Inorganic Chemistry

Article

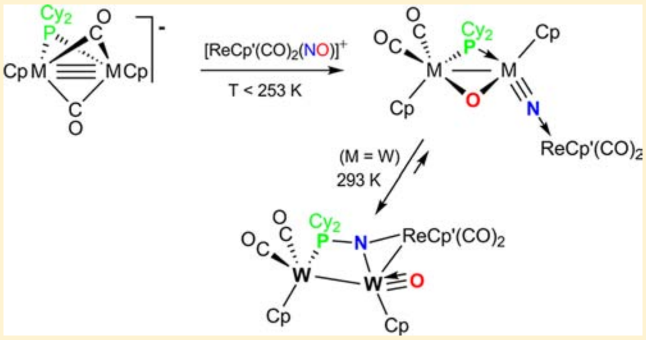
pubs.acs.org/IC

Low-Temperature N−O Bond Cleavage and Reversible N−P Bond Formation Processes in the Reactions of the Unsaturated Anions $[M_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}PCy_2)(\mu\text{-}CO)_2]^-$ (M = Mo, W) with the Nitrosyl Complex $[Re(\eta^5\text{-}C_5H_4Me)(CO)_2(NO)]^+$

M. Angeles Alvarez, M. Esther García, Miguel A. Ruiz,* Adrián Toyos, and M. Fernanda Vega

Departamento de Química Orgánica e Inorgánica/IUQOEM, Universidad de Oviedo, E-33071 Oviedo, Spain

Supporting Information



ABSTRACT: The unsaturated anion $[Mo_2Cp_2(\mu\text{-}PCy_2)(\mu\text{-}CO)_2]^-$ (Na^+ salt) reacted rapidly with $[ReCp'(CO)_2(NO)]BF_4$ in a dichloromethane solution at 253 K to give the oxo nitride tetracarbonyl complex $[Mo_2ReCp_2Cp'(\mu\text{-}N)(\mu\text{-}O)(\mu\text{-}PCy_2)(CO)_4]$ as the major product (Cp = η^5-C_5H_5; Cp′ = η^5-C_5H_4Me). This complex underwent spontaneous decarbonylation at room temperature to give the unsaturated tricarbonyl derivative $[Mo_2ReCp_2Cp'(\mu\text{-}N)(\mu\text{-}O)(\mu\text{-}PCy_2)(CO)_3]$, a very dioxygen-sensitive molecule rapidly evolving upon manipulation to give the dioxo nitride dicarbonyl complex $[Mo_2ReCp_2Cp'(\mu\text{-}N)(\mu\text{-}O)(\mu\text{-}PCy_2)(O)(CO)_2]$ in modest yield. The latter product was obtained as a mixture of isomers, with the major ones differing in the relative arrangement (cis and trans) of their MoCp moieties [Mo−Mo = 2.7707(8) Å in the cis isomer]. The ditungsten anion $[W_2Cp_2(\mu\text{-}PCy_2)(\mu\text{-}CO)_2]^-$ (Na^+ salt) also reacted rapidly with $[ReCp'(CO)_2(NO)]BF_4$ in a dichloromethane solution at 253 K to give an analogous oxo nitride complex, $[W_2ReCp_2Cp'(\mu\text{-}N)(\mu\text{-}O)(\mu\text{-}PCy_2)(CO)_4]$, but instead of releasing CO, this complex undergoes at room temperature a reversible insertion of the nitride ligand into a W−PCy_2 bond, to reach an equilibrium with its phosphinoimido-bridged isomer $[W_2ReCp_2Cp'(\mu_3\text{-}N{:}N{:}P\text{-}NPCy_2)(O)(CO)_4]$, which displays a V-shaped metal core [W−W = 3.0564(7) Å; W−Re = 2.9021(6) Å]. Decarbonylation of this mixture in a refluxing toluene solution led to partial degradation and condensation of these heterometallic species, to give $[ReCp'(CO)_3]$ and the pentanuclear oxo nitride complex $[W_4ReCp_4Cp'(\mu_2\text{-}N)(\mu_3\text{-}N)(\mu\text{-}O)(O)(\mu\text{-}PCy_2)_2(CO)_3]$, a very air-sensitive molecule displaying both linear and trigonal nitride ligands bound to rather unsaturated ditungsten centers [W−W = 2.7246(6) and 2.7900(6) Å].

■ INTRODUCTION

Nitrogen monoxide is a molecule of remarkable chemical behavior and is well-known within the field of coordination chemistry for being able to strongly bind to transition-metal atoms in high and low oxidation states, thus providing a wide diversity of stable coordination and organometallic complexes.[1,2] Besides, this molecule also is one of the important air pollutants requiring catalytic abatement (mainly through reduction or decomposition) from the corresponding effluents (vehicle engines, power stations, nitric acid plants and related industrial facilities, etc.).[3,4] However, after decades of intense research on the matter, mostly on heterogeneous systems, the need persists for more efficient and less expensive catalysts, and this ultimately relies on our ability to control the activation and eventual cleavage of the strong N−O bond of the NO molecule when bound to a metal atom.

The ability of organometallic compounds to cleave the N−O bond of the nitrosyl ligand is known, but the actual transformation of a well-defined nitrosyl complex into a nitride derivative has been observed in a few instances. These may involve a carbonyl cluster (eq 1)[5] or more discrete electron-deficient centers, either binuclear (eq 2)[6] or mononuclear (eq 3) ones.[7] Yet, another reported cleavage process is the abstraction of the O atom of a terminal nitrosyl ligand by a strongly oxophilic complex (eq 4).[8]

$$M_n(NO)(CO)_m \rightarrow M_n(\mu\text{-}N)(CO)_{m-1} + CO_2 \tag{1}$$

$$M(\mu\text{-}NO)M \rightarrow M{\equiv}N{-}M(O) \tag{2}$$

$$M(NO)R \rightarrow M(O)(NR) \tag{3}$$

$$M{-}NO + M' \rightarrow M{\equiv}N + M'(O) \tag{4}$$

Recently, we reported that the reactions of several anionic complexes of the group 6 metals $[MCp(CO)_2L]^-$ (Na^+ or K^+ salts; M = Mo, W; Cp = η^5-C_5H_5; L = CO, $P(OMe)_3$, PPh_3) with the electron-precise nitrosyl cations $[M'Cp'(CO)_2(NO)]^+$ (BF_4^- salts; M′ = Mn, Re; Cp′ = η^5-C_5H_4Me) take place readily

Received: December 13, 2012
Published: March 13, 2013

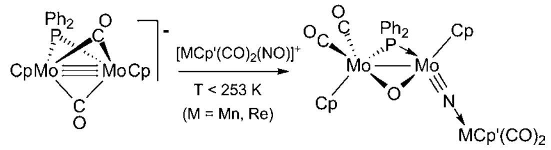
dx.doi.org/10.1021/ic3027489 | Inorg. Chem. 2013, 52, 3942−3952

at low temperatures and lead to the heterometallic nitride-bridged derivatives [MM′CpCp′(μ-N)(CO)$_3$L].[9] A density functional theory (DFT) study revealed that the N−O bond cleavage process yielding the nitride derivative follows from the orbital-controlled nucleophilic attack of the anion to the N atom of the nitrosyl ligand in the cation, eventually releasing CO$_2$ (eq 5).

$$[L_nM(CO)]^- + [ON-M'L'_m]^+ \rightarrow L_nM{\equiv}N-M'L'_m + CO_2 \qquad (5)$$

We then showed that the reactions of the unsaturated anion [Mo$_2$Cp$_2$(μ-PPh$_2$)(μ-CO)$_2$]$^-$ (Na$^+$ salt) with the same nitrosyl cations [M′Cp′(CO)$_2$(NO)]$^+$ also proceeded at low temperature with full cleavage of the nitrosyl N−O bond but now without release of CO$_2$, then yielding the corresponding oxo- and nitride-bridged heterometallic derivatives [Mo$_2$M′Cp$_2$Cp′(μ-N)(μ-O)(μ-PPh$_2$)(CO)$_4$] (Scheme 1).[10]

Scheme 1



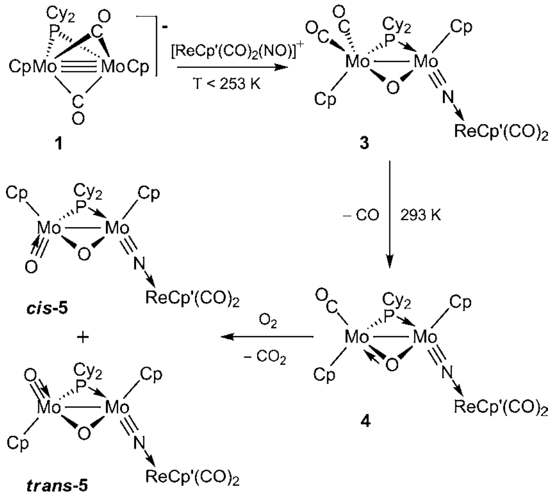
The latter complexes, however, were rather unstable species that would rapidly release CO and react with adventitious oxygen to yield different oxo nitride derivatives. It was thus of interest to examine the influence that the nature of the metal in the unsaturated anion and even that of the bridging phosphide ligand would have on the above N−O bond cleavage processes. To accomplish this, we have now studied the reactions of the same nitrosyl cations [M′Cp′(CO)$_2$(NO)]$^+$ with the Na$^+$ salts of the PCy$_2$-bridged unsaturated anions [M$_2$Cp$_2$(μ-PCy$_2$)(μ-CO)$_2$]$^-$ [M = Mo (**1**), W (**2**)].[11,12] Our previous studies on the general reactivity of these versatile species have revealed that the reactivity of the ditungsten anion **2** differs significantly from that of its dimolybdenum analogue **1**. As will be discussed next, while the influence of the phosphide ligand is quite modest, the metal at the unsaturated anion has a dramatic influence on the outcome of the reactions under study, this allowing inter alia the detection of a reversible and unprecedented P−N bond coupling process between nitride and diorganophosphide ligands.

■ RESULTS AND DISCUSSION

Reactions of the Dimolybdenum Anion 1. The unsaturated compound **1** reacts rapidly with [ReCp′(CO)$_2$(NO)]BF$_4$ in a dichloromethane solution at 253 K to give a brown solution shown by IR and NMR spectroscopy to contain the oxo nitride tetracarbonyl complex [Mo$_2$ReCp$_2$Cp′(μ-N)(μ-O)(μ-PCy$_2$)(CO)$_4$] (**3**) as the major product (Scheme 2).

Compound **3** can be purified through column chromatography and isolated as a solid in the usual way (ca. 60%), as long as the temperature is kept below 253 K. Above this temperature, however, spontaneous decarbonylation takes place to yield the unsaturated tricarbonyl derivative [Mo$_2$ReCp$_2$Cp′(μ-N)(μ-O)(μ-PCy$_2$)(CO)$_3$] (**4**) almost quantitatively. According to the EAN formalism, we might formulate a Mo−Mo double or single bond for this molecule, depending on the electron-donor ability of the bridging O atom, a matter to be addressed later on. We note at this point that the formation of compounds **3** and **4** completely reproduces the behavior of the related PPh$_2$-bridged complexes obtained in the reactions of the anion [Mo$_2$Cp$_2$(μ-PPh$_2$)(μ-CO)$_2$]$^-$.[10] In the latter case, the tricarbonyl analogue of **4** proved to be a very air-sensitive molecule, rapidly transforming into a dioxo nitride derivative displaying a transoid arrangement of the MoCp moieties. Compound **4** behaves analogously indeed, and it progressively evolves upon manipulation (rapidly in the presence of air) to give the dioxo nitride dicarbonyl derivative [Mo$_2$ReCp$_2$Cp′(μ-N)(μ-O)(μ-PCy$_2$)(O)(CO)$_2$] (**5**) in modest yield, presumably with evolution of CO$_2$. However, in contrast with the single isomer obtained for its PPh$_2$-bridged analogue, compound **5** is obtained as a mixture of isomers that could not be separated chromatographically, although there is no evidence of fast interconversion with each other. The major isomers display an O atom bridging the dimolybdenum center, while differing in the relative arrangement (cis and trans) of the MoCp moieties (Scheme 2), with the ratio *cis*-**5**/*trans*-**5** being ca. 1:2. We note that the assignment of the intermetallic bond order in these dioxo nitride complexes again is not straightforward, and this matter will be addressed in light of the structural data to be discussed below. Fortunately, we could obtain small amounts of pure isomers *cis*-**5** or *trans*-**5** by fractional crystallization of the above mixture, thus facilitating the structural characterization of these species.

Scheme 2



The reactions of the anion **1** with the manganese salt [MnCp′(CO)$_2$(NO)]BF$_4$ were much less selective than the one with the Re cation just discussed and led to complex mixtures of products irrespective of the reaction conditions. The major products identified in the corresponding mixtures were the homometallic species [Mn$_2$Cp′$_2$(CO)$_2$(NO)$_2$][13] and [Mo$_2$Cp$_2$(μ-PCy$_2$)(CO)$_3$(NO)],[14] obviously derived from undesired electron- and nitrosyl-transfer processes, respectively. We could also identify the presence of small amounts of a manganese analogue of the dioxo nitride complexes **5**, but this was not further investigated because of the very low yields of heterometallic products formed.

Structural Characterization of the Dioxo Nitride Complex 5. The molecule of the isomer *cis*-**5** in the crystal (Figure 1 and Table 1) is built up from two CpMo fragments arranged in a cisoid conformation and bridged by PCy$_2$ and oxo

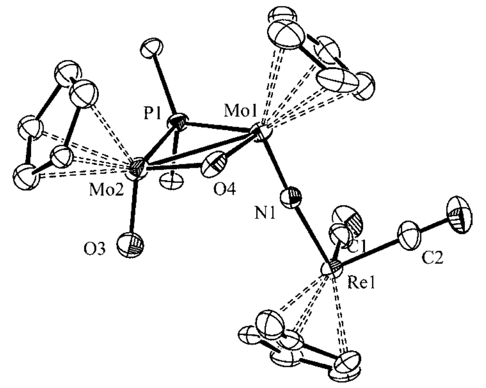


Figure 1. ORTEP diagram (30% probability) of compound *cis*-**5**, with H atoms and Cy groups (except their C^1 atoms) omitted for clarity.

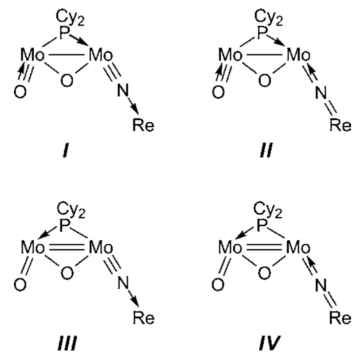
Table 1. Selected Bond Lengths (Å) and Angles (deg) for *cis*-5

Mo1−Mo2	2.7707(8)	Mo1−P1−Mo2	69.97(5)
Mo1−P1	2.383(2)	Mo1−O4−Mo2	91.5(2)
Mo2−P1	2.448(2)	Mo1−Mo2−O3	108.0(2)
Mo1−O4	1.955(5)	Mo2−Mo1−N1	102.3(2)
Mo2−O4	1.913(5)	P1−Mo1−N1	94.0(2)
Mo1−N1	1.743(5)	P1−Mo2−O3	102.4(2)
Mo2−O3	1.693(6)	Mo1−N1−Re1	172.9(3)
Re1−N1	1.971(5)	N1−Re1−C1	90.8(3)
Re1−C1	1.914(10)	N1−Re1−C2	97.6(3)
Re1−C2	1.878(8)	C1−Re1−C2	86.2(4)

ligands. Each metal atom carries out one further ligand, a terminal O atom on Mo2, and a nitride ligand acting as an essentially linear bridge between Mo1 and the ReCp′(CO)$_2$ fragment [Re−N−Mo = 172.9(3)°]. The overall geometrical parameters of *cis*-**5** are very similar to those measured in the PPh$_2$-bridged complex [Mo$_2$ReCp$_2$Cp′(μ-N)(μ-O)(μ-PPh$_2$)(O)(CO)$_2$],[10] except for the different conformation of the CpMo fragments, which in the latter compound is a transoid one. Therefore, a detailed analysis of the different interatomic lengths is not needed. Concerning the nitride ligand, the Mo−N and N−Re lengths of 1.743(5) and 1.971(5) Å, respectively, are comparable not only to the corresponding values in the mentioned PPh$_2$-bridged complex but also to those in the dimetallic nitride-bridged complex [WReCpCp′(μ-N)(CO)$_3${P(OMe)$_3$}] [W−N = 1.81(3) Å; N−Re = 1.97(3) Å].[9] As we noted then, these figures can be considered respectively as slightly longer and significantly shorter than the reference values for triple Mo≡N and single Re−N bonds, and this suggests some delocalization of the π interaction along the Mo−N−Re framework. This can be accounted for by using a combination of the canonical forms of Chart 1, with the latter also differing in the description of the terminal Mo−O interaction.

As for the terminal oxo ligand, we note its very short Mo−O length of 1.693(6) Å, as is usually found in organomolybdenum complexes having terminal oxo ligands, this being, in turn, indicative of the substantial multiplicity in the corresponding Mo−O bonds.[15] According to the EAN formalism, a Mo−Mo double bond might be formulated for compound **5** if considering the terminal O atom as a two-electron donor but a single intermetallic bond if considering it as a four-electron donor (forms III and IV vs forms I and II in Chart 1, respectively). Indeed, the Mo−Mo lengths in *cis*-**5** [2.7707(8) Å] and its PPh$_2$-bridged analogue (2.763(1) Å) are much shorter than the reference single-bond figures usually found in comparable structures (above ca. 2.9 Å) but still are somewhat longer than the reference values for related species having double Mo═Mo bonds, such as [Mo$_2$Cp$_2$(μ-N═CHPh)(μ-PCy$_2$)(CO)$_2$], [2.632(1) Å],[16a] [Mo$_2$Cp$_2$(μ-PCy$_2$)(μ-CCO$_2$Me)(CO)$_2$] [2.656(1) Å],[16b] and [Mo$_2$Cp$_2$(μ-PPh$_2$)$_2$(CO)$_2$] [2.716(1) Å].[17] Therefore. we conclude that the contributions of the canonical forms I−IV to the actual electronic structure of *cis*-**5** are all significant (however, only form I has been used to represent this complex in Scheme 2), thus yielding intermediate Mo−Mo, Mo−O, Mo−N, and Re−N bond orders.

Chart 1



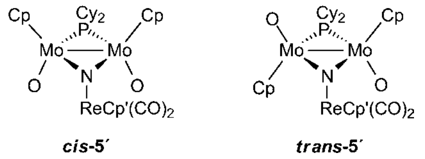
Solution Structure of Compound 5. As noted above, compound **5** is obtained as a mixture of isomers, but this is not reflected in its solution IR spectrum, which displays just two C−O stretches (Table 2), with the anticipated pattern (very strong and strong, in order of decreasing frequencies)[18] for a cisoid M(CO)$_2$ oscillator with a C−M−C angle of just below 90° [cf. 86.2(4)° for *cis*-**5** in the crystal] and with frequencies some 5 cm^{-1} lower than the corresponding values in [Mo$_2$ReCp$_2$Cp′(μ-N)(μ-O)(μ-PPh$_2$)(O)(CO)$_2$] (a molecule comparable to the isomer *trans*-**5**), as expected from the stronger donor properties of the PCy$_2$ (vs PPh$_2$) bridging ligand. The four isomers of compound **5** give rise to similar but separated ^{31}P NMR resonances at δ 201.2 (*cis*-**5**′), 201.0 (*cis*-**5**), 197.4 (*trans*-**5**′), and 197.1 (*trans*-**5**), and they can also be identified through their different proton Cp resonances (see the Experimental Section). The relative ratio estimated from the ^{1}H NMR spectra of the mixture after chromatography was ca. 1:15:2:30. As is also noted above, we could obtain pure crystalline samples of either *cis*-**5** (the one examined through X-ray diffraction) or *trans*-**5**. The stereochemistry in solution of these isomers was confirmed by the observation in the case of *trans*-**5** of a positive nuclear Overhauser enhancement between the Me group of the Cp′ ligand and one of the Cp resonances, while no such enhancement could be detected for *cis*-**5**. For the very minor isomers of type **5**′, however, we could not identify all of the relevant NMR resonances because of their very small relative ratio in all of the spectra, and therefore their nature is not so clear to us at the moment. Yet, by taking into consideration the structure of compound **8** (to be discussed later on), an attractive proposal for these minor isomers is a structure where the bridging oxo ligand and the terminal NReCp′(CO)$_2$ group exchange their positions in either the cis or trans isomers (Chart 2; no bond orders implied in this drawing). As deduced from the spectroscopic data of **8**, this exchange of positions should not modify the chemical shifts of

Table 2. Selected IR^a and $^{31}P\{^1H\}$ NMR^b Data for New Compounds

Compound	ν_{CO}	δ_P [J_{PW}]
Na[$W_2Cp_2(\mu\text{-}PCy_2)(\mu\text{-}CO)_2$] (**2**)^c		152.7 [378]
[$Mo_2ReCp_2Cp'(\mu\text{-}N)(\mu\text{-}O)(\mu\text{-}PCy_2)(CO)_4$] (**3**)	1963 (s), 1897 (vs), 1831 (s)	237.1^d
[$Mo_2ReCp_2Cp'(\mu\text{-}N)(\mu\text{-}O)(\mu\text{-}PCy_2)(CO)_3$] (**4**)	1941 (m), 1896 (vs), 1832 (s)	198.3
cis-[$Mo_2ReCp_2Cp'(\mu\text{-}N)(\mu\text{-}O)(O)(\mu\text{-}PCy_2)(CO)_2$] (*cis*-**5**)	1905 (vs), 1840 (s)	200.9^e
trans-[$Mo_2ReCp_2Cp'(\mu\text{-}N)(\mu\text{-}O)(O)(\mu\text{-}PCy_2)(CO)_2$] (*trans*-**5**)	1901 (vs), 1837 (s)	197.0^e
[$W_2ReCp_2Cp'(\mu\text{-}N)(\mu\text{-}O)(\mu\text{-}PCy_2)(CO)_4$] (**6**)	1951 (s), 1890 (vs), 1821 (s)	165.3 [362, 170]^f
[$W_2ReCp_2Cp'(\mu_3\text{-}N{:}N{:}P\text{-}NPCy_2)(O)(CO)_4$] (**7**)	1945 (s), 1894 (vs), 1881 (s, sh), 1803 (m)	52.1 [277, 57]^g
[$W_4ReCp_4Cp'(\mu_2\text{-}N)(\mu_3\text{-}N)(\mu\text{-}O)(O)(\mu\text{-}PCy_2)_2(CO)_3$] (**8**)	1882 (s), 1814 (vs)	129.6 [411, 379]^h
		112.9 [393, 366]^h

^{a}Recorded in a dichloromethane solution, with C–O stretching bands (ν_{CO}) in cm^{-1}. ^{b}Recorded in CD_2Cl_2 solutions at 290 K and 162.00 MHz (^{31}P) unless otherwise stated; δ in ppm relative to external 85% aqueous H_3PO_4; $J(^{31}P-^{183}W)$ in hertz. ^{c}Data recorded in a $Me_2CO\text{-}d_6$ solution, taken from ref 12. ^{d}Recorded at 233 K. ^{e}Recorded in C_6D_6. ^{f}Recorded at 268 K. ^{g}Recorded at 213 K. ^{h}Recorded in toluene.

Chart 2



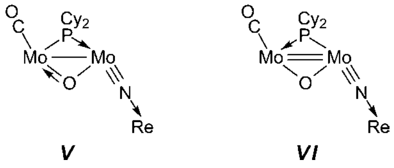
cis-**5′** *trans*-**5′**

the bridging PCy_2 groups to a great extent. Moreover, this proposal is consistent with the chemical equivalence of the Cp groups observed for either *cis*-**5′** (δ_H 5.01) or *trans*-**5′** (δ_H 4.75), the latter meaning that the ReCp′(CO)$_2$ fragment does not disturb at a significant extent the local symmetry at the Mo_2 unit in these molecules.

Structural Characterization of the Oxo Nitride Complexes 3 and 4. The spectroscopic data for these unstable species (Table 2 and the Experimental Section) are closely related to those of the corresponding PPh_2-bridged complexes [$Mo_2ReCp_2Cp'(\mu\text{-}N)(\mu\text{-}O)(\mu\text{-}PPh_2)(CO)_n$] ($n$ = 4, 3) previously reported by us,[10] after allowing for the expected changes upon replacement of the PPh_2 by a PCy_2 ligand (a moderate lowering in the C–O stretching bands and a significant deshielding of ca. 30 ppm in the ^{31}P NMR resonances),[19] and therefore a detailed analysis of the data is not required. Presumably, all of these molecules display a transoid arrangement of the corresponding MoCp moieties. For compound **4**, the presence of a carbonyl ligand terminally bound to molybdenum is denoted by the observation of an additional C–O stretching band at ca. 1940 cm^{-1} in the corresponding IR spectra (in addition to the characteristic bands due to the Re(CO)$_2$Cp′ fragment). As for the tetracarbonyl compound **3**, the presence of a Mo(CO)$_2$ oscillator is not immediately obvious in the IR spectrum, which exhibits just three C–O stretching bands, but is clearly denoted by the appearance of two deshielded resonances at δ 241.3 and 236.5 (apart from those of the Re-bound carbonyls) in the carbonyl region of the ^{13}C NMR spectrum. The very different P–C couplings of these two resonances (27 and ca. 0 Hz, respectively) indicate that both carbonyls must be bound to the same metal atom because this would then lead to very different C–Mo–P angles for these two ligands, a critical structural factor governing the magnitude of two-bond P–C couplings.[20]

According to the EAN formalism, the tetracarbonyl compound **3** is an electron-precise (34-electron) binuclear complex, and a single Mo–Mo bond must be formulated for this molecule. In contrast, the tricarbonyl compound **4** has two fewer electrons, and a Mo–Mo double bond might be formulated for it if we were to consider the bridging O atom as a two-electron donor (as we do for **5**). However, DFT calculations on the PPh_2-bridged analogue of complex **4** revealed that the bridging O atom in that molecule is involved in significant O → Mo π-bonding interaction with the dimetal center, leading to a reduction of the Mo–Mo bond order,[10] and the same presumably applies to compound **4**. As a result, the bonding in these tricarbonyl complexes is better represented by the combination of two extreme canonical forms (V and VI in Chart 3), implying Mo–Mo and Mo–O bond orders intermediate between 1 and 2. Of course, intermediate bond orders are also to be expected for the W–N and Re–N bonds involving the nitride ligand, and this can be represented through additional canonical forms, as discussed for **5** (not shown in Chart 3).

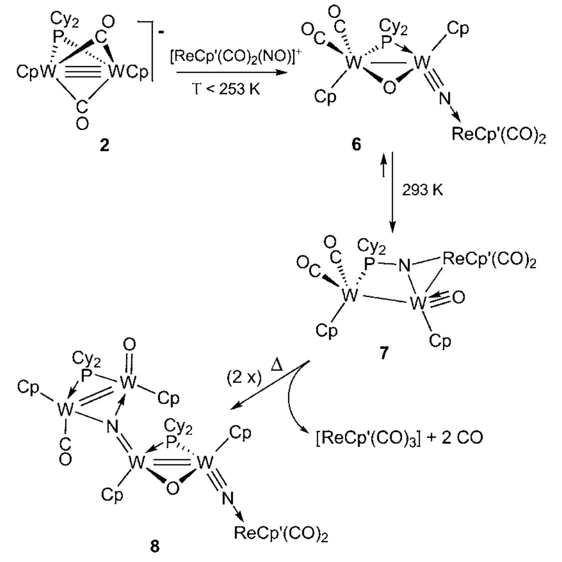
Chart 3



V *VI*

Reactions of the Ditungsten Anion 2. The unsaturated compound **2** reacts rapidly with [ReCp′(CO)$_2$(NO)]BF$_4$ in dichloromethane at 253 K to give a brown solution shown by IR and NMR spectroscopy to contain a mixture of different products, of which the major species eventually present at room temperature are the oxo nitride complex [$W_2ReCp_2Cp'(\mu\text{-}N)(\mu\text{-}O)(\mu\text{-}PCy_2)(CO)_4$] (**6**) and its oxo phosphinoimido isomer [$W_2ReCp_2Cp'(\mu_3\text{-}N{:}N{:}P\text{-}NPCy_2)(O)(CO)_4$] (**7**) (Scheme 3). Other minor species identified spectroscopically in the corresponding reaction mixtures were the known ditungsten complexes [$W_2Cp_2(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_4$] and [$W_2Cp_2(\mu\text{-}I)(\mu\text{-}PCy_2)(CO)_2$], which obviously follow from undesired proton- and electron-transfer side reactions, respectively.[21] The isomers **6** and **7** could be separated by column chromatography at 253 K, but as was the case of the dimolybdenum complex **5**, each of them seems to be accompanied by tiny amounts of a second isomer in each case (**6′** and **7′**) in a equilibrium ratio of ca. 1:10 relative to the major isomer. Independent experiments revealed that their solutions slowly equilibrate at room temperature to reach the same equilibrium ratio **6**/**7** of ca. 1:6 in a dichloromethane solution after ca. 1 h (starting from **7**) or ca. 6 h (from **6**). The

Scheme 3



overall ratios of isomers **6′**/**6**/**7′**/**7** thus reach the values of ca. 1:10:6:60 in a CD_2Cl_2 solution, as determined from the ^1H NMR spectrum. Finally, we note that monitoring of the above reactions revealed that the oxo nitride isomer **6** was the major isomer formed at 253 K, which then rearranges at room temperature to reach the mentioned equilibrium ratio with the phosphinoimido isomer **7** (Scheme 3).

The reactions of **2** with the manganese salt $[MnCp'(CO)_2(NO)]BF_4$ were again much less selective than the one with the Re cation just discussed and led to complex mixtures of products irrespective of the reaction conditions. No trinuclear complexes could be identified in the corresponding mixtures, and the major products were the homometallic species $[Mn_2Cp'_2(CO)_2(NO)_2]$[13] and $[W_2Cp_2(\mu\text{-}PCy_2)(CO)_3(NO)]$,[14] thus pointing once more to the prevalence, in these reactions, of undesired electron- and nitrosyl-transfer processes, respectively.

Solid-State Structure of Compound 7. The molecule of **7** in the crystal (Figure 2 and Table 3) displays a V-shaped W−W−Re chain (intermetallic angle ca. 120°) built up from $WCp(CO)_2$, $WCp(O)$, and $ReCp'(CO)_2$ units, which are triply bridged by a $NPCy_2$ ligand, with the latter being P-bound to the first fragment in a terminal way and bridging the latter two fragments through its N atom. The P and N atoms are close to the intermetallic plane, and the hydrocarbyl ligands are placed in mutually transoid (WW) or cisoid (WRe) positions, relative to that plane. The rather large intermetallic separations of 3.0564(7) Å (W−W) and 2.9021(6) Å (W−Re) are indicative of the presence of single metal−metal bonds [cf. 3.0027(1) Å for the W−W length in $[W_2Cp_2(\mu\text{-}P_2)(CO)_4]$[22] and 2.9085(6) Å for the W−Re length in $[WReCp^*(\mu\text{-}I)(\mu\text{-}CCPh)(CO)_5]$,[23] and the W−P length of 2.424(3) Å is comparable to the values of ca. 2.45 Å usually found for phosphine ligands bound to W atoms. The terminal oxo ligand on the central W2 atom is tightly bound to it as expected, with a quite short distance of 1.711(7) Å, comparable to those recently measured in the PCy_2-bridged complexes $[W_2Cp_2\{CH_2(p\text{-tol})\}(O)(\mu\text{-}PCy_2)(CO)_2]$ and $[W_2Cp_2\{\mu\text{-}C(O)CH_2(p\text{-tol})\}(O)(\mu\text{-}PCy_2)(CO)]$ (ca. 1.72 Å).[24]

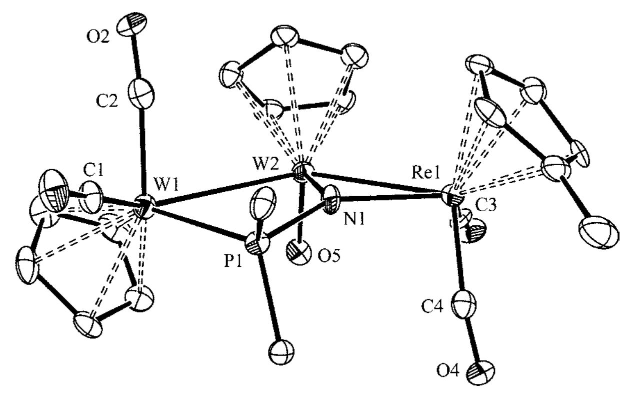


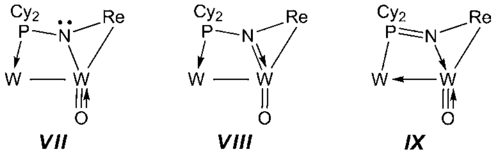
Figure 2. ORTEP diagram (30% probability) of compound **7**, with H atoms and Cy groups (except their C^1 atoms) omitted for clarity.

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

W1−W22	3.0564(7)	W1−W2−Re1	123.48(2)
W2−Re1	2.9021(6)	C1−W1−C2	78.5(5)
W1−P1	2.424(3)	W2−W1−P1	64.52(6)
W1−C1	1.94(1)	W1−P1−N1	102.5(4)
W1−C2	1.93(1)	P1−N1−W2	113.9(5)
W2−O5	1.711(7)	P1−N1−Re1	148.1(6)
W2−N1	1.91(1)	O5−W2−N1	108.5(4)
Re1−N1	2.134(8)	W2−N1−Re1	91.5(3)
Re1−C3	1.90(1)	N1−Re1−C3	110.0(4)
Re1−C4	1.87(1)	N1−Re1−C4	91.0(4)
P1−N1	1.633(8)	C3−Re1−C4	85.8(4)

The environment around the N atom in **7** is almost trigonal-planar (sum of the X−N−Y angles ca. 354°), thus allowing it to engage in π-donor interactions to any of the surrounding atoms. The Re−N length of 2.134(8) Å is ca. 0.15 Å longer than that in **5** and has a value comparable to those measured for the N → Re bonds in different $[ReCp(CO)_2L]$ complexes (L = pyridine or amine-type N-donor ligand), in the range 2.12−2.23 Å.[25] Therefore, the corresponding bond can be considered as essentially single, with a negligible π component. In contrast, the W2−N length of 1.91(1) Å is much shorter, even more after allowing for the ca. 0.1 Å larger covalent radius of W versus Re.[26] Indeed, this length is comparable to those measured in different amido complexes displaying trigonal $W\text{−}NR_2$ environments (ca. 1.94 Å for complexes of the type $[WCp^*(NR_2)(CH_2{}^tBu)(NO)]$).[27] Therefore, we conclude that the W−N bond in **7** has a significant π(N→W)-bonding contribution. Finally, the P−N length of 1.633(8) Å is significantly shorter than the reference single-bond value of ca. 1.78 Å[26] yet longer than the reference length for a double bond (e.g., 1.556 Å in $R^*P{=}N^tBu$; $R = 2,4,6\text{-}C_6H_2{}^tBu_3$).[28] Thus, the P−N link seems to have also a significant π-bonding contribution. We note that the measured P−N length in **7** is comparable to those in different dimetallic complexes having bridging phosphinoamido ($\mu\text{-}NRPR'_2$) ligands.[29] In all, the above data suggest that the electronic structure of complex **7** cannot be described in simple terms and is better described by using a combination of the canonical forms collected in Chart 4, which imply intermediate bond orders for the W−O, W−N, and N−P bonds. Unfortunately, we have no similar complexes at hand to be used for comparative purposes; compound **7** appears to be the first example of a complex containing a bridging NPR_2 ligand to be reported. In fact, only a few phosphinoimido complexes of any type have been reported previously, all of them displaying a terminal and almost linear

Chart 4



$M{-}N{-}PR_2$ coordination mode and multiple M–N bonding (M = Ti, V, Nb, W).[30]

Solution Structures of Compounds 6 and 7: The Reversible Formation of a P–N Bond. The IR spectrum of compound **6** in the C–O stretching region is very similar to that of the dimolybdenum complex **3** (Table 2), except that the bands in **6** are some 10 cm^{-1} less energetic, as expected when comparing analogous molybdenum and tungsten complexes.[19] The NMR spectra, however, reveal the presence of minor isomer **6′**, displaying very similar ^{31}P and ^{1}H NMR resonances (see the Experimental Section), with the ratio **6**/**6′** in a CD_2Cl_2 solution remaining ca. 10:1 in the range 213–293 K. This minor species might correspond to an isomer with a terminal O atom and a nitride ligand bridging the ditungsten unit and the rhenium fragment, as proposed for the dioxo nitride dimolybdenum complex **5** (Chart 2), although other alternatives cannot be excluded (i.e., cis/trans isomerism). As for the major isomer of **6**, it displays a ^{31}P NMR resonance at δ 165.3, a position some δ 70 more shielded than that of **3**, as expected from the change of the metal, and in any case consistent with the presence of a PCy_2 ligand bridging a ditungsten moiety with a single intermetallic bond (cf. δ_P 139.6 for $[W_2Cp_2(\mu\text{-H})(\mu\text{-PCy}_2)(CO)_4]$).[19] More informatively, this resonance displays two $^{183}W{-}^{31}P$ couplings very different from each other (362 and 169 Hz), which is fully consistent with the different coordination numbers of the W atoms of this molecule.[20a] The lowest value thus corresponds to the coupling with the atom having the highest coordination number, that is, the $W(CO)_2$ center, and indeed is comparable to the value of 182 Hz measured in the mentioned hydride complex. On the other hand, the highest coupling [corresponding to the W(N) center] is close to the values reported for ditungsten complexes of the type $[W_2Cp_2(PPh_2)_2(E)(CO)]$ having related multiple W–E bonds (ca. 380 Hz for E = O,[31] $N{-}NCPh_2$).[32]

The spectroscopic data for complex **7** are fully consistent with the structure found in the crystal. Thus, although the IR spectrum of **7** in the C–O stretching region is not very different from that of **6**, its ^{13}P NMR resonance appears at a much lower frequency (δ_P ca. 52), which is consistent with the presence of a phosphine-like P atom bound to a W atom. This resonance was rather broad above 243 K but sharp below 213 K, then displaying two very different P–W couplings of 277 and 57 Hz. The reduced magnitude of the latter value ensures that the P atom is not directly bound to one of the W atoms, as found in the solid state, and the one-bond coupling of 277 Hz to the $W(CO)_2$ center is comparable to the values measured for the diphosphine-bridged complexes $[W_2Cp_2(\mu\text{-}R_2PCH_2PR_2)(CO)_4]$ (224 Hz when R = Me and 340 Hz when R = Ph),[33] which are molecules with similar environments around their W atoms. As for the minor isomer **7′**, the fact that the corresponding ^{31}P and $^{1}H(Cp)$ NMR resonances are similar to those of the major isomer (see the Experimental Section) suggests that it might just differ (from the major isomer) in the relative conformation of any of the WCp or ReCp′ groups, although we have not investigated this in detail because of the low proportion of this minor isomer under all conditions examined. We finally note that, although the ^{31}P NMR resonances of both **7** and **7′** broaden significantly above 243 K, this is not paralleled by a significant broadening or coalescence of the corresponding ^{1}H NMR resonances. This implies that the observed broadening in the ^{31}P NMR spectra is not caused by the mutual exchange between isomers and possibly is caused by intermolecular interactions with the solvent. For instance, we have previously observed severe broadening in the ^{31}P NMR resonances of the phosphide-bridged complex $[W_2Cp_2(\mu\text{-PPh}_2)_2(CO)(O)]$ in the presence of small amounts of acid, as a result of the incipient protonation of the oxo ligand to give the corresponding hydroxo complex.[31]

The formation of **7** from **6** requires insertion of a nitride ligand into a W–P bond of a bridging PR_2 ligand. To our knowledge, this reaction has not been previously reported. We can only quote a few examples of related P–N bond-forming reactions through coupling between coordinated ligands, with these couplings taking place between imido and phosphide (NR/PR_2),[34] nitride and phosphine (N/PR_3),[35] and amido and phosphine (NR_2/PR_3) ligands.[36] The reverse reaction, that is, the cleavage of the P–N bond in **7** to give **6**, is also a most unusual reaction, especially when considering that this process occurs at room temperature. King et al. reported cleavage of the P–N bonds in several aminobis(difluorophosphine) ligands ($F_2PNR'PF_2$) during their reactions with several metal carbonyls, typically under forcing thermal or photochemical conditions,[37] and more recently an analogous P–N bond cleavage was reported to take place to a small extent in the reaction of $(PhO)_2PN(Ph)P(OPh)_2$ with $[Fe_2Cp_2(CO)_4]$ upon prolonged reflux in benzene solutions.[38] We should stress that, in any case, all of the above coupling and cleavage reactions are irreversible processes. The interconversion between the isomers **6** and **7** therefore seems to constitute the first example of a reversible P–N bond coupling taking place between N- and P-donor ligands of any type.

Decarbonylation of Compounds 6 and 7. The equilibrium between the nitride complex **6** and its phosphinoimido isomer **7** is obviously possible thanks to the stability of **6** toward spontaneous decarbonylation (a common observation in the comparison of related tungsten and molybdenum complexes): otherwise, **6** would have evolved irreversibly to give an unsaturated oxo nitride tricarbonyl complex analogous to **4**, as observed for the dimolybdenum complex **3**. In order to check whether an unsaturated ditungsten analogue of **4** could be obtained, we examined the thermal decarbonylation of the mixture of isomers **6** and **7** in a toluene solution. Decarbonylation indeed takes place at a significant rate above ca. 363 K, although it is more conveniently completed in refluxing conditions (ca. 45 min). The process, however, also implies a partial degradation of the parent trinuclear substrates, to eventually yield the very air-sensitive pentanuclear complex $[W_4ReCp_4Cp'(\mu_2\text{-N})(\mu_3\text{-N})(\mu\text{-O})(O)(\mu\text{-PCy}_2)_2(CO)_3]$ (**8**) and the mononuclear rhenium species $[ReCp'(CO)_3]$, with the latter being identified through its characteristic C–O stretching bands in the IR spectrum (Scheme 3).[39]

The structure of **8** (Figure 3 and Table 4) can be viewed as built from two transoid $W_2Cp_2(\mu\text{-PCy}_2)$ moieties. One of them bears terminal CO and O ligands and is also bridged by a nitride ligand (N1), which, in turn, acts as a terminal ligand to the second ditungsten unit. The latter is bridged by an O atom somewhat asymmetrically and bears a second nitride ligand (N2) linearly connected to a $ReCp'(CO)_2$ fragment. The

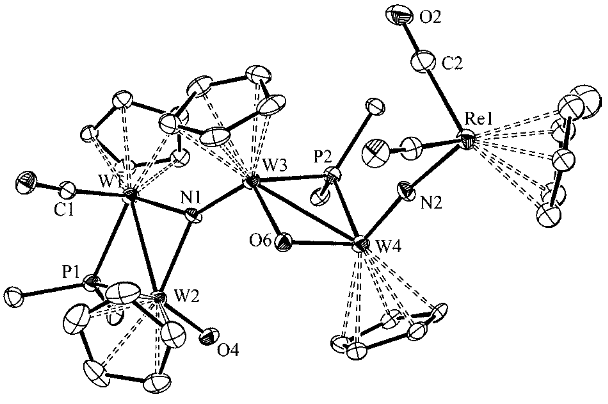


Figure 3. ORTEP diagram (30% probability) of compound **8**, with H atoms and Cy groups (except their C^1 atoms) omitted for clarity.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for 8

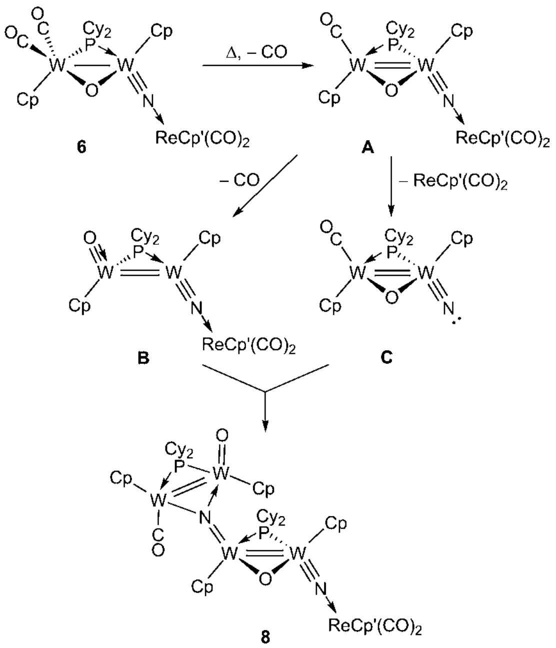
W1–W2	2.7246(6)	W1–P1–W2	69.74(7)
W1–P1	2.332(2)	W1–N1–W2	83.9(3)
W2–P1	2.431(2)	C1–W1–W2	85.4(3)
W1–N1	2.006(7)	O4–W2–W1	113.3(2)
W2–N1	2.071(7)	P1–W1–N1	105.3(2)
W1–C1	1.942(10)	P1–W1–C1	86.8(3)
W2–O4	1.743(7)	W1–N1–W3	143.4(4)
		W2–N1–W3	131.2(4)
W3–W4	2.7900(6)	W3–P2–W4	70.50(7)
W3–P2	2.438(2)	W3–O6–W4	90.7(3)
W4–P2	2.395(2)	W4–W3–N1	116.4(2)
W3–O6	1.927(6)	W3–W4–N2	99.9(3)
W4–O6	1.995(6)	P2–W3–N1	100.8(2)
W4–N2	1.747(8)	P2–W4–N2	94.5(3)
W3–N1	1.893(7)	W4–N2–Re1	170.1(5)
Re1–N2	2.025(8)	N2–Re1–C2	94.2(4)
Re1–C2	1.907(11)	N2–Re1–C3	90.3(4)
Re1–C3	1.878(11)	C2–Re1–C3	87.0(5)

overall structure and interatomic distances within this second ditungsten subunit are comparable to those measured in *cis*-**5** (except for the relative conformation of the Cp ligands) after replacement of the terminal oxo ligand in **5** with the nitride ligand N1 and need no further discussion. However, it should be recalled that the corresponding intermetallic separations in this subunit indicate the presence of intermediate Re–N2, W4–N2, and W3–W4 bond orders (not represented in Scheme 3). In contrast, the first ditungsten subunit displays a shorter intermetallic separation [2.7246(6) vs 2.7900(6) Å], now clearly approaching the values expected for a double W–W bond (cf. 2.677(2) Å in the 32-electron complex $[W_2Cp_2\{\mu\text{-}CNH(2,6\text{-}Me_2C_6H_3)\}(\mu\text{-}PCy_2)\{CN(2,6\text{-}Me_2C_6H_3)\}(CO)]$).[24] Indeed, a double intermetallic bond might be proposed for this subunit if considering the terminal oxo ligand as a two-electron donor and the nitride ligand as a three-electron donor to the ditungsten center. This is consistent respectively with the W2–O4 distance of 1.743(7) Å, ca. 0.05 Å longer than the corresponding distance in *cis*-**5**, and with the relatively large W1/W2–N1 lengths of 2.006(7) and 2.071(7) Å, which are comparable to the Mo–N lengths of ca. 2.07 Å measured in the azavinylidene complex $[Mo_2Cp_2(\mu\text{-}N{=}CHPh)(\mu\text{-}PCy_2)(CO)_2]$.[16a] The environment around the N1 atom is trigonal-planar (sum of the W–N–W angles ca. 359°), and the N1–W3 distance [1.893(7) Å] is ca. 0.15 Å shorter than the average N1–W1/W2 lengths, even slightly shorter than that measured in **7**; therefore, it can be considered as corresponding to an essentially double W–N bond. The coordination of this nitride ligand is thus comparable to that found in the trimolybdenum complex $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu_3\text{-}N)MoCp(O)(SMe)]$, with the latter also exhibiting one short Mo–N length of 1.849(7) Å.[40] However, μ_3-nitride ligands bridging Mo or W atoms more often display a T-shaped geometry, with M–N–M angles of ca. 90 or 180°.[5b,41]

Spectroscopic data for **8** (Table 2 and the Experimental Section) are consistent with the retention in solution of the essential geometric features present in the solid-state structure. The IR spectrum displays just two C–O stretches at 1882 and 1814 cm^{-1}, with the latter being of stronger intensity, because of the accidental superimposition of the stretch arising from the unique W(CO) group and the asymmetric stretch of the $Re(CO)_2$ oscillator.[18] The inequivalent and remote PCy_2 ligands of the molecule give rise to separate ^{31}P NMR resonances at similar shifts (δ 129.6 and 112.9), with negligible mutual coupling as expected. Both resonances display large P–W couplings (in the range 370–410 Hz) to inequivalent W atoms in each case, in agreement with their low coordination numbers. We finally note that the corresponding chemical shifts are significantly lower than those in **6**, which is consistent with the increased intermetallic bond order in the ditungsten subunits, now closer to a double bond (cf. δ_P 89.3 for $[W_2Cp_2(\mu\text{-}I)(\mu\text{-}PCy_2)(CO)_2]$).[12]

The formation of compound **8** can be rationalized by assuming for **6** a decarbonylation step similar to the one spontaneously occurring at the analogous dimolybdenum complex **3**, which would give in this case an unstable tricarbonyl intermediate **A** isostructural to complex **4** (Scheme 4). This intermediate would now evolve in two different ways: (a) by releasing a second CO molecule and then yielding a coordinatively unsaturated intermediate **B** and (b) by releasing its $ReCp'(CO)_2$ fragment, which rapidly would trap the CO available in the solution to yield the observed product

Scheme 4



[ReCp′(CO)$_3$]. This second process would yield an intermediate **C** having a terminal nitride ligand, which then might bind the unsaturated dimetal center of intermediate **B** to give the final product **8** after an exchange of positions (terminal/bridging) between the nitride and oxo ligands present there.

■ CONCLUDING REMARKS

The exact nature of the diorganophosphide ligand in the unsaturated anions [M$_2$Cp$_2$(μ-PR$_2$)(μ-CO)$_2$]$^-$ (M = Mo, W) has only a modest influence on their reactions with the nitrosyl cations [MCp′(CO)(NO)]$^+$ (M = Mn, Re), as shown by the fact that the reactions of the dicyclohexylphosphide-bridged anion [Mo$_2$Cp$_2$(μ-PCy$_2$)(μ-CO)$_2$]$^-$ with the mentioned cations proceed much in the same way as those of the PPh$_2$-bridged anion previously studied by us, with this implying a fast N−O cleavage step of the nitrosyl ligand, which is followed by spontaneous decarbonylation in the resulting oxo nitride complex **3**. The main differences are the appearance of minor geometrical isomers in some of the products and a significant increase of side products, resulting from undesired electron- and nitrosyl-transfer processes, with these being dominant in reactions with the manganese cation. The nature of the metal, however, has a much stronger influence on the output of the reactions under study. For the ditungsten anion [W$_2$Cp$_2$(μ-PCy$_2$)(μ-CO)$_2$]$^-$, the mentioned side reactions are more prevalent, and the yield of the heterometallic products is lower. The most significant difference, however, is that the oxo nitride complex [Mo$_2$ReCp$_2$Cp′(μ-N)(μ-O)(μ-PCy$_2$)(CO)$_4$] following from the initial N−O bond cleavage reaction does not undergo spontaneous decarbonylation at room temperature but instead undergoes a reversible insertion of its nitride ligand into a W−PCy$_2$ bond to reach an equilibrium with its [W$_2$ReCp$_2$Cp′(μ_3-*N*:*N*:*P*-NPCy$_2$)(O)(CO)$_4$], which displays an unprecedented bridging phosphinoimido ligand. The forced decarbonylation of this mixture shifts the equilibrium to the oxo nitride side, as expected, but also results in partial degradation and condensation reactions to eventually give a pentanuclear oxo nitride derivative. To our knowledge, the reversible coupling between N- and P-donor ligands has never been reported previously.

■ EXPERIMENTAL SECTION

General Procedures and Starting Materials. All manipulations and reactions were carried out under a nitrogen (99.999%) atmosphere using standard Schlenk techniques. Solvents were purified according to literature procedures and distilled prior to use.[42] Petroleum ether refers to that fraction distilling in the range 338−343 K. Tetrahydrofuran solutions/suspensions of the salts **1**[11] and **2**[12] were prepared in situ from the corresponding precursors [Mo$_2$Cp$_2$(μ-H)(μ-PCy$_2$)(CO)$_2$] and [W$_2$Cp$_2$(μ-H)(μ-PCy$_2$)(CO)$_4$] as described previously. Compounds [MCp′(CO)$_2$(NO)]BF$_4$ [M = Mn,[43] Re[44]] were prepared by literature procedures. All other reagents were obtained from the usual commercial suppliers and used as received. Chromatographic separations were carried out using jacketed columns cooled 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 under nitrogen with the appropriate amount of water to reach the activity desired. Filtrations were performed using diatomaceous earth unless otherwise stated. IR C−O stretching frequencies were measured in solution, are referred to as ν_{CO} (solvent), and are given in wavenumber units (cm^{-1}). NMR spectra were routinely recorded at 400.13 (^{1}H), 162.00 (^{31}P{^{1}H}), or 100.62 MHz (^{13}C{^{1}H}) at 290 K in CD$_2$Cl$_2$ solutions unless otherwise stated. Chemical shifts (δ) are given in ppm, relative to internal tetramethylsilane (^{1}H and ^{13}C) or an external 85% aqueous H$_3$PO$_4$ solution (^{31}P). Coupling constants (*J*) are given in hertz (Hz).

Preparation of 3. Solid [ReCp′(CO)$_2$(NO)]BF$_4$ (0.023 g, 0.052 mmol) was added to a suspension of compound **1**, freshly prepared from [Mo$_2$Cp$_2$(μ-H)(μ-PCy$_2$)(CO)$_2$] (0.030 g, 0.052 mmol), in dichloromethane (10 mL) and cooled at 253 K, and the mixture was stirred at that temperature for 45 min to yield a brown solution. The solvent was then removed under vacuum, the residue was extracted with dichloromethane/petroleum ether (1:2), and the extract was chromatographed on alumina (activity IV) at 253 K. Elution with the same solvent mixture gave a minor orange fraction containing some [Mo$_2$(μ-PCy$_2$)(CO)$_3$(NO)],[14] and other unidentified species. Elution with dichloromethane gave a major brown fraction, which yielded, after removal of solvents under vacuum at 253 K, compound **3** as a brown powder (0.030 g, 62%). This compound is thermally unstable and transforms into **4** above 273 K in a dichloromethane solution; thus, satisfactory elemental analysis for this compound could not be obtained. ^{1}H NMR (400.13 MHz, 233 K): δ 5.90, 5.54 (2s, 2 × 5H, Cp), 5.11, 4.96, 4.89, 4.80 (4m, 4 × 1H, C$_5$H$_4$), 2.05 (s, 3H, Me), 2.92−1.00 (m, 22 H, Cy). ^{13}C{^{1}H} NMR (100.63 MHz, 233 K): δ 241.3 (d, J_{CP} = 27, MoCO), 236.5 (s, MoCO), 206.9, 205.9 (2s, ReCO), 111.8 [s, C^1(C$_5$H$_4$)] 104.0, 96.9 (2s, Cp), 85.4, 82.3, 81.8, 81.6 [4s, CH(C$_5$H$_4$)], 50.8 [d, J_{PC} = 18, C^1(Cy)], 40.3 [d, J_{PC} = 13, C^1(Cy)], 35.0, 32.0, 31.3, 29.6 [4s, C^2(Cy)], 28.3 [d, J_{PC} = 10, C^3(Cy)], 27.4 [d, J_{PC} = 12, C^3(Cy)], 27.1 [d, J_{PC} = 9, C^3(Cy)], 27.0 [d, J_{PC} = 11, C^3(Cy)], 26.1, 25.8 [2s, C^4(Cy)], 13.5 (s, Me).

Preparation of 4. A crude brown solution of compound **3**, prepared at 253 K as described above, was further stirred at room temperature for 1 h to give a dark-green solution. The solvent was then removed under vacuum, the residue was extracted with dichloromethane/petroleum ether (1:4), and the extracts were chromatographed on alumina (activity IV) at 285 K. Elution with dichloromethane/petroleum ether (1:1) gave a minor brown fraction, which was discarded, and then a green fraction, which yielded, after removal of solvents under vacuum, compound **4** as an emerald-green, air-sensitive powder (0.023 g, 50%); thus, satisfactory elemental analysis for this compound could not be obtained. ^{1}H NMR (300.13 MHz): δ 5.99, 5.35 (2s, 2 × 5H, Cp), 4.78, 4.61 (2m, 2 × 1H, C$_5$H$_4$), 4.75 (m, 2H, C$_5$H$_4$), 2.60−1.00 (m, 22H, Cy), 1.62 (s, 3H, Me).

Preparation of 5. A crude green solution of compound **4**, prepared as described above from [Mo$_2$Cp$_2$(μ-H)(μ-PCy$_2$)(CO)$_2$] (0.060 g, 0.104 mmol) and [ReCp′(CO)$_2$(NO)]BF$_4$ (0.046 g, 0.104 mmol), was stirred at room temperature in the presence of air for 30 min to give a blue solution, which was filtered. The solvent was then removed 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 minor brown fraction, which was discarded. Elution with dichloromethane gave a dark-blue fraction, which yielded, after removal of solvents under vacuum, compound **5** as a blue microcrystalline solid (0.028 g, 30%). This solid was shown (by NMR) to be a mixture of the corresponding cis and trans isomers in a ca. 1:2 ratio, along with very small amounts (ca. 1:15) of the corresponding μ_3-N-bridged isomers **5′** (see the text). It was possible to obtain small amounts of the major cis and trans isomers upon fractional crystallization of the above mixture. The crystals of *cis*-**5** used in the X-ray study were grown by the slow diffusion of a layer of petroleum ether into a concentrated solution of the mixture of isomers in dichloromethane. Anal. Calcd for C$_{31}$H$_{41}$Cl$_2$Mo$_2$NO$_4$PRe (**5**·CH$_2$Cl$_2$): C, 38.32; H, 4.25; N, 1.44. Found: C, 38.58; H, 4.55; N, 1.71. Spectroscopic data for *cis*-**5**. ^{1}H NMR (300.13 MHz, C$_6$D$_6$): δ 5.68, 5.30 (2s, 2 × 5H, Cp), 5.18, 4.99, 4.86, 4.81 (4m, 4 × 1H, C$_5$H$_4$), 2.90−1.10 (m, 22H, Cy), 1.99 (s, 3H, Me). Spectroscopic data for *trans*-**5**. ^{1}H NMR (300.13 MHz, C$_6$D$_6$): δ 5.76, 5.72 (2s, 2 × 5H, Cp), 4.66, 4.61, 4.55, 4.47 (4m, 4 × 1H, C$_5$H$_4$), 3.10−1.00 (m, 22H, Cy), 1.91 (s, 3H, CH$_3$).

Reaction of Compound 2 with [ReCp′(CO)$_2$(NO)]BF$_4$. Solid [ReCp′(CO)$_2$(NO)]BF$_4$ (0.033 g, 0.074 mmol) was added to a suspension of compound **2**, freshly prepared from [W$_2$Cp$_2$(μ-H)(μ-

Table 5. Crystal Data for New Compounds

	cis-**5**	**7**	**8**
molecular formula	$C_{30}H_{39}Mo_2NO_4PRe$	$C_{32}H_{39}NO_5PReW_2$	$C_{53}H_{71}N_2O_5P_2ReW_4$
mol wt	886.68	1102.51	1799.63
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$C2/c$	$P2_1/c$
radiation (λ), Å	1.54184	1.54184	1.54184
a, Å	14.0692(3)	35.5058(19)	16.8430(8)
b, Å	16.5028(4)	11.0077(4)	22.4890(9)
c, Å	19.8725(5	17.6403(9)	15.6359(6)
α, deg	90	90	90
β, deg	133.3580(10)	113.516(6)	100.911(4)
γ, deg	90	90	90
V, Å^3	3354.75(14)	6321.9(5)	5815.5(4)
Z	4	8	4
calcd density, g cm^{-3}	1.756	2.317	2.055
abs coeff, mm^{-1}	13.639	21.294	19.041
temp, K	123.0(1)	150.0(1)	123.0(1)
θ range (deg)	4.07−74.31	4.24−72.69	3.32−73.98
index ranges (h; k; l)	−15, 17; −20, 14; −22, 24	−43, 40; −7, 13; −20, 21	−20, 16; −26, 27; −13, 19
no. of reflns collected	13695	11390	20703
no. of indep reflns (R_{int})	6633 (0.0446)	6032 (0.0439)	11283 (0.0749)
reflns with $I > 2\sigma(I)$	5164	5217	9410
R indexes [data with $I > 2\sigma(I)$]^a	$R_1 = 0.0447$, $wR_2 = 0.1103^b$	$R_1 = 0.0522$, $wR_2 = 0.15^c$	$R_1 = 0.0631$, $wR_2 = 0.1595^d$
R indexes (all data)^a	$R_1 = 0.0595$, $wR_2 = 0.12^b$	$R_1 = 0.0605$, $wR_2 = 0.1585^c$	$R_1 = 0.0719$, $wR_2 = 0.173^d$
GOF	1.037	1.067	1.042
no. of restraints/param	5/348	0/381	12/598
$\Delta\rho_{max}$, $\Delta\rho_{min}$, e Å^{-3}	1.034, −2.295	3.622, −3.311	2.591, − 2.877

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. $wR_2 = [\sum w(|F_o|^2 - |F_c|^2)^2/\sum w|F_o|^2]^{1/2}$. $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$. [b] $a = 0.0592$; $b = 2.0740$. [c] $a = 0.1081$; $b = 16.4689$. [d] $a = 0.1111$; $b = 0.0000$

$PCy_2)(CO)_4]$ (0.060 g, 0.074 mmol), in dichloromethane (10 mL) and cooled at 253 K, and the mixture was stirred at that temperature for 50 min to yield a brown solution, which was filtered. The solvent was then removed from the filtrate under vacuum, the residue was extracted with dichloromethane/petroleum ether (1:2), and the extract was chromatographed on alumina (activity IV) at 253 K. Elution with dichloromethane/petroleum ether (2:1) gave a major dark-brown fraction, which yielded, after removal of solvents, compound **7** (0.020 g, 25%) as a brown solid. Anal. Calcd for $C_{32}H_{39}NPO_5ReW_2$: C, 34.86; H, 3.57; N, 1.27. Found: C, 34.65; H, 3.53; N, 1.38. Elution with dichloromethane gave a minor brown fraction, yielding, after removal of solvents under vacuum at 253 K, compound **6** as a brown powder (0.005 g, 6%). Both compounds were obtained along with very small amounts of a second isomer in each case (**6′** and **7′**) in an equilibrium ratio of ca. 1:10 relative to the major isomer. In solution, however, isomers **6** and **7** interconvert slowly so as to reach an equilibrium ratio **6**:**7** of ca. 1:6 at room temperature after ca. 1 h (from **7**) or ca. 6 h (from **6**). The overall equilibrium ratio of isomers **6′**:**6**:**7′**:**7** was ca. 1:10:6:60 in a CD_2Cl_2 solution at room temperature, as determined from the ^1H NMR spectrum. The crystals of **7** used in the X-ray study were grown by the slow diffusion of a layer of petroleum ether into a concentrated solution of the mixture of isomers in dichloromethane at 253 K. Spectroscopic data for **6**. ^1H NMR (268 K): δ 6.00, 5.66 (2s, 2 × 5H, Cp), 5.02, 4.97, 4.88, 4.84 (4m, 4 × 1H, C_5H_4), 2.01 (s, 3H, Me), 2.90−1.00 (m, 22H, Cy). Spectroscopic data for **6′**. $^{31}P\{^1H\}$ NMR (268 K): δ 165.9. ^1H NMR (268 K): δ 6.01, 5.68 (2s, 2 × 5H, Cp); other resonances were obscured by those of the major isomer. Spectroscopic data for **7**. ^1H NMR (213 K): δ 6.33, 5.43 (2s, 2 × 5H, Cp), 5.74, 4.61 (2m, 2 × 1H, C_5H_4), 5.32 (m, 2H, C_5H_4), 2.59 (s, 3H, Me), 2.70−1.10 (m, 22H, Cy). $^{31}P\{^1H\}$ NMR (268 K): δ 52.4 (br). ^1H NMR (268 K): δ 6.29, 5.38 (2s, 2 × 5H, Cp), 5.72, 5.32, 5.22, 4.78 (4m, 4 × 1H, C_5H_4), 2.50 (s, 3H, Me), 2.30−1.10 (m, 22H, Cy). Spectroscopic data for **7′**. $^{31}P\{^1H\}$ NMR (213 K): δ 53.2. ^1H NMR (213 K): δ 6.35, 5.56 (2s, 2 × 5H, Cp), 6.22, 5.28 (2m, 2 × 1H, C_5H_4); other resonances were obscured by those of the major isomer. $^{31}P\{^1H\}$ NMR (268 K): δ 52.4 (br). ^1H NMR (268 K): δ 6.31, 5.52 (2s, 2 × 5H, Cp); other resonances were obscured by those of the major isomer.

Preparation of 8. A toluene solution (8 mL) of a mixture of isomers **6** and **7** (0.025 g, 0.023 mmol) was refluxed for 45 min to give a black solution. After removal of the solvent under vacuum, the residue was washed with petroleum ether (5 mL) to remove most of the $[ReCp'(CO)_3]$ formed. The washed residue was dissolved in the minimum amount of dichloromethane/petroleum ether (2:1) and chromatographed on alumina (activity IV) at 253 K. Elution with dichloromethane/petroleum ether (9:1) gave a dark-blue fraction, yielding, after removal of solvents, compound **8** as a dark-blue, extremely air-sensitive solid (0.010 g, 50%); thus, satisfactory elemental analysis for this compound could not be obtained. The crystals used in the X-ray study were grown by the slow diffusion of a layer of petroleum ether into a concentrated solution of the complex in toluene at 253 K. ^1H NMR (300.13 MHz): δ 6.13, 6.06, 5.87, 5.69 (4s, 4 × 5H, Cp), 5.00 (m, 2H, C_5H_4), 4.96, 4.78 (2m, 2 × 1H, C_5H_4), 2.80−1.00 (m, 22H, Cy), 2.10 (s, 3H, Me).

X-ray Structure Determination for Compounds *cis*-5, 7, and 8. Data collections were performed at 123 K (**5** and **8**) or 150 K (**7**) on an Oxford Diffraction Xcalibur Nova single-crystal diffractometer, using Cu Kα radiation (Table 5). Images were collected respectively at a 63, 75, and 65 mm fixed crystal−detector distance, using the oscillation method, with 1° oscillation and fixed (1.5 s for **5** and **7**) or variable (43−105 s for **8**) exposure times per image. The data collection strategy was calculated with the program *CrysAlis Pro CCD*.[45] Data reduction and cell refinement were performed with the program *CrysAlis Pro RED*.[45] An empirical absorption correction was applied using the *SCALE3 ABSPACK* algorithm, as implemented in the program *CrysAlis Pro RED*. Using the program suite *WinGX*,[46] the structure was solved using Patterson interpretation and phase expansion and refined with full-matrix least squares on F^2 using *SHELXL97*.[47] In general, all non-H atoms were refined anisotropically, and all H atoms were geometrically placed and refined using a riding model with an overall isotropic parameter. For compound *cis*-**5**, the Cp ligand on Mo1 was disordered over two positions and could be satisfactorily modeled with occupancy factors of 0.5/0.5, while that on Mo2 showed an incipient disorder that could not be modeled. All non-H atoms were refined anisotropically, except the C atoms of the disordered Cp ligand. There was also a heavily disordered dichloromethane molecule in the unit cell that could not be conveniently modeled; therefore, the *SQUEEZE*[48] procedure, as implemented in *PLATON*,[49] was used. For compound **8**, there was a toluene molecule in the unit cell, also highly disordered, that was treated analogously. In addition, the Cp′ ligand was disordered over two positions and could be satisfactorily modeled with occupancy factors of 0.5/0.5 and some restraints. All non-H atoms were refined anisotropically, except for the C atoms of the disordered Cp′ ligand.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

CIF file containing full crystallographic data for compounds *cis*-**5**, **7**, and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: mara@uniovi.es.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank the DGI of Spain for financial support (Projects CTQ2009-09444 and CTQ2012-33187) and a grant (to M.F.V.) and the Consejería de Educación del Principado de Asturias for a grant (to A.T.).

■ REFERENCES

(1) Ritcher-Addo, G. B.; Legzdins, P. *Metal Nitrosyls*; Oxford University Press: Oxford, U.K., 1992.

(2) (a) Roncaroli, F.; Videla, M.; Slep, L. D.; Olabe, J. A. *Coord. Chem. Rev.* **2007**, *25*, 1903. (b) Hayton, T. W.; Legzdins, P.; Sharp, W. B. *Chem. Rev.* **2002**, *102*, 935. (c) Ford, P. C.; Lorkovic, I. M. *Chem. Rev.* **2002**, *102*, 993. (d) Mingos, D. M. P.; Sherman, D. J. *Adv. Inorg. Chem.* **1989**, *34*, 293. (e) Gladfelter, W. L. *Adv. Organomet. Chem.* **1985**, *24*, 41.

(3) (a) *Reduction of Nitrogen Oxide Emissions*; Ozkan, U. S., Agarwal, S. K., Marcelin, G., Eds.; American Chemical Society: Washington, DC, 1995. (b) *Environmental Catalysis*; Armor, J. M., Ed.; American Chemical Society: Washington, DC, 1994. (c) *Catalytic Control of Air Pollution*; Silver, R. G., Sawyer, J. E., Summers, J. C., Eds.; American Chemical Society: Washington, DC, 1992. (d) *Energy and the Environment*; Dunderdale, J., Ed.; Royal Society of Chemistry: Cambridge, U.K., 1990. (e) *Pollution: Causes, Effects and Control*; Harrison, R. M., Ed.; Royal Society of Chemistry: Cambridge, U.K., 1990.

(4) (a) Granger, P.; Parvulescu, V. I. *Chem. Rev.* **2011**, *111*, 3155. (b) Basu, S. *Chem. Eng. Commun.* **2007**, *194*, 1374. (c) Tayyeb, J. M.; Naseem, I.; Gibbs, B. M. *J. Environ. Manage.* **2007**, *83*, 251. (d) Wallington, T. J.; Kaiser, E. W.; Farrell, J. T. *Chem. Soc. Rev.* **2006**, *35*, 335. (e) McMillan, S. A.; Broadbelt, L. J.; Snurr, R. Q. *Environ. Catal.* **2005**, 287. (f) Curtin, T. *Environ. Catal.* **2005**, 197.

(5) (a) Fjare, D. E.; Gladfelter, W. L. *J. Am. Chem. Soc.* **1984**, *106*, 4799. (b) Feasey, N. D.; Knox, S. A. R.; Orpen, A. G. *J. Chem. Soc., Chem. Commun.* **1982**, 75.

(6) Legzdins, P.; Young, M. A. *Comments Inorg. Chem.* **1995**, *17*, 239.

(7) (a) Blackmore, I. J.; Jin, X.; Legzdins, P. *Organometallics* **2005**, *24*, 4088. (b) Sharp, W. B.; Daff, P. J.; McNeil, W. S.; Legzdins, P. *J. Am. Chem. Soc.* **2001**, *123*, 6272.

(8) (a) Veige, A. S.; Slaughter, LeG. M.; Lobkovsky, E. B.; Wolczansky, P. T.; Matsunaga, N.; Decker, S. A.; Cundari, T. R. *Inorg. Chem.* **2003**, *42*, 6204. (b) Odom, A. L.; Cummins, C. C.; Protasiewicz, J. D. *J. Am. Chem. Soc.* **1995**, *117*, 6613.

(9) García, M. E.; Melón, S.; Ruiz, M. A.; López, R.; Sordo, T.; Marchiò, L.; Tiripicchio, A. *Inorg. Chem.* **2008**, *47*, 10644.

(10) García, M. E.; García-Vivó, D.; Melón, S.; Ruiz, M. A.; Graiff, C.; Tiripicchio, A. *Inorg. Chem.* **2009**, *48*, 9282.

(11) (a) García, M. E.; Melón, S.; Ramos, A.; Ruiz, M. A. *Dalton Trans.* **2009**, 8171. (b) García, M. E.; Melón, S.; Ramos, A.; Riera, V.; Ruiz, M. A.; Belletti, D.; Graiff, C.; Tiripicchio, A. *Organometallics* **2003**, *22*, 1983.

(12) Alvarez, M. A.; García, M. E.; García-Vivó, D.; Ruiz, M. A.; Vega, M. F. *Organometallics* **2010**, *29*, 512.

(13) James, T. A.; McCleverty, J. A. *J. Chem. Soc. A* **1970**, 850.

(14) The complexes $[M_2Cp_2(\mu\text{-}PCy_2)(CO)_3(NO)]$ (M = Mo, W) have been prepared independently from $[Mo_2Cp_2(\mu\text{-}PCy_2)(\mu\text{-}CO)_2]^-$ and $[W_2Cp_2(H)(\mu\text{-}PCy_2)(CO)_2]$ through specific synthetic routes (García, M. E.; Ramos, A.; Ruiz, M. A.; Vega, M. F., unpublished results). Their spectroscopic data are comparable to those of the PPh_2-bridged complex $[Mo_2Cp_2(\mu\text{-}PPh_2)(CO)_3(NO)]$ reported earlier by us. See: García, M. E.; Riera, V.; Rueda, M. T.; Ruiz, M. A.; Lanfranchi, M.; Tiripicchio, A. *J. Am. Chem. Soc.* **1999**, *121*, 4060.

(15) Bottomley, F.; Sutin, L. *Adv. Organomet. Chem.* **1988**, *28*, 339.

(16) (a) Alvarez, M. A.; García, M. E.; Ramos, A.; Ruiz, M. A. *Organometallics* **2007**, *26*, 1461. (b) García, M. E.; García-Vivó, D.; Ruiz, M. A. *Organometallics* **2008**, *27*, 543.

(17) Adatia, T.; McPartlin, M.; Mays, M. J.; Morris, M. J.; Raithby, P. R. *J. Chem. Soc., Dalton Trans.* **1989**, 1555.

(18) Braterman, P. S. *Metal Carbonyl Spectra*; Academic Press: London, 1975.

(19) García, M. E.; Riera, V.; Ruiz, M. A.; Sáez, D. *Organometallics* **2002**, *21*, 5515.

(20) A general trend established for $^2J_{XY}$ in complexes of the type $[MCpXYL_2]$ is that $|J_{cis}| > |J_{trans}|$. See, for instance: (a) Jameson, C. J. In *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*; Verkade, J. G., Quin, L. D., Eds.; VCH: Deerfield Beach, FL, 1987; Chapter 6. (b) Wrackmeyer, B.; Alt, H. G.; Maisel, H. E. *J. Organomet. Chem.* **1990**, *399*, 125.

(21) It should be recalled that compound **2** is prepared in situ by reducing $[W_2Cp_2(\mu\text{-}I)(\mu\text{-}PCy_2)(CO)_2]$ with Na(Hg). Therefore, all of the subsequent reactions are carried out in the presence of NaI.

(22) Davies, J. E.; Klunduk, M. C.; Mays, M. J.; Raithby, P. R.; Shields, G. P.; Tompkin, P. K. *J. Chem. Soc., Dalton Trans.* **1997**, 715.

(23) Pin, C. W.; Peng, J. J.; Shiu, C. W.; Chi, Y.; Peng, S. M.; Lee, G. H. *Organometallics* **1998**, *17*, 438.

(24) Alvarez, M. A.; García, M. E.; Ruiz, M. A.; Vega, M. F. *Dalton Trans.* **2011**, *40*, 8294.

(25) (a) Pyshnograeva, N. I.; Setkina, V. N.; Andrianov, V. G.; Struchkov, Y. T.; Kursanov, D. N. *J. Organomet. Chem.* **1978**, *157*, 431. (b) Enders, M.; Kohl, G.; Pritzkow, H. *J. Organomet. Chem.* **2001**, *622*, 66. (c) Wang, T. F.; Hwu, C.; Wen, Y. *J. Organomet. Chem.* **2004**, *689*, 411.

(26) Cordero, B.; Gómez, V.; Platero-Prats, A. E.; Revés, M.; Echeverría, J.; Cremades, E.; Barragán, F.; Alvarez, S. *Dalton Trans.* **2008**, 2832.

(27) Tsang, J. Y. K.; Fujita-Takayama, C.; Buschhaus, M. S. A.; Patrick, B. O.; Legzdins, P. *J. Am. Chem. Soc.* **2006**, *128*, 14762.

(28) Chernega, A. N.; Antipin, M. Y.; Struchkov, Y. T.; Ruban, A. V.; Romanenko, V. D. *Zh. Strukt. Khim.* **1987**, *28*, 106.

(29) For some recent X-ray structures, see: (a) Thapa, I.; Gambarotta, S.; Korobkov, I.; Duchateau, R.; Kulangara, S. V.; Chevalier, R. *Organometallics* **2010**, *29*, 4080. (b) Greenwood, B. P.; Rowe, G. T.; Chen, C. H.; Foxman, B. M.; Thomas, C. M. *J. Am. Chem. Soc.* **2010**, *132*, 44. (c) Cooper, B. G.; Fafard, C. M.; Foxman, B. M.; Thomas, C. M. *Organometallics* **2010**, *29*, 5179. (d) Majoumo-Mbe, F.; Kuhl, O.; Lonnecke, P.; Silaghi-Dumitrescu, I.; Hey-Hawkins, E. *Dalton Trans.* **2008**, 3107.

(30) (a) Etienne, M.; Mathieu, R.; Donnadieu, B. *J. Am. Chem. Soc.* **1997**, *119*, 3218. (b) Fickes, M. G.; Odom, A. L.; Cummins, C. C. *Chem. Commun.* **1997**, 1993. (c) Brask, J. K.; Fickes, M. G.;

Sangtrirutnugul, P.; Dura-Vila, V.; Odom, A. L.; Cummins, C. C. *Chem. Commun.* **2001**, 1676. (d) Basuli, F.; Watson, L. A.; Huffman, J. C.; Mindiola, D. J. *Dalton Trans.* **2003**, 4228. (e) Cowley, A. R.; Dilworth, J. R.; Naim, A. K.; Robbie, A. J. *Dalton Trans.* **2005**, 680. (f) Agarwal, P.; Piro, N. A.; Meyer, K.; Muller, P.; Cummins, C. C. *Angew. Chem., Int. Ed.* **2007**, *46*, 3111.

(31) García, M. E.; Riera, V.; Rueda, M. T.; Ruiz, M. A.; Halut, S. *J. Am. Chem. Soc.* **1999**, *121*, 1960.

(32) García, M. E.; García-Vivó, D.; Ruiz, M. A.; Herson, P. *Organometallics* **2008**, *27*, 3879.

(33) Alvarez, M. A.; García, M. E.; Riera, V.; Ruiz, M. A.; Falvello, L. R.; Bois, C. *Organometallics* **1997**, *16*, 354.

(34) (a) Baranger, A. M.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1993**, *115*, 7890. (b) Baranger, A. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1994**, *116*, 3822.

(35) (a) Morello, M.; Yu, P.; Carmichael, C. D.; Patrick, B. O.; Fryzuk, M. D. *J. Am. Chem. Soc.* **2005**, *127*, 12796. (b) Spencer, L. P.; MacKay, B. A.; Patrick, B. O.; Fryzuk, M. D. *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103*, 17094.

(36) Adhikari, D.; Basuli, F.; Fan, H.; Huffman, J. C.; Pink, M.; Mindiola, D. J. *Inorg. Chem.* **2008**, *47*, 4439.

(37) (a) King, R. B. *Acc. Chem. Res.* **1980**, *13*, 243. (b) Newton, M. G.; King, R. B.; Lee, T. W.; Norskov-Lauritzen, L.; Kumar, V. *J. Chem. Soc., Chem. Commun.* **1982**, 201.

(38) Balakrishna, M. S.; Krishnamurthy, S. S. *Indian J. Chem.* **1991**, *30A*, 536.

(39) Caulton, K. G.; Lewis, L. N. *Inorg. Chem.* **1981**, *20*, 1139.

(40) Schollhammer, P.; Petillon, F. Y.; Talarmin, J.; Muir, K. W. *J. Organomet. Chem.* **1998**, *560*, 245.

(41) (a) Chisholm, M. H.; Folting, K.; Huffman, J. C.; Leonelli, J.; Marchant, N. S.; Smith, C. A.; Taylor, L. C. E. *J. Am. Chem. Soc.* **1985**, *107*, 3722. (b) Fenske, D.; Godemeyer, T.; Dehnicke, K. *Z. Naturforsch. B* **1988**, *43*, 12. (c) Gebeyehu, Z.; Weller, F.; Neumuller, B.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1991**, *593*, 99.

(42) Armarego, W. L. F.; Chai, C. *Purification of Laboratory Chemicals*, 5th ed.; Butterworth-Heinemann: Oxford, U.K., 2003.

(43) Connelly, N. G. *Inorg. Synth.* **1974**, *15*, 91.

(44) Tam, W.; Liu, G. Y.; Wang, K. W.; Kiel, W. A.; Wong, V. K.; Gladysz, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 141.

(45) *CrysAlis Pro*; Oxford Diffraction Ltd.: Oxford, U.K., 2006.

(46) Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837.

(47) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **2008**, *64*, 112.

(48) Van der Sluis, P.; Spek, A. L. *Acta Crystallogr., Sect. A* **1990**, *46*, 194.

(49) (a) Spek, A. L. *Acta Crystallogr., Sect. A* **1990**, *46*, C34. (b) Spek, A. L. *PLATON, A Multipurpose Crystallographic Tool*; Utrecht University: Utrecht, The Netherlands, 2010.