

ARTICLE

Hydride, Gold(I) and Related Derivatives of the Unsaturated Ditungsten Anion $[\text{W}_2\text{Cp}_2(\mu\text{-PCy}_2)(\mu\text{-CO})_2]^{-\dagger}$

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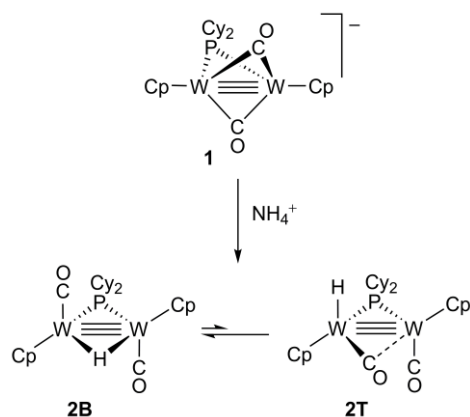
Protonation of the title anion with $[\text{NH}_4]\text{PF}_6$ gave $[\text{W}_2\text{Cp}_2(\text{H})(\mu\text{-PCy}_2)(\text{CO})_2]$ (**2**), which in solution exists as an equilibrium mixture of two isomers having either bridging (major) or terminal (minor) hydrides. Both molecules retain short intermetallic distances (*ca.* 2.54 Å), with the H-bridged isomer being almost 15 kJ/mol more stable than the terminal one, according to density functional theory calculations. Further protonation with acids having weakly coordinating anions (BF_4^- or BAR'_4^- ; $\text{Ar}' = 3,5\text{-C}_6\text{H}_3(\text{CF}_3)_2$), yielded isomeric cations also displaying bridging and terminal hydride ligands ($[\text{W}_2\text{Cp}_2(\mu\text{-H})(\text{H})(\mu\text{-PCy}_2)(\text{CO})_2]^+$ and $[\text{W}_2\text{Cp}_2(\text{H})_2(\mu\text{-PCy}_2)(\text{CO})_2]^+$), with the latter being only slightly more energetic (by *ca.* 4 kJ/mol). In contrast, protonation of **2** with carboxylic acids yielded carboxylate-bridged derivatives $[\text{W}_2\text{Cp}_2(\mu\text{-PCy}_2)(\mu\text{-O}:O'\text{-O}_2\text{CR})(\text{CO})_2]$ [$\text{R} = \text{Ph}, \text{CF}_3$] following from dihydrogen elimination. The title anion also reacted readily with metal-based electrophiles such as ClSnPh_3 and $[\text{AuCl}(\text{PR}_3)]$ ($\text{R} = i\text{Pr}, p\text{-tol}$) to give the corresponding heterometallic clusters $[\text{W}_2\text{Cp}_2(\mu\text{-PCy}_2)(\mu\text{-SnPh}_3)(\text{CO})_2]$ and $[\text{AuW}_2\text{Cp}_2(\mu\text{-PCy}_2)(\text{CO})_2(\text{PR}_3)]$, these having the added electrophile placed at the bridging position and formally retaining triple W–W bonds. The gold complexes, however, were rather unstable species decomposing spontaneously to give the tetranuclear clusters $[\text{Au}_2\text{W}_2\text{Cp}_2(\mu\text{-PCy}_2)(\text{CO})_2(\text{PR}_3)_2]\text{X}$ ($\text{W}–\text{W} = 2.5803(6)$ Å and $\text{Au}–\text{Au} = 2.8050(6)$ Å when $\text{R} = i\text{Pr}$ and $\text{X} = \text{PF}_6$), which could be prepared more conveniently by adding two equivalent of $[\text{AuCl}(\text{PR}_3)]$ to the anion, as expected. In contrast, reaction of the title anion with ClPbPh_3 led to the formation of the phenyl-bridged complex $[\text{W}_2\text{Cp}_2(\mu\text{-PCy}_2)(\mu\text{-Ph})(\text{CO})_2]$, following from formal loss of PbPh_2 .

Introduction

Transition-metal carbonylates are classical building blocks in organometallic synthesis, mainly due to their enhanced nucleophilicity, which allows them to react with a wide variety of electrophiles under mild conditions to give products having new M–E bonds ($\text{E} = \text{H}, \text{C}, p\text{- or } d\text{-block element, etc.}$).¹ To date the vast majority of these systems are based on mononuclear or polynuclear species, whereas metal–metal bonded binuclear anions are much more scarce, and those having multiple M–M bonds can still be considered a rarity. Among the latter complexes we can quote the iron complexes $[\text{Fe}_2(\mu\text{-P}^t\text{Bu}_2)_2(\text{CO})_5]^{-,2}$ and $[\text{Fe}_2(\mu\text{-PPh}_2)(\text{CO})_6]^{-,3}$ the manganese hexacarbonyls $[\text{Mn}_2(\mu\text{-PPh}_2)(\mu\text{-H})_2(\text{CO})_6]^{-,4}$ and $[\text{Mn}_2(\text{CO})_6(\mu\text{-Ph}_2\text{PCH}_2\text{PPh}_2)]^{2-,5}$ and the group-6 element dihydrides $[\text{M}_2(\mu\text{-H})_2(\text{CO})_8]^{2-}$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$).⁶ Far from being just chemical curiosities, the unusual combination of negative charge and a multiple M–M bond confers a remarkably wide synthetic potential to these complexes. Some

time ago our group implemented high-yield routes leading to the 30-electron dimolybdenum anions $[\text{Mo}_2\text{Cp}_2(\mu\text{-PR}_2)(\mu\text{-CO})_2]^{-}$ ($\text{R} = \text{Cy}, \text{Ph}, \text{OEt}$),⁷ this allowing us to develop a systematic study on the reactivity of the PCy_2 -bridged anion, which turned to be a highly active and versatile intermediate displaying two distinct nucleophilic sites located at the Mo and O atoms.^{7,8} Remarkably, this anionic compound turned to be a key synthetic intermediate to a variety of novel unsaturated derivatives such as the hydride $[\text{Mo}_2\text{Cp}_2(\mu\text{-H})(\mu\text{-PCy}_2)(\text{CO})_2]$,⁹ the methoxycarbonyl $[\text{Mo}_2\text{Cp}_2(\mu\text{-COMe})(\mu\text{-PCy}_2)(\mu\text{-CO})]^{10}$ or the agostic alkyls $[\text{Mo}_2\text{Cp}_2(\mu\text{-CHR})(\mu\text{-PCy}_2)(\text{CO})_2]$ ($\text{R} = \text{H}, \text{Ph}$),¹¹ all of them displaying a rich chemistry, as shown by independent studies. As a natural extension of this work, we recently developed a synthetic route to prepare an analogous ditungsten anion $[\text{W}_2\text{Cp}_2(\mu\text{-PCy}_2)(\mu\text{-CO})_2]^{-}$ (**1**) (Na^+ salt).¹² Interestingly, our preliminary studies on this compound revealed that metal substitution (W instead of Mo) had significant effects on the reactivity of these anions, and also on

the structure of some of their derivatives. Thus, we first found that the ditungsten system had enhanced nucleophilicity at the O site, this allowing the formation of unprecedented phosphinoylcarbene (COPR₂) complexes, *inter alia*.¹² Interestingly, protonation of **2** with weak acids such as [NH₄]PF₆ led to the corresponding hydride [W₂Cp₂(H)(μ-PCy₂)(CO)₂] (**2**) (Scheme 1),¹³ which in solution exists as a mixture of two isomers displaying either terminal or bridging hydride ligands,¹² in stark contrast with the exclusive bridging disposition found for its dimolybdenum analogue.⁹ Then, it was of interest to further explore the potential of ditungsten anion **1** to build new unsaturated hydrides and related species, which is the main purpose of this work. In this paper we give full details of the protonation reactions of **1**, which we have now extended to other Brønsted acids and also to H⁺-related electrophiles such as gold(I) complexes [AuCl(PR₃)] and organometal chlorides ClEPh₃ (E = Sn, Pb). As it will be shown below, most of these reactions involve the addition of the corresponding electrophile at the dimetal site of the anion, to give new unsaturated compounds related to those obtained for the dimolybdenum analogue of **1**. In contrast, only the ditungsten anion **1** is able to undergo double protonation to give stable dihydride derivatives, which are relatively stable towards dehydrogenation in the absence of coordinating anions.



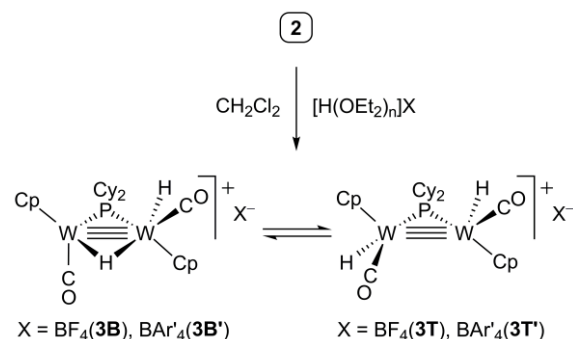
Scheme 1

Results and Discussion

Protonation of compounds **1** and **2**

The sodium salt of anion **1** is easily protonated in tetrahydrofuran solution by weak acids such as [NH₄]PF₆ to give the neutral unsaturated hydride [W₂Cp₂(H)(μ-PCy₂)(CO)₂] (**2**) almost quantitatively. In solution, this compound exists as a mixture of two interconverting isomers having either a bridging hydride (**2B**) or terminal hydride and semibridging carbonyl ligands (**2T**, Scheme 1), in a ratio **2B**/**2T** of *ca.* 3. A second protonation requires the use of stronger acids such as HBF₄·OEt₂ or [H(OEt₂)₂]BAR'₄ [Ar' = 3,5-C₆H₃(CF₃)₂], and is better performed by starting from the isolated hydride **2** in dichloromethane solution, then leading again to a mixture of two dihydride isomers: one having a bridging hydride ligand

[W₂Cp₂(H)(μ-H)(μ-PCy₂)(CO)₂]X [X = BF₄(**3B**), BAR'₄(**3B'**)] and another one bearing only terminal hydrides [W₂Cp₂(H)₂(μ-PCy₂)(CO)₂]X (**3T** and **3T'**) (Scheme 2). These isomers seem to be also in equilibrium in solution, and a ratio of *ca.* 6:5 was found in both cases. Unfortunately, these species could not be isolated as pure solids and decomposed progressively upon attempted purification, but their structures are well supported by spectroscopic data and DFT calculations (see below). In any case we note that the nature of the metal (W instead of Mo) is having a critical role in the stability of these products, because protonation of the Mo₂ analogue of **2** fails to yield any observable dihydrides and leads instead to complex mixtures of products that could not be isolated or characterized.



Scheme 2

To gain further insight into the role of the external anion in these reactions, we also examined reactions of **2** with some acids having coordinating anions. In particular, we have used three carboxylic acids of increasing acidity: acetic, benzoic and trifluoroacetic acid. No reaction was observed for the weaker acetic acid, but reaction of **2** with a slight excess of benzoic or trifluoroacetic acid gave the corresponding carboxylate-bridged complexes [W₂Cp₂(μ-PCy₂)(μ-O:O'-O₂CR)(CO)₂] [R = Ph(**4a**), CF₃(**4b**)] (Chart 1), with the latter reaction taking place instantaneously at room temperature, while the former one requires thermal activation (completed within 30 min in refluxing toluene). There are two points of interest in these reactions: first, their rates correlate with the relative strength of these acids (CF₃CO₂H >> PhCO₂H > CH₃CO₂H), which suggests that initial protonation to give cations analogous to **3** might be the first step of the process; secondly, the formation of the carboxylate complexes **4a,b** requires release of hydrogen, likely occurring at a subsequent step. In agreement with this proposed sequence, an independent experiment revealed that a dichloromethane solution of dihydride **3** reacted with sodium benzoate at room temperature to give **4a**.

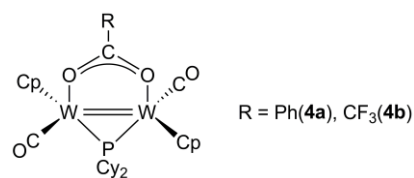


Chart 1

Structural characterization of compound 2

The presence of two isomers in the solutions of **2** is immediately apparent from the IR spectrum, which displays three instead of two C–O stretching bands (Table 1). While the first two bands have the pattern expected for transoid $M_2(CO)_2$ oscillators,¹⁴ the appearance of a third band at lower frequency (1739 cm^{-1}) is only compatible with the presence in solution of a second isomer having a bridging or semibringing ligand, as confirmed by low-temperature NMR data. Indeed, although the room temperature ^{31}P NMR spectrum of **2** displays a unique broad resonance, the latter eventually splits upon cooling, to give at 213 K two well-resolved resonances at 193.6 and 167.2 ppm, which are assigned to the terminal (minor, **2T**) and bridging (major, **2B**) isomers, respectively. In agreement with this assignment, the resonance of the symmetric isomer **2B** (C_2 symmetry) displays just one set of ^{183}W satellites, while that of **2T** displays two quite different sets ($J_{PW} = 240$ and 379 Hz), reflecting the difference in the coordination numbers of both metal atoms in this isomer.¹⁵ In any case, the chemical shifts of both resonances are quite high and comparable to those observed for related tungsten complexes having PCy_2 ligands bridging formally triple metal–metal bonds (*cf.* 150 ppm for **1**).

Similar changes with temperature were observed in the 1H and ^{13}C NMR spectra of **2**, with average resonances being observed at room temperature which eventually split upon cooling to give separate sets of resonances for both isomers at 213 K (see the Experimental Section). The C_2 symmetry axis in the major isomer **2B** relates pairs of Cp, CO and Cy groups, this reducing the number of resonances accordingly, while the bridging hydride ligand gives rise to a moderately shielded resonance strongly coupled to the ^{183}W nuclei ($\delta = -6.7$ ppm, $J_{WH} = 121$ Hz), thus reflecting the low coordination number of the metal atoms. This chemical shift is comparable to that measured for $[Mo_2Cp_2(\mu-H)(\mu-PCy_2)(CO)_2]$ (-6.9 ppm), and significantly lower than the values measured for the corresponding 34-electron complexes $[M_2Cp_2(\mu-H)(\mu-PCy_2)(CO)_4]$, [$\delta_H = -13.2$ ppm (Mo), -16.4 ppm (W), $J_{WH} = 40$ Hz].¹⁶ We have attributed this effect to the strong magnetic anisotropy of the multiple metal–metal bonds in the unsaturated hydrides.⁹ In fact, even stronger deshielding effects have been observed for bridging hydrides in related 30-electron complexes such as the diphosphine-bridged cations $[W_2Cp_2(\mu-H)(CO)_2(\mu-R_2PCH_2PR_2)]^+$ (δ_H *ca.* -2.5 ppm).¹⁷

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

Compound	$\nu(CO)$	$\delta(P)$ [J_{PW}]
$Na[W_2Cp_2(\mu-PCy_2)(\mu-CO)_2]$ (1)	1546 (s) ^c	152.7 [378] ^c
$[W_2Cp_2(H)(\mu-PCy_2)(CO)_2]$ (2) ^d	1864 (w, sh), 1822 (vs), 1739 (w)	193.6 [240, 379] (T) ^e 167.2 [318] (B) ^e
$[W_2Cp_2(H)_2(\mu-PCy_2)(CO)_2](BF_4)$ (3) ^d	1990 (m, sh), 1952 (vs), 1934 (s, sh), 1902 (s)	282.8 [246] (T) 242.4 [383, 218] (B)
$[W_2Cp_2(H)_2(\mu-PCy_2)(CO)_2](BAR'_4)$ (3') ^d	1995 (w, sh), 1954 (vs), 1934 (s), 1904 (s)	282.4 [247] (T) 242.7 [382, 216] (B)
$[W_2Cp_2(\mu-O:O'-O_2CPh)(\mu-PCy_2)(CO)_2]$ (4a)	1803 (m, sh), 1768 (vs), 1532 (w)	98.5 [230] ^f
$[W_2Cp_2(\mu-O:O'-O_2CCF_3)(\mu-PCy_2)(CO)_2]$ (4b)	1807 (m, sh), 1780 (vs), 1633 (w)	104.8 [236] ^f
$[W_2Cp_2(\mu-SnPh_3)(\mu-PCy_2)(CO)_2]$ (5)	1879 (m), 1821 (vs)	178.5 [305] (67) ^g
$[W_2Cp_2(\mu-PCy_2)(\mu-Ph)(CO)_2]$ (6)	1844 (w, sh), 1806 (vs)	109.3 [295]
$[AuW_2Cp_2(\mu-PCy_2)(CO)_2(P^iPr_3)]$ (7p)	1783 (s)	144.4 [293] (10) ^h ($\mu-P$) 101.2 [54] (10) ^h (AuP)
$[AuW_2Cp_2(\mu-PCy_2)(CO)_2\{P(p-tol)_3\}]$ (7t)	1787 (s)	161.2 [285] ($\mu-P$) 77.0 [55] (AuP) ⁱ
$[Au_2W_2Cp_2(\mu-PCy_2)(CO)_2(P^iPr_3)_2](PF_6)$ (8p)	1868 (w, sh), 1841 (vs)	175.1 [287] ($\mu-P$) 102.8 [43] (AuP) ^j
$[Au_2W_2Cp_2(\mu-PCy_2)(CO)_2\{P(p-tol)_3\}_2](PF_6)$ (8t)	1868 (w, sh), 1844 (vs)	180.1 [288] ($\mu-P$) 73.3 [44] (AuP) ^j

^a Recorded in dichloromethane solution, with C–O stretching bands ($\nu(CO)$) in cm^{-1} . ^b Recorded in CD_2Cl_2 solutions at 293 K and 162.00 MHz unless otherwise stated; δ in ppm relative to external 85% aqueous H_3PO_4 , J_{PW} in Hz. ^c Data taken from reference 12, with IR recorded in THF and ^{31}P NMR in acetone-*d*₆. ^d This complex displays in solution two interconverting isomers (**B** and **T**, see text). ^e Recorded at 213 K. ^f Recorded at 121.50 MHz. ^g Value for the $P_{-117/119}Sn$ couplings. ^h Value of J_{PP} . ⁱ Recorded in CH_2Cl_2 . ^j The spectrum also displays a septet resonance at -144.4 ppm ($J_{PF} = 711$ Hz) due to the PF_6^- anion.

In contrast, the minor isomer **2T** has no symmetry elements, and accordingly displays separate resonances for the pairs of Cy, Cp, and CO groups, with the strong deshielding of one of the latter resonances (272.7 ppm) further confirming the semibringing coordination of one of the carbonyls in this isomer. The presence of a terminal hydride is denoted by the

relatively low shielding of the hydride ($\delta_H = -0.71$ ppm), a value comparable to that observed for the isoelectronic and crystallographically characterized complex $[Mo_2Cp_2(H)(\mu-PCy_2)_2(CO)]^+$ ($\delta_H = -1.45$ ppm),¹⁸ while its high coupling to phosphorus ($J_{PH} = 31$ Hz) reveals a *cis* positioning relative to the PCy_2 ligand.¹⁹

DFT calculations of compound 2

The above structural proposals for the observed isomers of **2** were fully supported by DFT calculations (see the Experimental Section and Supplementary Information). The most stable structure computed is that having a bridging hydride ligand (**B** in Figure 1), which is some 15 kJ/mol below the structure having a terminal hydride (*cis* to the PCy₂ group) and a semibridging carbonyl ligand (**T**), in agreement with the observed prevalence of isomer **B** in solution and with all spectroscopic data. A third isomer displaying a semibridging hydride and bridging and terminal carbonyls (**C** in Figure 1) was significantly higher in energy (67 kJ/mol above **B**), and will not be further discussed.

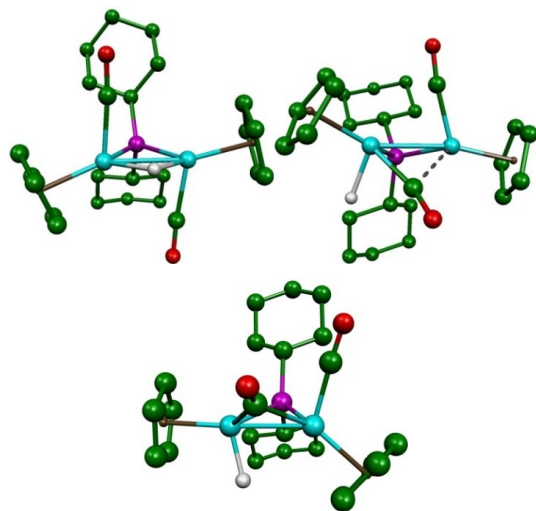


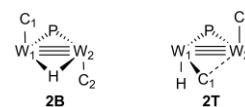
Figure 1: DFT-optimized structures of isomers for compound **2** (**B**, upper left; **T**, upper right; **C**, below), with H atoms (except hydrides) omitted for clarity. Relative Gibbs free energies were 0, 15 and 67 kJ/mol, respectively.

In spite of their different structures, isomers **2B** and **2T** display similarly short intermetallic separations of 2.545 and 2.536 Å respectively (Table 2), in turn comparable to the corresponding length computed for the molybdenum hydride [Mo₂Cp₂(μ-H)(μ-PCy₂)(CO)₂] (2.535 Å),⁹ all of them in agreement with the metal–metal triple bond to be proposed for these molecules on application of the 18-electron rule.¹³ A similar bonding picture is obtained from the analysis of the electron density under the *Atoms in Molecules* (AIM) scheme,²⁰ this yielding for **2B** and **2T** almost identical and quite high electron densities at the corresponding intermetallic bond critical points (*ca.* 0.64 eÅ⁻³). For comparison, the corresponding value at the triply-bonded [W₂Cp₂(CO)₄] was computed to be 0.652 eÅ⁻³ at the same level of theory (W–W = 2.518 Å). The remaining structural parameters of the bridged isomer **2B** are almost identical to those of its molybdenum analogue and deserve no particular comments. In isomer **2T**, the two WCp fragments are bridged by the PCy₂ group and a linear semibridging carbonyl spanning a relatively short M⋯C distance to the second metal atom (2.438 Å). In contrast, both the hydride and the second CO ligand are terminally coordinated, although the latter group is slightly bent over the

intermetallic vector, yet too far away from the second metal atom (2.795 Å) so as to be involved in bonding with it.

Table 2. Selected DFT-Computed Bond Lengths (Å) and Angles (deg) for isomers **2B** and **2T**.

Parameter	2B	2T
W1–W2	2.545	2.536
W1–P	2.429	2.467
W2–P	2.439	2.400
W1–H	1.870	1.707
W2–H	1.867	
W1–C1	1.956	1.978
W1–C2		2.795
W2–C1		2.438
W2–C2	1.946	1.945
W1–H–W2	85.8	
W1–C1–W2		69.2
W1–W2–C2	81.4	75.9
W2–W1–C1	87.1	
W2–W1–H		106.4



Solution structure of compounds 3

As noted above, compounds **3** and **3'** are obtained as a mixture of two interconverting isomers in each case. The available spectroscopic data for both salts (Table 1 and Experimental Section) are very similar to each other, suggesting that no significant anion–cation interactions occur in solution, therefore only data for the BF₄[−] salt (**3**) will be discussed. The presence of two species in the solutions of **3** is first indicated by its IR spectrum, which displays four (instead of two) high-frequency C–O stretching bands corresponding to terminal carbonyls. Moreover its ³¹P NMR spectrum displays two highly deshielded resonances, at 242.4 and 282.8 ppm, which are assigned respectively to isomers **3B** (major) and **3T** (minor, Scheme 2), on the basis of their different P–W couplings. Thus, isomer **3B** displays two very different couplings (383 and 218 Hz), in agreement with a structure in which the coordination numbers of the two metal atoms differ by one unit. In contrast, the minor isomer **3T** must display equivalent W centres, since just one set of satellite lines with a relatively low P–W coupling (246 Hz) is observed. We note that the chemical shifts of both resonances are much higher than those of its precursor **2**, they being actually comparable to the values measured for several 30-electron dimolybdenum cations such as [Mo₂Cp₂(μ-COMe)₂(μ-PCy₂)]⁺ (264.2 ppm),¹⁰ and [Mo₂Cp₂(μ-COH)(μ-CPh)(μ-PCy₂)]⁺ (254.8 ppm).²¹

The major isomer **3B** displays two distinct hydride resonances coupled to phosphorus, corresponding respectively to a terminal ligand *cis* to the PCy₂ ligand (δ_{H} 0.13 ppm; J_{HP} = 32 Hz) and a bridging ligand (δ_{H} = −3.96 ppm; J_{HP} = 3 Hz) strongly coupled to inequivalent tungsten atoms (J_{HW} = 109, 107 Hz). In contrast, the equivalent hydrides in **3T** give rise to a poorly shielded resonance (δ_{H} −0.19 ppm), retaining a high

H–P coupling (37 Hz) indicative of a *cis* disposition of these two H atoms with respect to the PCy₂ ligand.¹⁹

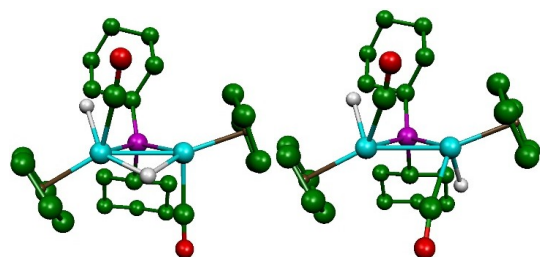
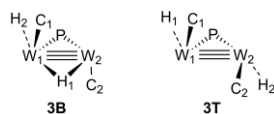


Figure 2: DFT-optimized structures of the cations in isomers **3B** (left) and **3T** (right), with H atoms (except hydrides) omitted for clarity. Relative Gibbs free energies were 0 and 4 kJ/mol, respectively.

Table 3: Selected DFT-Computed Bond Lengths (Å) and Angles (deg) for isomers **3B** and **3T**.

Parameter	3B	3T
W1–W2	2.557	2.544
W1–H1	1.865	1.704
W2–H1	1.877	
W1–H2	1.717	
W2–H2		1.702
W1–P	2.504	2.449
W2–P	2.402	2.469
W1–C1	2.011	1.994
W2–C2	1.979	1.991
W1–C2		2.691
W2–C1		2.711
W1–H1–W2	86.2	
P–W1–H1	101.8	72.6
P–W1–H2	69.6	72.4
P–W1–W2–H1	161.3	



Unfortunately we were unable to grow crystals of any of these cations, so we carried out DFT calculations to further support our proposals (Figure 2 and Table 3). First, we found that both proposed structures are almost isoenergetic, with the bridged isomer **3B** being only slightly more stable (by 4 kJ/mol), in full agreement with the observed ratio of isomers in solution. The optimized structures are closely related to those discussed above for **2B** and **2T**, by just adding another proton at one of the metal positions, with little effect on the rest of the molecule. Indeed, both isomers of **3** retain short intermetallic separations (*ca.* 2.55 Å) comparable to those computed for the neutral hydrides **2**, in turn consistent with the metal–metal triple bonds to be formulated for these cations. In line with this, the electron densities at the corresponding intermetallic bond critical points (*ca.* 0.61 eÅ⁻³) are only marginally lower than those computed for the isomers of **2**, which suggests that attachment of the second proton mainly involves non-bonding electron density at the metal atoms. In the case of **3B**, the different coordination numbers of the metals is partially balanced by a somewhat asymmetric coordination of the phosphide ligand ($\Delta d(\text{W}–\text{P})$ *ca.* 0.1 Å), with the P atom being

closer to the M(CO) fragment. Other relevant feature of this structure is the puckering of the central W₂PH ring, as opposed to the almost perfectly flat disposition of the central W₂PH ring in the neutral **2B**, which might be a geometrical distortion encompassing some displacement of the carbonyl ligand of the Mo(H)(CO) fragment towards the bridging region. On the other hand, the structure of the minor isomer **3T** is much more symmetrical, with a C₂-related terminal coordination of the carbonyl and hydride ligands. We finally note that the terminal hydride ligands in both isomers display acute H–W–P angles of *ca.* 70°, fully consistent with the high H–P couplings of *ca.* 30 Hz observed in solution.

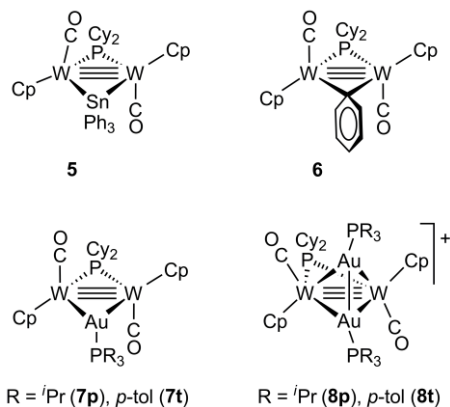
Solution structure of carboxylate complexes **4a,b**

Spectroscopic data for compounds **4a,b** (Table 1 and Experimental Section) are similar to each other and indicative of an overall C₂ symmetry and an *O:O'*-bridging coordination of the carboxylate groups (Chart 1). Thus, the IR spectra of these compounds display three C–O stretching bands, with the two more energetic ones having relative intensities characteristic of transoid M₂(CO)₂ oscillators,¹⁴ and frequencies significantly lower than those of the parent hydride **2**, as expected from replacement of the bridging hydride with a 3-electron donor carboxylate ligand. A third band is observed at lower frequency [1532 (**4a**) and 1633 (**4b**) cm⁻¹], which is assigned to the asymmetric C–O stretch of the carboxylate groups. Although we have not identified the corresponding symmetric stretches in the IR spectra, expected *ca.* 125 cm⁻¹ below the asymmetric stretch for *O:O'*-bridging carboxylates (*cf.* 1565 and 1430 cm⁻¹ for [Mn₂(μ-H)(μ-*O:O'*-O₂CMe)(CO)₆(μ-Ph₂PCH₂PPh₂)]),²² the low frequency of the observed asymmetric bands rules out an alternative *O:O*-bridging coordination of the carboxylate, which would yield a much more energetic C–O stretch (around 1700 cm⁻¹).²³ The 32-electron complexes **4** give rise to relatively shielded ³¹P NMR resonances (δ_{P} *ca.* 100 ppm), as observed for the isoelectronic iodide complex [W₂Cp₂(μ-I)(μ-PCy₂)(CO)₂] (δ_{P} 89.3 ppm, $J_{\text{PW}} = 292$ Hz). However, their coupling to tungsten is much lower [230 (**4a**) and 236 Hz (**4b**)], thus providing additional support for the proposed *O:O'*-bridging coordination of the carboxylate ligand in these compounds, since the latter implies the presence of an additional donor atom around the metals (hence a reduced P–W coupling),¹⁵ when compared to the *O:O*-bridging coordination mode.

Reactions of **1** with ClEPh₃ (E = Sn, Pb) and gold(I) cations

The high nucleophilicity of anion **1** can be exploited for the preparation of different unsaturated heterometallic derivatives not accessible using conventional routes. For instance, addition of ClSnPh₃ to THF suspensions of **1** gives rapidly the stannyl derivative [W₂Cp₂(μ-SnPh₃)(μ-PCy₂)(CO)₂] (**5**) in high yield (Chart 2), with the SnPh₃⁺ electrophile incorporated at the dimetal site, as previously observed for the molybdenum analogue of **1**.^{8b} In any case, the bridging disposition of the SnR₃ group can still be considered a rarity in the chemistry of these groups, which more typically display a terminal

coordination. In fact, we can only quote two other families of compounds displaying this unusual bridging coordination, the manganese complexes $[\text{Mn}_2\{\mu\text{-SnR}_2\text{OP}(\text{OEt}_2)\}(\text{CO})_6\text{L}]$ ($\text{R} = \text{Bu}, \text{Ph}$; $\text{L} = \text{CO}$, tertiary phosphine),²⁴ and the germanium cluster $[\text{K}(2,2,2\text{-crypt})][\text{Ge}_9(\mu_2\text{-SnPh}_3)]$ ($2,2,2\text{-crypt} = \text{C}_{18}\text{H}_{36}\text{N}_2\text{O}_6$).²⁵



In contrast, reaction of **1** with ClPbPh_3 did not lead to the expected heterometallic cluster, but instead to the phenyl-bridged derivative $[\text{W}_2\text{Cp}_2(\mu\text{-PCy}_2)(\mu\text{-Ph})(\text{CO})_2]$ (**6**) as major product (Chart 2), along with small amounts of the chloride-bridged complex $[\text{W}_2\text{Cp}_2(\mu\text{-Cl})(\mu\text{-PCy}_2)(\text{CO})_2]$, a product related to the iodide complex mentioned above, which was not fully characterized. A similar Ph-bridged product was formed when using the Mo_2 analogue of **1**,⁹ in a process most likely involving the formation of a PbPh_3 -bridged intermediate (not observed) akin to compound **5**, which in a second step would evolve *via* Ph migration to the dimetal centre and formal elimination of PbPh_2 , the latter likely undergoing disproportionation to give elemental lead and PbPh_4 . Such a proposal is based on the reported photochemical decomposition of $[\text{WCp}(\text{PbPh}_3)(\text{CO})_3]$ to give the phenyl derivative $[\text{WCp}(\text{Ph})(\text{CO})_3]$ along with Pb and PbPh_4 .²⁶ A significant difference between these two processes is that the required 1,2-phenyl shift takes place much more easily in our dinuclear compounds (thermal reaction at room temperature), surely facilitated by the electronic and coordinative unsaturation of the metal core at the PbPh_3 -bridged intermediate presumably formed in the initial stage of this reaction.

We have also studied reactions of **1** with some electrophilic gold (I) complexes of type $[\text{AuCl}(\text{PR}_3)]$. By recalling the isolobal relationship between the $[\text{Au}(\text{PR}_3)]^+$ cations and a proton,²⁷ it can be expected that these reactions would give products related to the hydrides following from protonation, a principle which has provided a general route for the preparation of heterometallic clusters of the transition metals having group 11 metal fragments.²⁷⁻³⁰ Indeed, the ditungsten anion **1** reacts with one equivalent of $[\text{AuCl}(\text{PR}_3)]$ to give instantaneously green-brownish solutions of the new trinuclear clusters $[\text{AuW}_2\text{Cp}_2(\mu\text{-PCy}_2)(\text{CO})_2(\text{PR}_3)]$ [$\text{R} = i\text{Pr}$ (**7p**), $p\text{-tol}$ (**7t**)] (Chart

2). These products, however, are only moderately stable and evolve spontaneously in solution to give the corresponding cationic compounds $[\text{Au}_2\text{W}_2\text{Cp}_2(\mu\text{-PCy}_2)(\text{CO})_2(\text{PR}_3)_2]^+$ (Chart 2), presumably as the corresponding Cl^- salts, along with other unidentified species. This decomposition was faster for **7t**, then preventing a complete spectroscopic characterization, while it was slower for **7p**, presumably due to the higher steric protection provided by the bulkier $i\text{Pr}$ groups. As expected, the above cationic clusters could be more conveniently prepared as the corresponding PF_6^- salts $[\text{Au}_2\text{W}_2\text{Cp}_2(\mu\text{-PCy}_2)(\text{CO})_2(\text{PR}_3)_2]\text{PF}_6$ [$\text{R} = i\text{Pr}$ (**8p**), $p\text{-tol}$ (**8t**)] by reaction of **1** with two equivalent of $[\text{AuCl}(\text{PR}_3)]$, followed by anion exchange using $\text{Ti}(\text{PF}_6)$. The formation of these tetranuclear clusters indicate that the neutral compounds **7p,t** still retain significant electron-donor ability at their intermetallic positions, as also found for the related dimolybdenum analogues.^{8b}

Structural characterization of compounds **5** and **6**.

The structure of **5** was reported in our preliminary work,¹² and is not very different from that of its Mo_2 analogue, therefore only a brief comment is needed now, to be found in the Supplementary Information. On the other hand, spectroscopic data for the phenyl complex **6** (Table 1 and Experimental section) indicate a close structural similarity with the molybdenum complex $[\text{Mo}_2\text{Cp}_2(\mu\text{-PCy}_2)(\mu\text{-Ph})(\text{CO})_2]$, a molecule characterized crystallographically,⁹ therefore a detailed analysis is neither needed. We just note that NMR data for **6** also denotes the presence of a π -bonding interaction between the bridging phenyl ligand and the unsaturated dimetal centre, which must be essentially analogous to that identified for its Mo_2 analogue on the basis of DFT calculations. This interaction is most clearly evidenced by the anomalous ^{13}C chemical shifts of the *ipso* (116.2 ppm) and *ortho* (168.3 ppm) atoms of the Ph group, which are more shielded and deshielded, respectively, than those values typically observed for conventional phenyl ligands in either terminal or bridging complexes. In the same line, the ^{31}P chemical shift of **6** (109.3 ppm) is relatively low for a 30 electron complex. In fact, this shift is closer to that of the 32-electron complex $[\text{W}_2\text{Cp}_2(\mu\text{-I})(\mu\text{-PCy}_2)(\text{CO})_2]$ (89.3 ppm)¹² than to the corresponding figure in the 30-electron hydride **2B** (167.2 ppm).

Solution structure of compounds **7p,t**

Spectroscopic data obtained from impure samples of the heterometallic clusters **7** (Table 1 and Experimental section) indicate a strong relationship with their Mo_2 analogues $[\text{AuMo}_2\text{Cp}_2(\mu\text{-PCy}_2)(\text{CO})_2(\text{PR}_3)]$ previously prepared by us,^{8b} and a similar geometry is assumed for these molecules, with the gold(I) fragment symmetrically bridging the tungsten atoms (Chart 2). In agreement with this, the IR spectra of compounds **7** display bands characteristic of *transoid* $\text{M}_2(\text{CO})_2$ oscillators, although the weak symmetrical stretch is obscured in each case by the strong band of the corresponding cationic complex **8** invariably present in the reaction mixtures. In any case, these frequencies are well below (*ca.* 40 cm^{-1}) those measured for hydride **2B**, as expected from the replacement of H by a gold(I)

fragment of comparatively lower electronegativity. The ^{31}P NMR spectra of these complexes display two weakly coupled resonances in each case [$J_{\text{PP}} = 10$ (**7p**), ~ 0 (**7t**) Hz], as anticipated for a three-bond P–P coupling in this type of clusters,^{29,30} and the PCy_2 resonance retains the high P–W couplings (*ca.* 300 Hz) characteristic of the low-coordination environment of the tungsten atoms in $[\text{W}_2\text{Cp}_2(\mu\text{-PCy}_2)(\mu\text{-X})(\text{CO})_2]$ complexes.^{12,16}

Structural characterization of compounds **8p,t**

The structure of compound **8p** was determined through an X-ray diffraction analysis (Figure 4 and Table 4). The geometry of the cation resembles that of its dimolybdenum analogue $[\text{Au}_2\text{Mo}_2\text{Cp}_2(\mu\text{-PCy}_2)(\text{CO})_2(\text{P}^i\text{Pr}_3)_2]^+$,^{8b} and displays a quite regular tetrahedral W_2Au_2 core. The coordination sphere of the W atoms is completed with transoid Cp and CO ligands at each site and with a symmetrically bridging PCy_2 ligand. The Au–Au bond is almost perpendicular to the W–W vector, with its centroid lying close to the W_2P plane. Finally, each Au atom bears a phosphine ligand, with the P atom located close to the corresponding W_2Au plane. A metal–metal triple bond should be formulated for this cation on the basis of the 18-electron rule, which is in agreement with the relatively short W–W length of 2.5803(6) Å, a figure comparable to that measured for its Mo_2 analogue (2.5673(3)Å),^{8b} and for the stannyl complex **5**. We also note the proximity of these figures to the value of 2.545 Å computed for the hydride-bridged isomer **2B**. As a result of the slightly tilted coordination of the Au_2 fragment there are two different W–Au distances differing by *ca.* 0.1 Å, but both are still comparable to the average value measured for the electron-precise cluster $[\text{AuMo}_2\text{Cp}_2(\mu\text{-PPh}_2)(\text{CO})_4(\text{PPh}_3)]$.³¹ A salient feature in the structure of **8p** is the presence of a strong Au–Au bonding interaction, as deduced from the distance of 2.8050(6) Å, which falls on the short side of the range usually found in heterometallic clusters having gold(I)–gold(I) bonding interactions (2.70–3.10 Å).²⁸ Finally, the carbonyl ligands display slightly different environments, with one of them leaning over the W–W bond while the second carbonyl is pointing away from it, and both seem involved in very weak semi-bridging interactions with the gold atoms, as suggested by the relatively short Au–C lengths [2.607(9) and 2.65(1)Å] and deviation from linearity (W–C–O angles *ca.* 172°). We must note that similar weak interactions are not uncommon in heterometallic carbonyl clusters having gold phosphine fragments,²⁸ but might not be of a truly bonding nature in all cases.

Spectroscopic data in solution for compounds **8p,t** are similar to each other, indicating that both share the same structural features, consistent with the solid-state structure just discussed. Thus, the retention of essentially terminal CO ligands is denoted in the IR spectra by the appearance of two C–O stretching bands with pattern characteristic of *transoid* $\text{M}_2(\text{CO})_2$ oscillators. As expected, the equivalent gold-bound phosphine ligands give rise to just one ^{31}P NMR resonance, while the phosphide ligand gives rise to a strongly deshielded resonance close to those of dihydrides **3** and retaining large

W–P couplings characteristic of low-coordination environments of tungsten atoms. Yet, because of the overall C_2 symmetry of the cation, the Me groups within each ^iPr substituent remain diastereotopic and give rise to separated resonances. Other spectroscopic parameters are as expected, and deserve no additional comments.

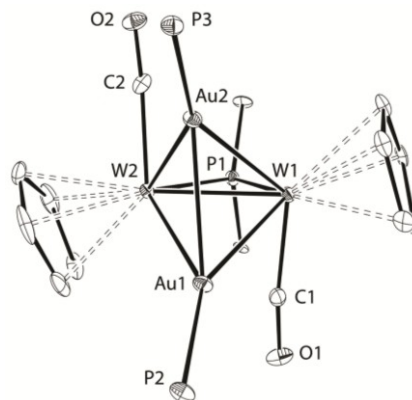


Figure 3: ORTEP diagram (30% probability) of the cation in compound **8p** with H atoms, ^iPr and Cy groups (except their C1 atoms) omitted for clarity.

Table 4: Selected Bond Lengths (Å) and Angles (deg) for the cation in **8p**.

W1–W2	2.5803(6)	W2–W1–Au2	61.12(2)
W1–Au1	2.8061(6)	W2–W1–Au1	64.88(2)
W1–Au2	2.8933(6)	W2–Au1–W1	53.79(2)
W2–Au1	2.8958(6)	W2–Au2–W1	53.91(1)
W2–Au2	2.7959(6)	W1–P3–W2	65.5(1)
W1–P3	2.377(3)	C1–W1–W2	93.6(3)
W2–P3	2.395(6)	C2–W2–W1	84.4(3)
Au1–P1	2.323(3)	W1–C1–O1	172.2(8)
Au2–P2	2.309(3)	W2–C2–O2	172.2(8)
W1–C1	1.96(1)	W1–W2–C2	93.6(3)
W2–C2	1.94(1)	W2–W1–C1	84.4(3)
Au1–C1	2.607(9)		
Au2–C2	2.65(1)		
Au1–Au2	2.8050(6)		

Is it there a dihydrogen analogue of digold clusters **8**?

On the basis of the H/Au(PR₃) isolobal analogy, the digold clusters **8** can be obviously related to an hypothetical dihydrogen-bridged complex $[\text{W}_2\text{Cp}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-H}_2)(\mu\text{-PCy}_2)(\text{CO})_2]^+$, which actually would be an isomer of cations **3B** and **3T**. Since their discovery by Kubas in 1984,³² dihydrogen complexes have attracted considerable attention from both basic and applied perspectives.^{33,34} Yet, 30 years later, all dihydrogen complexes characterized so far display terminal coordination to a single metal atom. Very recently, theoretical work by Simandiras *et al.* predicted that some dihydrogen-bridged structures might be stable at ditungsten carbonyl environments.³⁵ It was thus of interest for us to check whether the cation $[\text{W}_2\text{Cp}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-H}_2)(\mu\text{-PCy}_2)(\text{CO})_2]^+$ could possibly be a viable isomer, even if more energetic, of dihydrides **3B** and **3T**. A DFT calculation, however, revealed that such a structure was not a true minimum on the potential energy surface of **3**, but instead evolved to a dihydride-bridged structure **3HH** (Figure 4), still more energetic than the observed

isomers of **3** (25 kJ/mol above **3B**). Apparently, the ditungsten centre in **3** is too electron rich, a circumstance favouring dihydride structures with respect to the corresponding dihydrogen isomers, *via* back-bonding to the $\sigma^*(\text{H}-\text{H})$ orbital of the H_2 ligand. We note that, in spite of the presence of two bridging hydrides, the molecule of isomer **3HH** displays a very short intermetallic separation of 2.570 Å and an electron density at the corresponding bond critical point of $0.652 \text{ e}\text{\AA}^{-3}$, a figure identical to the one computed for the triply bonded $[\text{W}_2\text{Cp}_2(\text{CO})_4]$, even if the latter complex displays a shorter intermetallic length (computed to be 2.518 Å).

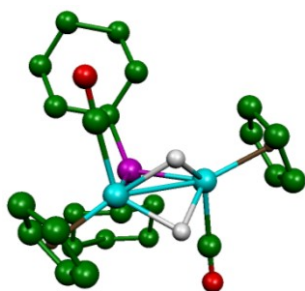


Figure 4: DFT-optimized structure of the cation $[\text{W}_2\text{Cp}_2(\mu\text{-H})_2(\mu\text{-PCy}_2)(\text{CO})_2]^+$ (**3HH**), with H atoms (except hydrides) omitted for clarity. Selected bond lengths (Å): W–W = 2.570; W–P = 2.436, 2.452; W–H = 1.877 to 1.913; W–CO = 2.000, 2.004; H···H = 1.902.

Conclusions

The ditungsten anion **1** behaves quite differently from its dimolybdenum analogue, particularly as the protonation reactions are concerned. A first proton can be readily added on **1** which, however, gives a mixture of two interconverting isomers of formula $[\text{W}_2\text{Cp}_2(\text{H})(\mu\text{-PCy}_2)(\text{CO})_2]$ (**2**) displaying either bridging or terminal hydrides, with the former being some 15 kJ/mol more stable, according to DFT calculations. In contrast, reactions of **1** with some H^+ -related, metal-based electrophiles such as ECIPh_3 ($\text{E} = \text{Sn}, \text{Pb}$) and $[\text{AuCl}(\text{PR}_3)]$ reproduce the reactivity pattern observed for its dimolybdenum analogue, that its, preferential binding of the electrophile at the dimetal centre, followed when $\text{E} = \text{Pb}$ by formal loss of PbPh_2 to render a phenyl-bridged derivative. All these neutral derivatives retain substantial electron density at the ditungsten site, as denoted by the formation of cationic W_2Au_2 clusters upon further reaction of $[\text{AuW}_2\text{Cp}_2(\mu\text{-PCy}_2)(\text{CO})_2(\text{PR}_3)]$ with $[\text{AuCl}(\text{PR}_3)]$, or by the reactions of hydride **2** with strong acids having weakly coordinating anions to give cationic dihydrides of formula $[\text{W}_2\text{Cp}_2(\text{H})_2(\mu\text{-PCy}_2)(\text{CO})_2]^+$. The latter cations can display either bridging or terminal hydrides, with their relative energies following the order $(\mu\text{-H})(\text{H}) \leq (\text{H})(\text{H}) \ll (\mu\text{-H})(\mu\text{-H})$, according to experiment and DFT calculations. No related dihydrides can be obtained from the Mo_2 analogue of **1**, thus proving the critical influence of the metal on the relative stability of these products. Yet, in the presence of coordinating anions, the above tungsten dihydrides evolve *via* dehydrogenation and anion coordination, as shown by the

reactions of **2** with carboxylic acids to give carboxylate-bridged derivatives.

Acknowledgments

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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,³⁶ and distilled prior to use. Petroleum ether refers to that fraction distilling in the range 338–343 K. Suspensions of compound $\text{Na}[\text{W}_2\text{Cp}_2(\mu\text{-PCy}_2)(\mu\text{-CO})_2]$ (**1**) in THF were prepared as described previously.¹² Complexes $[\text{AuCl}(\text{PR}_3)]$ ($\text{R} = p\text{-tol}, ^i\text{Pr}$),³⁷ and $[\text{H}(\text{OEt}_2)_2]\text{BAr}'_4$ ($\text{Ar}' = 3,5\text{-C}_6\text{H}_3(\text{CF}_3)_2$),³⁸ were prepared by literature procedures, and all other reagents were obtained from the usual commercial suppliers and used as received. Chromatographic separations were carried out using jacketed columns, kept at the desired temperature with tap water or with a cryostat. Commercial alumina (activity I, 150 mesh) was degassed under vacuum prior to use. The latter was mixed under nitrogen with the appropriate amount of water to reach the activity desired. IR C–O bond stretching frequencies were measured in solution or Nujol mulls, are given in cm^{-1} and are referred to as $\nu(\text{CO})$ (solvent/Nujol) respectively. Nuclear magnetic resonance (NMR) spectra were routinely recorded at 400.13 (^1H), 162.00 ($^{31}\text{P}\{^1\text{H}\}$) or 100.63 MHz ($^{13}\text{C}\{^1\text{H}\}$) at 293 K in CD_2Cl_2 solutions unless otherwise stated. Chemical shifts (δ) are given in ppm, relative to internal tetramethylsilane (^1H and ^{13}C), CFCl_3 (^{19}F) or external 85% aqueous H_3PO_4 solutions (^{31}P). Coupling constants (J) are given in Hertz.

Preparation of $[\text{W}_2\text{Cp}_2(\text{H})(\mu\text{-PCy}_2)(\text{CO})_2]$ (2**).** A suspension containing *ca.* 0.90 mmol of compound **1** in tetrahydrofuran (10 mL) was stirred with an excess $(\text{NH}_4)\text{PF}_6$ (*ca.* 0.25 g, 1.53 mmol) for 3 min to give a dark brown solution. Solvent was then removed under vacuum and the residue was extracted with dichloromethane-petroleum ether (1:4) and chromatographed through an alumina column (activity IV) at 253 K. A brown fraction was eluted using the same solvent mixture. Removal of solvents from this fraction gave compound **2** as a brown solid (0.536 g, 79%). Anal. Calcd for $\text{C}_{24}\text{H}_{33}\text{O}_2\text{PW}_2$: C, 38.32; H, 4.42; Found: C, 38.05; H, 4.27. $^{31}\text{P}\{^1\text{H}\}$ NMR (293 K, averaged spectrum): δ 170.2 (s, br, $J_{\text{PW}} = 316$). ^1H NMR (293 K, averaged spectrum): δ 5.24 (s, 10H, Cp), 2.50–1.00 (m, 22H, Cy), -5.20 (d, br, $J_{\text{PH}} = 9$, $J_{\text{HW}} = 103$, 1H, W–H). ^1H NMR (193 K): δ 5.42, 5.39 (2s, br, 2 x 5H, Cp, isomer **T**), 5.21 (s, 10H, Cp, isomer **B**), -0.71 (d, $J_{\text{PH}} = 31$, $J_{\text{HW}} = 99$, 1H, W–H, **T**), -6.77 (s, $J_{\text{HW}} = 121$, 1H, $\mu\text{-H}$, **B**); ratio **B/T** = 3. $^{13}\text{C}\{^1\text{H}\}$ NMR (293 K,

averaged spectrum): δ 237.8 (s, br, WCO), 87.8 (s, Cp), 51.9 [d, J_{CP} = 23, C^1 (Cy)], 34.0, 33.6 [2s, C^2 (Cy)], 28.7, 28.0 [2d, J_{CP} = 12, C^3 (Cy)], 26.6 [s, C^4 (Cy)]. $^{13}C\{^1H\}$ NMR (193 K): δ 272.7 (s, br, μ -CO, T), 244.2 (s, br, CO, T), 233.5 (s, br, 2CO, B), 94.1, 90.3 (2s, Cp, T), 87.2 (s, 2Cp, B).

Reaction of compound 2 with $HBf_4 \cdot OEt_2$. Neat $HBf_4 \cdot OEt_2$ (4 μ L, 0.029 mmol) was added to a solution of compound 2 (0.020 g, 0.027 mmol) in dichloromethane (4 mL) at 233 K, and the mixture was stirred for 10 min to give an orange solution containing an inseparable mixture of isomers **3B** and **3T** in a ratio of ca. 6:5 in CD_2Cl_2 solution at either 293 K or 213 K. The solvent was then removed under vacuum and the resulting residue washed with petroleum ether (3 x 3 mL) and dried under vacuum to yield compound **3** as an air-sensitive orange solid (0.018 g, 80%). $\nu(CO)$ (Nujol): 1996 (w, sh), 1947 (s, sh), 1918 (vs), 1902 (s). *Spectroscopic data for isomer 3B*: 1H NMR (300.13 MHz): δ 5.79, 5.47 (2s, 2 x 5H, Cp), 3.00-1.00 (m, 22H, Cy), 0.13 (dd, J_{HP} = 32, J_{HH} = 9, 1H, W-H), -3.96 (dd, J_{HH} = 9, J_{HP} = 3, J_{HW} = 109, 107, 1H, μ -H). *Spectroscopic data for isomer 3T*: 1H NMR (300.13 MHz): 5.71 (s, 10H, Cp), 3.00-1.00 (m, 22H, Cy), -0.19 (d, J_{HP} = 37, J_{HW} = 53, 2H, W-H).

Reaction of compound 2 with $[H(OEt_2)_2]BAr^*_4$. The procedure and workup is identical to that described for the reaction with HBf_4 , but using $[H(OEt_2)_2]BAr^*_4$ instead (0.027 g, 0.027 mmol). This yielded compound **3'** as an air-sensitive orange solid (0.034 g, 82%). This solid was shown (by NMR) to contain a mixture of isomers **3B'** and **3T'**, in a ratio of ca. 6:5 in CD_2Cl_2 solution at 293 K, which could not be separated from each other. *Spectroscopic data for isomer 3B'*: 1H NMR: δ 7.72 (s, 8H, Ar *), 7.56 (s, 4H, Ar *), 5.72, 5.42 (2s, 2 x 5H, Cp), 2.60-1.00 (m, 22H, Cy), 0.12 (dd, J_{HP} = 31, J_{HH} = 9, 1H, W-H), -4.00 (dd, J_{HH} = 9, J_{HP} = 3, J_{HW} = 109, 107, 1H, μ -H). *Spectroscopic data for isomer 3T'*: 1H NMR: δ 7.72 (s, 8H, Ar *), 7.56 (s, 4H, Ar *), 5.65 (s, 10H, Cp), 2.60-1.00 (m, 22H, Cy), -0.20 (d, J_{HP} = 37, J_{HW} = 53, 2H, W-H).

Preparation of $[W_2Cp_2(\mu-O:O'-O_2CPh)(\mu-PCy_2)(CO)_2]$ (4a**).** Compound 2 (0.020 g, 0.027 mmol) and benzoic acid (0.005 g, 0.04 mmol) were stirred in refluxing toluene (4 mL) for 0.5 h to give an orange solution. Solvent was then removed and the residue was washed with petroleum ether (3 x 3 mL) and dried under vacuum to yield compound **4a** as an orange microcrystalline solid (0.011 g, 47%). Anal. Calcd for $C_{31}H_{37}O_4PW_2$: C, 42.69; H, 4.28. Found: C, 42.38; H, 4.11. 1H NMR (300.09 MHz): δ 8.02 (m, 2H, Ph), 7.50 (m, 3H, Ph), 5.63 (d, J_{HP} = 1, 10H, Cp), 2.60-1.00 (m, 22H, Cy). $^{13}C\{^1H\}$ NMR: δ 220.4 (d, J_{CP} = 6, WCO), 184.0 (s, CO_2Ph), 132.2 [s, $C^4(Ph)$], 130.4 [s, $C^2(Ph)$], 129.4 [s, $C^1(Ph)$], 128.5 [s, $C^3(Ph)$], 91.2 (s, Cp), 48.1 [d, J_{CP} = 23, $C^1(Cy)$], 33.7 [d, J_{CP} = 3, $C^2(Cy)$], 32.9 [s, $C^2(Cy)$], 28.3 [d, J_{CP} = 11, $2C^3(Cy)$], 26.7 [s, $C^4(Cy)$].

Preparation of $[W_2Cp_2(\mu-O:O'-O_2CCF_3)(\mu-PCy_2)(CO)_2]$ (4b**).** Neat CF_3CO_2H (4 μ L, 0.052 mmol) was added to a stirred solution of compound 2 (0.020 g, 0.027 mmol) in dichloromethane (4 mL), and the mixture was further stirred at room temperature for 5 min to give an orange solution. Solvent was then removed under vacuum and the residue was washed with petroleum ether (3 x 3 mL) to yield compound **4b** as an orange solid (0.021 g, 90%). Anal. Calcd for

$C_{26}H_{32}F_3O_4PW_2$: C, 36.14; H, 3.73. Found: C, 35.85; H, 3.50. 1H NMR (300.09 MHz): δ 5.60 (d, J_{HP} = 1, 10H, Cp), 2.60-1.00 (m, 22H, Cy). $^{19}F\{^1H\}$ NMR (282.33 MHz): δ -72.4 (s, CF_3). $^{13}C\{^1H\}$ NMR: δ 218.5 (d, J_{CP} = 6, WCO), 113.2 (q, J_{CF} = 285, CF_3), 91.2 (s, Cp), 48.3 [d, J_{CP} = 24, $C^1(Cy)$], 33.4 [d, J_{CP} = 3, $C^2(Cy)$], 32.9 [s, $C^2(Cy)$], 28.2 [d, J_{CP} = 11, $C^3(Cy)$], 28.18 [d, J_{CP} = 13, $C^3(Cy)$], 26.6 [s, $C^4(Cy)$]; the resonance for the carboxylic C atom could not be identified in this spectrum.

Preparation of $[W_2Cp_2(\mu-SnPh_3)(\mu-PCy_2)(CO)_2]$ (5**).** A suspension containing ca. 0.040 mmol of **1** in tetrahydrofuran (5 mL) was stirred with $ClSnPh_3$ (0.017 g, 0.045 mmol) for 15 min to give a dark brown solution. Solvent was then removed under vacuum and the residue was extracted with toluene and filtered. Solvent was removed again from the filtrate and the residue was extracted with dichloromethane/petroleum ether (1:6) and chromatographed through an alumina column (activity IV) at 288 K. Elution with the same solvent mixture gave a purple fraction yielding, after removal of solvents, compound **5** as a red-purple solid (0.033 g, 75%). Anal. Calcd for $C_{42}H_{47}O_2PSnW_2$: C, 45.81; H, 4.30. Found: C, 45.68; H, 4.23. 1H NMR: δ 7.46 [false d, J_{HSn} = 42, 6H, $H^2(Ph)$], 7.33-7.23 (m, 9H, Ph), 4.78 (s, 10H, Cp), 2.60-0.80 (m, 22H, Cy).

Preparation of $[W_2Cp_2(\mu-PCy_2)(\mu-Ph)(CO)_2]$ (6**).** A suspension containing ca. 0.062 mmol of **1** in tetrahydrofuran (4 mL) was stirred with $CIPbPh_3$ (0.040 g, 0.084 mmol) for 5 min to give a brown solution. Solvent was then removed under vacuum and the residue was extracted with dichloromethane and filtered through diatomaceous earth. Solvent was removed again from the filtrate and the residue was extracted with dichloromethane/petroleum ether (1:4) and chromatographed through an alumina column (activity IV) at 253 K. Elution with the same solvent mixture gave a brown fraction yielding, after removal of solvents, compound **6** as a red solid (0.039 g, 76%). Anal. Calcd for $C_{30}H_{37}O_2PW_2$: C, 43.50; H, 4.50. Found: C, 43.88; H, 4.21. 1H NMR: δ 8.88 [false d, J_{HH} = 7, 2H, $H^2(Ph)$], 8.14 [t, J_{HH} = 7, 1H, $H^4(Ph)$], 6.84 [false t, J_{HH} = 7, 2H, $H^3(Ph)$], 4.93 (s, 10H, Cp), 2.60-1.20 (m, 22H, Cy). $^{13}C\{^1H\}$ NMR: δ 240.5 (d, J_{CP} = 6, WCO), 168.3 [s, $C^2(Ph)$], 133.7 [s, $C^4(Ph)$], 122.7 [s, $C^3(Ph)$], 116.2 [s, $C^1(Ph)$], 86.8 (s, Cp), 51.8 [d, J_{CP} = 24, $C^1(Cy)$], 34.1, 33.4 [2s, $C^2(Cy)$], 28.6 [d, J_{CP} = 12, $C^3(Cy)$], 28.4 [d, J_{CP} = 11, $C^3(Cy)$], 26.8 [s, $C^4(Cy)$].

Preparation of $[AuW_2Cp_2(\mu-PCy_2)(CO)_2(P^iPr_3)]$ (7p**).** A suspension containing ca. 0.037 mmol of **1** in tetrahydrofuran (5 mL) was stirred with $[AuCl(P^iPr_3)]$ (0.015 g, 0.038 mmol) for 15 min to give a dark green solution. Solvent was then removed under vacuum and the residue was extracted with dichloromethane and filtered through diatomaceous earth. Removal of solvent from the filtrate under vacuum yielded compound **7p** as a green solid (0.025 g, ca. 60%). Pure samples of **7p** could not be obtained due to its progressive decomposition upon manipulation. 1H NMR: δ 5.00 (s, 10H, Cp), 2.42 (m, 3H, CH), 1.33 (m, 18H, CH_3), 2.60-1.00 (m, 22H, Cy). 1H NMR (213 K): δ 5.04 (s, 10H, Cp), 2.45 (m, 3H, CH), 1.33 (m, 18H, CH_3), 2.60-1.00 (m, 22H, Cy). $^{31}P\{^1H\}$ NMR (213 K): δ 145.5 (s, br, J_{PW} = 293, $\mu-PCy_2$), 100.5 (d, J_{PP} = 9, J_{PW} = 53, AuP). $^{13}C\{^1H\}$ NMR (233 K): δ 231.4 (s, WCO), 86.1 (s, Cp), 48.0

[d, $J_{CP} = 22$, $C^1(Cy)$], 33.9 [s, br, $C^2(Cy)$], 27.9 [d, $J_{CP} = 11$, $C^3(Cy)$], 26.4 [s, $C^4(Cy)$], 23.3 [d, $J_{CP} = 19$, $C^1(^iPr)$], 20.5 [s, $C^2(^iPr)$].

Preparation of $[AuW_2Cp_2(\mu-PCy_2)(CO)_2\{P(p-tol)_3\}]$ (7t**).** The procedure and workup is identical to that described for **7p**, but using $[AuCl\{P(p-tol)_3\}]$ (0.020 g, 0.0374 mmol). This yielded compound **7t** as a green-brownish solid (0.028 g, ca. 60%). Pure samples of **7t** could not be obtained due to its progressive decomposition upon manipulation.

Preparation of $[Au_2W_2Cp_2(\mu-PCy_2)(CO)_2\{P^iPr_3\}_2](PF_6)$ (8p**).** A suspension containing ca. 0.037 mmol of **1** in tetrahydrofuran (5 mL) was stirred with $[AuCl(P^iPr_3)]$ (0.030 g, 0.076 mmol) for 30 min to give a dark green solution. Then, solid $Tl(PF_6)$ (0.035 g, 0.10 mmol) was added and the mixture was stirred for 5 min to give a green-brownish solution. Solvent was then removed under vacuum and the residue extracted with dichloromethane (3 x 5 mL) and filtered through diatomaceous earth. Solvent was removed again from the filtrate and the residue was dissolved in dichloromethane and chromatographed through an alumina column (activity IV) at 263 K. Elution with the same solvent gave a green fraction yielding, after removal of solvent, compound **8p** as a green solid (0.033 g, 55%). The crystals used in the X-ray diffraction study were grown by the slow diffusion of a layer of diethyl ether into a concentrated dichloromethane solution of the complex at 253 K. Anal. Calcd for $C_{42}H_{74}Au_2F_6O_2P_4W_2$: C, 31.32; H, 4.63; Found: C, 31.13; H, 4.49. $\nu(CO)$ (Nujol): 1861 (m), 1832 (vs). 1H NMR (400.13 MHz): δ 5.11 (s, 10H, Cp), 2.55 (m, 6H, CH), 1.37, 1.34 (2dd, $J_{PH} = 15$, $J_{HH} = 7$, 2 x 18H, CH_3), 2.61-1.29 (m, 22H, Cy).

Preparation of $[Au_2W_2Cp_2(\mu-PCy_2)(CO)_2\{P(p-tol)_3\}_2](PF_6)$ (8t**).** The procedure and workup is identical to that described for **8p**, but using $[AuCl\{P(p-tol)_3\}]$ instead (0.040 g, 0.075 mmol). This yielded compound **8t** as a green solid (0.030g, 46%). Anal. Calcd for $C_{54}H_{74}Au_2F_6O_2P_4W_2$: C, 38.96; H, 4.25; Found: C, 38.60; H, 4.05. 1H NMR (400.13 MHz): δ 7.60-7.00 (m, 24H, C_6H_4), 5.06 (s, 10H, Cp), 2.38 (s, 18H, CH_3), 2.70-1.00 (m, 22H, Cy).

X-Ray structure determination of compound **8p.** X-ray intensity data were collected on a Kappa-Appex-II Bruker diffractometer, using graphite-monochromated MoK_{α} radiation at 100 K. The software APEX³⁹ was used for collecting frames with the ω/ϕ scans measurement method. The Bruker SAINT software was used for data reduction,⁴⁰ and a multi-scan absorption correction was applied with SADABS.⁴¹ Using the program suite WinGX,⁴² the structure was solved by Patterson interpretation and phase expansion using SHELXL97, and refined with full-matrix least squares on F^2 using SHELXL97.⁴³ One of the isopropyl groups was found to be disordered over two positions, conveniently modelled with occupancy factors of 0.75/0.25. However, an incipient disorder in one of the cyclopentadienyl ligands could not be properly modelled. During the final stages of refinement, all the positional parameters and the anisotropic temperature factors of all non-H atoms were refined anisotropically, except for the carbon atoms involved in disorder, which were refined isotropically. Moreover, atoms C(3) and C(5) had to be refined in combination with the instructions DELU and SIMU. All hydrogen atoms were geometrically placed and refined using a riding model.

Table 5. Crystal Data for Compound **8p**.

mol formula	$C_{42}H_{74}Au_2F_6O_2P_4W_2$
mol wt.	1610.53
cryst syst	triclinic
space group	$P-1$
radiation (λ , Å)	0.71073
a , Å	9.7938(13)
b , Å	14.502(2)
c , Å	17.625(2)
α , deg	88.717(7)
β , deg	77.756(7)
γ , deg	83.607(7)
V , Å ³	2431.1(6)
Z	2
calcd density, gcm ⁻³	2.200
absorpt. coeff., mm ⁻¹	10.92
temperature, K	110.0(1)
θ range (deg)	1.18 to 26.44
index ranges	-11, 12; -18, 18;
(h, k, l)	0, 22
no. of reflns collected	38744
no. of indepreflns (R_{int})	9951 (0.0441)
reflns with $I > 2\sigma(I)$	7146
R indexes [data with $I > 2\sigma(I)$] ^a	$R_1 = 0.0387$ $wR_2 = 0.079^b$
R indexes (all data) ^a	$R_1 = 0.0733$ $wR_2 = 0.0944^b$
GOF	1.035
no. of restraints/params	15 / 534
$\Delta\rho$ (max, min), e Å ⁻³	1.954, -1.791

$$^aR = \sum |F_o| - |F_c| / \sum |F_o|, wR = [\sum w(|F_o|^2 - |F_c|^2)^2 / \sum w|F_o|^2]^{1/2}. w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP] \text{ where } P = (F_o^2 + 2F_c^2)/3. ^b a = 0.0241, b = 25.2180.$$

Computational details. All computations were carried out using the GAUSSIAN03 package,⁴⁴ in which the hybrid method B3LYP was used with the Becke three parameters exchange functional⁴⁵ and the Lee-Yang-Parr correlation functional.⁴⁶ Effective core potentials (ECP) and their associated double- ζ LANL2DZ basis set were used for the metal atoms.⁴⁷ The light elements (P, O, C and H) were described with 6-31G* basis.⁴⁸ Geometry optimizations were performed under no symmetry restrictions, using initial coordinates derived from X-ray data of closely related compounds, and frequency analyses were performed for all the stationary points to ensure that a minimum structure with no imaginary frequencies was achieved. The topological analysis of the electron density was carried out with the *Xaim* routine.⁴⁹

Notes and references

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†Electronic supplementary information (ESI) available: A PDF file containing comments on the structure of compound **5**, the complete reference 44 and results of DFT calculations, and a CIF file for compound **8p**. CCDC-1009449 (**8p**). DOI: 10.1039/b000000x/

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