

A Glimpse Into the Chemical Reactivity of the Unsaturated Hydride [MoWCp₂(H)(μ-PCy₂)(CO)₂]

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Abstract

The title hydride reacted rapidly with stoichiometric amounts of different isocyanides at room temperature to give two types of formimidoyl derivatives: the symmetrically bridged complexes [MoWCp₂(μ-η²:η²-CHNR)(μ-PCy₂)(CO)₂] (R = ^tBu, 4-C₆H₄OMe), and the asymmetrically bridged complex [MoWCp₂(μ-1κ^C:2κ^N-HCNR)(μ-PCy₂)(CO)₂] (R = Xyl), with the latter compound undergoing slow rearrangement above 293 K to give the aminocarbyne isomer [MoWCp₂{μ-CN(Xyl)}(μ-PCy₂)(CO)₂]. The reaction of the title complex with excess CN^tBu led to the double addition product [MoWCp₂(μ-H)(μ-PCy₂)(1κ-CN^tBu)(2κ-CN^tBu)(1κ-CO)(2κ-CO)], whereas the reaction with excess CN(4-C₆H₄OMe) at room temperature gave a mixture of two complexes having 5-electron donor aminocarbene-iminoacyl ligands: [MoWCp₂(μ-1η²:2κ^C,κ^C-HCN(4-C₆H₄OMe)C{N(4-C₆H₄OMe)})(μ-PCy₂)(CO)₂] and [MoWCp₂(μ-1κ^C,κ^C:2η²-HCN(4-C₆H₄OMe)C{N(4-C₆H₄OMe)})(μ-PCy₂){2κ-CN(4-C₆H₄OMe)}(1κ-CO)] following from formimidoyl-isocyanide coupling. The title compound reacted with N₂CH(SiMe₃) to give the addition product [MoWCp₂(1κ-H)(μ-PCy₂)(2κ-CO)₂{1κ-N₂CH(SiMe₃)}], in which the coordinated diazoalkane acts formally as an imido-like four-electron donor group. Reaction with N₂CPh₂ led instead to a mixture of four products derived from the addition of either one molecule of diazoalkane: [MoWCp₂(1κ-H)(μ-PCy₂)(2κ-CO)₂(1κ-N₂CPh₂)] and [MoWCp₂(2κ-H)(μ-PCy₂)(1κ-CO)₂(2κ-N₂CPh₂)], or two molecules of the reagent: [MoWCp₂(2κ-H)(μ-PCy₂)(2κ-CO)₂(1κ-N₂CPh₂)₂] and [MoWCp₂(1κ-H)(μ-PCy₂)(1κ-CO)₂(2κ-N₂CPh₂)₂]. These latter products lack of metal–metal bond due to a dissimilar electron donation from the diazoalkane ligands which, act as 2- and 4-electron donors, respectively. Reaction of the title compound with excess (*p*-tol)C(O)H (*p*-tol = 4-MeC₆H₄) in refluxing toluene gave the oxoacyl complex [MoWCp₂{μ-1κ^C:2η²-C(O)CH₂(*p*-tol)}(1κ-O)(μ-PCy₂)(2κ-CO)] as the unique product, following from C–O bond cleavage of the incoming reagent. Finally, the title compound reacted with HC₂(*p*-tol) at room temperature to give a mixture of the α-substituted alkenyls *trans*-[MoWCp₂{μ-κ:η²-C(*p*-tol)CH₂}(μ-PCy₂)(CO)₂] and *cis*-[MoWCp₂{μ-1κ:2η²-C(*p*-

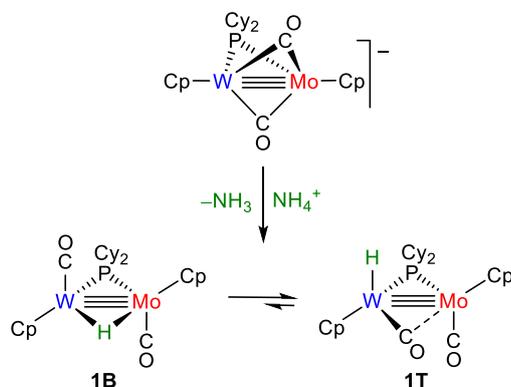
tol)CH₂}(μ-PCy₂)(CO)₂] in a ratio *ca.* 7/1, whereas the reaction in refluxing toluene led to mixtures of the β-substituted alkenyls *trans*-[MoWCp₂{μ-1κ:2η²-CHCH(*p*-tol)}(μ-PCy₂)(CO)₂] and *cis*-[MoWCp₂{μ-κ:η²-CHCH(*p*-tol)}(μ-PCy₂)(CO)₂] in a ratio *ca.* 10/1, with the former α-substituted complexes fully rearranging into the β-substituted alkenyls rapidly at 363 K, as shown by independent experiments.

Keywords: Heterometallic complexes; Metal–metal interactions; Hydride complexes; Formimidoyl complexes; Diazoalkane complexes; Alkenyl complexes.

1. Introduction

Over the last decade there has been an increasing interest in the preparation and chemical study of new transition-metal complexes having two different metal atoms (heterometallic complexes). This interest stems from their potential to promote novel reactions which depart significantly from those of their corresponding homometallic analogues, thanks to the presence of synergistic effects enabled by the unique electronic and coordinative preferences of the different metals [1]. In fact, nature has been exploiting such effects to accomplish many relevant biological processes, which are then effectively catalyzed by enzymes having heterometallic active centers (*ie.* Cu–Mo, Cu–Fe, Mo–Fe, Ni–Fe, Fe–Zn, etc.) [2]. As commonly found for homometallic systems, the presence of metal-metal multiple bonds in the heterometallic compounds is a natural way to further enhance the chemical reactivity of these complexes [3-7] and, not surprisingly, this approach has been successfully exploited for the development of new catalytic processes in which the combination of both, electronic unsaturation (multiple bond) and bond polarity (heterometallic bond) are key enabling factors [5,8]. However, the current knowledge of the chemical behavior of these complexes is rather limited (especially for organometallic compounds), mainly due to the synthetic difficulties associated to their preparation or due to the low stability of most of these compounds. In this area of work, our group recently reported the synthesis of the heterometallic anion $[\text{MoWCp}_2(\mu\text{-PCy}_2)(\mu\text{-CO})_2]^-$, which reacted rapidly with different electrophiles to give new Mo–W heterometallic complexes having double and triple metal-metal bonds in combination with alkyl, hydride, or carbyne ligands [9]. Amongst all these new compounds, stands out the heterometallic hydride $[\text{MoWCp}_2(\text{H})(\mu\text{-PCy}_2)(\text{CO})_2]$ (**1**) (Scheme 1), which in solution exists as an equilibrium mixture of two isomers displaying either a bridging (**1B**) or a terminal (**1T**) hydride ligand, in a compound also featuring a metal-metal triple bond [10,11]. Although this compound is structurally related to the corresponding homometallic hydrides $[\text{Mo}_2\text{Cp}_2(\mu\text{-H})(\mu\text{-PCy}_2)(\text{CO})_2]$ (bridging isomer only) and $[\text{W}_2\text{Cp}_2(\text{H})(\mu\text{-PCy}_2)(\text{CO})_2]$ (bridging and terminal isomers), at the time we identified a genuine heterometallic structural effect, as in solution compound **1** displays a prevalence of the terminal isomer when compared to both homometallic analogues. Furthermore, DFT calculations allowed us to estimate the existence of a *ca.* 20 kJ·mol⁻¹ thermodynamic preference for the terminal coordination of the hydride ligand at the W site (*vs.* Mo) [9]. The consequences of all these structural features on the chemical reactivity of this compound is yet to be explored even if, as nicely exemplified by all the chemistry developed around its homometallic Mo₂ and W₂ analogues [12,13-16], the combined presence of a metal-metal triple bond and a hydride ligand in **1** is expected to confer great synthetic potential to this compound. In addition,

the above-mentioned studies on the homometallic complexes revealed a remarkable influence of the metal atom (Mo vs. W) on the chemical behavior of these unsaturated compounds. For instance, while the protonation of the Mo₂ hydride led to complex mixtures of products, the protonation of the W₂ compound led to the formation of new cationic dihydrides which remained stable in the absence of coordinating anions [13]. A comparable situation was also found in the reactions with diazoalkanes, which only for the W₂ system led to new isolable compounds having N-bound diazoalkanes [14], while the Mo₂ hydride just catalyzed the decomposition of the organic reagent [15]. Finally, the reaction with some isocyanides and alkynes were also substantially different, as the W₂ compound displayed an uncommon preference to incorporate two molecules of the reagent (rather than one for the Mo₂ compound), then leading to the formation of products following from C–N or C–C coupling processes [15,16]. It was then clear that compound **1** was an ideal substrate to further explore the chemical effects of the nature of the metals present in the dimetallic center of this family of unsaturated hydrides. Although similar comparative studies between homometallic and heterometallic complexes for related unsaturated hydrides are extremely scarce, we can quote here the comparative study of Suzuki *et al.* on the reactivity of the 30-electron hydride [Cp*₂Ru(μ-H)₄OsCp*], which in fact undergoes addition reactions much faster than its homometallic (Ru₂ or Os₂) analogues, then pointing to the synthetic utility of the heterometallic compound [17]. In this paper we report the reactions of the unsaturated hydride **1** toward small organic molecules containing C–C, C–O, C–N or N–N multiple bonds, such as alkynes, aldehydes, isocyanides and diazo compounds. These reactions provide a glimpse of the wide synthetic potential of this hydride complex for the preparation of new heterometallic compounds having a wide variety of functional groups, while also pinpointing some genuine heterometallic effects even if the overall chemical behavior of the compound rather resembles the known chemistry of the W₂ analogue.



Scheme 1

2. Results and Discussion

2.1. Reactions of compound **1** with isocyanides.

Isocyanides give addition products easily in their reactions with binuclear unsaturated hydrides, although in most cases the initial addition products evolve through insertion processes to finally give complexes with formimidoyl ligands. These latter ligands commonly adopt a 3-electron donor bridging coordination (**A** in Chart 1), as found in the reactions of the hydrides $[\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}]$ [18], $[\text{Re}_2(\mu\text{-H})_2(\text{CO})_6(\mu\text{-L}_2)]$ [19], $[\text{Mn}_2(\mu\text{-H})_2(\text{CO})_6(\mu\text{-L}_2)]$ [20] and $[\text{Mo}_2\text{Cp}_2(\mu\text{-H})(\mu\text{-PPh}_2)(\mu\text{-SMe})_2]$ [21], with different isocyanides. However, in the case of the reactions of the Mo_2 and W_2 analogues of compound **1**, most of the resulting formimidoyl ligands adopt a 5-electron donor coordination mode instead (**B** in Chart 1), this effectively providing electronic and coordinative saturation to the dimetallic centers [15,16b]. Yet there is another potential outcome for these reactions, this now formally involving the migration of the hydride ligand to the N atom of the incoming reagent, to generate an aminocarbyne group $[\text{C}=\text{N}(\text{H})\text{R}]$ (**C** in Chart 1). However, the actual mechanism by which the aminocarbyne group might be formed in these reactions is uncertain, and it seems to depend on the particular system under study, as both intramolecular processes (H-shift from formimidoyl ligands) and deprotonation/reprotonation sequences have been invoked to account for these transformations [18,22]. In particular, we observed a “direct” thermal transformation from **A** to **C** isomers for the W_2 analogue of compound **1** when the isocyanide used had the bulky xylyl group ($\text{Xyl} = 2,6\text{-Me}_2\text{C}_6\text{H}_4$) [16b].

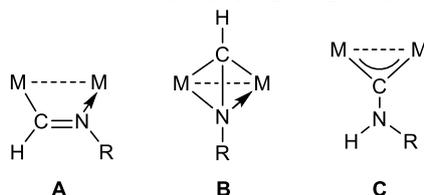
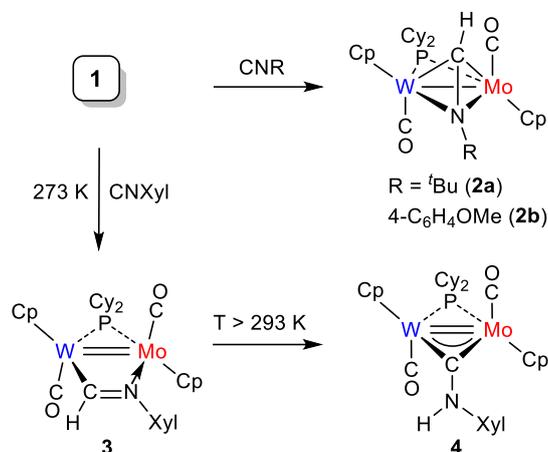


Chart 1

2.1.1. Stoichiometric reactions

As observed for the homometallic analogues, the reactions of **1** with isocyanides CNR (tBu , 4- $\text{C}_6\text{H}_4\text{OMe}$ and Xyl) are strongly dependent on the nature of the substituent R and on the experimental conditions. Under stoichiometric conditions the reactions take place rapidly even at 273 K to give two types of formimidoyl derivatives: the type **B** complexes $[\text{MoWCp}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-CHNR})(\mu\text{-PCy}_2)(\text{CO})_2]$ ($\text{R} = \text{tBu}$ (**2a**), 4- $\text{C}_6\text{H}_4\text{OMe}$ (**2b**)), and the type **A** complex $[\text{MoWCp}_2\{\mu\text{-}1\kappa\text{C:}2\kappa\text{N-HCN}(\text{Xyl})\}(\mu\text{-PCy}_2)(\text{CO})_2]$ (**3**), in which the carbon atom of the ligand is bonded specifically to the W atom (Scheme 2). As found for the W_2 derivatives, while compounds **2** are stable in solution at room

temperature, compound **3** undergoes a slow isomerization to give the corresponding aminocarbyne derivative $[\text{MoWCp}_2\{\mu\text{-CNH(Xyl)}\}(\mu\text{-PCy}_2)(\text{CO})_2]$ (**4**), a transformation also taking place rapidly upon attempted chromatographic purification of compound **3** on alumina columns.



2.1.2. Structural characterization of formimidoyl complexes **2** and **3**.

Spectroscopic data for the formimidoyl complexes **2a,b** (Table 1 and Experimental section) are comparable to those of the related homometallic complexes $[\text{M}_2\text{Cp}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-CHNR})(\mu\text{-PCy}_2)(\text{CO})_2]$ ($\text{M} = \text{Mo}$, $\text{R} = \text{tBu}$, *p*-tol; $\text{M} = \text{W}$, $\text{R} = \text{tBu}$, 4- $\text{C}_6\text{H}_4\text{OMe}$) [15,16b], which have been thoroughly characterized by spectroscopic methods and X-ray diffraction studies for the ^tBu substituted derivatives, then only relevant details will be discussed here. IR solution spectra of these compounds display two C–O stretching bands with weak and strong relative intensities in order of decreasing frequency as expected for *transoid* $\text{MM}'(\text{CO})_2$ oscillators [23]. However, the available NMR data for compounds **2a,b** are indicative of the existence of two isomers (**E** and **F**) in solution for both compounds. This is first indicated by their $^{31}\text{P}\{^1\text{H}\}$ NMR spectra, which display two very close resonances in each case at *ca.* 104 (**2a**) and 107 (**2b**) ppm, with chemical shifts which are, as expected, intermediate between those of the Mo_2 and W_2 analogues (*ie.* 155 and 56 ppm for the CN^tBu derivatives, respectively). As also observed for the W_2 compounds, these resonances display relatively high P–W couplings of *ca.* 290 Hz, actually close to the value of the parent hydride **1** (*ca.* 330 Hz for the bridging isomer), a situation with no obvious explanation taking into account the usual decrease of the value of $^1J_{\text{PW}}$ couplings upon increasing the number of donor atoms around the corresponding W atoms. The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of compounds **2a,b** confirmed the presence of two isomers in solution and, more importantly, the retention of a 5-electron coordination of their formimidoyl ligands. Actually, isomers **E** and **F** would differ only in the actual metal atom (Mo/W) present at each of the two non-equivalent metal sites: i) one bearing a CO group leaning towards the intermetallic bond

and ii) another one bearing a CO group pointing away from the dimetal centre. In fact, DFT calculations at the B3LYP/6-31G(d)/LANL2DZ level allowed us to locate the two structures proposed (**2aE** and **2aF**) as true minima in the corresponding Potential Energy Surface and, not surprisingly, they are almost isoenergetic (difference *ca.* 3 kJ·mol⁻¹) (Figure 1), hence supporting its coexistence in solution, with a measured ratio of *ca.* 3:1 in C₆D₆. However, we must note that this ratio was not affected by the solvent used, this rather suggesting that the above isomers do not interconvert in solution, a circumstance not further explored. Comparison of the carbonyl ¹³C NMR resonances for the major isomer of compound **2a** (239.8 and 231.7 ppm) in solution with those of the homometallic analogues (W₂: 231.0 and 227.6 ppm, Mo₂: 242.1 and 238.2 ppm) indicates that this isomer is the one bearing the W bound CO ligand leaning towards the intermetallic bond (type E), more deshielded in relative terms.

Table 1. Selected IR^a and NMR Data^b for New Compounds.^c

Compound	$\nu(\text{CX})$	$\delta(\text{P}) [J_{\text{PW}}]$
[MoWCp ₂ (μ - η^2 : η^2 -CHN ^t Bu)(μ -PCy ₂)(CO) ₂] (2a)	1844 (m, sh), 1818 (vs)	104.1 [287] ^d
[MoWCp ₂ { μ - η^2 : η^2 -CHN(4-C ₆ H ₄ OMe)}(μ -PCy ₂)(CO) ₂] (2b)	1854 (m, sh), 1828 (vs)	107.3 [287] ^e
[MoWCp ₂ (μ -1 κ _C :2 κ _N -HCNXYl)(μ -PCy ₂)(CO) ₂] (3)	1833 (s), 1792 (vs)	81.2 [218] ^e
[MoWCp ₂ (μ -CNHXYl)(μ -PCy ₂)(CO) ₂] (4)	1865 (m, sh), 1843 (vs)	78.1 [297]
[MoWCp ₂ (μ -H)(μ -PCy ₂)(1 κ -CN ^t Bu)(2 κ -CN ^t Bu)(1 κ -CO)(2 κ -CO)] (5)	2093 (w), 2049 (w), 1900 (w), 1801 (vs)	159.3 [210]
[MoWCp ₂ (μ -1 η^2 :2 κ _C : κ _C -HCN(4-C ₆ H ₄ OMe)C{N(4-C ₆ H ₄ OMe)})(μ -PCy ₂)(CO) ₂] (6)	1881 (m, sh), 1860 (vs)	107.4 [228] ^e
[MoWCp ₂ (μ -1 κ _C : κ _C :2 η^2 -HCN(4-C ₆ H ₄ OMe)C{N(4-C ₆ H ₄ OMe)})(μ -PCy ₂){1 κ -CN(4-C ₆ H ₄ OMe)}(CO)] (7)	1994 (w), 1854 (vs)	118.0 [186] ^e
[MoWCp ₂ (1 κ -H)(μ -PCy ₂)(2 κ -CO) ₂ {1 κ -N ₂ CH(SiMe ₃)}] (8c)	1895 (vs), 1805 (vs)	210.8 [190] ^{d,e}
[MoWCp ₂ (1 κ -H)(μ -PCy ₂)(2 κ -CO) ₂ (1 κ -N ₂ CPh ₂)] (8d-W)	1895 (vs), 1800 (vs)	215.8 [192] ^f
[MoWCp ₂ (2 κ -H)(μ -PCy ₂)(1 κ -CO) ₂ (2 κ -N ₂ CPh ₂)] (8d-Mo)	1891 (vs), 1801 (vs)	203.5 [242] ^g
[MoWCp ₂ (2 κ -H)(μ -PCy ₂)(2 κ -CO) ₂ (1 κ -N ₂ CPh ₂) ₂] (9d-Mo)	1897 (vs), 1803 (s)	46.3 [308] ^h
[MoWCp ₂ (1 κ -H)(μ -PCy ₂)(1 κ -CO) ₂ (2 κ -N ₂ CPh ₂) ₂] (9d-W)	1896 (vs), 1805 (s)	28.1 [174] ^g
[MoWCp ₂ { μ -1 κ _C :2 η^2 -C(O)CH ₂ (<i>p</i> -tol)}(1 κ -O)(μ -PCy ₂)(2 κ -CO)] (10)	1850 (vs)	194.0 [304] ^e
<i>trans</i> -[MoWCp ₂ { μ - κ : η^2 -C(<i>p</i> -tol)CH ₂ }(μ -PCy ₂)(CO) ₂] (trans-11)	1886 (s), 1859 (vs), 1782 (m)	106.5 [245] ⁱ
<i>cis</i> -[MoWCp ₂ { μ -1 κ :2 η^2 -C(<i>p</i> -tol)CH ₂ }(μ -PCy ₂)(CO) ₂] (cis-11)	1920 (m)	144.5 [358]
<i>trans</i> -[MoWCp ₂ { μ -1 κ :2 η^2 -CHCH(<i>p</i> -tol)}(μ -PCy ₂)(CO) ₂] (trans-12)	1874 (m), 1815 (vs), 1796 (sh, s)	113.3 [317] ^h
<i>cis</i> -[MoWCp ₂ { μ - κ : η^2 -CHCH(<i>p</i> -tol)}(μ -PCy ₂)(CO) ₂] (cis-12)	1921 (w)	105.4

^a Recorded in dichloromethane solution, with C–X stretching bands [$\nu(\text{CO})$ and $\nu(\text{CN})$] in cm⁻¹.

^b Recorded in CD₂Cl₂ solution at 162.16 MHz and 298 K, unless otherwise stated, with chemical shifts (δ) in ppm and ³¹P–¹⁸³W couplings (J_{PW}) in Hz.

^c When two isomers coexist in solution the data provided correspond only to the major one.

^d Recorded in C₆D₆.

^e Recorded at 121.49 MHz.

^f Recorded at 213 K.

^g Recorded at 193 K.

^h Recorded at 233 K.

ⁱ Recorded at 203 K.

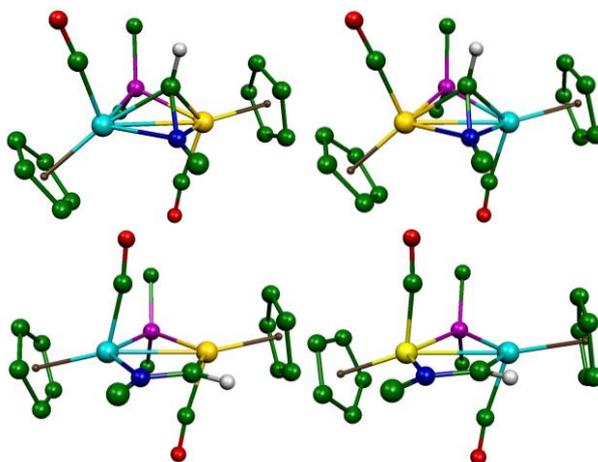


Figure 1. B3LYP-optimized structures for isomers **2aE** (top left), **2aF** (top right) and hypothetical isomers having 3-electron donor formimidoyl groups C-bound to the W (yellow) atom **3a-W** (bottom left) or Mo (blue) atom **3a-Mo** (bottom right). Cy groups (except C1 atoms) and most hydrogens omitted for clarity. Relative Gibbs free energies at 298 K were +3, 0, +16 and +27 kJ/mol, respectively.

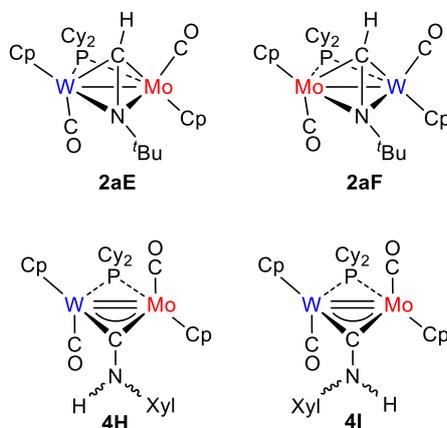


Chart 2

As for compound **3**, there is an obvious spectroscopic support for the change in the coordination mode of the formimidoyl ligand (Table 1 and Experimental section). Thus, the ¹H and ¹³C NMR resonances of this group in **3** are significantly deshielded (11.96 and 217.1 ppm, respectively) when compared to those in compounds **2**, with figures now falling within the range usually found for complexes having $\mu\text{-}\kappa\text{N}:\kappa\text{C}\text{-HC=NR}$ ligands [18-21], including its W₂ analogue [16b]. Furthermore, its ¹³C NMR resonance is also informative of the coordination mode of the formimidoyl ligand, as it displays a high C–W coupling of 84 Hz, which is only compatible with a structure in which the C atom is directly attached to the W atom. We must note that the 3-electron donor (type A) coordination of the formimidoyl ligand in our binuclear complexes has only been

observed when R = Xylyl, and we have previously shown for the W₂ complexes that this has a steric origin [16b]. In contrast, the preference for a W–C / Mo–N coordination of the formimidoyl group seems to have an electronic origin since DFT calculations for the two hypothetical complexes of type **A** bearing a ^tBu substituted formimidoyl ligand (**3a-Mo** and **3a-W** in Figure 1) proved that this coordination is favoured by *ca.* 11 kJ·mol⁻¹ when compared with the alternative W–N / Mo–C coordination mode. Other spectroscopic features of compound **3** are as expected and will not be discussed.

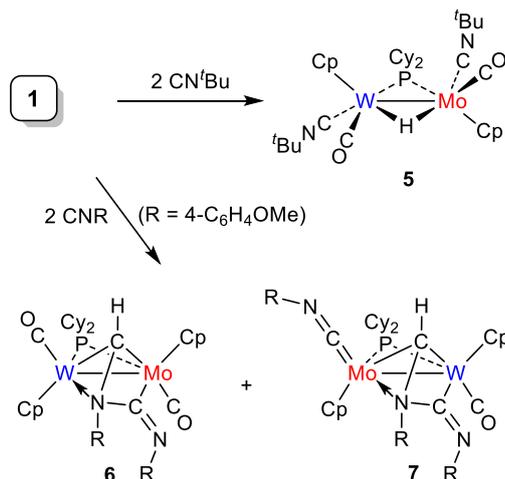
2.1.3. Structural characterization of the aminocarbyne complex **4**.

The aminocarbyne complex **4** shares spectroscopic features with the large family of dicarbonylic complexes *trans*-[M₂Cp₂(μ-PCy₂)(μ-X)(CO)₂] previously prepared by us, particularly with the W₂ analogue [W₂Cp₂{μ-CN(H)Xyl}(μ-PCy₂)(CO)₂], hence a detailed discussion is not required (Table 1 and Experimental section). However, in contrast with the latter compound, the available NMR data are also indicative of the existence of two isomers in solution (**H/I** in Chart 2) in a *ca.* 3:2 ratio, which are assigned to the two different orientations of the H and Xylyl groups of the aminocarbyne group with respect to the different metal centers, a situation arising from the restricted rotation around the C–N bond of the carbyne ligand, also observed for the W₂ compound [16b]. Besides this, the main spectroscopic feature of these isomers comes from the presence of aminocarbyne ligands, these giving rise to characteristic strongly deshielded ¹H and ¹³C NMR resonances at *ca.* 10 and 344 ppm, respectively (*cf.* 9.92 and 336.6 ppm in the W₂ complex). The newly formed carbyne ligands are 3-electron donors, so a metal-metal double bond must be formulated for these isomers, which agrees with the poorly deshielded resonances observed in the corresponding ³¹P NMR spectra (*ca.* 78 ppm), while the relatively high one bond P–W couplings of *ca.* 300 Hz is consistent with the relatively low coordination number of the W atom in this molecule (*cf.* J_{PW} = 291 and 301 Hz for the W₂ analogue).

2.1.4. Reactions with excess isocyanide

The reactions of hydride **1** with excess isocyanide allow for the formation of products of double addition of the organic reagent, then resembling the known chemistry of the W₂ analogue rather than that of the Mo₂ system (Scheme 3). Thus, reaction with excess CN^tBu at low temperature gives selectively the “trivial” addition product of formula [MoWCp₂(μ-H)(μ-PCy₂)(1κ-CN^tBu)(2κ-CN^tBu)(1κ-CO)(2κ-CO)] (**5**), in which one molecule of the reagent is added at each metal center. A more interesting reaction takes place with excess CN(4-C₆H₄OMe) at room temperature, this yielding a mixture of two complexes having a 5-electron donor aminocarbene-iminoacyl ligand: [MoWCp₂(μ-1η²:2κ_C,κ_C-HCN(4-C₆H₄OMe)C{N(4-C₆H₄OMe)})](μ-PCy₂)(CO)₂]

(6) and $[\text{MoWCp}_2(\mu\text{-}1\kappa_{\text{C}},\kappa_{\text{C}}:2\eta^2\text{-HCN}(4\text{-C}_6\text{H}_4\text{OMe})\text{C}\{\text{N}(4\text{-C}_6\text{H}_4\text{OMe})\})(\mu\text{-PCy}_2)\{2\kappa\text{-CN}(4\text{-C}_6\text{H}_4\text{OMe})\}(1\kappa\text{-CO})]$ (7), both following from the formal coupling of formimidoyl and isocyanide ligands and, in the case of compound 7, additional carbonyl substitution by isocyanide specifically at the Mo atom. This reaction outcome parallels that of the W_2 analogue [16b], with the exception that the formation of compound 7 highlights a greater trend of the heterometallic center to undergo additional carbonyl substitution reactions, probably facilitated by the higher lability of Mo-bound carbonyls when compared to W-bound ones.



Scheme 3

2.1.5. Structural characterization of complex 5.

Compound 5 is structurally related to the tetracarbonyl hydride $[\text{MoWCp}_2(\mu\text{-H})(\mu\text{-PCy}_2)(\text{CO})_4]$ [9], by just replacing a carbonyl ligand at each metal by an isocyanide molecule. A similar structure has been previously observed by us in the homometallic complex $[\text{Mo}_2\text{Cp}_2(\mu\text{-H})(\mu\text{-PCy}_2)\{\text{CN}(p\text{-tol})\}_2(\text{CO})_2]$, a compound formed in small amounts upon addition of $\text{CN}(p\text{-tol})$ to the unsaturated Mo_2 hydride [15]. In the latter case, however, both isocyanides coordinate at the same Mo atom to form a quite asymmetric compound. In the case of compound 5, however, the available spectroscopic data are indicative of a more symmetrical structure. Thus, its $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum displays two P-coupled resonances (ca. 193 ppm and 23 Hz) for the CN^tBu ligands, a situation which supports a *cisoid* disposition of these ligands relative to the bridging PCy_2 group [24,25], and also rules out the alternative coordination of the two isocyanides ligands at the same metal centre. Incorporation of two molecules of isocyanide provides electronic saturation to the dimetallic center in 5, which is consistent with the moderately deshielded ^{31}P resonance of this compound ($\delta_{\text{P}} = 159.3$ ppm, $J_{\text{PW}} = 210$ Hz) and with the significant shielding of the hydride in the ^1H NMR spectrum ($\delta_{\text{H}} = -15.73$ ppm). As expected, these figures are close to those of the

isoelectronic hydride complex $[\text{MoWCp}_2(\mu\text{-H})(\mu\text{-PCy}_2)(\text{CO})_4]$ ($\delta_{\text{P}} = 178.9$ ppm and $\delta_{\text{H}} = -14.56$ ppm) [9].

2.1.6. Structural characterization of aminocarbene-iminoacyl complexes **6** and **7**.

Spectroscopic data for compounds **6** and **7** (Table 1 and Experimental section) are similar to those of the related W_2 complex $[\text{W}_2\text{Cp}_2(\mu\text{-}\eta^2\text{:}\kappa_{\text{C}},\kappa_{\text{C}}\text{-HCN}\{4\text{-C}_6\text{H}_4\text{OMe}\}\text{C}\{\text{N}(4\text{-C}_6\text{H}_4\text{OMe})\})](\mu\text{-PCy}_2)(\text{CO})_2]$ (whose structure was determined through an X-ray diffraction analysis), thus confirming the presence of a bridging aminocarbene-iminoacyl group formed upon N–C coupling between formimidoyl and isocyanide ligands. In addition to this, our data indicate that in the case of compound **7** one of the carbonyl ligands has been further replaced by a third molecule of isocyanide. Thus, while the IR spectrum of compound **6** displays two C–O stretches with the pattern characteristic of *transoid* $\text{M}_2(\text{CO})_2$ oscillators, the spectrum of **7** displays just one strong C–O stretching band at 1854 cm^{-1} . In addition, this spectrum also displays a comparatively weak and broad band at 1994 cm^{-1} , consistent with the presence of a bent isocyanide ligand, a type of conformation which has been previously associated with an increased metal to ligand back-donation (*ie.* $\text{M}=\text{C}=\text{NR}$), not uncommon in this sort of compounds with rather electron-rich dimetallic centers. Obviously, the stronger support for the formation of the new CNC bridging ligands in these compounds come from the corresponding $^{13}\text{C}\{^1\text{H}\}$ NMR spectra, which display resonances consistent with the presence of M–CN₂ [δ_{C} 194.7 (**6**) and 177.5 (**7**) ppm] and bridging C(H)N groups [δ_{C} 101.8 (**6**) and 98.9 (**7**) ppm] in the expected regions (*cf.* 178.8 and 89.2 ppm for the W_2 analogue, respectively [16b]). However, the actual chemical shifts of these resonances indicate that the CN₂ group of the bridging ligand is likely to be attached at the Mo atom in **6**, but at the W atom in **7**. Moreover, the additional isocyanide ligand in **7** gives rise to a highly deshielded resonance (208.0 ppm) consistent with the presence of a bent terminal Mo–CNR group, as suggested by the IR data.

2.2. Reactions of compound **1** with diazoalkanes.

As briefly mentioned in the Introduction, the Mo_2 and W_2 unsaturated hydrides behave in completely different ways in their reactions with diazoalkanes. Thus, while the Mo_2 compound only catalyzed the decomposition of the reagent [15], the W_2 analogue gave isolable single and double addition products with terminally bound imido-like diazoalkanes [14], except in the reactions with the most reactive N_2CH_2 , for which denitrogenation also took place, then leading to products having methyl groups formed through methylene insertion into W–H bonds. Apart from these previous studies, only a limited number of studies of reactions of diazoalkanes with complexes having unsaturated $\text{M}_2(\mu\text{-H})_x$ cores have been reported [26-30]. Even if the outcome of

the latter reactions depended critically on the nature of the diazoalkane, they never led to the isolation of stable diazoalkane addition products, in contrast with the results obtained for our W_2 hydride. In fact, in most cases the products isolated from these previous reactions follow from N_2 loss of the incoming reagent and only in a few cases the outcome was different: these being the formation of a hydrazonide ligand ($NHNCPh_2$) [26c,27a] and the cleavage of the N–N bond in the diazoalkane molecule to give nitride and imido ligands [29].

Reaction of compound **1** with $N_2CH(SiMe_3)$ takes place rapidly at room temperature to give the addition product $[MoWCp_2(1\kappa-H)(\mu-PCy_2)(2\kappa-CO)_2\{1\kappa-N_2CH(SiMe_3)\}]$ (**8c**) (Chart 3), in which a terminal imido-like diazoalkane (4-electron coordination) is specifically bound at the W atom. In contrast, the reaction with N_2CPh_2 under similar conditions led to the formation of mixtures containing at least four new products derived from the addition of either one molecule of diazoalkane: $[MoWCp_2(1\kappa-H)(\mu-PCy_2)(2\kappa-CO)_2(1\kappa-N_2CPh_2)]$ (**8d-W**) and $[MoWCp_2(2\kappa-H)(\mu-PCy_2)(1\kappa-CO)_2(2\kappa-N_2CPh_2)]$ (**8d-Mo**), or two molecules of the reagent $[MoWCp_2(2\kappa-H)(\mu-PCy_2)(2\kappa-CO)_2(1\kappa-N_2CPh_2)_2]$ (**9d-Mo**) and $[MoWCp_2(1\kappa-H)(\mu-PCy_2)(1\kappa-CO)_2(2\kappa-N_2CPh_2)_2]$ (**9d-W**) (Chart 3). Unexpectedly, the ratio of these compounds (*ca.* 2:1:2:4) turned out to be essentially independent of the stoichiometry of the diazoalkane used, this rather pointing to the presence of independent reaction pathways for the single and double addition products. We also note that the major product within each pair of isomers correspond in both cases to the isomer bearing the hydride ligand bound to the W atom, as expected. On the other hand, we note that reactions of compound **1** with other diazoalkanes such as N_2CH_2 or N_2CHCO_2Et only led to complex mixtures from which we could not isolate new organometallic compounds, with the exception of the known methyl derivative $[MoWCp_2(\mu-Me)(\mu-PCy_2)(CO)_2]$ [9], a complex formed in small amounts in the reaction with diazomethane.

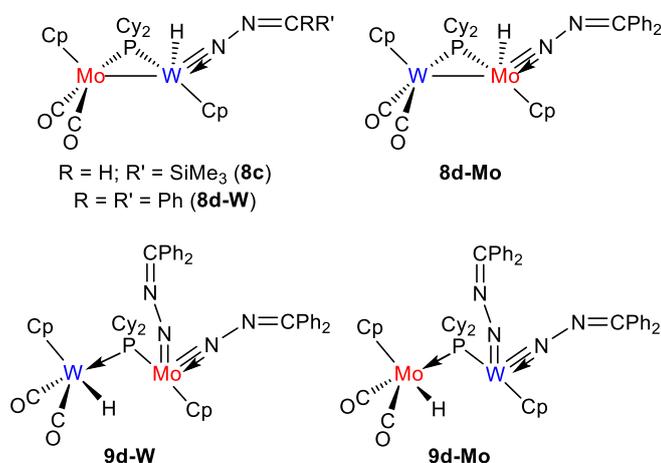


Chart 3

2.2.1. Structural characterization of compounds **8**.

The structure of complexes **8c**, **8d-W** and **8d-Mo** (Chart 3) are analogous to those of the related W_2 compounds $[W_2Cp_2(H)(\mu-PCy_2)(CO)_2(N_2CRR')]$ ($R = H$, $R' = SiMe_3$; $R = R' = Ph$) and it is built from $MCp(CO)_2$ and $M'Cp$ fragments arranged in a *transoid* disposition and bridged by a PCy_2 ligand, with the coordination sphere of the latter metal being completed by a hydride and a N-bound diazoalkane [14]. Accordingly, the IR spectra of these complexes display two strong C–O stretching bands of almost identical intensity and separated by *ca.* 100 cm^{-1} , as expected for compounds containing a $M(CO)_2$ fragment with carbonyl ligands in a mutual *cisoid* disposition (C–M–C angles around 90°) [23]. The bridging PCy_2 group in these compounds gives rise to a moderately deshielded resonance (*ca.* 210 ppm) which fall in the region expected for compounds having metal–metal single bonds (*ie.* 179 ppm for $[MoWCp_2(\mu-H)(\mu-PCy_2)(CO)_4]$ [9]), while retaining medium-strength W–P couplings similar to those found in the W_2 analogues. Valuable information for the identification of the ligands around each metal atom in these complexes could be obtained from the 1H NMR spectra. In particular, the poorly shielded hydride resonances (δ_H *ca.* -0.5 ppm) indicate a terminal coordination of this ligand, and their relatively high two-bond P–H coupling of *ca.* 32 Hz indicate a *cisoid* arrangement of this ligand relative to the P atom [24,25]. However, one-bond W–H coupling was only observed for compounds **8c** and isomer **8d-W**, whereas the absence of such a coupling for **8d-Mo** denote the coordination of the hydride ligand to the Mo atom in this isomer. Other spectroscopic parameters are similar to those of the W_2 complexes and will not be discussed.

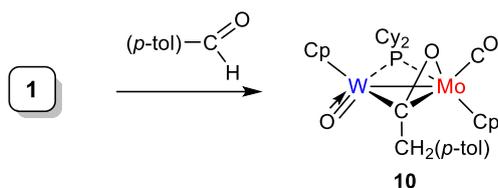
2.2.2. Structural characterization of compounds **9d**.

The structure proposed for isomers **9d-Mo** and **9d-W** (Chart 3) is based on that determined crystallographically for the W_2 complex $[W_2Cp_2H(\mu-PCy_2)(CO)_2(N_2CPh_2)_2]$, and it consists on $MCpH(CO)_2$ and $M'Cp(N_2CPh_2)_2$ fragments bridged by a PCy_2 ligand [14]. As found for complexes of type **8**, the IR spectra of isomers **9d-Mo/W** is clearly indicative of the presence of *cisoid* $M(CO)_2$ fragments in these compounds. However, their ^{31}P resonances are significantly more shielded, appearing now in the 30–50 ppm region, a circumstance that can be only attributed to the lack of M–M' bond in these complexes. This, in turn, requires that the diazoalkane ligands would effectively provide a total of 6 electrons to the complex, a circumstance likely achieved through a dissimilar coordination of these ligands: a four-electron coordination (imido-like) of one of them and a two-electron coordination of the second one, a situation which was supported by crystallographic data for the related W_2 compound [14]. Finally, as found for isomers **8d-Mo/W**, the presence or absence of

one-bond W–H couplings in the ^1H NMR resonances of the hydride ligands in these compounds allowed us to establish the connectivity of the groups, with a direct W–H bond being present only in **9d-W**, this corresponding to a $\text{WCpH}(\text{CO})_2$ fragment, while **9d-Mo** would then contain a $\text{MoCpH}(\text{CO})_2$ fragment instead.

2.3. Reaction of compound **1** with (*p*-tolyl)aldehyde.

The reactions of the homometallic analogues of **1** with (*p*-tolyl)aldehyde also revealed a significant influence of the metal on the reactivity of these systems. Thus, the Mo_2 complex reacted with this reagent in refluxing toluene to give the unstable alkoxide $[\text{Mo}_2\text{Cp}_2\{\mu\text{-OCH}_2(\textit{p}\text{-tol})\}(\mu\text{-PCy}_2)(\text{CO})_2]$ [31]. Under the same conditions, the W_2 hydride also reacted with this reagent, but the final outcome of the reaction would depend on the amount of reagent used. When using a great excess of the aldehyde, a mixture of the alkoxide $[\text{W}_2\text{Cp}_2\{\mu\text{-OCH}_2(\textit{p}\text{-tol})\}(\mu\text{-PCy}_2)(\text{CO})_2]$ and the carboxylate $[\text{W}_2\text{Cp}_2\{\mu\text{-}\kappa\text{:}\kappa\text{-O}_2\text{C}(\textit{p}\text{-tol})\}(\mu\text{-PCy}_2)(\text{CO})_2]$ was formed [32], whereas reactions with a slight excess led to the formation of mixtures of the oxo alkyl $[\text{W}_2\text{Cp}_2\{\text{CH}_2(\textit{p}\text{-tol})\}(\text{O})(\mu\text{-PCy}_2)(\text{CO})_2]$ and the oxoacyl complex $[\text{W}_2\text{Cp}_2\{\mu\text{-}\kappa\text{:}\eta^2\text{-C}(\text{O})\text{CH}_2(\textit{p}\text{-tol})\}(\text{O})(\mu\text{-PCy}_2)(\text{CO})]$ instead [33]. The reaction of the hydride **1** with (*p*-tolyl)aldehyde resembles in part the known chemistry of the W_2 complex, yet it only takes place selectively using a slight excess of the reagent in refluxing toluene, to give the oxoacyl complex $[\text{MoWCp}_2\{\mu\text{-}1\kappa\text{C:}2\eta^2\text{-C}(\text{O})\text{CH}_2(\textit{p}\text{-tol})\}(1\kappa\text{-O})(\mu\text{-PCy}_2)(2\kappa\text{-CO})]$ (**10**) (Scheme 4) as unique product, while other reaction conditions did not yield new isolable organometallic compounds. The origin of the oxo ligand in **10** has not been determined, but likely is originated from traces of dioxygen present in the reaction medium.



Scheme 4

2.3.1. Solid-state and solution structure of compound **10**.

The molecule of **10** in the crystal (Figure 2 and Table 2) is built from two *transoid* MCp fragments bridged by a PCy_2 group and an acyl ligand. The latter group displays an alkenyl-like coordination, it being κ^1 -bonded to the W atom and η^2 -bound to the Mo atom, with the M–C distances [$\text{W–C} = 2.12(1)$ Å and $\text{Mo–C} = 2.18(1)$ Å] being somewhat shorter than those in complexes with terminal acyls (*ca.* 2.26 Å for compounds $[\text{MoCp}\{\text{C}(\text{O})\text{CH}_3\}(\text{CO})_2(\text{PR}_3)]$ [34] or $[\text{WCp}\{\text{C}(\text{O})\text{CH}_3\}(\text{CO})_2(\text{PPh}_3)]$ [35]), while the Mo–O length of 2.171(5) Å is within the range typically found for these

ligands. The oxo ligand is tightly bound to the tungsten atom, with a short W–O bond length of 1.713(5) Å, indicative of the existence of significant multiplicity in this bond. We have previously found that oxo ligands can easily modify their degree of π interaction with the metal depending on the rest of the ligands present at the dimetallic center, then acting as formal donors of somewhere between 2 to 4 electrons [36]. Obviously, this has a direct effect on the M–M bonding in the resulting complexes, as is the case of compound **10**, which displays an intermetallic separation of 2.8767(6) Å, consistent with the formulation of a Mo–W single bond, actually a situation similar to that found for the related W_2 complex (2.8509(1) Å) [33], therefore indicative of a 4-electron contribution of the oxo ligand to the dimetal centre.

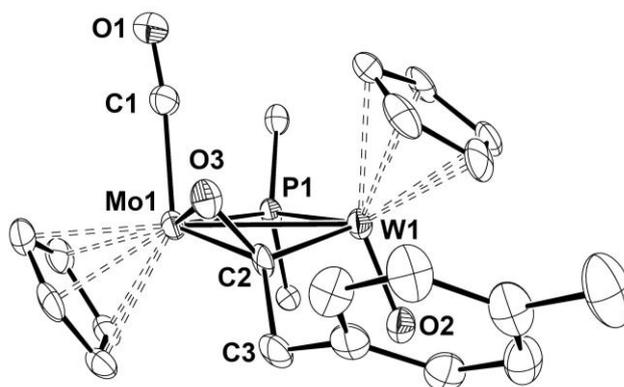


Figure 2. ORTEP diagram (30% probability) of compound **10**, with Cy groups (except their C¹ atoms), H atoms and co-crystallized solvent molecules omitted for clarity.

Table 2. Selected bond lengths (Å) and angles (°) for **10**

W(1)–Mo(1)	2.8767(6)	Mo(1)–P(1)–W(1)	73.86(5)
W(1)–P(1)	2.430(2)	W(1)–Mo(1)–C(1)	94.0(2)
Mo(1)–P(1)	2.367(2)	O(2)–W(1)–Mo(1)	111.2(2)
W(1)–O(2)	1.713(5)	C(2)–O(3)–Mo(1)	73.3(4)
Mo(1)–O(3)	2.171(5)	W(1)–C(2)–Mo(1)	83.9(2)
W(1)–C(2)	2.12(1)	O(3)–Mo(1)–C(2)	34.4(2)
Mo(1)–C(2)	2.18(1)	O(1)–C(1)–Mo(1)	173.3(6)
Mo(1)–C(1)	1.95(1)		
C(2)–O(3)	1.29(1)		
C(2)–C(3)	1.51(1)		

Spectroscopic data in solution for compound **10** (Table 1 and Experimental section) are similar to those of the W_2 analogue, and fully consistent with the solid-state structure just discussed. The acyl group gives rise to a characteristically deshielded ^{13}C NMR resonance at *ca.* 218 ppm, some 10 ppm above that of the W_2 analogue. The presence of a terminal carbonyl ligand at the Mo atom is supported by the presence of a single C–O stretching band (1850 cm^{-1}) in the IR spectrum, and a single highly deshielded ^{13}C NMR resonance at *ca.* 244 ppm. The $^{31}P\{^1H\}$ NMR spectrum shows a single resonance at 194 ppm ($J_{PW} = 304$ Hz), a chemical shift comparable to those of

compounds of type **8** and consistent with the metal–metal single bond inferred from the solid-state data. Other spectroscopic data for **10** are as expected and deserve no particular comments.

2.4. Reactions of Compound **1** with (*p*-tolyl)acetylene.

Unsaturated hydrides usually are quite reactive towards alkynes to give, typically, new alkenyl-bridged complexes. This is, indeed, the case of the homometallic analogues of compound **1** which display a tremendously rich chemistry in their reactions with alkynes [16a,16c]. Most of these reactions led to the formation of new alkenyl derivatives (α - or β -substituted, *cis/trans* isomers, etc.), yet for the W₂ analogue novel products derived from selective alkenyl/alkyne coupling were also observed when using excesses of activated alkynes. As expected, compound **1** reacts rapidly with HC≡C(*p*-tol) in toluene at room temperature to give a mixture of the α -substituted alkenyl isomers *trans*-[MoWCp₂{ μ - κ : η^2 -C(*p*-tol)CH₂}(μ -PCy₂)(CO)₂] (***trans*-11**) and *cis*-[MoWCp₂{ μ -1 κ :2 η^2 -C(*p*-tol)CH₂}(μ -PCy₂)(CO)₂] (***cis*-11**) in a ratio of *ca.* 7/1 (Chart 4). In contrast, when the same reaction is carried out in refluxing toluene it leads to mixtures of the corresponding β -substituted alkenyls *trans*-[MoWCp₂{ μ -1 κ :2 η^2 -CHCH(*p*-tol)}(μ -PCy₂)(CO)₂] (***trans*-12**) and *cis*-[MoWCp₂{ μ - κ : η^2 -CHCH(*p*-tol)}(μ -PCy₂)(CO)₂] (***cis*-12**) in a ratio *ca.* 10/1 (Chart 4). The α -substituted alkenyl ***trans*-11** can be identified as kinetic product of the reaction, as it evolves rapidly at 383 K to the corresponding β -substituted alkenyl ***trans*-12**, an isomerization process formally requiring a [2,1]-hydrogen shift, which has also been observed for the related Mo₂ and W₂ complexes [16a,16c]. Unfortunately, we have not been able to find suitable reaction conditions for the selective preparation of the *cis* isomers, nor we could separate them from the corresponding *trans* isomers; therefore, the available spectroscopic data for these compounds are quite limited and were obtained from the above mentioned mixtures.

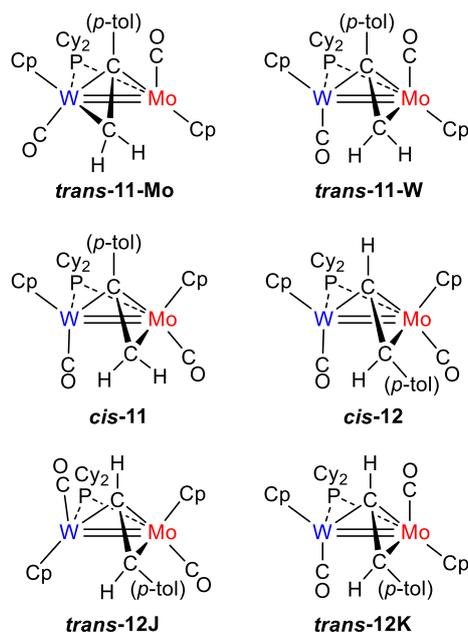


Chart 4

2.4.1. Structural characterization of alkenyl derivatives.

The spectroscopic data for the alkenyls **trans-11** and **trans-12** are comparable to those of the alkenyl complexes $trans\text{-}[M_2Cp_2\{\mu\text{-}\kappa\text{-}\eta^2\text{-CRCH(R')}\}\{\mu\text{-PCy}_2\}(CO)_2]$ previously prepared by us from related reactions of the Mo₂ and W₂ analogues of **1**, and which have been discussed thoroughly, then making unnecessary a lengthy discussion here [16a,16c]. Thus, once excluded the bands corresponding to the symmetric stretches (strong bands) of the *cis* isomers, which are always present in small amounts [1920 (**cis-11**) and 1921 cm⁻¹ (**cis-12**)], the IR spectra of these compounds display three and four C–O stretching bands respectively. This can be accounted for by assuming the presence in solution of two isomers for each compound (**trans-11-Mo/W** and **trans-12J/K** in Chart4), which are involved in fast equilibria, as the room temperature NMR spectra for these compounds are consistent with the presence of single species in solution in both cases. Following from our studies on the homometallic analogues, it seems likely that these isomers differ on the actual conformation of the two MCp(CO) fragments. Thus, the IR of these compounds would consist on an overlap of bands corresponding to species having an almost perfectly antiparallel arrangement of CO ligands with relative angles close to 180° (**trans-11-W** and **trans-12K**), these being characterized by a strong asymmetric stretching band, and those derived from species with CO ligands defining mutual angles now approaching 90° (**trans-11-Mo** and **trans-12J**), which in turn give rise to two C–O stretches of similar intensity and greatly separated from each other (*ca.* 100 cm⁻¹). As mentioned before, the room temperature ³¹P{¹H} NMR spectra of these species are deceptively simple and consistent with the presence of only two species in solution (*cis* and *trans* isomers), these being characterized by moderately deshielded

resonances (144–112 ppm), as expected for compounds having Mo=W bonds (*cf.* 81 ppm for **3**). In the case of *trans*-**11**, when the spectra was recorded at 203 K the signal split into two well-resolved resonances corresponding to the *trans*-**11-Mo** and *trans*-**11-W** isomers (ratio *ca.* 8:1), a situation not observed for the β -substituted complex *trans*-**12**, for which the dynamic process was fast at all temperatures attained. The ^{31}P – ^{183}W couplings in all these compounds bring out relevant information about the actual coordination mode of the alkenyl groups. Thus, the resonance for *cis*-**11** retains a very high P–W coupling of *ca.* 360 Hz which would be compatible only with a $1\kappa:2\eta^2$ coordination, in which the W atom retains a low number of donor groups around it, as it is not involved in the π coordination of the ligand. Unfortunately, we have not been able to measure the value of the P–W coupling for *cis*-**12** due to broadness of the resonance and, hence, we lack of enough information to ascertain the actual coordination mode of the alkenyl group in this compound. In the case of *trans*-**11** isomers, a comparatively low P–W coupling is observed for *trans*-**11-Mo** at 203 K (*ca.* 245 Hz), this being indicative of a $1\eta^2:2\kappa$ coordination, with the alkenyl ligand now π -bonded to the W atom. However, since the value of this coupling increases to 288 Hz in the averaged resonance at room temperature, we must conclude that the coordination of the alkenyl is reversed in the minor isomer *trans*-**11-W** ($1\kappa:2\eta^2$ coordination) for which we have not been able to measure directly the value of the P–W coupling in the low temperature spectra. In contrast, a fast dynamic process was observed at all accessible temperatures studied for *trans*-**12** and, hence, we can only access the value of the average P–W coupling (*ca.* 319 Hz), a comparatively high value which in this case can only be explained if both isomers (**J/K**) have the same $1\kappa:2\eta^2$ coordination of the alkenyl ligand, that is σ bound to W and π bound to the Mo atom.

The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of these compounds display resonances for the alkenyl ligands within the range usually found for a wide number di- or trinuclear Mo/W [16a,16c,36], Mn [38], Re [39], Fe [40], Ru [40i,41], Os [42] or Ir [22b] compounds having σ/π -bound bridging alkenyl ligands. In particular, α -substitution in compounds *trans*-**11** is evident from the low value of the “geminal” coupling between the hydrogen atoms of the CH_2 group (2 Hz), while this coupling is much higher for “vicinal” hydrogens in the β -substituted compound *trans*-**12** (11 Hz). Finally, the ^{13}C resonances of the C_β atoms provide additional support to the coordination modes proposed for the alkenyl ligands. Thus, the value of 59.1 ppm for this signal in the isomer *trans*-**11-Mo** (π bonding to W) is almost identical to that of the W_2 analogue (51.3 ppm) [16c], while the averaged resonance for the two isomers of *trans*-**12** (π bonding to Mo) at 95.6 ppm is now similar to that of the analogous Mo_2 alkenyl complex (100.9 ppm) [16a].

3. Conclusions

The heterometallic hydride $[\text{MoWCp}_2(\text{H})(\mu\text{-PCy}_2)(\text{CO})_2]$ (**1**) displays a rich and varied chemical behavior derived from its unsaturated nature, as it is the case of their homometallic analogues. In reactions with isocyanides it behaves essentially in a similar way to the W_2 analogue, it being able to reproduce uncommon C–N couplings between formimidoyl and isocyanide ligands for the $\text{CN}(4\text{-C}_6\text{H}_4\text{OMe})$ derivatives. Yet in these reactions we have also identified some genuine heterometallic effects: i) the potential to add up to three molecules of the reagent by additional carbonyl substitution taking place specifically at the Mo atom and, ii) the thermodynamic preference for a selective W–C/Mo–N coordination of the 3-electron formimidoyl ligand HCNXyl . The reactions of **1** with diazoalkanes also resemble the known chemistry of the W_2 analogue, with the $\text{N}_2\text{CHSiMe}_3$ addition taking place exclusively at the W atom, whereas little addition specificity was observed for N_2CPh_2 . In contrast, the reaction of **1** with (*p*-tol)C(O)H is more selective than those of the homometallic analogues, since it renders as major product a stable oxo acyl compound with the acyl group specifically κ^1 -bound to the W atom and η^2 -bound to the Mo centre. Such a preference for the σ -coordination at the W atom was only partially retained in the alkenyl derivatives formed upon reaction of **1** with $\text{HC}_2(\textit{p}\text{-tol})$. Thus, the α -substituted alkenyls displayed a solution equilibrium between isomers changing the metal involved into σ -coordination, whereas for the β -substituted isomer, σ -coordination takes place selectively at the W atom.

4. Experimental

All manipulations and reactions were carried out under an argon (99.995%) atmosphere using standard Schlenk techniques. Solvents were purified according to literature procedures, and distilled prior to use [43]. Compound **1** was prepared as described previously [9]. Petroleum ether refers to that fraction distilling in the range 338–343 K. Filtrations were carried out through diatomaceous earth unless otherwise stated. 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, 70-290 mesh) was degassed under vacuum prior to use. The latter was mixed under argon with the appropriate amount of water to reach activity IV. IR stretching frequencies were generally measured in solution, are referred to as $\nu(\text{solvent})$, and are given in cm^{-1} . Nuclear magnetic resonance (NMR) spectra were routinely recorded at 400.13 (^1H), 162.16 ($^{31}\text{P}\{^1\text{H}\}$) and 100.73 ($^{13}\text{C}\{^1\text{H}\}$) MHz, at 298 K in CD_2Cl_2 solution unless otherwise stated. Chemical shifts (δ) are given in ppm, relative to internal tetramethylsilane (^1H , ^{13}C) or external 85% aqueous H_3PO_4 solutions (^{31}P). Coupling constants (J) are given in hertz.

4.1. Preparation of $[\text{MoWCp}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-CHN}^t\text{Bu})(\mu\text{-PCy}_2)(\text{CO})_2]$ (**2a**).

Neat CN^tBu (4 μ L, 0.035 mmol) was added to a solution of compound **1** (0.020 g, 0.030 mmol) in dichloromethane (6 mL) at 273 K, and the mixture was stirred for 10 min to give an orange solution. The solvent was then removed under vacuum, the residue was extracted with dichloromethane/petroleum ether (1/7) and the extracts were chromatographed on an alumina column at 288 K. Elution with the same solvent mixture gave an orange fraction yielding, after removal of solvents, compound **2a** as an orange solid (0.017 g, 76%). This product was shown (by NMR) to contain a mixture of two isomers (**2aE** and **2aF**) in a ratio of *ca.* 3:1 which could not be separated. Anal. Calcd for C₂₉H₄₂MoNO₂PW: C, 46.60; H, 5.66; N, 1.87. Found: C, 46.88; H, 5.81; N, 1.52. $\nu(\text{CO})$ (CH₂Cl₂): 1844 (m, sh), 1818 (vs). *Isomer 2aE*: ³¹P{¹H} RMN (C₆D₆): δ 104.1 (s, $J_{\text{PW}} = 287$). ¹H NMR (C₆D₆): δ 5.24, 5.03 (2d, $J_{\text{HP}} = 1$, 2 x 5H, Cp), 2.80 (d, $J_{\text{HP}} = 2$, 1H, CHN), 2.03-0.94 (m, 22H, Cy), 0.76 (s, 9H, ^tBu). ¹³C{¹H} RMN (C₆D₆): δ 92.3, 86.0 (2s, Cp), 52.9 [s, C¹(^tBu)], 51.5 (d, $J_{\text{CP}} = 31$, CHN), 49.3 [d, $J_{\text{CP}} = 17$, C¹(Cy)], 44.1 [d, $J_{\text{CP}} = 10$, C¹(Cy)], 35.9, 34.3 [2s, C²(Cy)], 34.2 [d, $J_{\text{CP}} = 3$, C²(Cy)], 33.8 [s, C²(Cy)], 30.9 [s, C²(^tBu)], 28.9-28.0 [m, 4C³(Cy)], 27.0, 26.7 [2s, C⁴(Cy)]. ¹³C{¹H} RMN (243 K): δ 239.8 (d, $J_{\text{CP}} = 6$, MoCO), 231.7 (d, $J_{\text{CP}} = 2$, WCO), 92.4, 86.4 (2s, Cp), 52.9 [s, C¹(^tBu)], 52.5 (d, $J_{\text{CP}} = 31$, CHN), 49.1 [d, $J_{\text{CP}} = 19$, C¹(Cy)], 42.7 [d, $J_{\text{CP}} = 10$, C¹(Cy)], 35.6 [d, $J_{\text{CP}} = 2$, C²(Cy)], 34.1 [s, C²(Cy)], 33.8 [d, $J_{\text{CP}} = 3$, C²(Cy)], 33.0 [s, C²(Cy)], 30.8 [s, C²(^tBu)], 28.7 [d, $J_{\text{CP}} = 11$, C³(Cy)], 28.2 [m, 3C³(Cy)], 26.8, 26.6 [2s, C⁴(Cy)]. *Isomer 2aF*: ³¹P{¹H} RMN (C₆D₆): δ 103.6 (s, $J_{\text{PW}} = 297$, μ -PCy₂). ¹H RMN (C₆D₆): δ 5.14, 5.11 (2d, $J_{\text{HP}} = 1$, 2 x 5H, Cp), 3.34 (d, $J_{\text{HP}} = 1$, 1H, CHN), 2.03-0.94 (m, 22H, Cy), 0.75 (s, 9H, ^tBu). ¹³C{¹H} RMN (C₆D₆): δ 89.5, 88.1 (2s, Cp), 56.1 (d, $J_{\text{CP}} = 28$, CHN), 53.4 [s, C¹(^tBu)], 48.5 [d, $J_{\text{CP}} = 16$, C¹(Cy)], 43.9 [d, $J_{\text{CP}} = 10$, C¹(Cy)], 35.9, 34.4 [2s, C²(Cy)], 34.1 [d, $J_{\text{CP}} = 4$, C²(Cy)], 33.7 [s, C²(Cy)], 30.9 [s, C²(^tBu)], 28.9-28.0 [m, 4C³(Cy)], 26.6, 26.3 [2s, C⁴(Cy)] ppm.

4.2. Preparation of [MoWCp₂{ μ - η^2 : η^2 -CHN(4-C₆H₄OMe)}(μ -PCy₂)(CO)₂] (**2b**).

A solution of CN(4-C₆H₄OMe) in dichloromethane (1 mL of 0.03 M solution, 0.030 mmol) was added to a solution of compound **1** (0.020 g, 0.030 mmol) in dichloromethane (3 mL) at 273 K, and the mixture was stirred at the same temperature for 10 min to give a dark orange solution. The solvent was then removed under vacuum, the residue was extracted with dichloromethane/petroleum ether (1/5) and the extracts were chromatographed on an alumina column at 253 K. Elution with dichloromethane/petroleum ether (1/2) gave an orange fraction yielding, after removal of solvents, compound **2b** as an orange solid (0.018 g, 75%). This product was shown (by NMR) to contain a mixture of two isomers (**2bE** and **2bF**) in a ratio of *ca.* 3:2 which could not be separated. $\nu(\text{CO})$ (CH₂Cl₂): 1854 (m, sh), 1828 (vs). *Isomer 2bE*: ³¹P{¹H} RMN (121.49 MHz): δ 107.3 (s, $J_{\text{PW}} = 287$, μ -PCy₂). ¹H RMN: δ 5.31, 5.02

(2d, $J_{HP} = 1$, 2 x 5H, Cp), 3.72 (s, 3H, OMe), 3.25 (d, $J_{HP} = 2$, 1H, CHN), 2.21-0.74 (m, 22H, Cy). *Isomer 2bF*: $^{31}\text{P}\{^1\text{H}\}$ RMN (121.49 MHz): δ 106.4 (s, $J_{PW} = 291$, $\mu\text{-PCy}_2$). ^1H RMN: δ 5.31, 5.08 (2d, $J_{HP} = 1$, 2 x 5H, Cp), 3.34 (d, $J_{HP} = 1$, 1H, CHN), 3.72 (s, 3H, OMe), 2.21-0.72 (m, 22H, Cy). The resonances corresponding to the aromatic protons could not be assigned unambiguously for each isomer.

4.3. Reaction of compound **1** with CNXyl.

A solution of CNXyl in petroleum ether (600 μL of 0.05 M solution, 0.030 mmol) was added to a solution of compound **1** (0.020 g, 0.030 mmol) in dichloromethane (6 mL) at 273 K, and the mixture was stirred at the same temperature for 5 min to give a dark green solution which was shown (by NMR) to contain compound $[\text{MoWCp}_2(\mu\text{-}1\kappa\text{C}:2\kappa\text{N}\text{-HCNXyl})(\mu\text{-PCy}_2)(\text{CO})_2]$ (**3**) as major species. All attempts to further purify this product resulted in its progressive transformation into compound $[\text{MoWCp}_2(\mu\text{-CNHXyl})(\mu\text{-PCy}_2)(\text{CO})_2]$ (**4**), which could not be further purified either, and was shown (by NMR) to exist as a mixture of two isomers (**4H** and **4I**) in a ratio of *ca.* 3:2 which could not be separated.

Data for 3. $\nu(\text{CO})$ (CH_2Cl_2): 1833 (s), 1792 (vs). $^{31}\text{P}\{^1\text{H}\}$ RMN (121.49 MHz): δ 81.2 (s, $J_{PW} = 218$, $\mu\text{-PCy}_2$). ^1H RMN (300.13 MHz): δ 11.96 (d, $J_{HP} = 3$, 1H, CH), 7.34-6.78 (m, 3H, C_6H_3), 5.36, 5.00 (2s, 2 x 5H, Cp), 2.30, 2.25 (2s, 2 x 3H, CH_3), 2.07-0.98 (m, 22H, Cy). $^{13}\text{C}\{^1\text{H}\}$ RMN (75.47 MHz): δ 244.7 (d, $J_{CP} = 14$, MoCO), 237.9 (d, $J_{CP} = 7$, WCO), 217.1 (s, $J_{CW} = 84$, CHN), 156.4 [s, $\text{C}^1(\text{Xyl})$], 132.9, 132.7 [2s, $\text{C}^{2,6}(\text{Xyl})$], 128.7, 128.3, 124.9 [3s, $\text{C}^{3,4,5}(\text{Xyl})$], 90.7, 89.1 (2s, Cp), 48.6 [d, $J_{CP} = 24$, $\text{C}^1(\text{Cy})$], 41.9 [d, $J_{CP} = 18$, $\text{C}^1(\text{Cy})$], 36.5, 35.9, 34.8, 34.3 [4s, $\text{C}^2(\text{Cy})$], 29.0-28.0 [m, $4\text{C}^3(\text{Cy})$], 26.7 [s, $2\text{C}^4(\text{Cy})$], 19.0 (s, 2CH_3).

Data for 4. $\nu(\text{CO})$ (CH_2Cl_2): 1865 (m, sh), 1843 (vs). *Isomer 4H.* $^{31}\text{P}\{^1\text{H}\}$ RMN: δ 78.1 (s, $J_{PW} = 297$, $\mu\text{-PCy}_2$). ^1H RMN: δ 10.31 (s, 1H, NH), 7.31-7.22 (m, 3H, C_6H_3), 5.40, 4.90 (2s, 2 x 5H, Cp), 2.33 (s, 6H, CH_3), 2.49-0.93 (m, 22H, Cy). $^{13}\text{C}\{^1\text{H}\}$ RMN: δ 344.4 (d, $J_{CP} = 4$, $\mu\text{-CN}$), 233.8 (d, $J_{CP} = 10$, MoCO), 219.3 (d, $J_{CP} = 5$, WCO), 145.2 [s, $\text{C}^1(\text{Xyl})$], 137.0, 136.4 [2s, $\text{C}^{2,6}(\text{Xyl})$], 128.9, 128.3, 127.6 [3s, $\text{C}^{3,4,5}(\text{Xyl})$], 89.9, 87.6 (2s, Cp), 46.6 [d, $J_{CP} = 24$, $\text{C}^1(\text{Cy})$], 44.5 [d, $J_{CP} = 22$, $\text{C}^1(\text{Cy})$], 36.5, 35.9, 34.8, 34.2 [4s, $\text{C}^2(\text{Cy})$], 29.0-28.1 [m, $4\text{C}^3(\text{Cy})$], 26.7 [s, $2\text{C}^4(\text{Cy})$], 19.0 (s, 2CH_3). *Isomer 4I.* $^{31}\text{P}\{^1\text{H}\}$ RMN: δ 79.0 (s, $J_{PW} = 309$, $\mu\text{-PCy}_2$). ^1H RMN: δ 10.09 (s, 1H, NH), 7.31-7.22 (m, 3H, C_6H_3), 5.41, 4.88 (2s, 2 x 5H, Cp), 2.36 (s, 6H, CH_3), 2.49-0.93 (m, 22H, Cy). $^{13}\text{C}\{^1\text{H}\}$ RMN: δ 343.2 (d, $J_{CP} = 4$, $\mu\text{-CN}$), 228.9 (d, $J_{CP} = 11$, MoCO), 225.7 (d, $J_{CP} = 5$, WCO), 146.1 [s, $\text{C}^1(\text{Xyl})$], 137.2, 137.0 [2s, $\text{C}^{2,6}(\text{Xyl})$], 128.8, 128.3, 127.7 [3s, $\text{C}^{3,4,5}(\text{Xyl})$], 89.0, 88.3 (2s, Cp), 46.7 [d, $J_{CP} = 24$, $\text{C}^1(\text{Cy})$], 44.5 [d, $J_{CP} = 21$, $\text{C}^1(\text{Cy})$], 36.6, 35.9, 35.1, 33.7 [4s, $\text{C}^2(\text{Cy})$], 29.0-28.1 [m, $4\text{C}^3(\text{Cy})$], 26.7 [s, $2\text{C}^4(\text{Cy})$], 19.0, 18.7 (2s, CH_3).

4.4. Preparation of $[MoWCp_2(\mu-H)(\mu-PCy_2)(1\kappa-CN^tBu)(2\kappa-CN^tBu)(1\kappa-CO)(2\kappa-CO)]$ (**5**).

Neat CN^tBu (35 μ L, 0.300 mmol) was added to a solution of compound **1** (0.020 g, 0.030 mmol) in dichloromethane (1 mL) at 243 K, and the mixture was stirred for 1 min to give an orange solution. The solvent was then removed under vacuum, the residue was extracted with dichloromethane/petroleum ether (1:1), and the extracts were chromatographed through an alumina column (activity IV) at 285 K. Elution with the same solvent mixture gave an orange fraction yielding, after removal of solvents under vacuum, compound **5** as an orange solid (0.018 g, 72%). Anal. Calcd for $C_{34}H_{51}MoN_2O_2PW$: C, 49.17; H, 6.19; N, 3.37. Found: C, 49.00; H, 6.58; N, 3.28. $\nu(CX)$ (CH_2Cl_2): 2093 (w), 2049 (w), 1900 (w), 1801 (vs). $^{31}P\{^1H\}$ RMN (C_6D_6): δ 158.7 (s, $J_{PW} = 211$, $\mu-PCy_2$). $^{31}P\{^1H\}$ RMN: δ 159.3 (s, $J_{PW} = 210$, $\mu-PCy_2$). 1H RMN: δ 5.16, 5.10 (2s, 2 x 5H, Cp), 1.62-1.02 (m, 22H, Cy), 1.48, 1.44 (2s, 2 x 9H, tBu), -15.73 (d, $J_{HP} = 29$, $J_{HW} = 38$, 1H, $\mu-H$). $^{13}C\{^1H\}$ RMN (C_6D_6): δ 243.5 (s, MoCO), 231.0 (s, WCO), 193.8 (d, $J_{CP} = 22$, MoCN), 192.0 (d, $J_{CP} = 25$, WCN), 89.0, 86.9 (2s, Cp), 58.6, 58.0 [2s, $C^1(^tBu)$], 40.3 [d, $J_{CP} = 19$, $2C^1(Cy)$], 32.9, 32.8 [2s, $C^2(Cy)$], 31.7, 30.5 [2s, $C^2(^tBu)$], 30.7, 30.5 [2d, $J_{CP} = 5$, $C^2(Cy)$], 29.0, 28.9 [2d, $J_{CP} = 9$, $C^3(Cy)$], 28.2, 28.1 [2d, $J_{CP} = 13$, $C^3(Cy)$], 27.8, 27.7 [2s, $C^4(Cy)$].

4.5. Reaction of **1** with $CN(4-C_6H_4OMe)$ in excess.

A solution of compound **1** (0.020 g, 0.030 mmol) in dichloromethane (5 mL) was added dropwise to a solution of $CN(4-C_6H_4OMe)$ (0.012 g, 0.090 mmol) in dichloromethane (3 mL) for 15 min, and the mixture was further stirred at room temperature for 30 min. The solvent was then removed under vacuum, the residue was extracted with dichloromethane/petroleum ether (1:1), and the extracts were chromatographed through an alumina column at 253 K. Elution with dichloromethane gave an orange fraction yielding, after removal of solvents under vacuum, compound $[MoWCp_2(\mu-1\eta^2:2\kappa_C,\kappa_C-HCN(4-C_6H_4OMe)C\{N(4-C_6H_4OMe)\})(\mu-PCy_2)(CO)_2]$ (**6**) as an orange solid (0.013 g, 47%). Elution with dichloromethane/tetrahydrofuran (1:1) gave a red fraction yielding, after removal of solvents under vacuum, compound $[MoWCp_2(\mu-1\kappa_C,\kappa_C:2\eta^2-HCN(4-C_6H_4OMe)C\{N(4-C_6H_4OMe)\})(\mu-PCy_2)\{2\kappa-CN(4-C_6H_4OMe)\}(1\kappa-CO)]$ (**7**) as a red solid (0.011 g, 35%).

Data for 6. $\nu(CO)$ (CH_2Cl_2): 1881 (m, sh), 1860 (vs). $^{31}P\{^1H\}$ RMN (121.50 MHz): δ 107.4 (s, $J_{PW} = 228$, $\mu-PCy_2$). 1H RMN (300.09 MHz): δ 7.10 (m, 2H, C_6H_4), 6.79 (m, 4H, C_6H_4), 6.54 (m, 2H, C_6H_4), 5.87 (d, $J_{HP} = 2$, 1H, CHN), 5.29, 4.95 (2s, 2 x 5H, Cp), 3.78, 3.76 (2s, 2 x 3H, OMe), 2.03-0.98 (m, 22H, Cy). 1H RMN (253 K): δ 7.09 (false d, $J_{HH} = 9$, 2H, C_6H_4), 6.82 (false d, $J_{HH} = 9$, 2H, C_6H_4), 6.79 (false d, $J_{HH} = 9$, 2H,

C₆H₄), 6.59 (false d, $J_{\text{HH}} = 9$, 2H, C₆H₄), 5.93 (d, $J_{\text{HP}} = 1$, 1H, CHN), 5.30, 4.93 (2s, 2 x 5H, Cp), 3.79, 3.77 (2s, 2 x 3H, OMe), 2.13-0.91 (m, 22H, Cy). ¹³C{¹H} RMN (253 K): δ 249.1 (d, $J_{\text{CP}} = 10$, MoCO), 226.0 (s, WCO), 194.7 (s, MoCN₂), 157.5, 154.8 [2s, C⁴(C₆H₄)], 145.6, 141.2 [2s, C¹(C₆H₄)], 124.6, 122.9 [2s, C²(C₆H₄)], 113.3, 113.1 [2s, C³(C₆H₄)], 101.8 (d, $J_{\text{CP}} = 30$, CHN), 90.4, 87.9 (2s, Cp), 55.8, 55.6 (2s, OMe), 49.5 [d, $J_{\text{CP}} = 18$, C¹(Cy)], 41.3 [d, $J_{\text{CP}} = 7$, C¹(Cy)], 35.5 [s, C²(Cy)], 35.4 [d, $J_{\text{CP}} = 5$, C²(Cy)], 34.6 [d, $J_{\text{CP}} = 4$, C²(Cy)], 32.5 [s, C²(Cy)], 28.8 [d, $J_{\text{CP}} = 12$, C³(Cy)], 28.4 [d, $J_{\text{CP}} = 12$, C³(Cy)], 28.3 [d, $J_{\text{CP}} = 8$, C³(Cy)], 28.1 [d, $J_{\text{CP}} = 10$, C³(Cy)], 26.7, 26.5 [2s, C⁴(Cy)].

Data for 7. $\nu(\text{CX})$ (CH₂Cl₂): 1994 (w), 1854 (vs). ³¹P{¹H} RMN (121.50 MHz): δ 118.0 (s, $J_{\text{PW}} = 186$, μ -PCy₂). ¹H RMN: δ 7.16 (false d, $J_{\text{HH}} = 9$, 2H, C₆H₄), 6.78 (m, 6H, C₆H₄), 6.54 (s, 4H, C₆H₄), 5.29 (s, 5H, Cp), 5.08 (s, 1H, CHN), 5.05 (s, 5H, Cp), 3.79, 3.77, 3.67 (3s, 3 x 3H, OMe), 2.03-0.92 (m, 22H, Cy) ppm. ¹³C{¹H} RMN: δ 239.8 (d, $J_{\text{CP}} = 7$, WCO), 208.0 (bs, MoCNR), 177.5 (s, WCN₂), 157.9, 157.5, 157.4 [3s, C⁴(C₆H₄)], 146.9, 142.8, 127.7 [3s, C¹(C₆H₄)], 126.2, 125.0, 122.9 [3s, C²(C₆H₄)], 114.8, 113.8, 113.3 [3s, C³(C₆H₄)], 98.9 (d, $J_{\text{CP}} = 29$, CHN), 92.0, 85.4 (2s, Cp), 55.9, 55.8, 55.6 (3s, OMe), 49.8 [d, $J_{\text{CP}} = 15$, C¹(Cy)], 44.4 [d, $J_{\text{CP}} = 9$, C¹(Cy)], 35.3 [d, $J_{\text{CP}} = 3$, C²(Cy)], 35.0 [d, $J_{\text{CP}} = 5$, C²(Cy)], 34.9 [d, $J_{\text{CP}} = 3$, C²(Cy)], 33.8 [s, C²(Cy)], 28.7 [m, 4C³(Cy)], 27.0, 26.8 [2s, C⁴(Cy)].

4.6. Preparation of [MoWCp₂(1 κ -H)(μ -PCy₂)(2 κ -CO)₂{1 κ -N₂CH(SiMe₃)}] (**8c**).

A solution of N₂CH(SiMe₃) in petroleum ether (30 μ L of 2 M solution, 0.060 mmol) was added to a solution of compound **1** (0.020 g, 0.030 mmol) in dichloromethane (6 mL), and the mixture was stirred for 2 min to give a dark purple solution. The solvent was then removed under vacuum, the residue was extracted with dichloromethane/petroleum ether (1:5), and the extracts were chromatographed through an alumina column at 253 K. Elution with the same solvent mixture gave a purple fraction yielding, after removal of solvents under vacuum, compound **8c** as a purple solid (0.016 g, 68%). Anal. Calcd for C₂₈H₄₃MoN₂O₂PSiW: C, 43.20; H, 5.57; N, 3.60. Found: C, 42.96; H, 5.25; N, 3.51. $\nu(\text{CO})$ (CH₂Cl₂): 1895 (vs), 1805 (vs). ³¹P{¹H} RMN (C₆D₆, 121.50 MHz): δ 210.8 (s, $J_{\text{PW}} = 190$, μ -PCy₂). ¹H RMN (C₆D₆): δ 8.14 (s, $J_{\text{HSi}} = 14$, 1H, CHSi), 5.46, 5.08 (2s, 2 x 5H, Cp), 2.67-0.75 (m, 22H, Cy), -0.02 (s, 9H, SiMe₃), -0.25 (d, $J_{\text{HP}} = 32$, $J_{\text{HW}} = 126$, 1H, H-W). ¹³C{¹H} RMN (C₆D₆): δ 238.6 (d, $J_{\text{CP}} = 24$, MoCO), 237.2 (s, MoCO), 167.8 (s, NCHSi), 95.6, 88.5 (2s, Cp), 47.1 [d, $J_{\text{CP}} = 16$, C¹(Cy)], 45.4 [d, $J_{\text{CP}} = 23$, C¹(Cy)], 34.8, 34.3, 33.9, 33.5 [4s, C²(Cy)], 28.5, 28.4 [2d, $J_{\text{CP}} = 11$, C³(Cy)], 28.3 [d, $J_{\text{CP}} = 12$, C³(Cy)], 28.2 [d, $J_{\text{CP}} = 11$, C³(Cy)], 27.0, 26.8 [2s, C⁴(Cy)], -3.2 (s, SiCH₃).

4.7. Reaction of **1** with N₂CPh₂.

Compound **1** (0.070 g, 0.105 mmol) and N₂CPh₂ (4 mL of a *ca.* 0.05 M solution in dichloromethane, 0.200 mmol) were stirred in dichloromethane (6 mL) at room temperature for 5 min to give a purple solution containing a mixture of compounds [MoWCp₂(1κ-H)(μ-PCy₂)(2κ-CO)₂(1κ-N₂CPh₂)] (**8d-W**), [MoWCp₂(2κ-H)(μ-PCy₂)(1κ-CO)₂(2κ-N₂CPh₂)] (**8d-Mo**), [MoWCp₂(2κ-H)(μ-PCy₂)(2κ-CO)₂(1κ-N₂CPh₂)₂] (**9d-Mo**) and [MoWCp₂(1κ-H)(μ-PCy₂)(1κ-CO)₂(2κ-N₂CPh₂)₂] (**9d-W**) in a ratio of *ca.* 2:1:2:4. Solvent was then removed under vacuum, the residue was extracted with dichloromethane/petroleum ether (1:5), and the extracts were chromatographed through an alumina column (activity II) at 243 K. Elution with the same solvent mixture gave a red fraction, yielding, after removal of solvents, compound **9d-Mo** as a red solid (0.010 g, 9%). Elution with the same solvent mixture gave first a fraction containing compound **8d-W** as major product along with small amounts of **9d-Mo** and, secondly a fraction containing compound **8d-Mo** as major product along with small amounts of **9d-W**. Finally, elution with dichloromethane/petroleum ether (1:1) gave a purple fraction yielding, after removal of solvents under vacuum, compound **9d-W** as a purple solid (0.032 g, 29%). Compounds **9d-Mo/W** are thermally unstable and, in order to prevent their progressive decomposition, their solutions should be kept below 273 K. Alternatively, the residue obtained upon solvent removal from the initial reaction mixture was extracted with dichloromethane/petroleum ether (1:5), and the extracts were chromatographed through a silica gel column at 243 K. Elution with the same solvent mixture gave first a green fraction yielding, after removal of solvents under vacuum, compound **8d-W** as a green solid (0.018 g, 20%) and, secondly a blue fraction yielding, after removal of solvents under vacuum, compound **8d-Mo** as a green solid (0.007 g, 8%). With this solid phase compounds **9d-Mo/W** could not be eluted from the chromatographic column.

Data for 8d-W. ν(CO) (CH₂Cl₂): 1895 (vs), 1800 (vs). ³¹P{¹H} RMN: δ 212.7 (s, br, μ-PCy₂). ³¹P{¹H} RMN (213 K): δ 215.8 (s, *J*_{PW} = 192, μ-PCy₂). ¹H RMN: δ 7.93-6.94 (m, 10H, Ph), 5.26, 5.16 (2s, 2 x 5H, Cp), 2.35-0.58 (m, 22H, Cy), -1.09 (d, *J*_{HP} = 32, *J*_{HW} = 130, 1H, H-W). ¹³C{¹H} RMN: δ 239.8 (d, *J*_{CP} = 23, MoCO), 238.3 (d, *J*_{CP} = 3, MoCO), 163.0 (d, *J*_{CP} = 2, NCPh₂), 138.1, 135.7 [2s, C¹(Ph)], 130.7-127.4 [m, C^{2,3,4}(Ph)], 95.2, 88.6 (2s, Cp), 47.0 [d, *J*_{CP} = 17, 2C¹(Cy)], 34.9 [d, *J*_{CP} = 2, C²(Cy)], 34.2 [s, br, C²(Cy)], 34.0, 33.9 [2s, C²(Cy)], 28.7, 28.5 [2d, *J*_{CP} = 12, C³(Cy)], 28.5, 28.4 [2d, *J*_{CP} = 11, C³(Cy)], 27.0, 26.8 [2s, C⁴(Cy)].

Data for 8d-Mo. ν(CO) (CH₂Cl₂): 1891 (vs), 1801 (vs). ³¹P{¹H} RMN: δ 199.3 (s, br, μ-PCy₂). ³¹P{¹H} RMN (193 K): δ 203.5 (s, *J*_{PW} = 242, μ-PCy₂). ¹H RMN: δ 7.68-7.20 (m, 10H, Ph), 5.21, 5.18 (2s, 2 x 5H, Cp), 2.21-1.02 (m, 22H, Cy), -0.32 (d, *J*_{HP} = 32, 1H, H-Mo).

Data for 9d-Mo. $\nu(\text{CO})$ (CH_2Cl_2): 1897 (vs), 1803 (s). $^{31}\text{P}\{^1\text{H}\}$ RMN: δ 47.2 (s, br, $\mu\text{-PCy}_2$). $^{31}\text{P}\{^1\text{H}\}$ RMN (233 K): δ 46.3 (s, $J_{\text{PW}} = 308$, $\mu\text{-PCy}_2$). ^1H RMN: δ 7.83-7.15 (m, 20H, Ph), 5.38 (s, 5H, Cp), 5.31 (d, $J_{\text{HP}} = 1$, 5H, Cp), 2.33-0.65 (m, 22H, Cy), -4.99 (d, br, $J_{\text{HP}} = 52$, 1H, H-Mo). ^1H RMN (233 K): δ 7.91-7.18 (m, 20H, Ph), 5.38, 5.32 (2s, 2 x 5H, Cp), 2.75-0.73 (m, 22H, Cy), -4.90 (d, $J_{\text{HP}} = 57$, 1H, H-Mo).

Data for 9d-W. $\nu(\text{CO})$ (CH_2Cl_2): 1896 (vs), 1805 (s). $^{31}\text{P}\{^1\text{H}\}$ RMN: δ 31.8 (s, br, $\mu\text{-PCy}_2$). $^{31}\text{P}\{^1\text{H}\}$ RMN (193 K): δ 28.1 (s, $J_{\text{PW}} = 174$, $\mu\text{-PCy}_2$). ^1H RMN (273K): δ 7.80-7.05 (m, 20H, Ph), 5.40, 5.26 (2s, 2 x 5H, Cp), 2.55-1.12 (m, 22H, Cy), -5.90 (d, br, $J_{\text{HP}} = 60$, $J_{\text{HW}} = 49$, 1H, H-W). ^1H RMN (193 K): δ 7.75-7.10 (m, 20H, 2Ph), 5.40, 5.23 (2s, 2 x 5H, Cp), 3.07 (m, 1H, Cy), 3.08-1.12 (m, 21H, Cy), -6.27 (d, br, $J_{\text{HP}} = 60$, 1H, H-W). $^{13}\text{C}\{^1\text{H}\}$ RMN (193 K): δ 243.9, 238.6 (2s, br, WCO), 142.3, 136.8 [2s, $\text{C}^1(\text{Ph})$], 134.4, 131.2 (2s, br, NCPH_2), 129.9-128.5 [m, $\text{C}^{2,3}(\text{Ph})$], 127.5-126.9 [m, $\text{C}^4(\text{Ph})$], 107.5 (s, br, MoCp), 88.5 (s, WCp), 46.9 [s, br, $\text{C}^1(\text{Cy})$], 36.7 [s, br, $\text{C}^1(\text{Cy})$], 33.3-26.3 [m, $\text{C}^{2,3,4}(\text{Cy})$].

4.8. Preparation of $[\text{MoWCp}_2\{\mu\text{-}1\kappa\text{C}:2\eta^2\text{-C(O)CH}_2(p\text{-tol})\}(1\kappa\text{-O})(\mu\text{-PCy}_2)(2\kappa\text{-CO})]$ (**10**).

A freshly prepared solution of compound **1** (0.015 g, 0.023 mmol) and (*p*-tol)C(O)H (4 μ L, 0.034 mmol) in toluene-*d*₈ (0.5 mL) was transferred to a J-Young NMR tube and heated at 393 K for 2 h to give an orange solution. The solvent was then removed under vacuum and the residue was extracted with dichloromethane/petroleum ether (1:7) and chromatographed through an alumina column at 285 K. Elution with dichloromethane/petroleum ether (1:1) gave an orange fraction yielding, after removal of solvents under vacuum, compound **10** as an orange solid (0.014 g, 78%). The crystals used in the X-ray diffraction study of **10** were grown by the slow diffusion of layers of petroleum ether and toluene into a concentrated dichloromethane solution of the complex at 253 K. Anal. Calcd for $\text{C}_{32}\text{H}_{41}\text{MoO}_3\text{PW}$: C, 49.00; H, 5.27. Found: C, 49.34; H, 5.55. $\nu(\text{CO})$ (CH_2Cl_2): 1850 (vs). $^{31}\text{P}\{^1\text{H}\}$ RMN (121.50 MHz): δ 194.0 (s, $J_{\text{PW}} = 304$, $\mu\text{-PCy}_2$). ^1H RMN: δ 7.52, 7.25 (2 false d, $J_{\text{HH}} = 8$, 2 x 2H, C_6H_4), 5.17 (d, $J_{\text{HP}} = 1$, 5H, Cp), 5.05 (s, 5H, Cp), 4.69, 3.75 (2d, $J_{\text{HH}} = 11$, 2 x 1H, CH_2), 2.55 (m, 1H, Cy), 2.41 (s, 3H, CH_3), 2.36-0.95 (m, 21H, Cy). $^{13}\text{C}\{^1\text{H}\}$ RMN: δ 243.8 (d, $J_{\text{CP}} = 11$, MoCO), 217.8 (s, $\mu\text{-C}$), 140.3 [s, $\text{C}^1(\text{C}_6\text{H}_4)$], 136.0 [s, $\text{C}^4(\text{C}_6\text{H}_4)$], 130.3, 129.2 [2s, $\text{C}^{2,3}(\text{C}_6\text{H}_4)$], 100.4, 89.7 (2s, Cp), 67.4 (s, CH_2), 55.5 [d, $J_{\text{CP}} = 10$, $\text{C}^1(\text{Cy})$], 50.1 [d, $J_{\text{CP}} = 22$, $\text{C}^1(\text{Cy})$], 36.5 [d, $J_{\text{CP}} = 4$, $\text{C}^2(\text{Cy})$], 35.3 [s, $\text{C}^2(\text{Cy})$], 34.7 [d, $J_{\text{CP}} = 6$, $\text{C}^2(\text{Cy})$], 34.1 [s, $\text{C}^2(\text{Cy})$], 28.8 [d, $J_{\text{CP}} = 13$, $2\text{C}^3(\text{Cy})$], 28.7, 28.4 [2d, $J_{\text{CP}} = 11$, $\text{C}^3(\text{Cy})$], 26.8, 26.8 [2s, $\text{C}^4(\text{Cy})$], 21.3 (s, CH_3).

4.9. Room temperature reaction of **1** with $\text{HC}_2(p\text{-tol})$.

Neat HC≡C(*p*-tol) (8 μL, 0.063 mmol) was added to a solution of compound **1** (0.020 g, 0.030 mmol) in toluene (6 mL), and the mixture was stirred in a Schlenk tube equipped with a Young valve for 4 h to give a green yellowish solution which contains compound *trans*-[MoWCp₂{μ-κ:η²-C(*p*-tol)CH₂}(μ-PCy₂)(CO)₂] (***trans*-11**) as major product, along with small amounts of *cis*-[MoWCp₂{μ-1κ:2η²-C(*p*-tol)CH₂}(μ-PCy₂)(CO)₂] (***cis*-11**). The solvent was then removed under vacuum and the residue was extracted with dichloromethane/petroleum ether (1:7) and chromatographed through an alumina column at 253 K. Elution with dichloromethane/petroleum ether (1:5) gave a green fraction yielding, after removal of solvents under vacuum, compound ***trans*-11** as a green solid (0.022 g, 93%). This product was shown (by NMR) to contain a mixture of two isomers (***trans*-11-Mo** and ***trans*-11-W**) in a ratio of ca. 8:1 (at 203 K), this precluding the identification of most of the NMR signals for the minor isomer. Compounds ***trans*-11** and ***cis*-11** are thermally unstable, and their solutions evolve progressively to give compounds ***trans*-12** and ***cis*-12**, respectively. ν(CO) (CH₂Cl₂): 1920 (m), 1886 (s), 1859 (vs), 1782 (m). *Data for trans-11-Mo*. ³¹P{¹H} RMN (203 K): δ 106.5 (s, *J*_{PW} = 245, μ-PCy₂). ¹H RMN (203 K): δ 7.05 (false d, *J*_{HH} = 7, 2H, C₆H₄), 6.65 (m, 2H, C₆H₄), 5.48, 5.23 (2s, 2 x 5H, Cp), 5.12, 4.87 (2s, 2 x 1H, C_βH₂), 2.52 (m, 2H, Cy), 2.31 (s, 3H, CH₃), 2.22 (m, 2H, Cy), 2.03-0.64 (m, 18H, Cy). ¹³C{¹H} RMN (203 K): δ 241.6 (d, *J*_{CP} = 12, MoCO), 236.6 (d, *J*_{CP} = 6, WCO), 183.1 (s, C_α), 152.3 [s, C¹(C₆H₄)], 136.0 [s, C⁴(C₆H₄)], 128.6 [s, br, C²(C₆H₄)], 128.0 [s, 2C³(C₆H₄)], 127.0 [bs, C²(C₆H₄)], 91.0, 88.2 (2s, Cp), 59.1 (s, C_βH₂), 50.3 [d, *J*_{CP} = 28, C¹(Cy)], 37.2 [d, *J*_{CP} = 18, C¹(Cy)], 34.8, 34.0, 33.1 [3s, C²(Cy)], 30.4 [d, *J*_{CP} = 2, C²(Cy)], 28.6-27.3 [m, 4C³(Cy)], 26.4, 26.2 [2s, C⁴(Cy)], 21.2 (s, CH₃). *Data for trans-11-W*. ³¹P{¹H} RMN (203 K): δ 114.5 (s, br, μ-PCy₂). ¹H RMN (203 K): δ 4.95, 4.69 (2s, 2 x 5H, Cp). ¹³C{¹H} RMN (203 K): δ 87.6, 84.9 (2s, Cp). Other resonances of this isomer were not identified in the spectra of the mixture of isomers. *Data for cis-11*. ³¹P{¹H} RMN: δ 144.5 (s, *J*_{PW} = 358, μ-PCy₂).

4.10. High temperature reaction of **1** with HC₂(*p*-tol).

Neat HC≡C(*p*-tol) (8 μL, 0.063 mmol) was added to a solution of compound **1** (0.020 g, 0.030 mmol) in toluene (6 mL), and the mixture was refluxed for 30 min to obtain a brown solution which contains compound *trans*-[MoWCp₂{μ-1κ:2η²-CHCH(*p*-tol)}(μ-PCy₂)(CO)₂] (***trans*-12**), along with small amounts of *cis*-[MoWCp₂{μ-κ:η²-CHCH(*p*-tol)}(μ-PCy₂)(CO)₂] (***cis*-12**) in a ratio ca. 10:1. The solvent was then removed under vacuum and the residue was extracted with petroleum ether and chromatographed through an alumina column at 253 K. Elution with dichloromethane/petroleum ether (1:1) gave a green fraction yielding, after removal of solvents under vacuum, a mixture of compounds ***cis*-12** and ***trans*-12** (0.021 g, 90%). Anal. Calcd for C₃₃H₄₁MoO₂PW: C,

50.79; H, 5.30. Found: C, 50.41; H, 5.05. $\nu(\text{CO})$ (CH_2Cl_2): 1921 (w), 1874 (m), 1815 (vs), 1796 (s, sh). *Data for trans-12.* $^{31}\text{P}\{^1\text{H}\}$ RMN (233 K): δ 113.3 (s, $J_{\text{PW}} = 317$, $\mu\text{-PCy}_2$). ^1H RMN (233 K): δ 9.53 (dd, $J_{\text{HH}} = 11$, $J_{\text{HP}} = 1$, 1H, C_αH), 7.32-6.98 (m, 4H, C_6H_4), 6.31 (d, $J_{\text{HH}} = 11$, 1H, C_βH), 5.51, 5.02 (2s, 2 x 5H, Cp), 2.38 (s, 3H, CH_3), 2.36-1.00 (m, 22H, Cy). $^{13}\text{C}\{^1\text{H}\}$ RMN (233 K): δ 241.9 (s, br, MoCO), 237.1 (d, $J_{\text{CP}} = 10$, WCO), 143.2 [s, $\text{C}^1(\text{C}_6\text{H}_4)$], 141.9 (s, C_αH), 135.9 [s, $\text{C}^4(\text{C}_6\text{H}_4)$], 129.4, 127.0 [2s, br, $\text{C}^{2,3}(\text{C}_6\text{H}_4)$], 95.6 (s, C_βH), 90.5, 88.5 (2s, Cp), 46.4, 44.8 [2d, $J_{\text{CP}} = 24$, $\text{C}^1(\text{Cy})$], 34.2 [s, $2\text{C}^2(\text{Cy})$], 32.7, 32.1 [2s, $\text{C}^2(\text{Cy})$], 28.1 [d, $J_{\text{CP}} = 12$, $\text{C}^3(\text{Cy})$], 28.1 [d, $J_{\text{CP}} = 13$, $\text{C}^3(\text{Cy})$], 27.8 [d, $J_{\text{CP}} = 10$, $\text{C}^3(\text{Cy})$], 26.6 [d, $J_{\text{CP}} = 11$, $\text{C}^3(\text{Cy})$], 26.4, [s, $2\text{C}^4(\text{Cy})$], 21.3 (s, CH_3). *Data for cis-12.* $^{31}\text{P}\{^1\text{H}\}$ RMN: δ 105.4 (s, $\mu\text{-PCy}_2$).

4.11. X-Ray Structure Determination of Compound **10·0.5C₆H₁₄**.

Data collection for **10·0.5C₆H₁₄** was performed at 150(3) K on an Oxford Diffraction Xcalibur Nova single crystal diffractometer, using Cu-K α radiation ($\lambda = 1.5418$ Å). Images were collected at a 62 mm fixed crystal-detector distance, using the oscillation method, with 1.0° oscillation and variable exposure time per image (90.0-15.0 s). Data collection strategy was calculated with the program CrysAlis Pro CCD [44]. Data reduction and cell refinement was performed with the program CrysAlis Pro RED [44]. An empirical absorption correction was applied using the SCALE3 ABSPACK algorithm as implemented in the program CrysAlis Pro RED [44]. Using the program suite WINGX [45], the structure was solved by Patterson interpretation and phase expansion using SHELXL2016 and refined with full-matrix least squares on F^2 using SHELXL2016 [46]. The complex was found to crystallize with a molecule of hexane placed on the symmetry operation $-x+1, -y+1, -z+1$. All non-hydrogen atoms were refined anisotropically and all hydrogen atoms were geometrically placed and refined using a riding model.

4.12. Computational Details.

All DFT calculations were carried out using the GAUSSIAN03 package [47], in which the hybrid method B3LYP was used with the Becke three-parameter exchange functional [48], and the Lee-Yang-Parr correlation functional [49]. A pruned 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 Mo and Re atoms [50]. The light elements (P, N, O, C and H) were described with the 6-31G* basis [51]. Geometry optimizations were performed under no symmetry restrictions, using initial coordinates derived from the X-ray data of related compounds. Frequency analyses were performed for all the stationary points to ensure that a

minimum structure with no imaginary frequencies was achieved. Molecular diagrams and vibrational modes were visualized using the MOLEKEL program [52].

Table 3. Crystal Data for New Compounds

<i>10·0.5C₆H₁₄</i>	
mol formula	C ₃₅ H ₄₈ MoO ₃ P ₁ W
mol wt	827.48
cryst syst	triclinic
space group	<i>P</i> -1
radiation (λ , Å)	1.54184
<i>a</i> , Å	9.9654(4)
<i>b</i> , Å	14.2188(8)
<i>c</i> , Å	14.3937(9)
α , deg	61.308(6)
β , deg	73.440(4)
γ , deg	71.095(4)
<i>V</i> , Å ³	1671.87(18)
<i>Z</i>	2
calcd density, g cm ⁻³	1.644
absorp coeff, mm ⁻¹	10.033
temperature, K	150(3)
θ range (deg)	4.75 to 69.37
index ranges (<i>h</i> , <i>k</i> , <i>l</i>)	-11, 8; -16, 17; -17, 17
no. of reflns collected	12470
no. of indep reflns (<i>R</i> _{int})	6128(0.0573)
reflns with <i>I</i> > 2 σ (<i>I</i>)	4869
<i>R</i> indexes	<i>R</i> ₁ = 0.0418
[data with <i>I</i> > 2 σ (<i>I</i>)] ^a	<i>wR</i> ₂ = 0.1045 ^b
<i>R</i> indexes (all data) ^a	<i>R</i> ₁ = 0.0569
	<i>wR</i> ₂ = 0.1205 ^b
GOF	1.063
no. of restraints/params	0/372
$\Delta\rho$ (max., min.), eÅ ⁻³	1.673, -1.236
CCDC deposition no	2041372

^a $R = \sum(|F_o| - |F_c|) / \sum|F_o|$. $wR = [\sum w(|F_o|^2 - |F_c|^2)^2 / \sum w|F_o|^2]^{1/2}$. $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$. ^b $a = 0.0633$, $b = 0.5141$.

Acknowledgment.

We thank the MICINN of Spain and FEDER for financial support (Projects CTQ2015-63726-P and PGC2018-097366-B-I00) and a grant (to E. H.), the SCBI of the Universidad de Málaga and the CMC of the Universidad de Oviedo for access to computing facilities, and the X-Ray unit of the Universidad de Oviedo for acquisition of diffraction data.

Declaration of Interests

None

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Appendix A. Supplementary Data

An XYZ file containing the Cartesian coordinates for all computed species. CCDC 2041372 contains the supplementary crystallographic data for compound **10**; these data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Synopsis

The heterometallic hydride $[\text{MoWCp}_2(\text{H})(\mu\text{-PCy}_2)(\text{CO})_2]$ (**1**) displays a rich and varied chemical behavior derived from its unsaturated nature, this allowing it to react with small organic molecules containing C–C, C–O, C–N or N–N multiple bonds, such as alkynes, aldehydes, isonitriles and diazo compounds. In most of these reactions it behaves similarly to its W_2 analogue, yet some genuine heterometallic effects have also been observed.

Pictogram for Graphical Abstract

