{-1} and to a ^{13}C NMR resonance at 224 ppm, as expected for a terminal ligand. The latter resonance appears as a triplet due to coupling with equivalent P nuclei (J_{PC} = 5 Hz), and accordingly, the PPh_2 ligands give rise to a single ^{31}P NMR resonance (δ_P 76.1 ppm). It is somewhat unexpected that this resonance displays comparable couplings to both tungsten atoms (J_{PW} = 315, 295 Hz) in spite of the different coordination numbers of these metal atoms,[25] which we interpret as another indication of the relative weakness of the nitrite coordination.

We recorded low-temperature ^{1}H and ^{31}P NMR spectra of **5** in search for dynamic processes. Although the ^{1}H NMR spectra showed no significant changes (except for a progressive broadening of all resonances), the unique ^{31}P resonance at ca. 76 ppm broadened upon cooling, and split reversibly below ca. 173 K in two resonances at ca. 79.9 and 76.5 ppm, with 5:1 relative intensities at 163 K. We identify the corresponding species respectively as the nitrito (major) and nitro (minor) isomers of this compound, with the former one being dominant both in solution and in the solid state. In agreement with this, DFT calculations indicate that the nitrito isomer **5** is somewhat more stable (by 15 kJ/mol in dichloromethane solution) than its nitro isomer (**5-N**, Figure 3 and Supporting Information), perhaps because of steric constraints in the latter which would preclude an optimal approach of the N atom to the metal center, a hypothesis supported by the rather large W−N separation of 2.302 Å (cf. 2.189(11) Å in $(PPh_4)[W(N\text{-}NO_2)(CO)_5]$).[26] Similar energetic differences have been recently computed for nitrito and nitro isomers of $[MoL_3(NO_2)]$ complexes (L_3 = triamide ligands), also revealing low kinetic barriers for the conversion between the different linkage isomers of the nitrite ligand.[27]

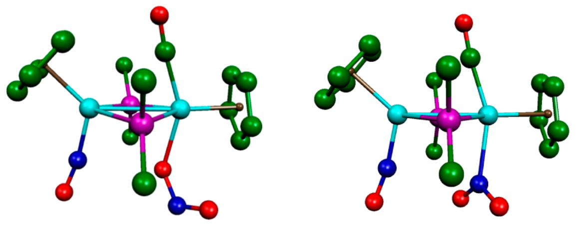


Figure 3. DFT-optimized structures of isomers **5** (left) and **5-N** (right), with H atoms and Ph groups (except their C^1 atoms) omitted for clarity. Selected bond lengths (Å) for **5**: W−W = 3.019; W−N = 1.792; W−P = 2.469−2.488; W−CO = 1.989; W−O = 2.184; WO−NO = 1.322; WON−O = 1.214; C−W−O = 149.8°. Selected bond lengths for **5-N**: W−W = 3.000; W−NO = 1.794; W−P = 2.466−2.484; W−CO = 1.990; W−NO_2 = 2.302; O−NO = 1.233, 1.241; C−W−N = 154.9°.

Stereoselectivity in the Reactions of 1 and 2 with NO. We have investigated the selective formation of either *cis* or *trans* dinitrosyl complexes with the help of DFT calculations on some of the critical steps (see the Experimental Section and Supporting Information). We have previously shown that carbonylation reactions of the triply bonded **2** and related complexes is initiated by coordination of CO to the metal site through the less congested region of the molecule (between CO and PR_2 bridging ligands) to give *cis*-dicarbonyl intermediates.[15] In the same way, we expect that addition of NO to compound **2** gives first a radical intermediate $[W_2Cp_2(\mu\text{-PPh}_2)_2(CO)(NO)]$ (**A**) with a *cis* arrangement of NO and CO ligands, in a process computed to be strongly favored thermodynamically (156 kJ/mol below reagents, Figure 4). This would occur almost barrierless, as we have failed to find the corresponding transition state. An analysis of the spin density in **A** reveals a strong localization of the unpaired electron on the carbonyl-bearing W atom (Mulliken spin density 0.67*e*), thus justifying the attack of the second NO molecule at that atom to yield a diamagnetic derivative. The latter proceeds opposite to the carbonyl though the transition state **TS1** to give an intermediate **B** having an η^2-bound cyclopentadienyl ligand that thus accommodates the added 3-electron donor nitrosyl. This step would provide the overall and relatively low kinetic barrier (54 kJ/mol) for the strongly exergonic formation of **4** (overall Gibbs free energy −292 kJ/mol). Intermediate **B**, which displays almost perfect trigonal bipyramidal geometry, then proceeds with a low barrier through transition state **TS2** by slipping the Cp ligand back to the η^5-mode with simultaneous displacement of CO, thus yielding the *trans* dinitrosyl complex **4** in a natural way. We should note that haptotropic shifts in cyclopentadienyl complexes induced by the addition of ligands are well-documented phenomena, although they usually involve η^5/η^3 or η^5/η^1 rearrangements, and frequently are reversible.[28] The η^5/η^2 rearrangement occurring in the formation of **2** obviously is derived from the need of the dimetal substrate to accommodate a 3-electron donor in an associative step, and it is facilitated by the fact that it requires no ring folding. In fact, recent calculations on the haptotropic shifts of cyclopentadienyl ligands during reactions involving the addition of 2-electron donors to mononuclear complexes suggest that, even in those cases, intermediates with η^2-Cp rings are favored over η^3-Cp ones because ring folding is thus avoided.[29]

To understand the selective formation of *cis*-dinitrosyl **3** in the reaction of *trans*-dicarbonyl **1** with NO we must recall that addition of a ligand (L) to this sort of unsaturated complexes is expected to take place easily and *cis* to one of the carbonyls to give electron-precise derivatives of type $[M_2Cp_2(\mu\text{-PR}_2)_2(CO)_2L]$, as observed in the carbonylation reactions of several dimolybdenum complexes of type $[Mo_2Cp_2(\mu\text{-PR}_2)(\mu\text{-X})(CO)_2]$ (X = PR'_2,[15] COMe,[30a] CRCHR′).[30b] Upon addition of NO, compound **1** thus would analogously yield a 35-electron intermediate **C** which rapidly would dissociate a

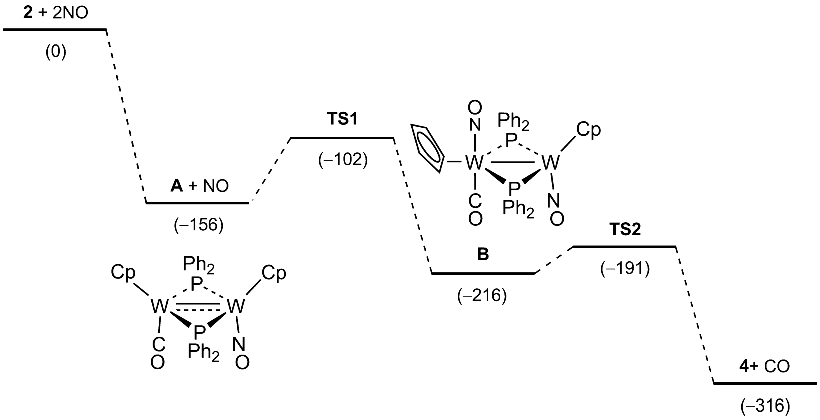
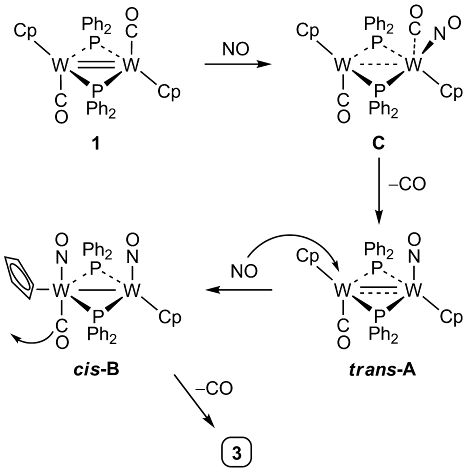


Figure 4. Energy profile for the reaction of **2** with NO, with structural diagrams of intermediates **A** and **B**, and DFT-computed Gibbs free energies relative to reactants in kJ/mol (dichloromethane solution).

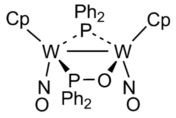
carbonyl ligand to yield a 33-electron intermediate *cis*-[$W_2Cp_2(\mu\text{-}PPh_2)_2(CO)(NO)$] (***trans*-A**) comparable to the intermediate **A** involved in the reactions of **2**, but now with a *trans* arrangement of NO and CO ligands (Scheme 2). Attack of a second molecule of NO would likely occur *trans* to the remaining carbonyl as discussed above, via an η^2-Cp intermediate ***cis*-B**, then leading to the *cis*-dinitrosyl **3** in a natural way.

Scheme 2



Thermal Reactions of the Nitrito Complex 5. In solution, compound **5** decomposes slowly at room temperature through a solvent-dependent process. Dichloromethane solutions of **5** yield 1:1 mixtures of dinitrosyl complexes **3** and **4** after 1 week, and a similar reaction time is required when using tetrahydrofuran as solvent, but then the *cis* dinitrosyl isomer **3** is the very major species formed. In contrast, when a suspension of **5** was stirred in toluene at room temperature, just a small degree of transformation (ca. 10%) was observed after 1 week, and the only new species being formed was the *trans* dinitrosyl **4**. However, temperature modifies drastically the course of this reaction. Thus, when compound **5** is stirred in refluxing toluene, full transformation takes place in 30 min, to give a mixture of the *cis*-dinitrosyl **3** and the new phosphinito complex *cis*-[$W_2Cp_2(\mu\text{-}OPPh_2)(\mu\text{-}PPh_2)(NO)_2$] (**6**), in a ratio of ca. 4:3 (Chart 3). A similar result was obtained when refluxing a tetrahydrofuran solution of **5**, although reaction time was substantially longer as expected, and the relative amount of **6** in the final mixture was slightly higher.

Chart 3



6

The IR spectrum of **6** displays two N−O stretches comparable to those of **3**, thus identifying it as a *cis*-dinitrosyl complex (Table 1). Moreover, the corresponding ^1H and ^{13}C NMR spectra (see the Experimental Section) indicate full inequivalence of Cp and Ph rings in the molecule. In agreement with this, its ^{31}P NMR spectrum displays two weakly coupled resonances, denoting the different environments of both PPh_2 groups. The most deshielded resonance (δ_P 145.5 ppm) displays one-bond P−W couplings with two distinct W atoms, while the second resonance appears much more shielded (δ_P 62.1 ppm) and displays one-bond coupling to just a single W atom, then being assigned to the phosphinito ligand. The chemical shift of the latter is ca. 50 ppm lower than those measured in related phosphinito dimolybdenum complexes,[31] as anticipated from the change in metal, while its coupling to the ^{183}W nucleus (381 Hz) is higher than those of the bridging PPh_2 ligand of the molecule (ca. 300 Hz), as expected when comparing terminal (M−P) with bridging (M−P−M) P-donor ligands.[25]

Pathways in the Nitrite to Nitrosyl Transformations of Compound 5. The nitrite anion is a classical reagent for the synthesis of nitrosyl complexes from suitable carbonyl precursors, a process resulting in O atom transfer from nitrite to a carbonyl ligand with eventual release of CO_2.[3] These reactions are supposed to involve the formation of chelate M{*C*,*N*-C(O)ON(O)} intermediates via nucleophilic attack of nitrite to the carbon atom of a metal-bound carbonyl at some intermediate stage, which in one case has been detected spectroscopically.[32] Alternatively, a metal-bound nitrite ligand also can act as an oxygen-transfer agent via analogous intermediates, as observed in the thermal reaction of the cationic nitro complex [$Fe(CO)_3(NO_2)(PPh_3)_2$]PF_6 to give the nitrosyl derivative [$Fe(CO)_2(NO)(PPh_3)_2$]PF_6.[33] In the case of compound **5**, with a nitrito ligand positioned in *trans* with respect to the unique carbonyl of the molecule, some previous rearrangements are obviously needed to bring the nitrite group

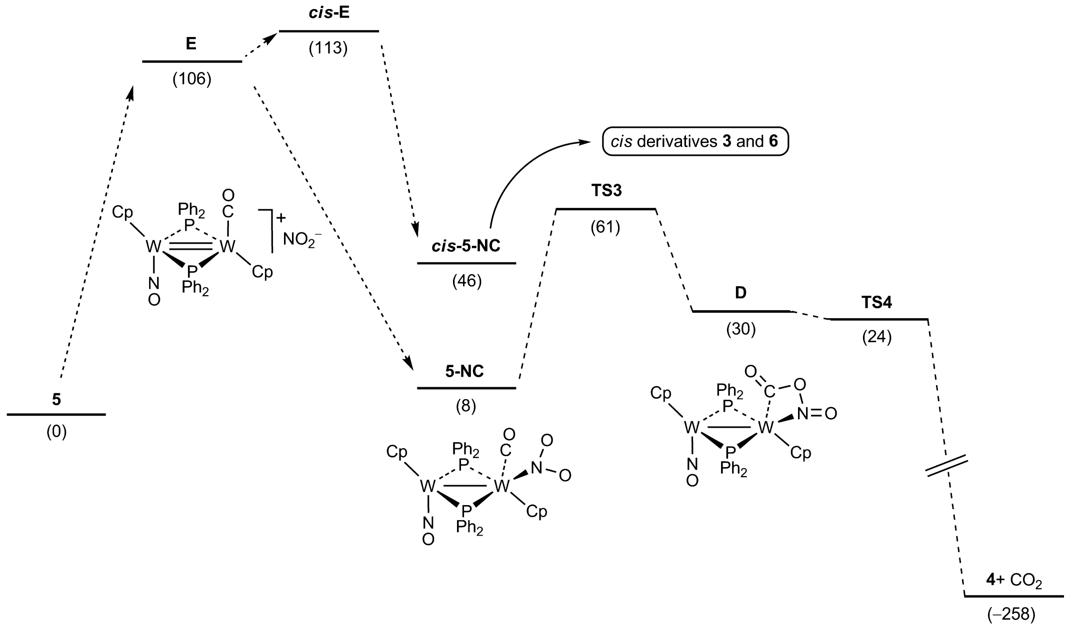


Figure 5. Energy profile for the thermal decomposition of compound **5** in dichloromethane solution, with structural diagrams of intermediates **5-NC**, **D**, and **E**, and DFT-computed Gibbs free energies in kJ/mol relative to **5**.

close to the carbonyl ligand. We have examined likely reaction pathways for the overall transformation of **5** into **4** through DFT calculations (Figure 5; see the Experimental Section and Supporting Information).

First we found that a nitro isomer of **5** with the NO_2 group positioned *cis* with respect to the carbonyl ligand (as required for subsequent O-transfer, **5-NC** in Figure 5) was only 8 kJ/mol more energetic than **5** in dichloromethane solution. This nitro isomer indeed evolves with a low barrier of 53 kJ/mol for coupling to the carbonyl ligand (**TS3**), to yield an intermediate **D** with the expected chelate W{*C*,*N*-C(O)ON(O)} ring. The interatomic distances within that ring are indicative of essentially single bonds (W—C = 2.198, W—N = 2.003, N—O = 1.562, C—O = 1.378 Å), while the exocyclic lengths of 1.209 (C═O) and 1.204 Å (N═O) are indicative of double bonds. Intermediate **D** then evolves almost barrierless for CO_2 dissociation through the transition state **TS4**, to give the *trans*-dinitrosyl **4** and CO_2.[34] The overall process (**5** → **4** + CO_2) is strongly exergonic ($\Delta G = -258$ kJ/mol in dichloromethane solution). However, since the latter reaction takes place slowly at room temperature, then a kinetic barrier of around 100 kJ/mol must be in operation, which obviously must correspond to the rearrangements needed to convert **5** into the cisoid isomer **5-NC**.

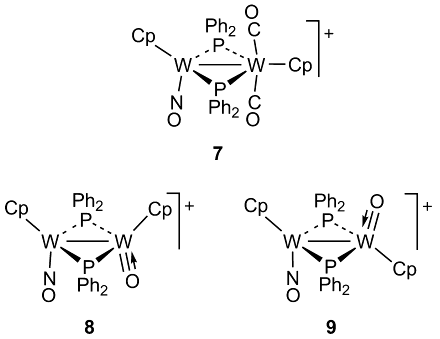
We have found that nitrite dissociation and recombination can account for the experimental kinetic barrier. Indeed, although nitrite dissociation from **5** to yield the unsaturated complex *trans*-$[W_2Cp_2(\mu\text{-}PPh_2)_2(CO)(NO)]NO_2$ (**E**) (W–W = 2.795 Å) is strongly disfavored in the gas phase (by 448 kJ/mol), it becomes affordable in dichloromethane solution (106 kJ/mol), actually matching the expected kinetic barrier. We then propose that **5** rearranges into **5-NC** via a dissociation/recombination process of the nitrite ligand, to eventually yield the *trans*-dinitrosyl **4**. This proposal is consistent with the observation of a very slow decomposition of **5** at room temperature in toluene, a solvent of low dielectric constant disfavoring the formation of charged species.

Formation of the *cis*-dinitrosyl **3** from **5** at room temperature in dichloromethane solution requires a *trans* to *cis* isomerization taking place at some stage of the previous reaction pathway. Although we have not studied this in detail, we note that a *cis* isomer ***cis*-E** of the unsaturated complex **E** is only some 7 kJ/mol less stable either in dichloromethane or in tetrahydrofuran solution. The latter solvent has good donor properties, and might even coordinate to these unsaturated cations thus facilitating this isomerization, which would explain the experimentally observed selective degradation of **5** into the *cis*-dinitrosyl **3** in tetrahydrofuran solution. In any event, nitrite recombination with intermediate ***cis*-E** would naturally yield an intermediate ***cis*-5-NC** (46 kJ/mol above **5**) with close nitro and carbonyl ligands that likely would evolve to the *cis*-dinitrosyl **3** with a low barrier, as discussed above for the *trans* isomer.

The formation of *cis*-dinitrosyl products **3** and **6** when refluxing toluene solutions of compound **5** might be analogously explained by assuming formation of the intermediate ***cis*-5-NC** via the unsaturated ***cis*-E**. In a solvent of low polarity such as toluene, however, nitrite dissociation probably occurs within the solvent cage, and does not proceed beyond a tight ion-pair. Yet, intermediate ***cis*-E** might be favored enough over its *trans* isomer **E** at high temperatures due to its higher entropic content (9 J/mol). At these temperatures, however, it seems that the nitrite ligand can get involved in two competitive O-transfer processes, either to the carbonyl ligand, then eventually yielding **3**, or to one of the phosphido ligands, to give the phosphinito complex **6**. We can quote no precedents for oxygen transfers from coordinated NO_2 to PR_2 ligands, although related O-transfers from added dioxygen,[31,35] or hydroxide,[36] have been reported.

Attempts To Obtain the Unsaturated Nitrosyl Cation $[W_2Cp_2(\mu\text{-}PPh_2)_2(CO)(NO)]^+$. As discussed above, the thermal transformations of **5** can be rationalized by assuming the operation of an energetically unfavorable dissociation of nitrite to yield the unsaturated cation $[W_2Cp_2(\mu\text{-}PPh_2)_2(CO)(NO)]^+$. We then considered the possibility of stabilizing this unstable cation through anion exchange of nitrite with a noncoordinating anion such as the borate $BAr'_4{}^-$ ($Ar' = 3,5\text{-}C_6H_3(CF_3)_2$). Indeed, the addition of $Na(BAr'_4)$ to a dichloromethane solution of **5** at room temperature caused an immediate reaction to occur, presumably caused by the precipitation of $NaNO_2$, but the unsaturated cation thus generated could not be even detected, with the IR and NMR spectra of the solution showing instead the presence of the electron-precise dicarbonyl complex $[W_2Cp_2(\mu\text{-}PPh_2)_2(CO)_2(NO)]BAr'_4$ (**7**) as the unique organometallic complex in the solution (Chart 4), which could be purified and fully characterized in a conventional way. As expected, the yield of **7** could be increased moderately by carrying out the above reaction under a CO atmosphere.

Chart 4



7

8

9

Attempts to form the putative complex $[W_2Cp_2(\mu\text{-}PPh_2)_2(CO)(NO)]BAr'_4$ through selective decarbonylation of **7** were unsuccessful too. No CO was released upon refluxing dichloroethane or toluene solutions of **7**, while photolysis of tetrahydrofuran solutions of this complex gave instead the oxo nitrosyl derivatives *cis*-$[W_2Cp_2(\mu\text{-}PPh_2)_2(O)(NO)]BAr'_4$ (**8**) and *trans*-$[W_2Cp_2(\mu\text{-}PPh_2)_2(O)(NO)]BAr'_4$ (**9**) as major products, along with small amounts of other uncharacterized species. A separate experiment revealed that compound **7** was not particularly air-sensitive itself, since its dichloromethane solutions could be stirred in the open air for several hours without noticeable decomposition. It is then concluded that photolysis of **7** likely forms significant amounts of the sought unsaturated cation which, being extremely air-sensitive, rapidly reacts with trace amounts of oxygen present in the reaction mixture, to give the corresponding oxo derivatives.

The structure of the cation in complexes **8** and **9** is comparable to that of the molybdenum complexes prepared some years ago by Mays and co-workers through the reaction of the oxo carbonyl complexes *trans*-$[Mo_2L_2(\mu\text{-}PPh_2)_2(O)(CO)]$ (L = Cp, $C_5H_4CO_2Me$), with $[NO]BF_4$.[37] Indeed, that synthetic procedure also is effective for our ditungsten substrates. Thus, reaction of the oxo complex *cis*-$[W_2Cp_2(\mu\text{-}PPh_2)_2(O)(CO)]$,[38] with $[NO]BF_4$ in dichloromethane solution, gave with good yield the tetrafluoroborate salt *cis*-$[W_2Cp_2(\mu\text{-}PPh_2)_2(O)(NO)]BF_4$ (**8′**) with retention of the overall cisoid stereochemistry of the dimetal substrate, as also found for the mentioned molybdenum complexes. Spectroscopic data for **8′** were comparable to those of the borate salt **8** (Table 1 and Experimental Section) and will not be further discussed.

Structure of Compound 7. The structure of the cation of **7** in the crystal (Figure 6 and Table 3) is very similar to that of the nitrito complex **5** after just replacing the NO_2 ligand with a carbonyl. This leaves two carbonyl ligands strongly opposed to each other, with an unusually large angle (for a four-legged piano stool geometry) of 148.5(2)°. As a result of this geometrical arrangement, the carbonyls are expected to exert a strong *trans* influence to each other, in agreement with the rather elongated W−C lengths of ca. 2.05 Å (cf. 1.97 Å in **5**), a circumstance also affecting the spectroscopic properties of these ligands, discussed below. Other geometrical parameters in this electron-precise complex (W−W = 2.9663(3) Å) are comparable to those in **5** and deserve no further comments.

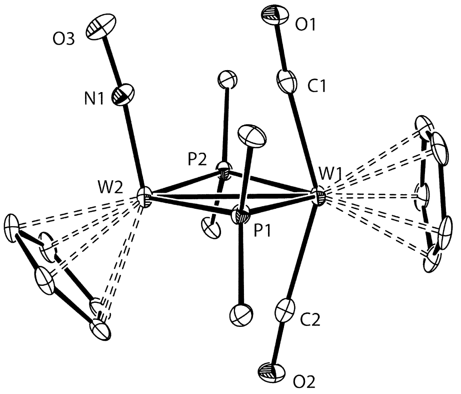


Figure 6. ORTEP diagram (30% probability) of compound **7** with H atoms and Ph groups (except their C^1 atoms) omitted for clarity.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Compound 7

W1−W2	2.9663(3)	W1−P1−W2	74.90(4)
W1−P1	2.440(1)	W1−P2−W2	75.16(4)
W1−P2	2.427(1)	W1−C1−O1	174.9(4)
W2−P1	2.439(1)	W1−C2−O2	175.9(5)
W2−P2	2.436(1)	W2−N1−O3	174.0(4)
W1−C1	2.048(5)	C1−W1−P1	78.5 (2)
W1−C2	2.068(5)	C1−W1−P2	78.3(2)
W2−N1	1.792(4)	C2−W1−P1	81.1(2)
C1−O1	1.143(7)	C2−W1−P2	84.2(2)
C2−O2	1.121(7)	C1−W1−W2	74.1(1)
N1−O3	1.199(6)	C2−W1−W2	74.5(1)
		C1−W1−C2	148.5(2)
		N1−W2−W1	101.7(1)

Spectroscopic data in solution for **7** (Table 1 and Experimental Section) are fully consistent with the structure of the cation found in the solid state. In particular, the transoid arrangement of the carbonyl ligands in this cation is denoted by the appearance of two high-energy C−O stretches, with the symmetric one being of very weak intensity.[17] These ligands give rise to distinct but unusually shielded ^{13}C NMR resonances at 200.2 and 185.2 ppm, which also display coupling to equivalent P atoms as expected. This unusual shielding (cf. δ_C 224.0 ppm for **5**) is likely related to the mutual weakening of the W−C bonds caused by the strongly transoid arrangement of these carbonyls. Finally we note that the P atoms are shielded by some 40 ppm relative to **5** and now display quite different couplings to the inequivalent W nuclei (305 and 224 Hz), with the lower coupling being consistent with the higher coordination number of the $W(CO)_2$ fragment, relative to the W(NO) one.[25]

Structure of Oxo Complexes 8 and 9. The crystals grown for **8** gave diffraction data of poor quality, and we could not refine satisfactorily the structure of this isomer. The main conformation of the molecule, however, could be established beyond doubt, displaying WCp fragments bridged by PPh_2 ligands, and bearing terminal nitrosyl and oxo ligands positioned on the same side of the almost flat W_2P_2 central skeleton (see the Supporting Information). The intermetallic distance of 2.980(2) Å is suggestive of the presence of a metal−metal single bond, a matter to be further discussed later on.

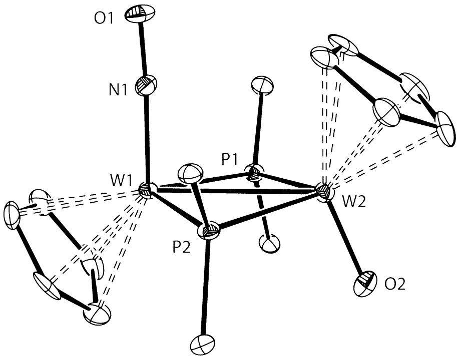


Figure 7. ORTEP diagrams (30% probability) of compound **9** with H atoms and Ph groups (except their C^1 atoms) omitted for clarity.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for Compound 9

W1−W2	3.0077(3)	W1−P1−W2	76.72(3)
W1−P1	2.387(1)	W1−P2−W2	77.13(3)
W1−P2	2.377(1)	W1−N1−O1	176.3(4)
W2−P1	2.459(1)	N1−W1−P1	92.1(1)
W2−P2	2.447(1)	N1−W1−P2	93.4(1)
W1−N1	1.795(4)	O2−W2−P1	101.8(1)
W2−O2	1.689(3)	O2−W2−P2	99.4(1)
N1−O1	1.208(5)	N1−W1−W2	88.3(1)
		O2−W2−W1	112.5(1)

The structure of **9** in the crystal (Figure 7 and Table 4) displays WCp fragments bridged asymmetrically by PPh_2 ligands (closer to W1) and bearing terminal nitrosyl (W1) and oxo (W2) ligands, with the former being placed almost perpendicular to the intermetallic vector and the oxo ligand pointing away from it (W−W−O ca. 113°). Interatomic distances involving the nitrosyl ligand are unremarkable, but the W−O length of the oxo ligand is very short (1.689(3) Å) and indicative of a strong π contribution to the corresponding bond. In agreement with this, the intermetallic length of 3.0077(3) Å is slightly longer than that in the dicarbonyl **7**, to be considered as corresponding to a single metal−metal bond, and there is a considerable lengthening of the W−C distances of the two cyclopentadienyl carbons positioned *trans* to the oxo ligand (ca. 2.45 Å, to be compared with 2.30 Å for the shortest W−C length involving this ring). We have noted previously that the intermetallic bond order in oxo complexes $[Mo_2Cp_2(\mu\text{-}PR_2)(\mu\text{-}X)(O)(CO)]$ (X = 3-electron donor ligand) depends strongly on the donor strength of the oxo ligand, with a formal contribution, affected by the nature of X, anywhere between 2 and 4 electrons. This in turn leads to formal intermetallic bond orders between 2 and 1, respectively.[11,39] Indeed, the intermetallic distances determined so far in complexes $[M_2Cp_2(\mu\text{-}PR_2)(\mu\text{-}X)(O)(CO)]$ span the range 2.80−2.95 Å.[37,39,40] In this context, the intermetallic separations of ca. 3.0 Å in isomers **8** and **9** are still longer, an effect that can be attributed to the presence of both the oxo and the nitrosyl ligand, with the latter providing an additional lengthening effect on the metal−metal bond, due to its excellent π bonding properties.

Spectroscopic data for compounds **8** and **9** are fully consistent with the structures found in the solid state. Both isomers give rise to a single ^{31}P NMR resonance at around 110 ppm, close to those found for dinitrosyls **3** and **4**, but now display couplings to inequivalent W atoms (ca. 350 and 320 Hz), as expected. The terminal nitrosyl ligand in the *cis* isomer **8** gives rise to a N−O stretch of frequency higher than that of the *trans* isomer **9** (1690 vs 1649 cm^{-1}), thus following the same trend observed for carbonyl complexes of type $[Mo_2Cp_2(\mu\text{-}PR_2)(\mu\text{-}X)(O)(CO)]$,[39,40a] while the presence of the terminal oxo ligand is denoted in the solid-state IR spectra by the appearance of a medium-intensity band at ca. 950 cm^{-1} in each case. Other spectroscopic features of these isomers are as expected and deserve no further comments.

■ CONCLUSION

The unsaturated complexes **1** and **2** react with NO with high stereoselectivity, to give, respectively, *cis*- and *trans*-dinitrosyl complexes $[W_2Cp_2(\mu\text{-}PPh_2)_2(NO)_2]$. This is derived from the transient formation of 33-electron intermediates $[W_2Cp_2(\mu\text{-}PPh_2)_2(CO)(NO)]$ selectively as *trans*- and *cis*-isomers, respectively, which undergo stereochemical inversion upon addition of a second NO molecule *trans* to the carbonyl ligand via an η^2-C_5H_5 intermediate displaying a trigonal bipyramidal local environment, according to our DFT calculations. Trace amounts of oxygen in the reaction of **2** with NO trigger the formation of $[W_2Cp_2(\mu\text{-}PPh_2)_2(ONO)(CO)(NO)]$, a thermally unstable molecule with a nitrito ligand which readily transfers an oxygen atom to either the carbonyl ligand, to yield dinitrosyls $[W_2Cp_2(\mu\text{-}PPh_2)_2(NO)_2]$ and CO_2, or to the phosphido ligand, to give the phosphinito derivative *cis*-$[W_2Cp_2(\mu\text{-}OPPh_2)(\mu\text{-}PPh_2)(NO)_2]$. The first reaction takes place at room temperature via a dissociation/recombination process of the nitrite ligand allowing its approach and coupling to the carbonyl ligand, to yield an intermediate with a chelate W{*C,N*-C(O)ON(O)} ring which then dissociates CO_2, according to our DFT calculations. At higher temperatures, the dissociative process is accompanied by an entropically favored *trans* to *cis* isomerization in the transient unsaturated intermediate $[W_2Cp_2(\mu\text{-}PPh_2)_2(CO)(NO)]^+$, thus explaining the formation of the less stable *cis* neutral isomers under these conditions.

■ EXPERIMENTAL SECTION

General Procedures and Starting Materials. All manipulations and reactions were carried out under a nitrogen (99.995%) atmosphere using standard Schlenk techniques. Solvents were purified according to literature procedures, and distilled prior to use.[41] Compounds *trans*-$[W_2Cp_2(\mu\text{-}PPh_2)_2(CO)_2]$ (**1**),[15] $[W_2Cp_2(\mu\text{-}PPh_2)_2(\mu\text{-}CO)]$ (**2**),[15] *cis*-$[W_2Cp_2(\mu\text{-}PPh_2)_2(O)(CO)]$,[38] and $Na[B\{3,5\text{-}C_6H_3(CF_3)_2\}_4]$($NaBAr'_4$),[42] were prepared as described previously, and all other reagents were obtained from the usual commercial suppliers and used as received, unless otherwise stated. Petroleum ether refers to that fraction distilling in the range 338−343 K. Photochemical experiments were performed using jacketed Pyrex Schlenk tubes, cooled by tap water (ca. 288 K). A 400 W mercury lamp placed ca. 1 cm away from the Schlenk tube was used for these experiments. Chromatographic separations were carried out using jacketed columns refrigerated by tap water (ca. 288 K) or by a closed

2-propanol circuit kept at the desired temperature with a cryostat. Commercial aluminum oxide (activity I, 150 mesh) was degassed under vacuum prior to use. The latter was mixed afterward under nitrogen with the appropriate amount of water to reach the activity desired. IR stretching frequencies of CO ligands and W−O bonds were measured in solution (using CaF_2 windows), in Nujol mulls (using NaCl windows) or in KBr pellets, and are referred to as ν(XO)(solvent), ν(XO)(Nujol), or ν(XO)(KBr), respectively. Nuclear magnetic resonance (NMR) spectra were routinely recorded at 300.13 (^{1}H), 121.50 (^{31}P{^{1}H}), or 75.47 MHz (^{13}C{^{1}H}) at 295 K in CD_2Cl_2 solution unless otherwise stated. Chemical shifts (δ) are given in ppm, relative to internal tetramethylsilane (^{1}H, ^{13}C) or external 85% aqueous H_3PO_4 (^{31}P). Coupling constants (J) are given in Hertz.

Preparation of *cis*-[$W_2Cp_2(\mu$-$PPh_2)_2(NO)_2$] (3). Nitric oxide (5% in N_2) was gently bubbled through a stirred dichloromethane solution (12 mL) of compound **1** (0.050 g, 0.054 mmol) at 273 K for 5 min to give a yellow solution. After removal of the solvent under vacuum, the residue was extracted with dichloromethane/petroleum ether (1:1), and the extracts were filtered through a diatomaceous earth pad. Removal of solvents from the filtrate gave compound **3** as a yellow microcrystalline solid (0.042 g, 83%). Anal. Calcd for $C_{34}H_{30}N_2O_2P_2W_2$: C, 43.99; H, 3.26; N, 3.02. Found: C, 43.54; H, 3.20; N, 2.86. ^{1}H NMR: δ 7.77−6.57 (m, 20H, Ph), 5.32 (s, 10H, Cp).

Preparation of *trans*-[$W_2Cp_2(\mu$-$PPh_2)_2(NO)_2$] (4). Nitric oxide (5% in N_2) was gently bubbled through a stirred dichloromethane solution (30 mL) of compound **2** (0.050 g, 0.056 mmol) at 273 K for 2 h to give a yellow solution. After removal of the solvent under vacuum, the residue was extracted with dichloromethane/petroleum ether (1:2), and the extracts were chromatographed on alumina (activity IV) at 285 K. Elution with dichloromethane/petroleum ether (1:1) gave a yellow fraction yielding, after removal of solvents, compound **4** as a yellow microcrystalline solid (0.040 g, 78%). Anal. Calcd for $C_{34}H_{30}N_2O_2P_2W_2$: C, 43.99; H, 3.26; N, 3.02. Found: C, 43.65; H, 3.21; N, 2.95. ^{1}H NMR: δ 7.60−7.30 (m, 20H, Ph), 5.00 (s, 10H, Cp).

Preparation of [$W_2Cp_2(\mu$-$PPh_2)_2$(ONO)(CO)(NO)] (5). Nitric oxide (5% in N_2) was thoroughly bubbled through a stirred dichloromethane solution (30 mL) of compound **2** (0.050 g, 0.056 mmol) at 223 K for 1 h, to give a red-brown solution. After removal of the solvent under vacuum, the residue was extracted with dichloromethane/petroleum ether (2:1), and the extracts were filtered through a diatomaceous earth pad. Removal of solvents from the filtrate gave compound **5** as an essentially pure brown microcrystalline solid (0.038 g, 71%). The crystals used in the X-ray diffraction study were grown by the slow diffusion of layers of toluene and petroleum ether into a concentrated dichloromethane solution of the complex at 253 K. Anal. Calcd for $C_{35}H_{30}N_2O_4P_2W_2$: C, 43.24; H, 3.11; N, 2.88. Found: C, 42.81; H, 3.15; N, 2.55. ^{1}H NMR (400.13 MHz, 293 K): δ 7.73−7.17 (m, 20H, Ph), 6.00, 5.21 (2s, 2 × 5H, Cp). ^{31}P{^{1}H} NMR (161.98 MHz, 293 K): δ 76.1 (s, J_{PW} = 315, 295). ^{1}H NMR (400.13 MHz, 193 K): δ 7.75−7.25 (m, 20H, Ph), 6.13, 5.22 (2s, 2 × 5H, Cp). ^{31}P{^{1}H} NMR (161.98 MHz, 193 K): δ 77.9 (s, br, J_{PW} ca. 305). ^{1}H NMR (400.13 MHz, 163 K): δ 7.80−7.25 (m, 20H, Ph), 6.19, 5.25 (2s, 2 × 5H, Cp). ^{31}P{^{1}H} NMR (161.98 MHz, 163 K): δ 79.9 (s, br, nitrito isomer), 76.5 (s, br, nitro isomer); ratio nitrito/nitro ca. 5/1. ^{13}C{^{1}H} NMR (75.47 MHz, 293 K): δ 224.0 (t, J_{CP} = 5, WCO), 142.9 (d, J_{CP} = 47, C^1−Ph), 138.4 (d, J_{CP} = 41, C^1−Ph), 135.9 (d, J_{CP} = 11, C^2−Ph), 135.4 (d, J_{CP} = 9, C^2−Ph), 128.9−127.7(m, Ph), 98.2, 90.5 (2s, Cp).

Preparation of *cis*-[$W_2Cp_2(\mu$-$OPPh_2)(\mu$-$PPh_2)(NO)_2$] (6). A toluene solution (15 mL) of compound **5** (0.050 g, 0.052 mmol) was refluxed for 30 min to give a yellow-brown solution. After removal of the solvent under vacuum, the residue was extracted with dichloromethane/petroleum ether (1:1) and the extracts were chromatographed on alumina (activity IV) at 285 K. Elution with the same solvent mixture gave a yellow fraction yielding, after removal of solvents, compound **3** as a yellow microcrystalline solid (0.022 g, 45%). Elution with tetrahydrofuran/petroleum ether (1:1) gave another yellow fraction yielding analogously compound **6** as a yellow microcrystalline solid (0.018 g, 35%). Anal. Calcd for $C_{34}H_{30}N_2O_3P_2W_2$: C, 43.25; H, 3.20; N, 2.97. Found: C, 42.90; H, 3.12; N, 2.74. ^{1}H NMR: δ 7.62−6.98 (m, 20H, Ph), 5.75, 5.13 (2s, 2 × 5H, Cp). ^{13}C{^{1}H} NMR: δ 147.5 (d, J_{CP} = 37, C^1−Ph), 146.3 (d, J_{CP} = 43, C^1−Ph), 142.5 (d, J_{CP} = 53, C^1−Ph), 135.7−128.1 (m, Ph), 100.7, 94.4 (2s, Cp).

Preparation of [$W_2Cp_2(\mu$-$PPh_2)_2(CO)_2$(NO)]BAr′$_4$ (7). Carbon monoxide was gently bubbled for 5 min through to a crude dichloromethane solution (30 mL) of compound **5**, obtained *in situ* at 223 K from compound **1** (0.050 g, 0.056 mmol) as described above. Then solid Na(BAr′$_4$) (0.050 g, 0.056 mmol) was added to the solution, and the mixture was stirred and then allowed to reach room temperature for 30 min, to give a yellow-orange solution. After removal of the solvent under vacuum, the residue was extracted with dichloromethane/petroleum ether (1:2), and the extracts were chromatographed on alumina (activity IV) at 253 K. Elution with dichloromethane/petroleum ether (2:1) gave a yellow fraction yielding, after removal of solvents, compound **7** as a yellow microcrystalline solid (0.048 g, 47%). The crystals used in the X-ray crystallographic study were grown by the slow diffusion of layers of toluene and petroleum ether into a concentrated dichloromethane solution of the complex at 253 K. Anal. Calcd for $C_{68}H_{44}BF_{24}NO_3P_2W_2$: C, 44.91; H, 2.31; N, 0.77. Found: C, 44.92; H, 2.32; N, 0.91. ^{1}H NMR: δ 7.73 (m, 8H, Ar′), 7.56 (m, 4H, Ar′), 7.65−7.30 (m, 20H, Ph), 6.22 (s, 5H, Cp), 5.29 (t, J_{HP} = 1, 5H, Cp). ^{13}C{^{1}H} NMR (100.61 MHz, 223 K): δ 200.2 (t, J_{CP} = 8, WCO), 185.2 (t, J_{CP} = 10, WCO), 162.1 (q, J_{CB} = 50, C^1−Ar′), 137.9 (m, J_{CP}+$J_{CP'}$ = 49, C^1−Ph), 136.0 (m, J_{CP}+$J_{CP'}$ = 44, C^1−Ph), 135.1 (s, C^2−Ar′), 133.9, 133.5 (2false t, J_{CP}+$J_{CP'}$ = 11, C^2−Ph), 131.1, 130.8 (2s, C^4−Ph), 129.8 (false t, J_{CP}+$J_{CP'}$ = 11, C^3−Ph), 129.2 (false t, J_{CP}+$J_{CP'}$ = 12, C^3−Ph), 129.0 (qq, J_{CF} = 32, J_{CB} = 3), 117.9 (septet, J_{CF} = 4, C^4−Ar′), 99.9, 89.5 (2s, Cp).

Preparation of *cis*- and *trans*-[$W_2Cp_2(\mu$-$PPh_2)_2$(O)(NO)]BAr′$_4$ (8 and 9). A tetrahydrofuran solution (15 mL) of compound **7** (0.050 g, 0.027 mmol) was irradiated at 285 K with vis−UV light for 50 min while gently bubbling N_2 (99.9999%) through the solution, to give an orange-greenish solution. After removal of the solvent under vacuum, the residue was extracted with dichloromethane/petroleum ether (1:3), and the extracts were chromatographed on alumina (activity IV) at 285 K. Elution with dichloromethane/petroleum ether (1:1) gave an orange fraction yielding, after removal of solvents, compound **9** as an orange microcrystalline solid (0.007 g, 14%). Elution with dichloromethane/petroleum ether (2:1) gave an orange fraction yielding analogously compound **8** as an orange microcrystalline solid (0.008 g, 17%). The crystals of **9** used for the X-ray diffraction study were grown by the slow diffusion of layers of toluene and petroleum ether into a concentrated dichloromethane solution of the complex at 253 K. Crystals of **8** were grown analogously, but gave diffraction data of poor quality. Data for **8** follow. Anal. Calcd for $C_{66}H_{42}BF_{24}NO_2P_2W_2$: C, 44.57; H, 2.36; N, 0.79. Found: C, 44.90; H, 2.41; N, 0.90. IR (Nujol): 1688 (vs) [ν(NO)], 952 (w, br) [ν(WO)]. ^{1}H NMR: δ 7.72 (m, 8H, Ar′), 7.55 (m, 4H, Ar′), 7.90−6.67 (m, 20H, Ph), 6.04, 5.63 (2s, 2 × 5H, Cp). Data for **9** follow. Anal. Calcd for $C_{66}H_{42}BF_{24}NO_2P_2W_2$: C, 44.57; H, 2.36; N, 0.79. Found: C, 45.02; H, 2.35; N, 0.92. IR (Nujol): 1649 (vs) [ν(NO)], 965 (m) [ν(WO)]. ^{1}H NMR: δ 7.72 (m, 8H, Ar′), 7.55 (m, 4H, Ar′), 7.96−7.34 (m, 20H, Ph), 5.40, 5.37 (2t, J_{HP} = 1, 2 × 5H, Cp).

Preparation of *cis*-[$W_2Cp_2(\mu$-$PPh_2)_2$(O)(NO)]BF_4 (8′). Solid [NO]BF_4 (0.010 g, 0.086 mmol) was added to a dichloromethane solution (15 mL) of *cis*-[$W_2Cp_2(\mu$-$PPh_2)_2$(O)(CO)] (0.050 g, 0.055 mmol) cooled at 273 K, and the mixture was stirred at that temperature for 15 min to give a yellow solution which was filtered through a diatomaceous earth pad. Removal of the solvent from the filtrate gave a yellow residue that was crystallized from dichloromethane/diethyl ether at 253 K to render compound **8′** as an orange microcrystalline solid (0.042 g, 76%). Anal. Calcd for $C_{34}H_{30}BF_4NO_2P_2W_2$: C, 40.79; H, 3.02; N, 1.40. Found: C, 40.35; H, 2.84; N, 1.22. IR (KBr): 1675 (vs) [ν(NO)], 1052 (br, vs) [ν(BF)], 951 (m) [ν(WO)]. ^{1}H NMR: δ 7.90−6.84 (m, 20H, Ph), 6.10, 5.71 (2s, 2 × 5H, Cp).

X-ray Crystal Structure Determination for Compounds 5, 7, and 9. Data collection for these compounds was performed at low

Table 5. Crystal Data for New Compounds

	5	**7**·CH_2Cl_2	**9**·C_7H_8
mol formula	$C_{35}H_{30}N_2O_4P_2W_2$	$C_{69}H_{44}BCl_2F_{24}NO_3P_2W_2$	$C_{73}H_{50}BF_{24}NO_2P_2W_2$
mol wt	972.25	1902.38	1869.59
cryst syst	monoclinic	triclinic	triclinic
space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
radiation (λ, Å)	1.541 84	1.541 84	1.541 84
a, Å	15.0876(3)	11.6012(4)	12.7992(4)
b, Å	11.0682(2)	16.5397(4)	14.3171(3)
c, Å	21.9755(6)	18.9692(3)	19.8093(5)
α, deg	90	81.165(2)	82.575(2)
β, deg	121.608(2)	83.415(2)	76.783(2)
γ, deg	90	76.575(2)	87.726(2)
V, Å^3	3125.35(14)	3486.51(16)	3504.02(16)
Z	4	2	2
calcd density, g cm^{-3}	2.066	1.81	1.772
absorp coeff, mm^{-1}	14.73	8.154	7.405
T, K	118(4)	130(7)	139(3)
θ range (deg)	4.14−68.91	2.77−69.35	3.55−69.32
index ranges (h, k, l)	−17, 17; −13, 9; −26, 24	−14, 13; −19, 20; −17, 22	−15, 15; −7, 17; −23, 23
no. reflns collected	12 033	29 366	31 075
no. indep reflns (R_{int})	5635 (0.041)	12 835 (0.0436)	12 898 (0.0341)
reflns with $I > 2\sigma(I)$	4880	11 323	11 729
R indexes [data with $I > 2\sigma(I)$][a]	R1 = 0.0347, wR2 = 0.088[b]	R1 = 0.0437, wR2 = 0.1129[c]	R1 = 0.0431, wR2 = 0.1098[d]
R indexes (all data)[a]	R1 = 0.0417, wR2 = 0.094[b]	R1 = 0.0495, wR2 = 0.1188[c]	R1 = 0.0472, wR2 = 0.114[d]
GOF	1.062	1.050	1.061
no. restraints/params	0/406	4/928	0/932
$\Delta\rho$(max, min), e Å^{-3}	1.365, −1.744	1.911, −1.906	1.968/− 2.477

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $wR = [\Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w|F_o|^2]^{1/2}$. $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$. [b] $a = 0.0523$, $b = 0.0000$. [c] $a = 0.0661$, $b = 9.2122$. [d] $a = 0.0621$, $b = 12.2283$.

temperature on an Oxford Diffraction Xcalibur Nova single crystal diffractometer, using Cu Kα radiation (λ = 1.5418 Å). Images were collected at a 65 mm (**5**) or 63 mm fixed crystal-detector distance, using the oscillation method, with 1° oscillation and variable exposure time per image (1.2−4.5 s for **5**, 1−1.74 s for **7**, and 1−1.05 s for **9**). Data collection strategy was calculated with the program CrysAlis Pro CCD.[43] Data reduction and cell refinement was performed with the program CrysAlis Pro RED.[43] An empirical absorption correction was applied using the SCALE3 ABSPACK algorithm as implemented in the program CrysAlis Pro RED. Using the program suite WinGX,[44] the structures were solved by Patterson interpretation and phase expansion using SHELXL97,[45] and refined with full-matrix least-squares on F^2 using SHELXL97. For all compounds, all non-hydrogen atoms were refined anisotropically, except those involved in disorder, and all hydrogen atoms were geometrically placed and refined using a riding model. Compound **7** crystallized with a molecule of disordered dichloromethane, in positions which could be satisfactorily refined with 0.5/0.5 occupancy factors while applying some restraints to the C−Cl distances. Two CF_3 groups of the borate anion were also disordered and refined with 0.5/0.5 occupancy factors. Compound **9** crystallized with a molecule of disordered toluene, in positions which could be satisfactorily refined with 0.5/0.5 occupancy factors. Three CF_3 groups of the borate anion were also disordered and refined with 0.55/0.45, 0.5/0.5, and 0.6/0.4 occupancy factors, respectively. Crystallographic data and structure refinement details are collected in Table 5.

Computational Details. All DFT calculations were carried out using the GAUSSIAN03 package,[46] in which the hybrid method B3LYP (UB3LYP for electron-odd species) was used with the Becke three-parameter exchange functional,[47] and the Lee−Yang−Parr correlation functional.[48] An accurate numerical integration grid (99,590) was used for all the calculations via the keyword Int=Ultrafine. Effective core potentials and their associated double-ζ LANL2DZ basis set were used for the metal atoms.[49] The light elements (P, O, C, and H) were described with the 6-31G* basis.[50] Geometry optimizations were performed under no symmetry restrictions, using initial coordinates derived from the X-ray data of compound **5**. Frequency analyses were performed to ensure that all the stationary points were either minima (no negative frequencies) or transition states (one negative frequency). Solvent effects (CH_2Cl_2 and C_4H_8O) were modeled using the polarized-continuum-model of Tomasi and co-workers (PCM),[51] by using the gas-phase optimized structures. The connectivity of the transition states was corroborated by IRC calculations in the forward and backward directions, followed by full optimization of the final points of the IRC calculation.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

CIF file containing full crystallographic data for compounds **5**, **7**, and **9** (CCDC 989248−989250). PDF file containing details of DFT calculations (drawings, atomic coordinates, and energies of compounds **3**−**5**, and some of the isomers, intermediates, and transition states connecting them) and structural data of compound **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank the DGI of Spain for financial support (Project CTQ2012-33187), the Consejería de Educación del Principado de Asturias for a grant (to A.T.), and the European

Commission (Project PERG08-GA-2010-276958). We also thank the CMC of the Universidad de Oviedo for access to computing facilities.

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