Insertion and C-C Coupling Processes in Reactions of the Unsaturated Hydride [W2Cp2(H)(μ-PCy2)(CO)2] with Alkynes.

Journal:	*Dalton Transactions*
Manuscript ID	DT-ART-12-2015-004724.R3
Article Type:	Paper
Date Submitted by the Author:	01-Feb-2016
Complete List of Authors:	Alvarez, M. Angeles; Universidad de Oviedo, Quimica Organica e Inorganica García, M. Esther; Universidad de Oviedo, Quimica Organica e Inorganica García-Vivó, Daniel; Universidad de Oviedo, Departamento de Química Orgánica E Inorgánica Ruiz, Miguel; Universidad de Oviedo, Departamento de Quimica Organica e Inorganica Vega, M. Fernanda; Universidad de Oviedo, Departamento de Química Orgánica E Inorgánica

Insertion and C–C Coupling Processes in Reactions of the Unsaturated Hydride [W$_2$Cp$_2$(H)(μ-PCy$_2$)(CO)$_2$] with Alkynes.†

M. Angeles Alvarez, M. Esther García, Daniel García-Vivó,* Miguel A. Ruiz* and M. Fernanda Vega

Abstract

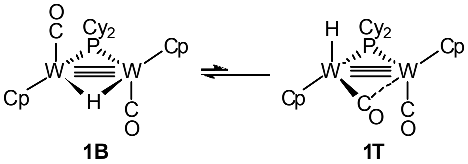
The title compound reacted with *p*-tolylacetylene at room temperature to give the 32-electron σ:π-bound alkenyl complexes *trans*-[W$_2$Cp$_2${μ-κ:η^2-C(*p*-tol)CH$_2$}(μ-PCy$_2$)(CO)$_2$] and *trans*-[W$_2$Cp$_2${μ-κ:η^2-CHCH(*p*-tol)}(μ-PCy$_2$)(CO)$_2$], with the former complex fully rearranging into the latter one after 1 h at 363 K. Both compounds exist in solution as an isomeric equilibrium mixture (rapid on the NMR timescale) involving the alternate π-coordination of the alkenyl ligand to each of the tungsten atoms. In the presence of CO or certain solvents (THF or CH$_2$Cl$_2$) the α-substituted alkenyl complex was transformed instead into the *cis*-dicarbonyl isomer *cis*-[W$_2$Cp$_2${μ-κ:η^2-C(*p*-tol)CH$_2$}(μ-PCy$_2$)(CO)$_2$] (W–W = 2.7273(8) Å). In contrast, the β-substituted alkenyl complex reacted with CO to give the saturated tricarbonyl [W$_2$Cp$_2${μ-κ:η^2-CHCH(*p*-tol)}(μ-PCy$_2$)(CO)$_3$], and with excess alkyne (under moderate heating) to yield the alkyne/alkenyl complex [W$_2$Cp$_2${μ-κ:η^2-CHCH(*p*-tol)}(μ-PCy$_2$){η^2-CHC(p-tol)}(CO)], with both products also displaying a cisoid disposition of the Cp ligands. In contrast, reactions of the title hydride with *tert*-butylacetylene were significantly slower and led to very air-sensitive compounds, the only isolable product from these reactions being the oxo alkenyl complex *trans*-[W$_2$Cp$_2${μ-κ:η^2-CHCH(^{t}Bu)}(O)(μ-PCy$_2$)(CO)]. The title hydride reacted with methyl propiolate at room temperature to give selectively the α-substituted alkenyl complex *cis*-[W$_2$Cp$_2${μ-κ:η^2-C(CO$_2$Me)CH$_2$}(μ-PCy$_2$)(CO)$_2$], but yielded instead the dienyl complex [W$_2$Cp$_2${μ-κ^2:η^3-CH(CO$_2$Me)CHC(CO$_2$Me)CH}(μ-PCy$_2$)(CO)$_2$] (W–W = 2.944(1) Å) when reaction was carried out at high temperature (393 K), with the latter following from an alkenyl/alkyne C–C coupling process. The title hydride also reacted with dimethyl acetylenedicarboxylate, to give three products mainly depending on the reaction temperature; at moderate temperature (343 K) this reaction led exclusively to the saturated alkenyl complex *trans*-[W$_2$Cp$_2${μ-κ_C,κ_O:η^2-C(CO$_2$Me)CH(CO$_2$Me)}(μ-PCy$_2$)(CO)$_2$] (W–W = 2.9329(8) Å), in which the σ:π-bound alkenyl ligand is additionally coordinated through the oxygen atom of the carboxylate group so as to render a *O*,*C*:*C*,*C*′ five-electron coordination mode. At 273 K this reaction led instead to a mixture of the unsaturated alkenyl *cis*-[W$_2$Cp$_2${μ-κ:η^2-C(CO$_2$Me)=CH(CO$_2$Me)}(μ-PCy$_2$)(CO)$_2$] and the dienyl complex [W$_2$Cp$_2${μ-κ_C,κ_O:η^2-

$C(CO_2Me)=C(CO_2Me)C(CO_2Me)=CH(CO_2Me)\}(\mu-PCy_2)(CO)_2]$ (W–W = 3.0273(6) Å).

Introduction

Recently we developed an efficient synthetic route to the unsaturated hydride $[W_2Cp_2(H)(\mu-PCy_2)(CO)_2]$ (**1**) (Chart 1),[1] a new addition to the rather reduced family of organometallic complexes having 30-electron $M_2(\mu-H)_x$ cores.[2] The electronic and coordinative unsaturation inherent to these species typically provides them with a high reactivity towards a wide variety of reagents under mild conditions, as exemplified by the extensive chemistry developed around the polyhydrides $[M_2Cp^*_2(\mu-H)_4]$ (M = Fe, Ru),[3] and $[M_2(\eta^6-C_6Me_6)_2(\mu-H)_3]^+$ (M = Ru, Os),[4] or that one carried out by our group for the dimolybdenum hydride $[Mo_2Cp_2(\mu-H)(\mu-PCy_2)(CO)_2]$.[5] Remarkably, our work with the ditungsten hydride **1** has revealed that the change of metal (W instead of Mo) has significant effects on the structure and reactivity of these unsaturated molecules. To begin with, compound **1** exists in solution as an equilibrium mixture of two isomers: a major one retaining the bridging disposition of the hydride ligand, as found in its Mo_2 analogue (**1B** in Chart 1), and a minor isomer displaying a terminal coordination of the hydride and a semibridging carbonyl ligand (**1T**).[1]

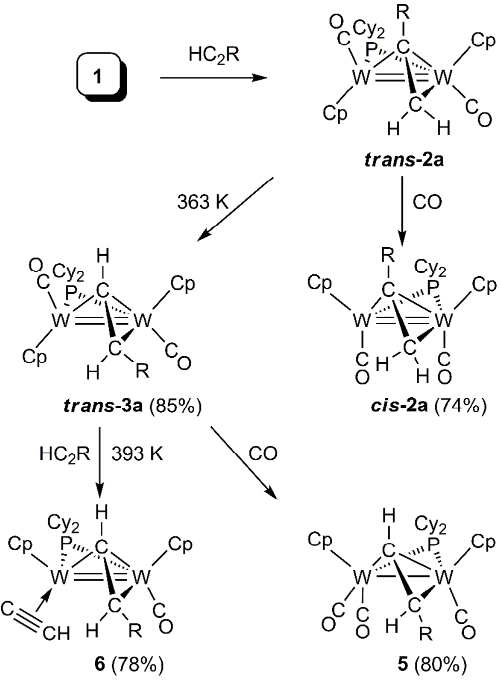
Chart 1



Besides this, the chemical behaviour of **1** also departs greatly from that of the Mo_2 counterpart. For instance, its protonation yields new cationic dihydrides which remain stable to dehydrogenation in the absence of coordinating anions,[1b] this being in stark contrast with the intractable mixtures of products obtained for the Mo_2 hydride. A similar stabilizing effect was observed in reactions of **1** with diazoalkanes, these leading to new isolable complexes with N-bound diazoalkanes,[6] instead of the accelerated diazoalkane decomposition observed in analogous reactions of the Mo_2 hydride.[7] A further point of divergence in the chemistry of these unsaturated hydrides is the ability of the ditungsten **1** to incorporate two molecules (rather than one) of some reagents. This has been observed in reactions with some transition-metal complexes, which lead to tetranuclear clusters,[8] rather than the trinuclear complexes formed in related reactions of the Mo_2 hydride,[9] and in reactions of **1** with some isocyanides, now leading to products following from C–N coupling of two molecules of reagent.[10] In a preliminary study on the reactivity of **1** we noticed that double addition processes might also occur in reactions with an activated alkyne such as dimethyl acetylenedicarboxylate (DMAD), this allowing the formation of a product having a 1,3-dienyl ligand via C–C coupling of two molecules of the alkyne.[11] This sort of coupling processes is a relatively rare outcome in reactions of unsaturated hydride-bridged complexes with alkynes, these more typically yielding alkenyl derivatives,[3,12-14] although some examples can be quoted. For instance, the osmium dihydride $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ has been shown to induce alkyne-alkyne couplings in its reactions with C_2Ph_2 or C_2H_2,[13,15] and the alkenyl-bridged diiron anion $[Fe_2(\mu\text{-}\kappa{:}\eta^2\text{-}CRCHR')(CO)_6]^-$ undergoes comparable couplings in reactions with alkynes.[16] All of this prompted us to study in more detail the reactions of **1** with alkynes, in search for further coupling processes of alkyne ligands at the ditungsten site, which is the main purpose of the present paper. We have done so by analyzing in detail the reactions of compound **1** not only with the internal alkyne DMAD, but also with different terminal alkynes HC≡CR (R = ^{t}Bu, *p*-tol, CO_2Me). As shown below, reactions of **1** with alkyl- or aryl-substituted alkynes essentially resemble those of the Mo_2 analogue, these mainly leading to formation of unsaturated alkenyl-bridged derivatives (either α- or β-substituted). In contrast, reactions with the most activated alkynes (those bearing carboxylate groups) yielded novel products following from selective alkenyl/alkyne coupling, these being processes not observed for the dimolybdenum analogue of **1**.

Results and Discussion

Reactions of Compound 1 with 1-Alkynes. The hydride **1** reacts slowly with HC≡C(*p*-tol) in toluene at room temperature to give, after 24 h, a mixture of the 32-electron α- and β-substituted alkenyl complexes *trans*-$[W_2Cp_2\{\mu\text{-}\kappa{:}\eta^2\text{-}C(p\text{-tol})CH_2\}(\mu\text{-}PCy_2)(CO)_2]$ (***trans*-2a**) and *trans*-$[W_2Cp_2\{\mu\text{-}\kappa{:}\eta^2\text{-}CHCH(p\text{-tol})\}(\mu\text{-}PCy_2)(CO)_2]$ (***trans*-3a**) respectively, in a ratio of ca. 8/1 (Scheme 1). The latter ratio, however, was highly dependent on the particular experimental conditions. In fact, separate experiments proved that the α-substituted alkenyl complex ***trans*-2a** was fully transformed into the β-substituted isomer ***trans*-3a** after 1 h at 363 K in toluene solution, a reaction also yielding small amounts of the oxo derivative *trans*-$[W_2Cp_2\{\mu\text{-}\kappa{:}\eta^2\text{-}CHCH(p\text{-tol})\}(O)(\mu\text{-}PCy_2)(CO)]$ (**4a**) (Chart 2), due to a side-reaction of these sensitive complexes with trace amounts of air in the reaction medium. Expectedly, the evolution of ***trans*-2a** at room temperature is much slower, yet not only involves $\alpha\rightarrow\beta$ isomerization at the alkenyl ligand but, alternatively, a *trans* to *cis* rearrangement of the carbonyl ligands so eventually, after seven days in toluene solution, a mixture of ***trans*-3a** and the *cis*-dicarbonyl isomer *cis*-$[W_2Cp_2\{\mu\text{-}\kappa{:}\eta^2\text{-}C(p\text{-tol})CH_2\}(\mu\text{-}PCy_2)(CO)_2]$ (***cis*-2a**) is obtained. Fortunately, we found that the latter compound could be prepared more selectively in a variety of ways: (a) by reacting **1** with HC≡C(*p*-tol) in THF or CH_2Cl_2 solution, (b) by placing toluene solutions of ***trans*-2a** under an atmosphere of carbon monoxide (Scheme 1) and (c) even when, after removing the solvent from a crude reaction mixture containing ***trans*-2a**, the residue so generated (retaining the excess alkyne used) was stored at 253 K for a few days. In contrast, the β-substituted alkenyl ***trans*-3a** does not undergo comparable *trans* to *cis* isomerizations. Instead, it reacts rapidly with CO to give the new tricarbonyl derivative [$W_2Cp_2\{\mu$-κ:η^2-CHCH(*p*-tol)\}(μ-PCy_2)$(CO)_3$] (**5**). On the other hand, in the presence of a large excess of alkyne and under slightly more forcing conditions (393 K), ***trans*-3a** undergoes carbonyl substitution by a second alkyne molecule to give the alkyne complex [$W_2Cp_2\{\mu$-κ:η^2-CHCH(*p*-tol)\}(μ-PCy_2)\{η^2-CHC(*p*-tol)\}(CO)] (**6**) (Scheme 1). In all, the above reactions are reminiscent of those observed for the Mo_2 analogue of **1**,[12] except for the formation of the alkyne complex **6**, this proving the ability of the ditungsten hydride to incorporate two molecules of alkyne at the dimetal site, a pre-requisite for induction of any C–C coupling processes between alkyne molecules. However, we note that such a coupling could not be induced on **6** even under more forcing conditions, although this takes place spontaneously when using more activated alkynes, as discussed later on.



Scheme 1. Reactions of **1** with HC≡CR (R = *p*-tol)

Compound **1** also reacts with a large excess of HC≡C^{t}Bu under moderate heating (313 K), to give the corresponding β-substituted alkenyl complex *trans*-[$W_2Cp_2\{\mu$-κ:η^2-CHCH(^{t}Bu)\}(μ-PCy_2)$(CO)_2$] (***trans*-3b**) as the essentially unique product (Chart 2). Unfortunately, this product was quite air-sensitive, and all attempts to isolate it resulted in its progressive decomposition, with the corresponding oxo derivative *trans*-[$W_2Cp_2\{\mu$-κ:η^2-CHCH(^{t}Bu)\}(O)(μ-PCy_2)(CO)] (**4b**) being the only product that could be isolated from the reaction mixture.

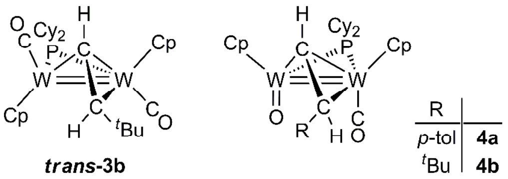
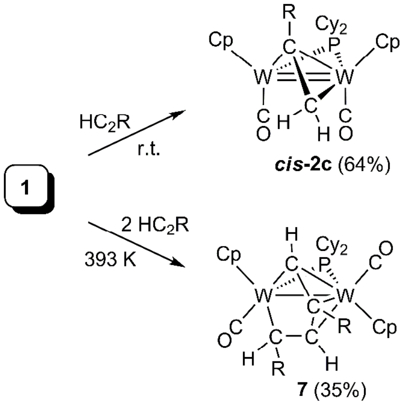


Chart 2

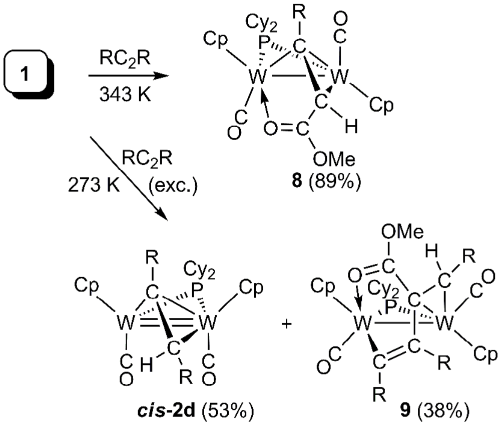
Reactions of **1** with a more activated alkyne such as methyl propiolate ($HC{\equiv}CCO_2Me$) yielded two products, mainly depending on the stoichiometry used. When using a slight excess of alkyne, then the corresponding α-substituted alkenyl complex *cis*-[$W_2Cp_2\{\mu$-κ:η^2-$C(CO_2Me)CH_2\}(\mu$-$PCy_2)(CO)_2$] (***cis*-2c**) was obtained in good yield (Scheme 2), irrespective of the temperature used which, however, modified the time for completion as expected (4 h at 298 K, 10 min at 393 K). A ^{31}P NMR monitoring of the room temperature reaction allowed us to detect the formation of an intermediate species (characterized by a broad resonance at δ_P 87.8 ppm) tentatively identified as the corresponding *trans*-dicarbonyl isomer; however, this compound could not be isolated, as it evolved rapidly to the final product ***cis*-2c**. Indeed, the selective formation of ***cis*-2c** in this reaction was quite surprising, because the related dimolybdenum compound was found to exist in solution as a solvent-dependent equilibrium mixture of the corresponding *cis* and *trans* isomers.[12]



Scheme 2. Reactions of **1** with $HC{\equiv}CR$ ($R = CO_2Me$)

In contrast, reaction of **1** with a large excess of methyl propiolate at 393 K led instead to the incorporation of two alkyne molecules and C–C coupling, to give the dienyl complex [$W_2Cp_2\{\mu$-κ^2:η^3-$CH(CO_2Me)CHC(CO_2Me)CH\}(\mu$-$PCy_2)(CO)_2$] (**7**) (Scheme 2). Although this molecule likely follows from an alkenyl/alkyne coupling, independent experiments proved that alkenyl ***cis*-2c** is not an intermediate in the formation of **7**, because it does not react with further alkyne even under more energetic conditions. Therefore it must be concluded that a different alkenyl complex would be involved in the formation of **7**, a matter to be discussed later on. In any case, we must note that formation of **7** was an unexpected outcome of this reaction, after recalling that the Mo_2 analogue of **1** reacted with methyl propiolate to yield only β-substituted alkenyls and the alkenylphosphine complex $[Mo_2Cp_2\{\mu\text{-}\kappa:\eta^2\text{-}Cy_2PCHCH(CO_2Me)\}(CO)_2]$,[12] a type of product not observed in any of the reactions of **1** with methyl propiolate.

Reactions of Compound 1 with DMAD. Compound **1** reacts rapidly with DMAD to yield three different products depending on experimental conditions (Scheme 3). When reaction is carried out at 343 K and using a slight excess of alkyne, then it is formed selectively the alkenyl derivative *trans*-$[W_2Cp_2\{\mu\text{-}\kappa_C,\kappa_O:\eta^2\text{-}C(CO_2Me)CH(CO_2Me)\}(\mu\text{-}PCy_2)(CO)_2]$ (**8**), in which a carboxylate group attached to the C_β atom of the alkenyl ligand is *O*-bound to one of the tungsten atoms. In contrast, if reaction is carried out at 273 K and using a large excess of reagent, then a mixture of the alkenyl *cis*-$[W_2Cp_2\{\mu\text{-}\kappa:\eta^2\text{-}C(CO_2Me){=}CH(CO_2Me)\}(\mu\text{-}PCy_2)(CO)_2]$ (***cis*-2d**) and the dienyl complex $[W_2Cp_2\{\mu\text{-}\kappa_C,\kappa_O:\eta^2\text{-}C(CO_2Me){=}C(CO_2Me)C(CO_2Me){=}CH(CO_2Me)\}(\mu\text{-}PCy_2)(CO)_2]$ (**9**) is obtained, with the latter following from a selective C–C alkenyl/alkyne coupling. A common intermediate to both products could be detected in this reaction, identified by a ^{31}P NMR resonance at 87.8 ppm ($^1J_{PW}$ = 317, 240 Hz), which can be tentatively identified as a *transoid* alkenyl complex, a matter to be discussed later on. Again this reactivity departs significantly from that of the Mo_2 analogue of **1**, which reacted with DMAD to only give *C*,*O*:*C*,*C′*-bound alkenyl products comparable to compound **8**.[12]



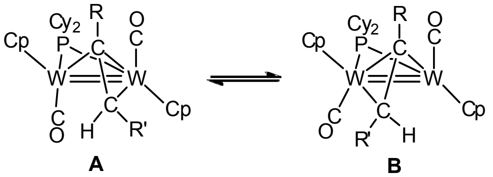
Scheme 3. Reactions of **1** with RC≡CR (R = CO_2Me)

Solution Structure of *trans*-Dicarbonyl Complexes 2 and 3. Spectroscopic data for compounds ***trans*-2** and ***trans*-3** (Table 1 and Experimental Section) are comparable to those of the alkenyl complexes *trans*-$[Mo_2Cp_2(\mu\text{-}\kappa:\eta^2\text{-}CRCHR')(\mu\text{-}PCy_2)(CO)_2]$ previously prepared by us from related reactions of the Mo_2 analogue of **1**,[12] or from reactions of the anion $[Mo_2Cp_2(\mu\text{-}PCy_2)(\mu\text{-}CO)_2]^-$ with different hydrocarbyl halides.[17] The structure of these dimolybdenum species has been already discussed at length, and only relevant details of the new ditungsten complexes will be discussed here. First we note that the IR spectra of compounds ***trans*-2a** and ***trans*-3a** display three C–O stretching bands rather than the two bands expected for a dicarbonyl complex.[18] This can be explained by assuming the presence in solution of two isomers (**A** and **B** in Scheme 4),[12,17] rapidly interconverting on the NMR timescale, since the room temperature NMR data of these compounds are consistent with the presence of a single species in each case.

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

compound	ν(CO)	δ_P [$^1J_{PW}$]	δ_H [J_{HH}]{$^2J_{HW}$}	δ_C [$^2J_{CP}$] {$^1J_{CW}$}
			H_α H_β	C_α C_β
trans-$[W_2Cp_2\{\mu\text{-}\kappa{:}\eta^2\text{-}C(p\text{-tol})CH_2\}(\mu\text{-}PCy_2)(CO)_2]$ (***trans*-2a**)	1891 (vs), 1869 (m), 1784 (s)	81.8 [311, 242]^{c,d,e}	6.23 [2]^{c,d} 5.02 [2]^{c,d}	174.6^{c,d} 57.3^{c,d}
cis-$[W_2Cp_2\{\mu\text{-}\kappa{:}\eta^2\text{-}C(p\text{-tol})CH_2\}(\mu\text{-}PCy_2)(CO)_2]$ (***cis*-2a**)	1919 (vs), 1830 (w)^f	102.9 [337, 265]^g	5.54 [2] {15} 4.21[2]	155.0 {114, 38}^{h,i} 39.4^{g,i}
cis-$[W_2Cp_2\{\mu\text{-}\kappa{:}\eta^2\text{-}C(CO_2Me)CH_2\}(\mu\text{-}PCy_2)(CO)_2]$ (***cis*-2c**)	1931 (vs), 1851 (m), 1678 (w)	113.2 [345, 267]^{g,h}	5.77 [3] {16}^{h,j} 4.33 [3]^{h,j}	132.8^{h,i} 33.3^{h,i}
cis-$[W_2Cp_2\{\mu\text{-}\kappa{:}\eta^2\text{-}C(CO_2Me){=}CH(CO_2Me)\}(\mu\text{-}PCy_2)(CO)_2]$ (***cis*-2d**)	1940 (vs), 1851 (w), 1697 (m), 1677 (w)	113.3 [351, 255]^h	5.22^h	154.1^h 33.5^h
trans-$[W_2Cp_2\{\mu\text{-}\kappa{:}\eta^2\text{-}CHCH(p\text{-tol})\}(\mu\text{-}PCy_2)(CO)_2]$ (***trans*-3a**)	1873 (vs), 1815 (m, sh), 1789 (s)	79.7 [314, 254]^g	10.13 [10]^j 6.02 [10]^j	144.7 {105, 21}^{i} 85.0^i
trans-$[W_2Cp_2\{\mu\text{-}\kappa{:}\eta^2\text{-}CHCH(^tBu)\}(\mu\text{-}PCy_2)(CO)_2]$ (***trans*-3b**)	1874 (vs), 1782 (s)	79.8 [317, 267]^h	9.43 [12]^h 6.28 [12]^h	135.8^{h,i} 83.0^{h,i}
$[W_2Cp_2\{\mu\text{-}\kappa{:}\eta^2\text{-}CHCH(p\text{-tol})\}(O)(\mu\text{-}PCy_2)(CO)]$ (**4a**)	1837 (s)^k	128.0 [330, 320]^h	8.47 [10] {6}^{h} 3.65 [10]^h	124.6^h 54.3^h
$[W_2Cp_2\{\mu\text{-}\kappa{:}\eta^2\text{-}CHCH(^tBu)\}(O)(\mu\text{-}PCy_2)(CO)]$ (**4b**)	1839 (s)^k	124.2 [333, 322]^{g,h}	7.85 [10]^{h,j} 2.22 [10]^{h,j}	
$[W_2Cp_2\{\mu\text{-}\kappa{:}\eta^2\text{-}CHCH(p\text{-tol})\}(\mu\text{-}PCy_2)(CO)_3]$ (**5**)	1933 (vs), 1862 (s), 1839 (s)	176.1 [374, 114]^g	8.30 [8]^j 2.33 [8]^j	113.6 [5] {44}^{i} 59.8^i
$[W_2Cp_2\{\mu\text{-}\kappa{:}\eta^2\text{-}CHCH(p\text{-tol})\}(\mu\text{-}PCy_2)\{\eta^2\text{-}CHC(p\text{-tol})\}(CO)]$ (**6**)	1825 (s)	114.6 [297, 224]^h	7.65 [10]^h 4.32 [10]^h	131.8 {98, 41}^{h,i} 56.2^{h,i}
$[W_2Cp_2\{\mu\text{-}\kappa^2{:}\eta^3\text{-}CH(CO_2Me)CHC(CO_2Me)CH\}(\mu\text{-}PCy_2)(CO)_2]$ (**7**)	1939 (m), 1928 (s), 1876 (vs), 1856 (w), 1721 (w), 1690 (w)^k	55.1 [181, 177]^h		
trans-$[W_2Cp_2\{\mu\text{-}\kappa_C,\kappa_O{:}\eta^2\text{-}C(CO_2Me)CH(CO_2Me)\}(\mu\text{-}PCy_2)(CO)_2]$ (**8**)	1885 (m), 1852 (vs), 1671 (w)	72.7 [213, 198]^h	4.57 {5}^{h}	122.2 [16]^h 30.1
$[W_2Cp_2\{\mu\text{-}\kappa_C,\kappa_O{:}\eta^2\text{-}C(CO_2Me){=}C(CO_2Me)C(CO_2Me){=}CH(CO_2Me)\}(\mu\text{-}PCy_2)(CO)_2]$ (**9**)	1893 (m), 1837 (vs), 1698 (s)^f	157.1 [224, 120]^g		

^{a} Recorded in toluene solution, unless otherwise stated, ν in cm^{-1}; bands in the range 2000–1800 cm^{-1} correspond to the C–O stretches of the carbonyl ligands; those in the range 1700–1600 cm^{-1} to the C–O stretches of the CO_2Me groups. ^{b} Recorded in CD_2Cl_2 at 400.13 (^1H), 162.01 (^{31}P) or 100.63 (^{13}C) MHz and 295 K unless otherwise stated, with coupling constants (J) in Hz; only selected resonances for alkenyl ligands given (labelled as α or β). ^{c} Recorded in toluene-d$_8$. ^{d} Recorded at 233 K. ^{e} The resonance of the minor isomer **A** appears at 76.8 ppm. ^{f} Recorded in CH_2Cl_2. ^{g} Recorded at 121.50 MHz. ^{h} Recorded in C_6D_6. ^{i} Recorded at 75.47 MHz. ^{j} Recorded at 300.09 MHz. ^{k} Recorded in petroleum ether.



Scheme 4. Isomerization Equilibrium Proposed for Compounds ***trans*-2** and ***trans*-3**

Although the above process was very fast for the Mo_2 complexes even at low temperature, this is not the case for ***trans*-2a**, which at low temperature yields separate ^{31}P and ^1H NMR resonances for both isomers (see the Experimental Section), with the **A**/**B** ratio being somewhat dependent on temperature (ca. 1/10 at 253 K, 1/15 at 233 K, in toluene-d_8). In any case, the interconversion process would involve the exchange of coordination of the alkenyl C_β atom between tungsten atoms, a common dynamic process (the windshield wiper movement) of alkenyl-bridged complexes, first studied by Shapley for the osmium cluster $[Os_3(\mu\text{-}CHCH_2)(\mu\text{-}H)(CO)_{10}]$.[19] We finally note that the ^{31}P NMR spectra of these isomers display poorly deshielded resonances at *ca.* 80 ppm, as usually found for related complexes having 32-electron counts, and display two different ^{31}P–^{183}W couplings (of ca. 310 and 250 Hz), which is consistent with the presence of two tungsten atoms with coordination numbers somewhat different.[20]

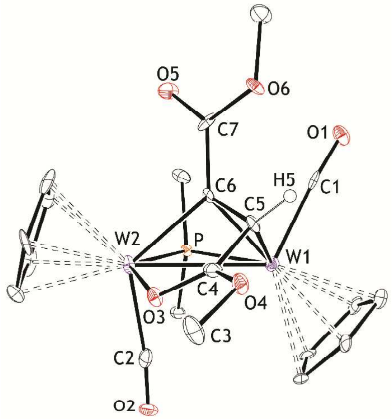


Figure 1. ORTEP diagram (30% probability) of compound **8** with H atoms (except H5) and Cy groups (except their C^1 atoms) omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Angles (°) for Compound **8**

W1–W2	2.9329(8)	W1–P1–W2	73.0(1)
W1–P1	2.473(3)	P1–W2–O3	136.4(2)
W2–P1	2.456(3)	O1–C1–W1	175(1)
W1–C1	1.97(2)	O2–C2–W2	173(1)
W2–C2	1.98(2)	C1–W1–W2	118.2(4)
W2–O3	2.222(8)	C2–W2–W1	78.8(4)
C5–C4	1.44(2)	O3–W2–P1	136.4(2)
C5–C6	1.47(2)	C5–C6–W1	74.0(8)
O5–C7	1.23(2)	W2–C6–W1	86.6(5)
O3–C4	1.26(2)	C4–C5–C6	111(1)
W1–C5	2.22(1)		
W1–C6	2.11(1)		
W2–C6	2.17(1)		

Structural Characterization of Compound 8. The molecule of **8** in the crystal (Figure 1 and Table 2) is similar to that previously determined by us for the analogous Mo_2 compound,[12] both in turn displaying a *C,O*:*C,C′* coordination of the alkenyl ligands closely related to those reported earlier for the related complexes *trans*-$[Mo_2Cp_2\{\mu\text{-}C(CO_2Me)CH(CO_2Me)\}(\mu\text{-}X)(CO)_2]$ (X = PPh_2, S^iPr)[21] and *trans*-$[Mo_2Cp_2\{\mu\text{-}CHCH(COPh)\}(\mu\text{-}PPh_2)(CO)_2]$.[22] Therefore a detailed discussion is not needed here. The molecule is built from two WCp(CO) fragments arranged in a quite distorted transoid disposition (C–W–W angles ca. 80 and 120°), and bridged by a PCy_2 ligand and by a five-electron donor alkenyl which is π-bound to one of the metals through the

C=C bond, while σ-bound to the other trough C_{α} and the carboxylic O atom of the carboxylate group attached to C_{β}, then forming an almost perfectly planar five-member WC_3O central ring. The intermetallic distance of 2.9329(8) Å is comparable to that of the analogous Mo_2 complex [2.9278(8) Å] and consistent with the formulation of a metal–metal single bond for this 34-electron complex, and the W–C lengths are indicative of strong σ [W–C_{α} = 2.17(1) Å] and π [W–C_{α} = 2.11(1) Å; W–C_{β} = 2.22(2) Å] interactions of the bridging alkenyl ligand. Notably, the W–O separation in **8** is *ca.* 0.04 Å shorter than the corresponding length in the related Mo_2 complex, indicating a somewhat stronger binding of the carboxylate group in the ditungsten complex.

Spectroscopic data available for **8** are essentially consistent with its solid-state structure. For instance, the IR spectrum displays two C–O stretching bands with the expected pattern for distorted *transoid* $M_2(CO)_2$ oscillators.[18] However, the ^{31}P NMR resonance of **8** appears at a chemical shift (72.7 ppm) unexpectedly low for a PCy_2 bridge in a 34-electron complex, actually being quite close to the shifts of ca. 80 ppm observed for the 32-electron complexes ***trans*-2** and ***trans*-3**. Yet, retention of the *O*-bound carboxylate in solution is supported by the observation of two similar and relatively weak P–W couplings (213 and 198 Hz), with values significantly lower than those measured in the alkenyls ***trans*-2** and ***trans*-3**, as expected by considering the increased coordination number of the metals in complex **8**. Although we currently do not have a satisfactory explanation for this low chemical shift, we note that a similar effect has been also observed for related 34-electron complexes with 5-electron-donor bridging ligands, such as the formimidoyl complexes $[W_2Cp_2(\mu\text{-}C,N{:}C,N\text{-HCNR})(\mu\text{-}PCy_2)(CO)_2]$ (δ_P ca. 60 ppm).[10] Other spectroscopic data are as expected and deserve no additional comments.

Structural Characterization of *cis*-Dicarbonyl Complexes 2. The molecule of ***cis*-2a** in the crystal (Figure 2 and Table 3) is made up from two WCp(CO) fragments arranged in a *cisoid* disposition and bridged by a PCy_2 ligand and a $\sigma{:}\pi$-bound alkenyl. The short intermetallic separation of 2.7273(8) Å is fully consistent with the metal–metal double bond to be formulated for this 32-electron complex according to the effective atomic number (EAN) formalism, and is significantly shorter than the corresponding length in the 34-electron complex **8**, while comparable to that measured in the isoelectronic alkenyl $[Mo_2Cp_2\{\mu\text{-}\kappa{:}\eta^2\text{-C(Me)CHMe}\}(\mu\text{-SPh})(CO)_2]$, even if the latter displays a transoid arrangement of the carbonyl ligands.[23] The parameters involving the alkenyl group indicate strong σ-binding [W–C_{α} = 2.10(2) Å] and π-coordination [W–C_{α} = 2.24(2) Å; W–C_{β} = 2.33(2) Å] of this ligand, while this intrinsic asymmetry is balanced by the phosphide ligand, *ca.* 0.04 Å closer to the tungsten atom σ-bound to the alkenyl. We finally note that the carbonyl ligands are parallel to each other, but deviates some 10° form the normal of the intermetallic vector to better accommodate the asymmetric bridging alkenyl ligand (C–W–W angles ca. 80 and 100°).

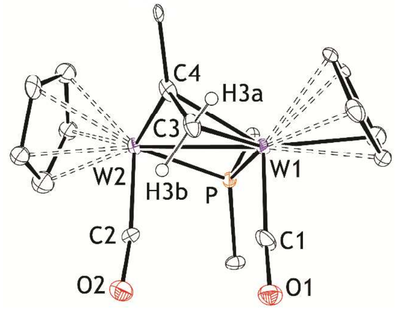


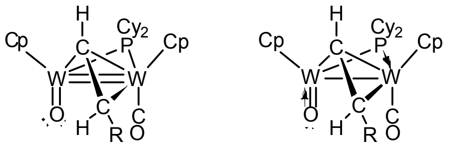
Figure 2. ORTEP diagram (30% probability) of compound ***cis*-2a** with H atoms (except H3a and H3b) and *p*-tol and Cy groups (except their C^1 atoms) omitted for clarity.

Table 3. Selected Bond Lengths (Å) and Angles (°) for Compound ***cis-2a***

W1–W2	2.728(1)	W1–C1–O1	175(2)
W1–P	2.425(5)	W2–C2–O2	172(2)
W2–P	2.382(5)	W1–P–W2	69.1(1)
W1–C3	2.33(2)	W1–C4–W2	77.8(6)
W1–C4	2.24(2)	W1–C3–C4	68(1)
W2–C4	2.10(2)	W2–C4–C3	121(1)
W1–C1	1.97(2)	C1–W1–C4	109.9(7)
W2–C2	1.94(2)	W1–W2–C2	82.1(5)
C3–C4	1.46(2)	W2–W1–C1	100.5(5)

Spectroscopic data for compounds ***cis*-2a-d** are similar to each other, indicating that they all share the same structural features, which in turn are consistent with the solid-state structure just discussed. Thus, the IR spectra of these compounds display two C–O stretches with relative intensities (strong and weak, in order of decreasing frequencies) indicative of the presence of *cisoid* $W_2(CO)_2$ oscillators having carbonyls almost parallel to each other.[18] The ^{31}P NMR resonances of these compounds appear around 130 ppm, figures which are *ca.* 30 ppm above those of the corresponding *trans* isomers, a recurrent trend found when comparing pairs of related *cis* and *trans* isomers, such as the Mo_2 alkenyls $[Mo_2Cp_2\{\mu\text{-}\kappa{:}\eta^2\text{-}CRCH_2\}(\mu\text{-}PCy_2)(CO)_2]$ ($\Delta\delta$ *ca.* 30 ppm),[12] and the bis(phosphide) complexes $[Mo_2Cp_2(\mu\text{-}PR_2)(\mu\text{-}PR'_2)(CO)_2]$ ($\Delta\delta$ *ca.* 45 ppm).[24] The ^1H and ^{13}C NMR spectra of all these complexes (see the Experimental Section) are as expected after considering the lack of any symmetry element in the corresponding molecules, except for the strong deshielding displayed by one of the carbonyl resonances in each case (δ_C ca. 245-250 ppm). This might be taken as an indication that, in solution, the carbonyl leaning towards the intermetallic bond might define a more acute angle than found in the crystal, so as to acquire an incipient semibridging character.

Solution Structure of Oxo Complexes 4. Compounds **4** are formally derived from replacement of a carbonyl ligand with a terminal oxygen atom in the corresponding dicarbonyl precursors. Indeed, the IR spectra of these compounds display just one C–O stretching band in each case, while the presence of a terminal oxo ligand was firmly supported by the appearance in the corresponding solid-state spectrum of a characteristic W–O stretch around 915 cm^{-1}. The high frequency of the C–O stretches in these compounds, *ca.* 1840 cm^{-1}, is indicative of a *cisoid* disposition of the terminal CO and oxo ligands, after recalling that *trans* isomers in this sort of oxocomplexes usually display significantly less energetic bands, as observed for example in the pairs of *cis*- and *trans* isomers of complexes [$Mo_2Cp_2(\mu\text{-}PCy_2)(\mu\text{-}CPh)(O)(CO)$] (1915/1895 cm^{-1}),[25] or [$Mo_2Cp_2(\mu\text{-}PPh_2)_2(O)(CO)$] (1859/1826 cm^{-1}).[26] The ^{31}P NMR resonances of these compounds appear around 130 ppm, retaining two sets of relatively high ^{183}W couplings. In general, replacement of CO by an oxo group in this type of complexes causes a strong deshielding of the corresponding ^{31}P nuclei, this possibly being a consequence of the presence of lone pairs at the O atom which can make this ligand to behave as a multielectron donor, then reducing the intermetallic interaction accordingly (see canonical forms ***I*** and ***II*** in Chart 3).[25] This is nicely exemplified by the pairs of compounds [$W_2Cp_2(\mu\text{-}PPh_2)_2L(CO)$] ($\delta_P$ 34.7/102.2 ppm for L = CO/O),[24,27] and [$Mo_2Cp_2(\mu\text{-}PPh_2)(\mu\text{-}CH_2PPh_2)L(CO)$] ($\delta_P$ 92.1/201.6 ppm for L = CO/O).[28,29] The corresponding deshielding in the case of compounds **4a,b** is more modest (*ca.* 40 ppm), then suggesting that the W–O interaction in these compounds might not be as strong as is in the above examples. Apart from this, the ^{1}H and ^{13}C NMR data are compatible with the lack of symmetry and with the $\sigma{:}\pi$-coordination of a β-substituted alkenyl in each case. We note that up to four different isomers might be compatible with the above conditionings, these involving different orientations of the alkenyl group with respect to the *cisoid* WCpL (L = CO/O) fragments. In the absence of additional structural data we have assumed for compounds **4** an alkenyl arrangement comparable to that found in the crystal structure of ***cis*-2a**, while keeping the π-interaction with the metal atom bearing the CO ligand (Charts 2 and 3), this likely rendering a more balanced electron distribution at the dimetal centre.



I *II*

Chart 3

Solution Structure of the Tricarbonyl Complex 5. Spectroscopic data for compound **5** (Table 1 and Experimental Section) are indicative of a strong relationship with the related dimolybdenum complexes [$Mo_2Cp_2(\mu\text{-}\kappa{:}\eta^2\text{-}CHCHR)(\mu\text{-}PCy_2)(CO)_3$] (R = H,[17] *p*-tol)[12] and [$Mo_2Cp_2\{\mu\text{-}\kappa{:}\eta^2\text{-}CRCHR'\}(\mu\text{-}PPh_2)(CO)_3$] (R, R' = H, Me, Et),[30] therefore, a similar geometry is assumed for all these compounds (Scheme 1). This implies a *cisoid* disposition of the Cp ligands with respect to the central W_2P plane, with the alkenyl group displaying π-coordination with the monocarbonyl metal fragment in order to balance the different number of CO ligands, as corroborated by X-ray crystallography.[17,30] This is particularly indicated by the identical pattern of the three C–O stretches appearing in the IR spectrum of all these compounds. As expected for a 34-electron complex, the ^{31}P resonance of **5** appears at a high chemical shift (δ_P 176.1 ppm), *ca.* 73 ppm downfield of the 32-electron dicarbonyl complex ***cis*-2a** while, quite unexpectedly, it displays two sets of very different couplings to the ^{183}W nuclei (374, 114 Hz). Such a strong difference does not have an obvious explanation if we keep in mind that the two metal centres might be considered to have the same coordination numbers, unless the π-interaction of the alkenyl ligand approaches the cyclopropane extreme. In line with this suspicion, we note that the C_β-bound H atom appears unusually shielded (δ_H 2.22 ppm), a situation also found for the ethenyl complexes $[Mo_2Cp_2\{\mu\text{-}\kappa{:}\eta^2\text{-}CHCH_2)\}(\mu\text{-}PR_2)(CO)_3]$ (R = Cy,[17] Ph),[30] a circumstance that seems to be related to a strong π-interaction of the alkenyl group with the monocarbonyl fragment in these tricarbonyl complexes.

Solution Structure of the Alkyne Complex 6. Spectroscopic data for **6** (Table 1 and Experimental Section) are consistent with this product following from replacement of a CO ligand with a second *p*-tolylacetylene molecule in the dicarbonyl complex ***trans*-3a**. Indeed compound **6** displays just one C–O stretch in its IR spectrum, and a single resonance (δ_C 220 ppm) in the carbonyl region of the ^{13}C NMR spectrum. Moreover, the ^1H and ^{13}C NMR spectra clearly indicates that two molecules of alkyne have been incorporated into **6**, displaying two sets of independent resonances which can be identified as derived from the presence of alkenyl and alkyne ligands, respectively. The latter is coordinated to one of the metal centres in a η^2-fashion, as indicated by the appearance of two ^{13}C resonances at 184.4 and 170.0 ppm, well within the range typically observed for terminally-bound alkynes (δ_C 250-150 ppm), as it is the case of complexes $[W(\eta^2\text{-}PhC{\equiv}CR)_3(CO)]$ (R = H, Ph),[31] and $[WCp(PMe_3)(\eta^2\text{-}RC{\equiv}COR')]$ (R = Me, *p*-tol; R' = Me, Et).[32] As a result, this complex might be formulated as a 32-electron compound (therefore, with an intermetallic double bond, according to the EAN formalism), which seems consistent with its relatively low ^{31}P chemical shift (δ_P 114.6 ppm), comparable to those of the 32-electron dicarbonyls ***cis*-2**; based on this similarity, it is likely that the terminal ligands are also arranged in a *cisoid* disposition. Yet, as noted for the oxo complexes **4**, four different isomers are possible depending on the relative arrangement of the alkenyl ligand with respect to the terminal ligands in **6**. However, based in the structure of ***cis*-2a**, it seems reasonable to assume that the alkenyl in **6** displays π-coordination to the monocarbonyl fragment of the molecule, because this involves lower steric repulsions with the relatively bulky (vs. CO) terminal alkyne (Scheme 1).

Structural Characterization of Compound 7. The asymmetric unit in the crystal of **7** displays two independent, but otherwise comparable molecules, so only the metric parameters of one will be discussed here (Figure 3 and Table 4). The molecule is built from two WCp(CO) fragments arranged in a *transoid* disposition and bridged by PCy_2 and by a dienyl ligand resulting from coupling of alkenyl and alkyne ligands. The dienyl ligand acts as a five-electron donor, being σ-bound to the W2 atom through the terminal atoms of the chain [W2–C6 = 2.28(1) Å; W2–C3 = 2.14(1) Å], and π-bound to the second W atom in a η^3-fashion [W1–C lengths 2.21(1)-2.34(1) Å] otherwise similar to that found in a number of tungsten complexes with η^3-coordinated allyl ligands.[33] This renders **7** as an electron-precise 34-electron compound for which a metal-metal single bond should be formulated, which is consistent with the relatively large intermetallic separation of 2.944(1) Å, a figure almost identical to that measured for the isoelectronic compound **8**. As found in the latter compound, the carbonyl ligands display a significant deviation from the ideal antiparallel disposition, with one of them leaning towards the intermetallic bond [W1–W2–C2 = 82.5(3)º] while the other one points away from the dimetal centre [W1–W2–C2 = 116.4(3)º].

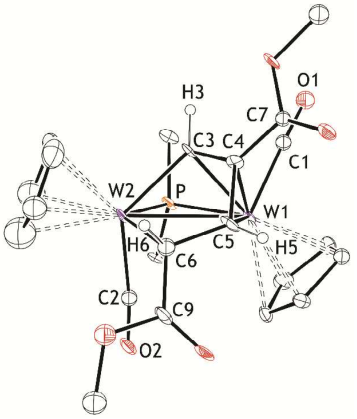


Figure 3. ORTEP diagram (30% probability) of one of the independent molecules of compound **7**, with H atoms (except H3, H5 and H6) and Cy groups (except their C^1 atoms) omitted for clarity.

Table 4. Selected Bond Lengths (Å) and Angles (°) for Compound **7**.

W1–W2	2.9440(9)	W2–W1–C1	116.6(3)
W1–P	2.477(3)	W1–W2–C2	82.5(3)
W2–P	2.427(3)	W1–P–W2	73.77(7)
W1–C1	1.96(1)	W1–C1–O1	177.8(9)
W2–C2	1.96(1)	W2–C2–O2	173.3(9)
W1–C3	2.21(1)	W2–C6–C5	103.1(7)
W2–C3	2.14(1)	W1–C5–C6	108.9(7)
W1–C5	2.34(1)	C3–C4–C5	108.8(9)
W1–C4	2.26(1)	C5–C6–C9	113.7(9)
W2–C6	2.28(1)	P–W1–C3	73.7(3)
C6–C5	1.47(1)	P–W2–C3	75.9(3)
C5–C4	1.41(1)	P–W2–C6	125.9(3)
C4–C3	1.44(1)		

Spectroscopic data in solution for compound **7** (Table 1 and Experimental Section) are essentially consistent with the solid-state structure just discussed. However, we note that its IR spectrum, when recorded in petroleum ether solution, displays four instead of the expected two C–O stretches (excluding those corresponding to the CO_2Me groups), which points to the coexistence of two similar dicarbonyl molecules in solution, possibly two conformers. In spite of this, all NMR data available for **7** (^{31}P, ^{1}H and ^{13}C) are indicative of the presence of a single species in solution, thus indicating that these conformers interconvert rapidly on the NMR timescale. For instance, the ^{31}P NMR spectrum of **7** displays just one resonance with two well defined sets of ^{183}W satellites. The small magnitude of the P–W couplings (181 and 177 Hz) is consistent with the relatively high coordination number of the tungsten atoms in this complex (compared to the alkenyl complexes **2** and **3**), but the corresponding chemical shift (δ_P 55.1 ppm) falls within the range observed for 32-electron complexes of the type $[W_2Cp_2(\mu\text{-}X)(\mu\text{-}PCy_2)(CO)_2]$ (δ_P 98-40 ppm when X = I,[1] PEt_2).[34] Yet, as noted above for compound **8**, a similar trend has been also observed for related 34-electron complexes with 5 electron-donor bridging ligands, such as the formimidoyl complexes $[W_2Cp_2(\mu\text{-}C,N{:}C,N\text{-}HCNR)(\mu\text{-}PCy_2)(CO)_2]$ (δ_P ca. 60 ppm).[10] Therefore it seems clear that the ^{31}P chemical shift is not a reliable indicator of the number of electrons provided by the polydentate hydrocarbyl ligands in these complexes. Other spectroscopic data for **7** are as expected and deserve no particular remarks.

Structural Characterization of Compound 9. The solid-state structure of **9** (Figure 4) was briefly discussed in a preliminary communication,[11] therefore a detailed analysis is not pertinent here. The most relevant aspect of the structure is the presence of a bridging dienyl ligand derived from an alkenyl/alkyne coupling comparable to that found in **7**, but displaying a coordination mode very different from that found in the latter compound. The C_4 chain now is σ-bound to one of the tungsten atoms through the alkenyl carbon [W1–C3 = 2.17(1) Å] while an oxygen atom of a pendant carboxylate group (O7) is also bound to the same metal centre. The ligand interacts with the second metal atom via π-bonding of the second C=C bond of the dienyl ligand (W–C lengths *ca*. 2.25 Å). In spite of this different coordination mode, the dienyl ligand in **9** still acts as a 5-electron donor, as it was the case in **7**, then leading to the electronic saturation of the dimetal centre, in agreement with the relatively large intermetallic separation of 3.0273(6) Å.

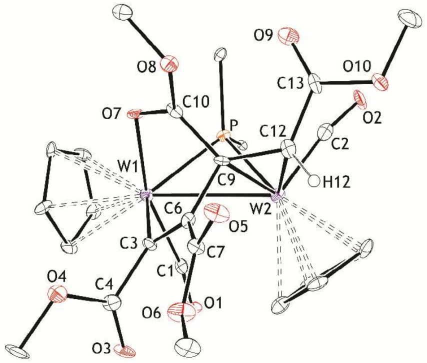
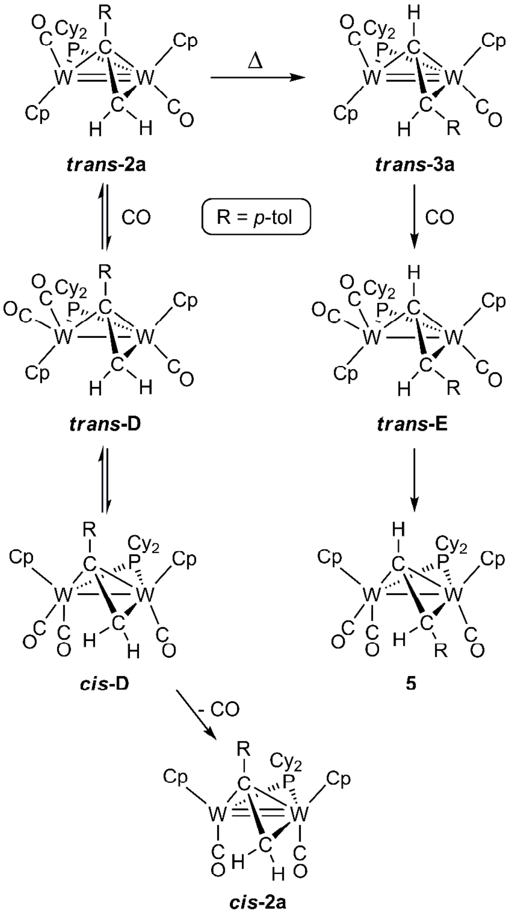


Figure 4. ORTEP diagram (30% probability) of compound **9** with H atoms (except H12) and Cy groups (except their C^1 atoms) omitted for clarity. Selected bond lengths (Å) and angles (deg) (taken from ref. 11): W1–W2 = 3.0273(6), W1–P1 = 2.433(3), W1–C1 = 1.99(1), W1–C3 = 2.17(1), W1–O7 = 2.24(1), W2–P1 = 2.475(3), W2–C2 = 1.94(1), W2–C9 = 2.24(1), W2–C12 = 2.26(1), C3–C6 = 1.35(1), C6–C9 = 1.49(1), C9–C12 = 1.44(1), C9–C10 = 1.46(1), C10–O7 = 1.24(1); W2–W1–C1 = 73.2(3), W1–W2–C2 = 118.4(3).

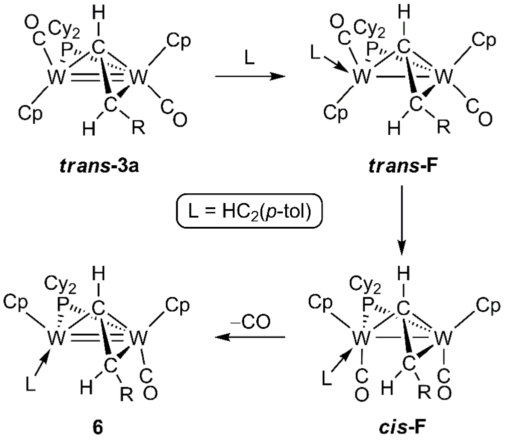
Spectroscopic data in solution for compound **9** are fully consistent with its solid-state data. Thus, the carbonyl region of the IR spectrum displays two C–O stretching bands with relative intensities indicative of the presence of a quite distorted *transoid* $M_2(CO)_2$ oscillator, in agreement with the strong deviation of the carbonyl ligands in the solid state from an ideal antiparallel disposition (W–W–C angles ca. 73 and 118°, C–W–W–C ca. 117°). The ^{31}P resonance of **9** appears *ca.* 85 ppm above that of **7**, with a chemical shift comparable to that of the isoelectronic tricarbonyl **5**, and the P–W couplings are significantly different from each other (224, 120 Hz), as expected for two tungsten atoms having different coordination numbers. Finally, the dienyl group gives rise to four ^{13}C resonances, with those corresponding to the alkenyl-like atoms [W–*C*=C (232.8 ppm) and W–C=*C* (163.8 ppm)] being similar to those observed in the terminal alkenyl complexes $[W(O)\{C(^tBu)=CH_2\}(OAr)_3]$ (213.4 and 114.0 ppm; Ar = 2,6-$C_6H_3{}^iPr_2$),[35] $[WCl\{C(Ph)=CPhH\}(NSi^tBu_3)]$ (192.6 and 139.8 ppm),[36] and those of the π-bound C=CH(CO_2Me) group remaining close to the resonances observed in the related ***cis*-2d**.



Scheme 5

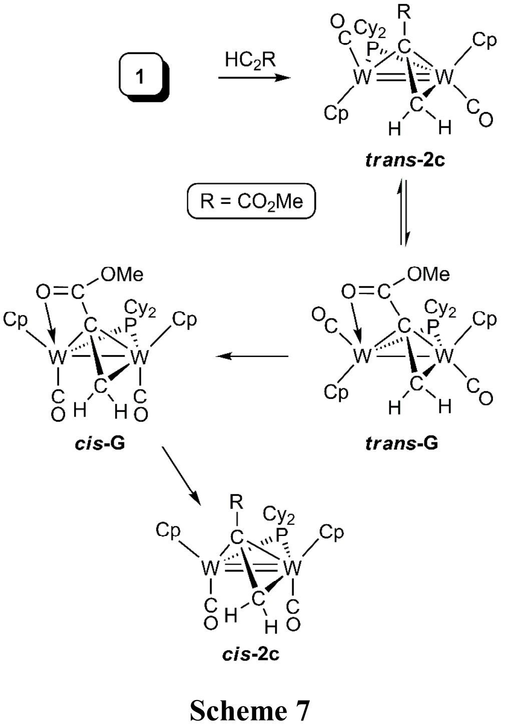
Pathways in Reactions of 1 with Alkynes. Reactions of **1** with HC≡C(*p*-tol) lead mainly to the formation of complexes bearing either *α*- or *β*-substituted alkenyl ligands (***trans*-2a** and ***trans*-3a**), depending on temperature and time. Since formation of ***trans*-2a** is favoured at room temperature, while ***trans*-3a** is mainly obtained from the former at higher temperatures, or after prolonged reaction times at room temperature, it is then clear that the *α*-substituted alkenyl complex is the kinetic product, while the *β*-substituted one is the thermodynamic one. Hence the exclusive formation of the *β*-substituted derivative ***trans*-3b** in reactions of **1** with HC≡C^{t}Bu, given the high temperatures required to induce addition of this less reactive alkyne. The *α*→*β* rearrangement formally requires a [2,1]-hydrogen shift (Scheme 5), a process also observed in the Mo_2 analogues of these complexes,[12] but otherwise rarely observed for alkenyl-bridged complexes under mild conditions. For instance, related rearrangements have been induced at elevated temperatures (*ca.* 393 K) on the dinuclear complexes $[Fe_2\{\mu\text{-}C(Ph)CH_2\}(\mu\text{-}PPh_2)(CO)_6]$,[37] and $[Ir_2Cp^*_2\{\mu\text{-}C(R)CH_2\}(\mu\text{-dppm})]^{+2}$.[38] It seems reasonable to assume that, in our case, the comparatively easy *α*→*β* isomerization can be attributed to the unsaturated nature of compounds **2**, this providing the required empty orbitals and coordination vacancy for activation of an alkenyl C–H bond, as required to accomplish isomerization *via* an hydride intermediate, as first proposed for the mentioned diiron complex.[37]

Carbonylation of the 32-electron alkenyl ***trans*-3a** yields the corresponding saturated tricarbonyl **5**, the latter displaying a *cisoid* disposition of the carbonyl (and Cp) ligands with respect to the central W_2P plane. Initial coordination of a CO molecule to ***trans*-3a** likely would lead to the formation of a (unobserved) *transoid* tricarbonyl intermediate (***trans*-E** in Scheme 5), which would evolve rapidly through a 180º rotation of the metal fragments around the W–W bond so as to render the final cisoid isomer **5**. In contrast, carbonylation of the α-substituted alkenyl ***trans*-2a** does not lead to a stable tricarbonyl derivative but to the *cis*-dicarbonyl ***cis*-2a**. This is itself not surprising by considering that related binuclear tricarbonyl complexes of the group 6 metals are rare species which typically evolve by releasing CO to give more stable dicarbonyl compounds.[24] In any case, the formation of ***cis*-2a** would follow a pathway similar to that leading to **5**, this involving initial carbonylation to give an undetected tricarbonyl species retaining the *transoid* disposition of the metal fragments (***trans*-D** in Scheme 5), which then would evolve rapidly to the corresponding *cis* isomer (***cis*-D**), which in turn would release CO spontaneously. A similar set of reactions would also explain the formation of the alkyne complex **6** from ***trans*-3a** at high temperature (Scheme 6) *via* a dicarbonyl alkyne intermediate (***trans*-F**) undergoing *trans* to *cis* rearrangement (to give intermediate ***cis*-F**) and then spontaneous decarbonylation. We finally note that a related sequence justifies the rare formation of ***cis*-2a** when just removing the solvent from a solution of ***trans*-2a** in the presence of excess alkyne and storing of the oily residue at low temperature for several days, this only requiring the formation of α-substituted analogues of intermediates **F** eventually undergoing release of the alkyne ligand instead of decarbonylation.



Scheme 6

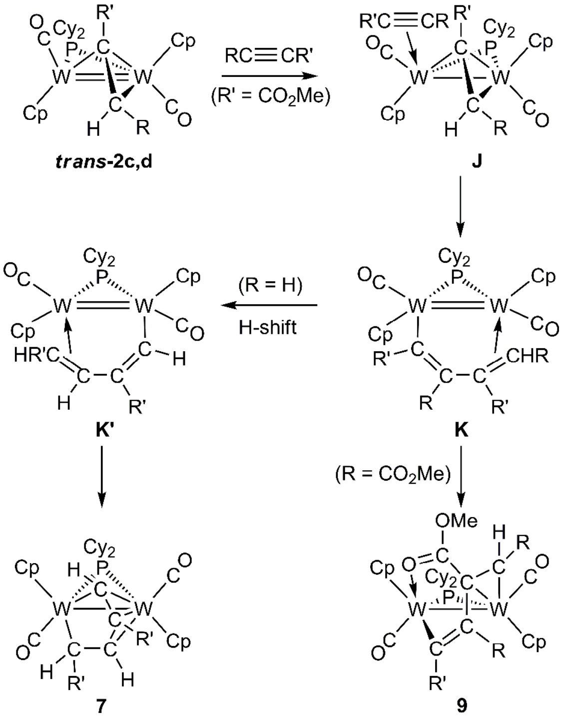
One of the main differences found in reactions of **1** with HC≡C(CO_2Me), when compared to those of the aryl- and alkyl-substituted acetylenes, is that no *β*-substituted alkenyls have been obtained or detected under any experimental conditions. Even at high temperature (393 K) the reaction leads rapidly (10 min) and selectively to the *α*-substituted alkenyl ***cis*-2c** if stoichiometric amounts of alkyne are used. Monitoring of the room temperature reaction allowed us to detect an intermediate species likely corresponding to the *transoid* alkenyl ***trans*-2c** (Scheme **7**), as noted above. The presence of pendant carboxylate groups in the alkenyl ligand of this intermediate would be critical to facilitate a *trans* to *cis* isomerization in the absence of added ligands (*i.e.* CO or excess alkyne). Thus, *O*-coordination of the carboxylate would generate an undetected intermediate (***trans*-G**) in which *trans* to *cis* isomerization would readily take place, as found for the isoelectronic tricarbonyls **D** and **E** mentioned above. This would be followed by de-coordination of the carboxylate group to finally render ***cis*-2c**. The fast formation of this product would prevail over any competitive *α*→*β* isomerization, since *cis* dicarbonyl isomers do not seem to undergo such rearrangement, as proven for the *p*-tol compound ***cis*-2a**. Finally, we must note that a similar mechanism would explain the formation of the alkenyl ***cis*-2d** in the low temperature reaction of **1** with $C_2(CO_2Me)$. Yet, we note that, in the presence of excess methyl propiolate, *α*→*β* isomerization must occur necessarily at some stage, after considering the structure of the dienyl complex **7**, next discussed.



Scheme 7

The formation of dienyl complexes **7** and **9** can be rationalized as following from coupling of an alkenyl ligand (formed after insertion of the first alkyne molecule into the W–H bond of **1**, as discussed above) with a second alkyne molecule. As noted above, independent experiments proved that in both cases the *cis*-dicarbonyl alkenyls ***cis*-2c,d** are not intermediates in the formation of the observed dienyl complexes. In fact, in both reactions we detected spectroscopically the formation of intermediates likely corresponding to *trans*-dicarbonyl alkenyls. In the DMAD reaction, such an intermediate would be the *trans* isomer of ***cis*-2d** (***trans*-2d** in Scheme 8). Coordination of a second molecule of alkyne to this alkenyl intermediate would give an alkenyl-alkyne intermediate **J** which, instead of releasing CO as proposed for the *p*-tol analogue (**F** in Scheme 6), would undergo a reductive C–C coupling to generate the dienyl ligand. In a way, this coupling could be related to the thiolate-alkyne-alkyne couplings observed in reactions of the cation $[Mo_2Cp_2(\mu\text{-}SMe)_3(NCMe)_2]^+$ with alkynes.[39] In any case, the coupling proposed would yield initially a 32 electron intermediate **K** which then would rearrange by coordinating one of its carboxylate groups in order to render the 34-electron complex **9** eventually isolated. In the methyl propiolate reaction (R = H in Scheme 8), intermediate **K** must be formed specifically *via* a head-to-tail coupling, as judged from the alternate distribution of carboxylate groups in the final product. However, since ***trans*-2c** seems to be a α-substituted alkenyl complex, as noted above, then intermediate **K** would have a CH_2 group, not present in the final product. Then, a H-shift must be proposed to occur at this unsaturated intermediate, perhaps analogous to the $\alpha \rightarrow \beta$ isomerization discussed for complexes ***trans*-2a,b** (i.e. *via* an hydride intermediate), which now would result in an overall [1,4]-H shift to yield a similar intermediate **K'** which would attain electronic saturation upon rearrangement into the $\kappa^2:\eta^3$ coordination mode, to yield the dienyl complex **7** eventually isolated.

Scheme 8



Conclusions

In reactions with *p*-tolylacetylene, the unsaturated hydride [$W_2Cp_2(H)(\mu\text{-}PCy_2)(CO)_2$] (**1**) behaves essentially in a way comparable to that of its dimolybdenum analogue. Thus, the main products obtained are unsaturated alkenyls of formulae *trans*-[$W_2Cp_2\{\mu\text{-}\kappa{:}\eta^2\text{-}C(R)CHR'\}(\mu\text{-}PCy_2)(CO)_2$], with the α-substituted alkenyl complex rearranging thermally into the β-substituted one, while its reaction with CO instead promotes a *trans* to *cis* isomerization *via* a cisoid tricarbonyl intermediate [$W_2Cp_2\{\mu\text{-}\kappa{:}\eta^2\text{-}C(R)CHR'\}(\mu\text{-}PCy_2)(CO)_3$] which, however, turned out to be a stable species when starting from the β-substituted alkenyl (R = H, R' = *p*-tol). Reaction of **1** with excess alkyne under more forcing conditions gives the alkenyl/alkyne complex [$W_2Cp_2\{\mu\text{-}\kappa{:}\eta^2\text{-}CHCH(p\text{-}tol)\}(\mu\text{-}PCy_2)\{\eta^2\text{-}CHC(p\text{-}tol)\}(CO)$], a product never observed in reactions of the analogous Mo_2 hydride with alkynes, thus illustrating the ability of the ditungsten hydride to incorporate two alkyne molecules, a pre-requisite for any subsequent C–C coupling reactions. A more substantial effect of the metal (W instead of Mo) was observed for reactions with alkynes bearing electron-withdrawing carboxylate substituents, particularly exemplified by the ability of the ditungsten hydride to form products following from alkenyl/alkyne coupling which were never observed in related reactions of the analogous Mo_2 hydride. Thus, reactions of **1** with $HC{\equiv}CCO_2Me$ give either a α-substituted alkenyl of *cisoid* geometry, following from a complete *trans* to *cis* isomerization facilitated by coordination of the O-atom of the carboxylate group at a transient stage, or the dienyl complex [$W_2Cp_2\{\mu\text{-}\kappa^2:\eta^3$-CH($CO_2$Me)CHC($CO_2$Me)CH}($\mu$-$PCy_2$)$(CO)_2$], generated from an alkenyl/alkyne coupling also involving a H-shift comparable to the $\alpha \rightarrow \beta$ isomerization observed in the alkenyl complexes. Reactions of **1** with dimethyl acetylenedicarboxylate also generates complexes bearing alkenyl ligands or dienyl ligands, but in most cases their coordination differ from those observed in the methyl propiolate derivatives because of the permanent binding of the oxygen atom of a carboxylate group to a tungsten atom so as to render electron-precise (34-electron) rather than unsaturated (32-electron) complexes.

Experimental Section

General Procedures and Starting Materials. All manipulations and reactions were carried out under a nitrogen (99.995%) atmosphere using standard Schlenk techniques. Solvents were purified according to literature procedures, and distilled prior to use.[40] Compound [W_2Cp_2(H)(μ-PCy_2)$(CO)_2$] (**1**) was prepared as described previously,[1] and all other reagents were obtained from the usual commercial suppliers and used as received, unless otherwise stated. Petroleum ether refers to that fraction distilling in the range 338-343 K. Filtrations were carried out through diatomaceous earth unless otherwise stated. Chromatographic separations were carried out using jacketed columns refrigerated by tap water (ca. 288 K) or by a closed 2-propanol circuit kept at the desired temperature with a cryostat. Commercial aluminium oxide (activity I, 70-290 mesh) was degassed under vacuum prior to use. The latter was mixed afterward under nitrogen with the appropriate amount of water to reach the activity desired (activity IV, unless otherwise stated). IR stretching frequencies of CO ligands were measured in solution (using CaF_2 windows), or in Nujol mulls (using NaCl windows), and are referred to as ν(CO)(solvent) and ν(CO)(Nujol), respectively. Nuclear magnetic resonance (NMR) spectra were routinely recorded at 400.13 (^{1}H), 162.00 ($^{31}P\{^1H\}$) or 100.63 MHz ($^{13}C\{^1H\}$), at 295 K in CD_2Cl_2 solution unless otherwise stated. Chemical shifts (δ) are given in ppm, relative to internal tetramethylsilane (^{1}H, ^{13}C) or external 85% aqueous H_3PO_4 (^{31}P). Coupling constants (J) are given in Hertz.

Reaction of 1 with HC_2(*p*-tol). A solution of compound **1** (0.040 g, 0.053 mmol) and HC_2(*p*-tol) (20 μL, 0.158 mmol) in toluene (4 mL) was stirred in a Schlenk flask equipped with a Young's valve for 24 h, to give a brown-greenish solution containing compound *trans*-[$W_2Cp_2\{\mu\text{-}\kappa:\eta^2$-C(*p*-tol)$CH_2$}($\mu$-$PCy_2$)$(CO)_2$] (***trans*-2a**) as major product, along with small amounts of *trans*-[$W_2Cp_2\{\mu\text{-}\kappa:\eta^2$-CHCH(*p*-tol)}($\mu$-$PCy_2$)$(CO)_2$] (***trans*-3a**). All attempts to isolate pure samples of compound ***trans*-2a** from these mixtures led to its complete transformation into ***trans*-3a**. *Spectroscopic data for* ***trans*-2a**: $^{31}P\{^1H\}$ NMR (toluene-d_8): δ 80.6 (br). $^{31}P\{^1H\}$ NMR (toluene-d_8, 273

K): δ 81.7 (s, br, $^1J_{PW}$ = 278, isomer **B**), 77.3 (br, isomer **A**). $^{31}P\{^1H\}$ NMR (toluene-d_8, 253 K): δ 81.7 (s, $^1J_{PW}$ = 311, 242, isomer **B**), 77.0 (s, br, $^1J_{PW}$ = 261, isomer **A**). $^{31}P\{^1H\}$ NMR (toluene-d_8, 233 K): δ 81.8 (s, $^1J_{PW}$ = 311, 242, isomer **B**), 76.8 (br, isomer **A**). ^1H NMR (toluene-d_8): δ 7.29, 6.73 (2d, $^3J_{HH}$ = 8, 2 x 2H, C_6H_4), 6.10 (s, br, 1H, CH_2), 5.02 (s, br, 5H, Cp), 4.89 (s, br, 1H, CH_2), 4.78 (s, br, 5H, Cp), 1.96 (s, 3H, Me), 2.40-1.10 (m, 22H, Cy). ^1H NMR (toluene-d_8, 273 K): δ 7.30, 6.70 (2d, $^3J_{HH}$ = 8, 2 x 2H, C_6H_4), 6.18 (s, br, 1H, CH_2), 5.13 (s, vbr, 5H, Cp), 4.90 (s, vbr, 6H, Cp and CH_2), 1.92 (s, 3H, Me), 2.40-1.00 (m, 22H, Cy). ^1H NMR (toluene-d_8, 253 K): *Isomer **B***: δ 7.30, 6.65 (2d, $^3J_{HH}$ = 8, 2 x 2H, C_6H_4), 6.22 (s, br, 1H, CH_2), 5.14, 4.88 (2s, 2 x 5H, Cp), 5.02 (s, br, 1H, CH_2), 1.89 (s, 3H, Me), 2.45-1.00 (m, 22H, Cy). *Isomer **A***: δ 5.89 (s, br, 1H, CH_2), 4.65, 4.23 (2s, br, 2 x 5H, Cp). Ratio **B**/**A** = 10. ^1H NMR (toluene-d_8, 233 K): *Isomer **B***: δ 7.31, 6.60 (2d, $^3J_{HH}$ = 8, 2 x 2H, C_6H_4), 6.23 (t, $^2J_{HH}$ = $^3J_{HP}$ = 2, 1H, CH_2), 5.14, 4.83 (2s, 2 x 5H, Cp), 5.02 (d, $^3J_{HH}$ = 2, 1H, CH_2), 1.85 (s, 3H, Me), 2.45-1.00 (m, 22H, Cy). *Isomer **A***: δ 5.89 (s, br, 1H, CH_2), 4.62, 4.20 (2s, br, 2 x 5H, Cp). Ratio **B**/**A** = 15. $^{13}C\{^1H\}$ NMR (toluene-d_8, 233 K, Isomer **B**): δ 235.6, 231.0 (2d, $^2J_{CP}$ = 4, WCO), 174.6 (s, C_α), 156.7 [s, C^1(*p*-tol)], 135.0 [s, C^4(*p*-tol)], 128.5, 128.3 [2s, $C^{2,3}$(*p*-tol)], 89.4, 87.5 (2s, Cp), 57.3 (s, C_β), 51.7 [d, $^1J_{CP}$ = 31, C^1(Cy)], 39.5 [d, $^1J_{CP}$ = 25, C^1(Cy)], 34.6, 34.4, 33.6, 31.2 [4s, C^2(Cy)], 28.0 [m, C^3(Cy)], 26.6, 26.3 [2s, C^4(Cy)], 21.2 (s, Me).

Preparation of *cis*-$[W_2Cp_2\{\mu\text{-}\kappa:\eta^2\text{-}C(p\text{-tol})CH_2\}(\mu\text{-}PCy_2)(CO)_2]$ (*cis*-2a). A freshly prepared solution of compound ***trans*-2a** (*ca.* 0.027 mmol) in toluene (4 mL) was stirred under an atmosphere of CO (1 atm) for 1 h to yield an orange solution. Solvent was then removed under vacuum, the residue was extracted with dichloromethane/petroleum ether (1/2) and the extracts were chromatographed through alumina at 263 K. A yellow-greenish fraction was eluted using the same solvent mixture which gave, upon removal of solvents, compound ***cis*-2a** as an air-sensitive orange solid (0.017 g, 74%). The crystals used in the X-ray study were grown by the slow diffusion of a layer of petroleum ether into a concentrated toluene solution of the complex at 253 K. Anal. Calcd for $C_{33}H_{41}O_2PW_2$: C, 45.65; H, 4.76. Found: C, 45.50; H, 4.73. ν(CO) (petroleum ether): 1936 (vs), 1857 (w). ^1H NMR: δ 6.83 (m, br, 2H, C_6H_4), 5.54 (dd, $^2J_{HH}$ = 1.5, $^3J_{HP}$ = 2.5, $^2J_{HW}$ = 15, 1H, CH_2), 5.23 (m, br, 2H, C_6H_4), 5.18, 4.55 (2s, 2 x 5H, Cp), 4.21 (d, $^2J_{HH}$ = 1.5, 1H, CH_2), 2.19 (s, 3H, Me), 2.70-1.00 (m, 22H, Cy). ^1H NMR (193 K): δ 7.54 (dd, $^4J_{HH}$ = 2, $^3J_{HH}$ = 8, 1H, C_6H_4), 7.05 (dd, $^4J_{HH}$ = 1.5, $^3J_{HH}$ = 8, 1H, C_6H_4), 6.67 (dd, $^4J_{HH}$ = 1.5, $^3J_{HH}$ = 8, 1H, C_6H_4), 5.57 (s, br, 1H, CH_2), 5.25 (s, 5H, Cp), 5.23 (dd, $^4J_{HH}$ = 2, $^3J_{HH}$ = 8, 1H, C_6H_4), 4.56 (s, 5H, Cp), 4.07 (s, 1H, CH_2), 2.21 (s, 3H, Me), 2.80-1.00 (m, 22H, Cy). $^{13}C\{^1H\}$ NMR (C_6D_6, 75.47 MHz): δ 247.7 (d, $^2J_{CP}$ = 2, $^1J_{CW}$ = 214, WCO), 227.5 (d, $^2J_{CP}$ = 2, $^1J_{CW}$ = 189, WCO), 161.4 [s, C^1(*p*-tol)], 155.0 (s, $^1J_{CW}$ = 114, 38, C_α), 133.2 [s, C^4(*p*-tol)], 127.9 [s, br, $C^{2,3}$(*p*-tol)], 87.2, 83.8 (2s, Cp), 53.0 [d,

$^1J_{CP}$ = 31, C^1(Cy)], 43.7 [d, $^1J_{CP}$ = 20, C^1(Cy)], 39.4 (s, C_β), 34.6 [s, C^2(Cy)], 34.2 [s, 2C^2(Cy)], 33.8 [s, C^2(Cy)], 28.6, 28.3 [2d, $^3J_{CP}$ = 13, C^3(Cy)], 28.1, 28.0 [2d, $^3J_{CP}$ = 12, C^3(Cy)], 27.0 [s, 2C^4(Cy)], 20.9 (s, Me). ^{13}C{^{1}H} NMR (193 K): δ 250.5, 230.0 (2s, WCO), 160.3 [s, C^1(*p*-tol)], 155.1 (s, C_α), 133.5 [s, C^4(*p*-tol)], 133.2, 128.0, 127.7, 122.6 [4s, C^{2,3}(*p*-tol)], 87.2, 84.2 (2s, Cp), 53.2 [s, br, C^1(Cy)], 42.2 [d, $^1J_{CP}$ = 21, C^1(Cy)], 39.0 (s, C_β), 33.9 [s, C^2(Cy)], 33.8 [s, 2C^2(Cy)], 32.9, [s, C^2(Cy)], 28.3 [d, $^3J_{CP}$ = 12, C^3(Cy)], 28.1 [d, $^3J_{CP}$ = 11, 2C^3(Cy)], 28.0 [d, $^3J_{CP}$ = 12, C^3(Cy)], 26.7 [s, 2C^4(Cy)], 21.1 (s, Me).

Preparation of *trans*-[W$_2$Cp$_2${μ-κ:η^2-CHCH(*p*-tol)}(μ-PCy$_2$)(CO)$_2$] (*trans*-3a). A solution of compound **1** (0.040 g, 0.053 mmol) and HC$_2$(*p*-tol) (16 μL, 0.126 mmol) in toluene (5 mL) was heated at 363 K for 1 h to give an orange-brown solution containing compound ***trans*-3a** as major product, along with small amounts of [W$_2$Cp$_2${μ-κ:η^2-CHCH(*p*-tol)}(O)(μ-PCy$_2$)(CO)] (**4a**). The solvent was then removed under vacuum, the residue was extracted with dichloromethane/petroleum ether (1/4) and the extracts were chromatographed through alumina at 253 K. An orange-brown fraction was eluted using the same solvent mixture which gave, after removal of solvents, compound ***trans*-3a** as an air-sensitive orange-brown solid (0.039 g, 85%). Elution with neat dichloromethane gave an orange fraction yielding analogously compound **4a** as an orange solid (0.006 g, 14%). *Data for **trans-3a**:* Anal. Calcd for $C_{33}H_{41}O_2PW_2$: C, 45.65; H, 4.76. Found: C, 45.40 H, 4.55. ν(CO) (petroleum ether): 1884 (vs), 1831 (w), 1803 (s). ^{1}H NMR (300.09 MHz): δ 10.13 (dd, $^3J_{HH}$ = 10, $^3J_{HP}$ = 1, 1H, C_αH), 7.15, 7.03 (2d, $^3J_{HH}$ = 8, 2 x 2H, C_6H_4), 6.02 (d, $^3J_{HH}$ = 10, 1H, C_βH), 5.50, 5.04 (2s, 2 x 5H, Cp), 2.36 (s, 3H, Me), 2.50-1.00 (m, 22H, Cy). ^{13}C{^{1}H} NMR (75.47 MHz): δ 236.4 (d, $^2J_{CP}$ = 4, $^1J_{CW}$ = 218, WCO), 227.5 (d, $^2J_{CP}$ = 5, $^1J_{CW}$ = 188, WCO), 144.9 [s, C^1(*p*-tol)], 144.7 (s, $^1J_{CW}$ = 105, 21, C_α), 135.6 [s, C^4(*p*-tol)], 129.3, 127.0 [2s, C^{2,3}(*p*-tol)], 88.7, 88.4 (2s, Cp), 85.0 (s, C_β), 49.6 [d, $^1J_{CP}$ = 28, C^1(Cy)], 44.7 [d, $^1J_{CP}$ = 24, C^1(Cy)], 34.5, 34.2 [2d, $^2J_{CP}$ = 3, C^2(Cy)], 34.0, 32.3 [2s, C^2(Cy)], 28.5 [d, $^3J_{CP}$ = 13, C^3(Cy)], 28.2 [d, $^3J_{CP}$ = 13, 2C^3(Cy)], 28.1 [d, $^3J_{CP}$ = 10, C^3(Cy)], 26.6, 26.5 [2s, C^4(Cy)], 21.1 (s, Me). *Data for **4a***: Anal. Calcd for $C_{32}H_{41}O_2PW_2$: C, 44.89; H, 4.83. Found: C, 44.56; H, 4.50. IR (Nujol): 1807 [vs, ν(CO)], 913 [m, ν(WO)]. ^{1}H NMR (C_6D_6): δ 8.47 (d, $^3J_{HH}$ = 10, $^2J_{HW}$ = 6, 1H, C_αH), 7.31, 7.05 (2d, $^3J_{HH}$ = 8, 2 x 2H, C_6H_4), 5.23 (s, 5H, Cp), 4.67 (d, $^3J_{HP}$ = 1, 5H, Cp), 3.65 (d, $^3J_{HH}$ = 10, 1H, C_βH), 2.19 (s, 3H, Me), 2.80-1.00 (m, 22H, Cy). ^{13}C{^{1}H} NMR (C_6D_6): δ 230.3 (d, $^2J_{CP}$ = 5, WCO), 147.3 [s, C^1(*p*-tol)], 133.6 [s, C^4(*p*-tol)], 129.4, 125.9 [2s, C^{2,3}(*p*-tol)], 124.6 (s, C_α), 99.1, 87.1 (2s, Cp), 55.7 [d, $^1J_{CP}$ = 16, C^1(Cy)], 54.3 (s, C_β), 48.2 [d, $^1J_{CP}$ = 25, C^1(Cy)], 37.1 [d, $^2J_{CP}$ = 4, C^2(Cy)], 36.5 [s, C^2(Cy)], 34.8 [d, $^2J_{CP}$ = 5, C^2(Cy)], 34.7 [s, C^2(Cy)], 28.9 [d, $^3J_{CP}$ = 14, C^3(Cy)], 28.8, 28.5 [2d, $^3J_{CP}$ = 11, C^3(Cy)], 28.2 [d, $^3J_{CP}$ = 10, C^3(Cy)], 27.0, 26.8 [2s, C^4(Cy)], 21.1 (s, Me).

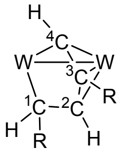
Preparation of [W$_2$Cp$_2${μ-κ:η^2-CHCH(*p*-tol)}(μ-PCy$_2$)(CO)$_3$] (5). A solution of compound ***trans*-3a** (0.020 g, 0.023 mmol) in toluene (4 mL) was stirred under an atmosphere of CO (1 atm) for 2 h to give an orange solution. Solvent was then removed under vacuum, the residue was extracted with dichloromethane/petroleum ether (1/1) and the extracts were chromatographed through alumina at 253 K. An orange fraction was eluted using the same solvent mixture, which gave, upon removal of solvents, compound **5** as an orange solid (0.016 g, 80%). Anal. Calcd for $C_{34}H_{41}O_3PW_2$: C, 45.56; H, 4.61. Found: C, 45.22; H, 4.52. ^{1}H NMR (300.09 MHz): δ 8.30 (dd, $^3J_{HH}$ = 8, $^3J_{HP}$ = 5, 1H, C$_\alpha$H), 7.00 (m, 4H, C_6H_4), 5.33, 5.20 (2s, 2 x 5H, Cp), 2.33 (dd, $^3J_{HH}$ = 8, $^3J_{HP}$ = 1, 1H, C$_\beta$H), 2.27 (s, 3H, Me), 2.80-1.00 (m, 22H, Cy). ^{13}C{^{1}H} NMR (75.47 MHz): δ 232.2 (d, $^2J_{CP}$ = 21, WCO), 231.3 (d, $^2J_{CP}$ = 13, WCO), 227.4 (s, WCO), 147.5 [s, C^1(*p*-tol)], 134.7 [s, C^4(*p*-tol)], 128.8, 124.9 [2s, C^{2,3}(*p*-tol)], 113.6 (d, $^2J_{CP}$ = 5, $^1J_{CW}$ = 44, C$_\alpha$), 92.0, 91.1 (2s, Cp), 61.0 [d, $^1J_{CP}$ = 20, C^1(Cy)], 59.8 (s, C$_\beta$), 43.3 [d, $^1J_{CP}$ = 23, C^1(Cy)], 37.3 [s, C^2(Cy)], 34.5 [d, $^2J_{CP}$ = 3, C^2(Cy)], 32.8 [s, C^2(Cy)], 29.4 [s, C^2(Cy)], 29.3 [d, $^3J_{CP}$ = 11, C^3(Cy)], 28.8 [d, $^3J_{CP}$ = 9, C^3(Cy)], 28.5 [d, $^3J_{CP}$ = 12, C^3(Cy)], 27.6 [d, $^3J_{CP}$ = 14, C^3(Cy)], 27.0, 26.7 [2s, C^4(Cy)], 21.0 (s, Me).

Preparation of [W$_2$Cp$_2${μ-κ:η^2-CHCH(*p*-tol)}(μ-PCy$_2$){η^2-CHC(*p*-tol)}(CO)] (6). A solution of compound **1** (0.030 g, 0.039 mmol) and HC$_2$(*p*-tol) (250 μL, 1.971 mmol) in toluene (5 mL) was refluxed for 2.5 h to give a maroon solution. Solvent was then removed under vacuum, the residue was extracted with dichloromethane/petroleum ether (1/3) and the extracts were chromatographed through alumina at 253 K. Elution with the same solvent mixture gave a violet fraction yielding, after removal of solvents, compound **6** as a violet solid (0.029 g, 78%). Anal. Calcd for $C_{41}H_{49}OPW_2$: C, 51.48; H, 5.16. Found: C, 51.05; H, 4.92. ^{1}H NMR (C_6D_6): δ 10.13 (d, $^3J_{HP}$ = 10, 1H, CH), 8.34 (d, $^3J_{HH}$ = 8, 2H, C_6H_4), 7.65 (d, $^3J_{HH}$ = 10, 1H, μ-CH), 7.37, 7.23, 7.05 (3d, $^3J_{HH}$ = 8, 3 x 2H, C_6H_4), 4.66, 4.28 (2s, 2 x 5H, Cp), 4.32 [d, $^3J_{HH}$ = 10, 1H, CH(*p*-tol)], 3.30-1.10 (m, 22H, Cy), 2.18, 2.15 (2s, 2 x 3H, Me). ^{13}C{^{1}H} NMR (C_6D_6, 75.50 MHz): δ 235.8 (d, $^2J_{CP}$ = 6, WCO), 188.4 [s, $^1J_{CW}$ = 35, C(*p*-tol)], 170.0 (d, $^2J_{CP}$ = 12, $^1J_{CW}$ = 44, CH), 148.8 [s, C^1(*p*-tol)], 139.3 [s, C^4(*p*-tol)], 134.0 [s, C^1(*p*-tol)], 133.3 [s, C^2(*p*-tol)], 133.2 [s, C^4(*p*-tol)], 131.8 (s, $^1J_{CW}$ = 98, 41, μ-CH), 130.4, 129.3, 125.8 [3s, C^{2,3}(*p*-tol)], 90.9, 86.5 (2s, Cp), 56.2 [s, CH(*p*-tol)], 53.4, 50.1 [2d, $^1J_{CP}$ = 20, C^1(Cy)], 38.0 [d, $^2J_{CP}$ = 8, C^2(Cy)], 37.9 [s, C^2(Cy)], 36.5 [d, $^2J_{CP}$ = 5, C^2(Cy)], 34.9 [d, $^2J_{CP}$ = 3, C^2(Cy)], 29.8, 29.1 [2d, $^3J_{CP}$ = 11, C^3(Cy)], 29.0 [d, $^3J_{CP}$ = 12, C^3(Cy)], 28.8 [d, $^3J_{CP}$ = 10, C^3(Cy)], 27.5, 27.4 [2s, C^4(Cy)], 21.6, 21.1 (2s, Me).

Preparation of *trans*-[W$_2$Cp$_2${μ-κ:η^2-CHCH(^{t}Bu)}(μ-PCy$_2$)(CO)$_2$] (*trans*-3b). A solution of compound **1** (0.020 g, 0.027 mmol) and HC$_2$(^{t}Bu) (100 μL, 0.812 mmol) in toluene (4 mL) was stirred in a Schlenk flask equipped with a Young's valve for 24 h at 313 K to give a brown-greenish solution containing compound ***trans*-3b** as the essentially unique product. Unfortunately, all attempts to isolate pure samples of this compound from these solutions led to its progressive transformation into [W_2Cp_2\{μ-κ:η^2-CHCH(^{t}Bu)\}(O)(μ-PCy_2)(CO)] (**4b**). The latter could be isolated in variable amounts after chromatographic workup as described for **4a**. *Data for **trans-3b**:* ^{1}H NMR (C_6D_6): δ 9.43 (dd, $^3J_{HH}$ = 12, $^3J_{HP}$ = 1, 1H, C_αH), 6.28 (d, $^3J_{HH}$ = 12, 1H, C_βH), 5.18 (s, br, 10H, Cp), 1.31 (s, 9H, ^{t}Bu), 2.50-0.50 (m, 22H, Cy). ^{13}C\{^{1}H\} NMR (C_6D_6): δ 239.2, 234.2 (2s, WCO), 135.8 (s, C_α), 87.8, 85.6 (2s, Cp), 83.0 (s, C_β), 51.3 [d, $^1J_{CP}$ = 31, C^1(Cy)], 43.7 [d, $^1J_{CP}$ = 34, C^1(Cy)], 39.5 [s, C^1(^{t}Bu)], 34.8, 34.3, 33.7, 32.1 [4s, C^2(Cy)], 31.8 [s, C^2(^{t}Bu)], 28.4 [m, 4C^3(Cy)], 26.6, 26.4 [2s, C^4(Cy)]. *Data for **4b***: Anal. Calcd for $C_{29}H_{43}O_2PW_2$: C, 42.36; H, 5.27. Found: C, 41.97; H, 4.90. IR (Nujol): 1824 [vs, ν(CO)], 924 [m, ν(WO)]. ^{1}H NMR (C_6D_6, 300.09 MHz): δ 7.85 (d, $^3J_{HH}$ = 10, 1H, C_αH), 5.21 (s, 5H, Cp), 4.95 (d, $^3J_{HP}$ = 1, 5H, Cp), 2.83 (m, 2H, Cy), 2.54 (m, 1H, Cy), 2.30 (m, 1H, Cy), 2.22 (d, $^3J_{HH}$ = 10, 1H, C_βH), 2.00-1.40 (m, 18H, Cy), 1.27 (s, 9H, ^{t}Bu).

Preparation of *cis*-[W_2Cp_2\{μ-κ:η^2-C(CO_2Me)CH_2\}(μ-PCy_2)$(CO)_2$] (*cis*-2c). A solution of compound **1** (0.020 g, 0.027 mmol) and $HC_2(CO_2Me)$ (15 μL, 0.167 mmol) in toluene (4 mL) was stirred at room temperature for 4 h to give a brown yellowish solution. Solvent was then removed under vacuum, the residue was extracted with dichloromethane/petroleum ether (1/1), and the extracts were chromatographed through alumina. Elution with the same solvent mixture gave a yellow-greenish fraction yielding, upon removal of solvents, compound ***cis*-2c** as a brown solid (0.014 g, 64%). Anal. Calcd for $C_{28}H_{37}O_4PW_2$: C, 40.21; H, 4.46. Found: C, 39.80; H, 4.40. ν(CO) (petroleum ether): 1940 (vs), 1863 (m), 1678 (w). ^{1}H NMR (C_6D_6, 300.09 MHz): δ 5.77 (dd, $^2J_{HH}$ = 3, $^3J_{HP}$ = 1, $^2J_{HW}$ = 16, 1H, CH_2), 5.27 (s, 5H, Cp), 4.37 (d, $^3J_{HP}$ = 0.6, 5H, Cp), 4.33 (s, br, 1H, CH_2), 3.13 (s, 3H, OMe), 2.40-0.20 (m, 22H, Cy). ^{13}C\{^{1}H\} NMR (C_6D_6, 75.47 MHz): δ 246.7 (d, $^2J_{CP}$ = 3, WCO), 225.9 (d, $^2J_{CP}$ = 2, WCO), 183.0 (s, *C*O_2Me), 132.8 (s, C_α), 87.3, 84.4 (2s, Cp), 51.5 [d, $^1J_{CP}$ = 31, C^1(Cy)], 49.9 (s, OMe), 43.4 [d, $^1J_{CP}$ = 31, C^1(Cy)], 37.0, 34.5, 33.6, 33.3 [4s, C^2(Cy)], 33.3 (s, C_β), 28.4, 28.3 [2d, $^3J_{CP}$ = 13, C^3(Cy)], 28.2 [d, $^3J_{CP}$ = 10, C^3(Cy)], 27.8 [d, $^3J_{CP}$ = 13, C^3(Cy)], 27.0, 26.9 [2s, C^4(Cy)].

Preparation of [W_2Cp_2\{μ-κ^2:η^3-CH(CO_2Me)CHC(CO_2Me)CH\}(μ-PCy_2)$(CO)_2$] (7). A solution of compound **1** (0.040 g, 0.054 mmol) and $HC_2(CO_2Me)$ (500 μL, 5.620 mmol) in toluene (5 mL) was refluxed for 2 h to give an orange solution. Solvent was then removed under vacuum, the residue was extracted with dichloromethane, and the extracts were chromatographed through alumina. Elution with the same solvent gave an orange fraction yielding, upon removal of solvent, compound **7** as an orange solid (0.018 g, 35%). The crystals used in the X-ray study were grown by the slow diffusion of a layer of petroleum ether into a concentrated dichloromethane solution of the complex at room temperature. Anal. Calcd for $C_{32}H_{41}O_6PW_2$: C, 41.76; H, 4.49. Found: C, 41.32; H, 4.42. ^{1}H NMR (C_6D_6): δ 6.45 (dd, $^3J_{HP}$ = 14, $^4J_{HH}$ = 4, 1H, H^4), 5.20 (d, $^3J_{HP}$ = 1, 5H, Cp), 5.02 (ddd, $^4J_{HH}$ = 4, $^3J_{HP}$ = 2, $^3J_{HH}$ = 1, 1H, H^2), 4.78 (d, $^3J_{HP}$ = 1, 5H, Cp), 4.76 (dd, $^3J_{HP}$ = 3, $^3J_{HH}$ = 1, 1H, H^1), 3.66, 3.57 (2s, 2 x 3H, OMe), 2.30-0.90 (m, 22H, Cy). $^{13}C\{^1H\}$ NMR (C_6D_6, 75.47 MHz): δ 240.3, 215.2 (2d, $^2J_{CP}$ = 6, WCO), 184.9, 172.8 (2s, *C*O$_2$Me), 104.0 (d, $^2J_{CP}$ = 21, C^4), 89.6, 86.2 (2s, Cp), 79.1 (d, $^2J_{CP}$ = 7, C^3), 77.1 (s, C^2), 51.1, 49.9 (2s, OMe), 49.5 [d, $^1J_{CP}$ = 18, C^1(Cy)], 44.6 [d, $^1J_{CP}$ = 7, C^1(Cy)], 36.9 [d, $^2J_{CP}$ = 2, C^2(Cy)], 35.6 [d, $^2J_{CP}$ = 6, C^2(Cy)], 35.5 [s, 2C^2(Cy)], 29.1 [d, $^3J_{CP}$ = 12, C^3(Cy)], 28.8 [d, $^3J_{CP}$ = 10, C^3(Cy)], 28.4 [d, $^3J_{CP}$ = 10, 2C^3(Cy)], 26.9, 26.6 [2s, C^4(Cy)], 21.4 (s, $^1J_{CW}$ = 43, C^1). Numbering scheme of the hydrocarbyl ligand according to the figure shown below.



Preparation of *trans*-[$W_2Cp_2\{\mu\text{-}\kappa_C,\kappa_O:\eta^2\text{-}C(CO_2Me)CH(CO_2Me)\}(\mu\text{-}PCy_2)(CO)_2$] (8). A solution of compound **1** (0.020 g, 0.027 mmol) and DMAD (16 μL, 0.130 mmol) in toluene (4 mL) was heated at 243 K for 15 min to give an orange solution. Solvent was then removed under vacuum, the residue was extracted with dichloromethane/petroleum ether (3/1), and the extracts were chromatographed through alumina. Elution with the same solvent mixture gave an orange fraction yielding, upon removal of solvents, compound **8** as an orange solid (0.021 g, 89%). The crystals used in the X-ray study were grown by the slow diffusion of a layer of petroleum ether into a concentrated toluene solution of the complex at room temperature. Anal. Calcd for $C_{30}H_{39}O_6PW_2$: C, 40.29; H, 4.40. Found: C, 40.36; H, 4.48. ^{1}H NMR (C_6D_6): δ 5.22 (d, $^3J_{HP}$ = 1, 5H, Cp), 4.83 (s, 5H, Cp), 4.57 (s, $^2J_{HW}$ = 5, 1H, CH), 3.76, 2.96 (2s, 2 x 3H, OMe), 2.80-1.00 (m, 22H, Cy). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 255.7 (d, $^2J_{CP}$ = 5, $^1J_{CW}$ = 156, WCO), 232.9 (d, $^2J_{CP}$ = 6, $^1J_{CW}$ = 186, WCO), 198.1 (s, *C*O$_2$Me), 184.4 (d, $^3J_{CP}$ = 2, *C*O$_2$Me), 122.2 (d, $^2J_{CP}$ = 16, C_α), 89.2, 87.6 (2s, Cp), 53.1 (s, OMe), 52.5 [d, $^1J_{CP}$ = 19, C^1(Cy)], 50.9 (s, OMe), 47.1 [d, $^1J_{CP}$ = 9, C^1(Cy)], 37.5 [d, $^2J_{CP}$ = 5, C^2(Cy)], 35.7 [d, $^2J_{CP}$ = 3, C^2(Cy)], 35.2 [d, $^2J_{CP}$ = 4, C^2(Cy)], 34.8 [d, $^2J_{CP}$ = 5, C^2(Cy)], 30.1 (s, C_β), 29.6 [d, $^3J_{CP}$ = 11, C^3(Cy)], 29.0, 28.6 [2d, $^3J_{CP}$ = 10, C^3(Cy)], 28.3 [d, $^3J_{CP}$ = 11, C^3(Cy)], 27.4, 26.8 [2s, C^4(Cy)].

Reaction of 1 with DMAD at 273 K. Neat DMAD (20 μL, 0.160 mmol) was added to a solution of compound **1** (0.040 g, 0.053 mmol) in toluene (4 mL) at 273 K, and the mixture was stirred at that temperature for 3 h to give a green solution. The solvent was then removed under vacuum, the residue was extracted with dichloromethane and the extract was chromatographed through an alumina column at 253 K. Elution with the same solvent gave two green fractions yielding respectively, after removal of solvent, compounds *cis*-[W$_2$Cp$_2${μ-κ:η^2-C(CO$_2$Me)=CH(CO$_2$Me)}(μ-PCy$_2$)(CO)$_2$] (***cis*-2d**), (0.025 g, 53%), and [W$_2$Cp$_2${μ-κ_C,κ_O:η^2-C(CO$_2$Me)=C(CO$_2$Me)C(CO$_2$Me)=CH(CO$_2$Me)}(μ-PCy$_2$)(CO)$_2$] (**9**) (0.021 g, 38%), both as green powders. *Data for compound* ***cis-2d****:* Anal. Calcd for $C_{30}H_{39}O_6PW_2$: C, 40.29; H, 4.40; Found: C, 40.03; H, 4.22. ^{1}H NMR (C_6D_6): δ 5.22 (s, 1H, CH), 5.16 (s, 5H, Cp), 4.77 (d, $^3J_{HP}$ = 1, 5H, Cp), 3.60, 3.59 (2s, OMe), 2.33-2.80 (m, 22H, Cy). ^{13}C{^{1}H} NMR (C_6D_6): δ 244.4, 222.6 (2s, WCO), 184.6, 176.8 (2s, *C*O$_2$Me), 154.1 (s, C$_\alpha$), 88.2, 87.0 (2s, Cp), 51.8 [d, $^1J_{CP}$ = 31, C^1(Cy)], 51.4, 50.8 (2s, OMe), 44.1 [d, $^1J_{CP}$ = 19, C^1(Cy)], 35.0, 34.3, 33.5, 33.3 [4s, C^2(Cy)], 33.5 (s, C$_\beta$H), 28.4 [d, $^3J_{CP}$ = 12, C^3(Cy)], 28.3 [d, $^3J_{CP}$ = 9, C^3(Cy)], 28.1, 27.8 [2d, $^3J_{CP}$ = 13, C^3(Cy)], 26.9, 26.8 [2s, C^4(Cy)]. *Data for compound* ***9****:* Anal. Calcd for $C_{36}H_{45}O_{10}PW_2$: C, 41.72; H, 4.38. Found: C, 41.49; H, 4.25. ^{1}H NMR (300.13 MHz): δ 5.61, 5.24 (2s, 2 x 5H, Cp), 3.79, 3.65, 3.56, 3.55 (4s, 4 x 3H, OMe), 3.11 (s, $^2J_{HW}$ = 5, 1H, CH), 2.80-0.50 (m, 22H, Cy). ^{13}C{^{1}H} NMR: δ 234.2 (d, $^2J_{CP}$ = 3, WCO), 233.3 (s, WCO), 232.8 (s, W–*C*=C), 186.6, 185.8, 178.5, 176.4 (4s, CO$_2$Me), 163.8 (s, W–C=*C*), 131.6 (s, *C*=CHCO$_2$Me), 98.6, 91.8 (2s, Cp), 55.5 (s, OMe), 55.0 [d, $^1J_{CP}$ = 23, C^1(Cy)], 51.8, 51.2, 50.5 (3s, OMe), 46.2 [d, $^1J_{CP}$ = 16, C^1(Cy)], 36.0 [s, C^2(Cy)], 34.0, 33.5 [2d, $^2J_{CP}$ = 3, C^2(Cy)], 32.3 [d, $^2J_{CP}$ = 5, C^2(Cy)], 29.5 [d, $^3J_{CP}$ = 13, C^3(Cy)], 28.8 [d, $^3J_{CP}$ = 9, C^3(Cy)], 28.6 [d, $^3J_{CP}$ = 12, C^3(Cy)], 28.4 [d, $^3J_{CP}$ = 11, C^3(Cy)], 27.0, 26.8 [2s, C^4(Cy)], 23.3 (s, $^1J_{CW}$ = 28, C=*C*HCO$_2$Me).

X-Ray Crystal Structure Determination of Compound *cis*-2a. X-ray intensity data were collected on a Smart-CCD-1000 Bruker diffractometer using graphite-monochromated Mo K$_\alpha$ radiation at 110 K. Cell dimensions and orientation matrixes were initially determined from least-squares refinements on reflections measured in 3 sets of 30 exposures collected in 3 different ω regions and eventually refined against all reflections. Twinning was found to occur in the crystal. The experimental data were treated as two domain twinned data, the second domain being rotated from first domain by 1.1 degrees about reciprocal axis 1.000, 0.824, –0.999 and real axis 1.000, 0.177, –0.342. The program Cell Now[41] was used to determine the twin law, the cell dimensions and orientation matrixes, and a multi-scan absorption correction was applied with TWINABS.[42] Using the program suite WINGX,[43] the structure was solved by direct methods using SIR92,[44] and refined with full-matrix least squares on F^2 using SHELXL2014.[45]All the positional parameters and the anisotropic temperature factors for all non-H atoms were refined anisotropically, and all hydrogen atoms were geometrically placed and refined using a riding model. After convergence the strongest residual peaks (3.35-2.32 eÅ^{-3}) were placed around the tungsten atoms (Table 5).

X-Ray Crystal Structure Determination of Compounds 7 and 8. X-ray intensity data for these compounds were collected on a Kappa-Appex-II Bruker diffractometer using graphite-monochromated MoK$_{\alpha}$ radiation at 100 K. The software APEX[46] was used for collecting frames with ω/ϕ scans measurement method. The SAINT software was used for data reduction,[47] and a multi-scan absorption correction was applied with SADABS.[48] The structures were solved and refined as described for **2a**. The asymmetric unit in compound **7** contains two independent molecules of the complex and one water molecule. Due to poor quality of the diffraction data (twinning was present in the crystal, but the twin law could not be determined) not all the positional parameters and anisotropic temperature factors could be freely refined for non-H atoms. Some atoms were refined anisotropically in combination with the instructions DELU and SIMU, and a significant number of atoms had to be refined isotropically to prevent their temperature factors from becoming non-positive definite. In addition, a disorder on C(10B) could not be conveniently modelled and was left unsolved. Moreover, the H atoms of the water molecule could not be found in the Fourier map and other residual electronic density was present around its O atom; therefore, the SQUEEZE procedure,[49] as implemented in PLATON,[50] was used. Upon squeeze application and convergence, the strongest residual peaks (5.5-5.0 eÅ^{-3}) were placed ca. 0.9 Å away from the tungsten atoms. Diffraction data for compound **8** were of poor quality too (twinning was also present in the crystal, with the second component being present in small proportion). After full convergence the strongest residual peaks (7.8 and 5.7 eÅ^{-3}) were placed ca. 1.0 Å away from the tungsten atoms.

Acknowledgment. We thank the DGI of Spain for financial support (Project CTQ2012-33187) and a grant (to M. F. V.). We also thank the X-Ray unit of the Universidad de Santiago de Compostela, Spain, for collection of diffraction data.

Table 5. Crystal Data for New Compounds

	***cis*-2a**	**7**	**8**
mol formula	$C_{33}H_{41}O_2PW_2$	$C_{32}H_{41}O_6PW_2$	$C_{30}H_{39}O_6PW_2$
mol wt	868.33	920.30	894.28
cryst syst	Monoclinic	Triclinic	Monoclinic
space group	$P2_1/c$	$P-1$	$P2_1/c$
radiation (λ, Å)	0.71073	0.71073	0.71073
a, Å	9.378(2)	11.744(5)	10.6093(13)
b, Å	21.148(6)	15.106(5)	15.7243(16)
c, Å	14.800(4)	19.242(5)	19.131(2)
α, deg	90	103.203(5)	90
β, deg	98.333(4)	105.118(5)	115.682(7)
γ, deg	90	93.143(5)	90
V, Å^3	2904.2(13)	3184.5(19)	2876.3(6)
Z	4	4	4
calcd density, g cm^{-3}	1.986	1.92	2.065
absorp coeff, mm^{-1}	7.999	7.31	8.09
temperature, K	110(2)	100.0(1)	100.0(1)
θ range (deg)	1.691 to 26.496	1.133 to 26.372	1.753 to 26.016
index ranges (h, k, l)	$-11 \leq h \leq 11$, $-26 \leq k \leq 26$, $0 \leq l \leq 18$	$-14 \leq h \leq 14$, $-18 \leq k \leq 18$, $0 \leq l \leq 24$	$-13 \leq h \leq 12$, $-19 \leq k \leq 0$, $-23 \leq l \leq 12$
no. of reflns collected	32760	75626	41104
no. of indep reflns (R_{int})	11748 (0.1673)	13010 (0.0730)	5658 (0.1345)
reflns with $I > 2\sigma(I)$	6967	10356	3887
R indexes [data with $I > 2\sigma(I)$]^a	$R_1 = 0.0909$ $wR_2 = 0.2246^b$	$R_1 = 0.0625$ $wR_2 = 0.1648^c$	$R_1 = 0.0598$ $wR_2 = 0.125^d$
R indexes (all data)^a	$R_1 = 0.1423$ $wR_2 = 0.2633^b$	$R_1 = 0.0794$ $wR_2 = 0.1759^c$	$R_1 = 0.0987$ $wR_2 = 0.1424^d$
GOF	1.009	1.074	1.045
no. of restraints/params.	384/345	7/633	0/354
$\Delta\rho$(max., min.), eÅ^{-3}	3.349, –3.885	5.527, –5.484	7.826, –2.758

[a] $R = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$. $wR = [\Sigma w(|F_o|^2 - |F_c|^2)^2 / \Sigma w|F_o|^2]^{1/2}$. $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$. [b] a = 0.1474, b = 0. [c] a = 0.1229, b = 0. [d] a = 0.0486, b = 51.4201.

Notes and References

Departamento de Química Orgánica e Inorgánica / IUQOEM, Universidad de Oviedo, E-33071 Oviedo, Spain. E-mail: garciavdaniel@uniovi.es (D.G.-V.), mara@uniovi.es (M.A.R.)

†Electronic supplementary information (ESI) available: a CIF file with full crystallographic data for compounds ***cis*-2a**, **7** and **8** (CCDC 1430471 to 1430473). See DOI: 10.1039/b000000x/

(1) (a) M. A. Alvarez, M. E. García, D. García-Vivó, M. A. Ruiz and M. F. Vega, *Organometallics,* 2010, **29**, 512. (b) M. A. Alvarez, M. E. García, D. García-Vivó, M. A. Ruiz and M. F. Vega, *Dalton Trans.,* 2014, **43**, 16044.

(2) In this paper we have adopted a “half-electron” counting convention for complexes having bridging hydrides or alkyls (when only bound through a single

C atom), so these ligands (X) are considered as one-electron donors. Then, complexes of formulae $[M_2Cp_2(\mu\text{-}X)(\mu\text{-}PCy_2)(CO)_2]$ (M = Mo, W) are regarded as having M≡M bonds. These "triple" bonds actually follow from the superimposition of two bicentric (M_2) bonding interactions and a tricentric one (M_2X). Yet, the electron density at the intermetallic bond critical points, structural features, and chemical behaviour of these unsaturated complexes are comparable to those of 30-electron complexes having more conventional M≡M bonds such as the dimers $[M_2Cp_2(CO)_4]$. Other authors, however, recommend the adoption for these systems of a "half-arrow" convention (see J. C. Green, M. L. H. Green and G. Parkin, *Chem. Commun.*, 2012, **48**, 11481 and references therein). Under such convention, the corresponding M–M bond orders appearing in this paper should be reduced in one unit per bridging ligand X present in a molecule. In particular, the "half-arrow" convention implies that the 30-electron hydride complexes $[M_2Cp_2(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_2]$ must be assimilated to the 32-electron complexes $[M_2Cp_2(\mu\text{-}Y)(\mu\text{-}PCy_2)(CO)_2]$ (Y = Cl, PRR′, O_2CR) and hence considered to have a double M═M bond, a relationship which we consider of little use to interpret the strong differences separating the structure, spectroscopic properties, and reactivity of these molecules.

(3) H. Suzuki, *Eur. J. Inorg. Chem.,* 2002, 1009, and references therein.

(4) G. Süss-Fink and B. Therrien, *Organometallics,* 2007, **26**, 766.

(5) D. García-Vivó, A. Ramos and M. A. Ruiz, *Coord. Chem. Rev.,* 2013, **257**, 2143.

(6) M. A. Alvarez, M. E. García, D. García-Vivó, E. Huergo, M. A. Ruiz and M. F. Vega, *Organometallics,* 2015, **34**, 3833.

(7) M. A. Alvarez, M. E. García, A. Ramos and M. A. Ruiz, *Organometallics,* 2007, **26**, 1461.

(8) M. A. Alvarez, M. E. García, M. A. Ruiz, A. Toyos and M. F. Vega, *Inorg. Chem.,* 2013, **52**, 7068.

(9) C. M. Alvarez, M. A. Alvarez, M. E. García, A. Ramos, M. A. Ruiz, C. Graiff and A. Tiripicchio, *Organometallics,* 2007, **26**, 321.

(10) M. A. Alvarez, M. E. García, D. García-Vivó, M. A. Ruiz and M. F. Vega, *Organometallics,* 2013, **32**, 4543.

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

(12) M. A. Alvarez, M. E. García, A. Ramos, M. A. Ruiz, M. Lanfranchi and A. Tiripicchio, *Organometallics,* 2007, **26**, 5454.

(13) (a) A. J. Deeming, *Adv. Organomet. Chem.,* 1986, **26**, 1. (b) K. Burgess, *Polyhedron,* 1984, **3**, 1175. (c) A. K. Smith, *Comprehensive Organometallic*

Chemistry, 2nd ed., E. W. Abel, F. G. A. Stone and G. Wilkinson (Eds), Pergamon, Oxford, U. K., 1995, vol. 7, Chapter 13.

(14) (a) Y. Takahashi, N. Murakami, K. Fujita and R. Yamaguchi, *Dalton Trans.,* 2009, 2029. (b) T. Shima, T. Ichikawa and H. Suzuki, *Organometallics,* 2007, **26**, 6329. (c) Y. Gao, M. C. Jennings and R. J. Puddephatt, *Dalton Trans.,* 2003, 261. (d) F. J. García-Alonso, V. Riera, M. A. Ruiz, A. Tiripicchio and M. Tiripicchio-Camellini, *Organometallics,* 1992, **11**, 370.

(15) A. J. Deeming, S. Hasso and M. Underhill, *J. Chem. Soc., Dalton Trans.,* 1975, 1614.

(16) (a) R. Yañez, J. Ros and R. Mathieu, *J. Organomet. Chem.,* 1990, **389**, 197. (b) J. Ros, X. Solans, M. Font-Altaba and R. Mathieu, *Organometallics,* 1984, **3**, 1014.

(17) M. A. Alvarez, M. E. García, A. Ramos and M. A. Ruiz, *J. Organomet. Chem.,* 2009, **694**, 3864.

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

(19) J. R. Shapley, S. I. Richter, M. Tachikawa and J. B. Keister, *J. Organomet. Chem.,* 1975, **94**, C43.

(20) C. J. Jameson, *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*, J. G., Verkade and L. D., Quin (Eds), VCH, Deerfield Beach, FL, 1987, Chapter 6.

(21) H. Adams, A. Biebricher, S. R. Gay, T. Hamilton, P. E. McHugh, M. J. Morris and M. J. Mays, *J. Chem. Soc., Dalton Trans.,* 2000, 2983.

(22) G. R. Doel, N. D. Feasey, S. A. R. Knox, A. G. Orpen and J. Webster, *J. Chem. Soc., Chem. Commun.,* 1986, 542.

(23) P. Schollhammer, F. Y. Pétillon, S. Poder-Guillou, J. Talarmin, K. W. Muir and D. S. Yufit, *J. Organomet. Chem.,* 1996, **513**, 181.

(24) M. E. García, V. Riera, M. A. Ruiz, M. T. Rueda and D. Sáez, *Organometallics,* 2002, **21**, 5515.

(25) M. A. Alvarez, M. E. García, D. García-Vivó, S. Menéndez and M. A. Ruiz, *Organometallics,* 2013, **32**, 218.

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

(27) M. E. García, V. Riera, M. T. Rueda and M. A. Ruiz, *J. Am. Chem. Soc.,* 1999, **121**, 1960.

(28) V. Riera, M. A. Ruiz, F. Villafañe, C. Bois and Y. Jeannin, *J. Organomet. Chem.,* 1989, **375**, C23.

(29) V. Riera, M. A. Ruiz, F. Villafañe, C. Bois and Y. Jeannin, *Organometallics,* 1993, **12**, 124.

(30) G. Conole, K. Henrick, M. McPartlin, A. D. Horton and M. J. Mays, *New J. Chem.,* 1988, **12**, 559.

(31) D. J. Wink and N. J. Cooper, *Organometallics,* 1991, **10**, 494.

(32) F. R. Kreissl, W. J. Sieber, P. Hofmann, J. Riede and M. Wolfgruber, *Organometallics,* 1985, **4**, 788.

(33) L. M. Atagi, S. C. Critchlow and J. M. Mayer, *J. Am. Chem. Soc.,* 1992, **114**, 1483, and references therein.

(34) M. A. Alvarez, M. E. García, D. García-Vivó, M. A. Ruiz and M. F. Vega, *Organometallics,* 2015, **34**, 870.

(35) J. H. Freudenberg and R. R. Schrock, *Organometallics,* 1986, **5**, 398.

(36) S. M. Homes, D. F. Schafer, P. T. Wolczanski and E. B. Lobkovsky, *J. Am. Chem. Soc.,* 2001, **123**, 10571.

(37) M. K. Anwar, G. Hogarth, O. S. Senturk, W. Clegg, S. Doherty and M. R. J. Elsegood, *J. Chem. Soc., Dalton Trans.,* 2001, 341.

(38) M. Akita, R. Hua, S. A. R. Knox, Y. Moro-oka, S. Nakanishi, M. I. Yates, *J. Organomet. Chem.,* 1998, **569**, 71.

(39) (a) P. Schollhammer, N. Cabon, J. F. Capon, F. Y. Pétillon and J. Talarmin, *Organometallics,* 2001, **20**, 1230. (b) J. F. Capon, P. Schollhammer, F. Y. Pétillon and J. Talarmin, *Organometallics,* 1999, **18**, 2055.

(40) W. L. F. Armarego and C. L. L. Chai, *Purification of Laboratory Chemicals, 5th ed.*, Butterworth-Heinemann, Oxford, UK, 2003.

(41) G. M. Sheldrick, *Cell Now*, University of Göttingen, Göttingen, Germany, 2008.

(42) G. M. Sheldrick, *TWINABS*, University of Göttingen, Göttingen, Germany, 2007.

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

(44) A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori and M. Camalli, *J. Appl. Crystallogr.,* 1994, **27**, 435.

(45) G. M. Sheldrick, *Acta Crystallogr.,* 2008, **A64**, 112.

(46) *APEX 2, version 2.0-1*, Bruker AXS Inc, Madison, WI, 2005.

(47) *SMART & SAINT Software Reference Manuals, Version 5.051*, Bruker Analytical X-ray Instruments, Madison WI, 1998.

(48) G. M. Sheldrick, *SADABS, Program for Empirical Absorption Correction*, University of Göttingen, Göttingen, Germany, 1996.

(49) P. Van der Sluis and A. L. Spek, *Acta Crystallogr.,* 1990, **A46**, 194.

(50) A. L. Spek, *PLATON, A Multipurpose Crystallographic Tool*, Utrecht University, Utrecht, The Netherlands, 2010.

For Table of Contents Use Only

Insertion and C–C Coupling Processes in Reactions of the Unsaturated Hydride $[W_2Cp_2(H)(\mu\text{-}PCy_2)(CO)_2]$ with Alkynes.†

M. Angeles Alvarez, M. Esther García, Daniel García-Vivó,* Miguel A. Ruiz* and M. Fernanda Vega

Text for Table of Contents

Alkyne insertion into the W–H bond invariably occurs in the title reactions, to give alkenyl complexes which may undergo further alkyne addition to yield hydrocarbyl-bridged derivatives following from alkenyl-alkyne coupling.

Graphic for Table of Contents