Transition-metal derivatives of the functionalized cyclopentadienyl ligand. XVI. Synthesis of the bridged complexes $[(\mu\text{-}\eta^5\text{-}C_5H_4PPh_2)M(CO)_2]_2$ (M = Cr, Mo, W). X-Ray crystal structure of the dihydride derivative $[(\mu\text{-}\eta^5\text{-}C_5H_4PPh_2)W(CO)_2H]_2$

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Four synthetical methods, implying basically the oxidation of the anionic species $[(\eta^5\text{-}C_5H_4PPh_2)M(CO)_3]^-$ [M = Cr, ($\mathbf{2a}^-$), Mo ($\mathbf{2b}^-$), W ($\mathbf{2c}^-$)] to produce the new homobimetallic derivatives $[(\mu,\eta^5\text{-}C_5H_4PPh_2)M(CO)_2]_2$ (*M*—*M*), [M = Cr (**1a**), Mo (**1b**), W (**1c**)] of the heterodifunctional diphenylphosphinocyclopentadienyl bridging ligand, have been investigated. The first approach proceeds in two steps: thus the electrochemical oxidation of the complexes $\mathbf{2a}^-$and $\mathbf{2b}^-$ leads to the metal–metal bonded dimetallic complexes $[(\eta^5\text{-}C_5H_4PPh_2)M(CO)_3]_2$ (*M*—*M*), [M = Cr (**5a**), Mo (**5b**)]; the irradiation of these complexes **5a** and **5b** with a high-pressure Hg lamp affords the corresponding decarbonylated bridged complexes **1a** and **1b**. The second method, using silver tetrafluoroborate as the oxidant of the anions $\mathbf{2a}^-$ to $\mathbf{2c}^-$, leads to the formation of tetrametallic cyclic complexes of silver and Group 6 transition metals $[(\mu\text{-}\eta^5\text{-}C_5H_4PPh_2[M(CO)_3Ag]_2$, [M = Cr (**6a**), Mo (**6b**), W (**6c**)] but the splitting of these compounds into bimetallic complexes **1a**–**c** and metallic silver appears neither easy nor selective. As a third procedure, the hydrido complexes $(\eta^5\text{-}C_5H_4PPh_2)M(CO)_3H$ [M = Cr (**3a**), Mo (**3b**), W (**3c**)] are irradiated with a high-pressure Hg lamp. This procedure is useful to prepare **1b** but is non-selective in the two other cases, affording mainly bimetallic dihydrido-bridged complexes $[(\mu\text{-}\eta^5\text{-}C_5H_4PPh_2)M(CO)_2H]_2$ [M = Mo (**7b**), W (**7c**)] and **1a** or **1b**, as a result of the expected competition between the dehydrogenation and the decarbonylation processes. The X-ray molecular structure of **7c** points out the transoïd disposition of the hydrido ligands, which could well be a factor of its inertness in a spontaneous dehydrogenation process towards **1c**. Finally, the most efficient method requires the preliminary preparation of the iodo complexes $(\eta^5\text{-}C_5H_4PPh_2)M(CO)_3I$ [M = Cr (**4a**), Mo (**4b**), W (**4c**)], which are reacted in toluene with their anionic parents $\mathbf{2}^-$. This last method is particularly useful for preparing **1a** and **1c**.

Complexes des métaux de transition avec les ligands cyclopentadienyles fonctionnalisés. XVI. Synthèse des complexes dimétalliques $[(\mu\text{-}\eta^5\text{-}C_5H_4PPh_2)M(CO)_2]_2$ (M = Cr, Mo, W). Structure moléculaire du derivé dihydrure $[(\mu\text{-}\eta^5\text{-}C_5H_4PPh_2)W(CO)_2H]_2$. Afin d'accéder à la série des complexes homobimétalliques pontés $[(\mu\text{-}\eta^5\text{-}C_5H_4PPh_2)M(CO_2)]_2$ (*M*—*M*), [M = Cr (**1a**), Mo (**1b**), W (**1c**)] du ligand hétérodifonctionnel pontant diphénylphosphinocyclopentadienyle, quatre possibilités de préparations ont´eté étudiées. Elles impliquent fondamentalement l'oxydation des anions $[(\eta^5\text{-}C_5H_4PPh_2)M(CO)_3]^-$ [M = Cr ($\mathbf{2a}^-$), Mo ($\mathbf{2b}^-$), W ($\mathbf{2c}^-$)]. La première approche met d'abord en jeu l'oxydation électrochimique de $\mathbf{2a}^-$ et $\mathbf{2b}^-$ conduisant aux complexes à liaison métal–métal $[(\eta^5\text{-}C_5H_4PPh_2)M(CO_3)]_2$ (*M*—*M*), [M = Cr (**5a**), Mo (**5b**)] dont l'irradiation sous UV conduit aux dérives recherchés **1a** et **1b**. La deuxième, utilisant comme oxydant le tétrafluoborate d'argent, conduit à la formation de complexes tétramétalliques cycliques $[(\mu\text{-}\eta^5\text{-}C_5H_4PPh_2)M(CO)_3Ag]_2$ [M = Cr (**6a**), Mo (**6b**), W (**6c**)]. La troisième voie met en jeux l'irradiation UV des hydrures $(\eta^5\text{-}C_5H_4PPh_2)M(CO)_3H$, [M = Cr (**3a**), Mo (**3b**), W (**3c**)]. Celle-ci se traduit par la deshydrogénation de **3b** en **1b**, mais la décarbonylation de **3c**, conduit au complexe dihydrure ponté $[(\mu\text{-}\eta^5\text{-}C_5H_4PPh_2)W(CO)_2H]_2$, **7c** dont la structure a été determinée. Finalement, la quatrième méthode exige la préparation préalable des iodures $(\eta^5\text{-}C_5H_4PPh_2)M(CO)_3I$ [M = Cr (**4a**), Mo (**4b**), W (**4c**)] qui réagissent aisément avec les anions correspondants $\mathbf{2a}^-$–$\mathbf{2c}^-$.

We are currently involved in the synthesis of various dinuclear compounds in which two functionalized cyclopentadienyls, acting as eight-electron ligands, bridge the two metallic centers. This bridging forces the metallic atoms to remain in close proximity and has been shown, specially in the case of rhodium(I) complexes,[1] to promote reactions in which the two metal centers cooperate.[2] In extending these studies to metal–metal bonded dimers of the Group 6 transition metals, we anticipated that bridging might stabilize new dimetallic species and modify the course of reactions in which homolytic or heterolytic splittings of the metal–metal bond play a prominent part.[3] In the present paper, we shall describe and compare synthetic processes affording the dinuclear complexes of the general formula $[(\mu\text{-}\eta^5\text{-}C_5H_4PPh_2)M(CO)_2]_2$ [M = Cr (**1a**), Mo (**1b**), W (**1c**)].

Using the monometallic anionic complexes $[(\eta^5\text{-}C_5H_4PPh_2)M(CO)_3]^-$[M = Cr ($\mathbf{2a}^-$), Mo ($\mathbf{2b}^-$), W ($\mathbf{2c}^-$)] as starting materials, four synthetic attempts implying basically oxidative processes were investigated, namely: (i) electro- and photo-chemical transformations of the anions $\mathbf{2a}^-$, $\mathbf{2b}^-$ and $\mathbf{2c}^-$; (ii) chemical oxidation of the anions $\mathbf{2a}^-$, $\mathbf{2b}^-$ and $\mathbf{2c}^-$ by

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silver tetrafluoroborate; (iii) photochemical dehydrogenation of the hydrides $(\eta^5\text{-}C_5H_4PPh_2)M(CO)_3H$ [M = Cr (**3a**), Mo (**3b**), W (**3c**)]; and (iv) metal–metal bond formation by reaction of the lithium salts [Li][**2**] with the corresponding iodo complexes $(\eta^5\text{-}C_5H_4PPh_2)M(CO)_3I$ [M = Cr (**4a**), Mo (**4b**), W (**4c**)].

Interestingly, the first process includes the primary formation of metal–metal bonded complexes $[(\eta^5\text{-}C_5H_4PPh_2)M(CO)_3]_2$ [M = Cr (**5a**), Mo (**5b**)], the second one affords novel tetrametallic M—Ag cyclic complexes $[(\mu\text{-}\eta^5\text{-}C_5H_4PPh_2)M(CO)_3Ag]_2$ [M = Cr (**6a**), Mo (**6b**), W (**6c**)] and the third one also leads to novel dimetallic dihydrides $[(\mu\text{-}\eta^5\text{-}C_5H_4PPh_2)M(CO)_2H]_2$ [M = Mo (**7b**), W (**7c**)]. The X-ray molecular structure of the dihydride **7c** is also presented and discussed in comparison with the already known parent compounds $[(\eta^5\text{-}C_5H_5)W(CO)_2(\mu\text{-}H)]_2$ ($W{=}W$), related to the series of non-bridged complexes.[4]

Preparations of the molybdenum complex **1b** and its X-ray crystal structure, together with that of one of the tetrametallic cyclic complexes $[(\mu\text{-}\eta^5\text{-}C_5H_4PPh_2)Mo(CO)_3Ag]_2$, have already been reported in two preliminary communications[5,6]

Results

The complex $[(\mu\text{-}\eta^5\text{-}C_5H_4PPh_2)Mo(CO)_2]_2$, **1b**, is an interesting example of a dinuclear complex having a metal–metal bond supported by ‘flexible’ bridging ligands. As described hereafter chromium and tungsten analogs have now been prepared. Beside elemental analysis data, the three compounds **1a**–**1c** have been identified by their mass spectra (DCI/NH_3), which are in good agreement with the expected isotopic pattern calculated for dimetallic complexes. In addition, they were also easily characterized by spectroscopic methods as shown below.

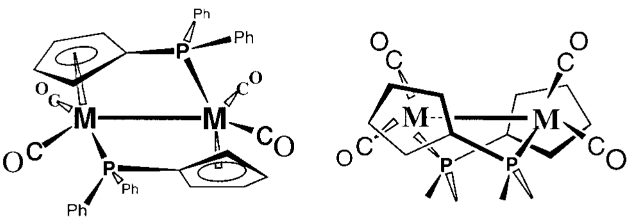
As shown in Table 1, the most evident analogies appear in the IR spectra in the C—O stretching frequency region, where the observation of four bands agrees with the expected C_{2v} symmetry. Moreover, comparison of these spectra with that of the centrosymmetric metal–metal bonded complex $[(\eta^5\text{-}C_5H_5)Mo(CO)_2PPh_3]_2$ [7] [1850 (s), 1831(vs) cm^{-1}] suggests the assignment of the two higher frequency bands of the C_{2v} bridged complexes **1a**–**1c**, to the in-phase stretching modes. The observed spectra of **1a**–**1c** are also comparable with that exhibited by the $[\mu\text{-}(Ph_2P)CH_2][M(\eta^5\text{-}C_5H_5)(CO)_2]_2$ complexes, which nevertheless, interestingly show a low frequency shift [1919(s), 1882(vs), 1848(m), 1828(s) for M = Mo[8a] and 1911(s), 1875(vs), 1837(m), 1815(s) for M = W[8b]] in the same solvent.

In the ^1H NMR spectra, the four protons of each cyclopentadienyl ligand are non-equivalent, confirming the absence of a symmetry plane in the C_5H_4—P fragment as shown in Scheme 1. From the values of the $J_{H\text{-}P}$ coupling constants, it is also suggested that the two signals at higher field in the three complexes **1a**–**1c** correspond to the protons in the α positions to the phosphorus atoms. Noticeably, the four cyclopentadienyl signals exhibit an important solvent effect (see Experimental). This last phenomena is most clearly observed with **1a** and **1b**. A last argument in favor of the equivalency of the two $[(\eta^5\text{-}C_5H_4PPh_2)M(CO)_2]$ fragments in **1a**–**1c** is provided by the $^{31}P\{^1H\}$ NMR spectra, which exhibit only one signal (Table 1). In all three cases, the chemical shifts appear as characteristic of the coordination of the phosphorus atom to the metal atom. In compound **1c**, each ^{31}P nucleus is coupled with one ^{183}W leading to a low intensity doublet that brackets the uncoupled singlet; the isotopic figure corresponds to the isotopic ratio $^{183}W/W$ (14.28%).

Table 1 Spectral characteristics of the bridged complexes **1a**-**1c**

	IR/cm^{-1} [a]	$^{31}P\{^1H\}$ NMR/ppm
$[(\mu\text{-}\eta^5\text{-}C_5H_4PPh_2)Cr(CO)_2]_2$	1941 vs	88.5[b]
1a	1890 vs	
	1864 w	
	1844 s	
$[(\mu\text{-}\eta^5\text{-}C_5H_4PPh_2)Mo(CO)_2]_2$	1943 vs	68.2[c]
1b	1888 vs	
	1868 w	
	1846 s	
$[(\mu\text{-}\eta^5\text{-}C_5H_4PPh_2)W(CO)_2]_2$	1938 vs	39.9 ($J_{P\text{-}W}$ = 140 Hz)[b]
1c	1892 vs	35.0 ($J_{P\text{-}W}$ = 164 Hz)[c]
	1863 w	
	1838 s	

[a] In toluene solution. [b] 81.015 MHz, $[^2H_6]$acetone [c] 32.40MHz, $[^2H_6]$benzene.



1a–1c

Scheme 1

Preparation of the diphenylcyclopentadienyl monometallic starting materials

Fig. 1 sums up the various synthetic pathways used to prepare the three dimetallic complexes **1a**–**1c** *via* four methods, each starting from the anionic complexes $[(\eta^5\text{-}C_5H_4PPh_2)M(CO)_3]^-$, **2a**$^-$–**2c**$^-$. These anions were prepared from the lithium diphenylphosphinocyclopentadienyde using tricarbonyl metal derivatives since the reactions with the hexacarbonyl complexes produce largely the monomeric pentacarbonyl anion $[(\eta^1\text{-}PPh_2C_5H_4)M(CO)_5]^-$ (in which the phosphorus atom is bonded to the metal).

By using the heptatrienyl tricarbonyl complexes $(\eta^6\text{-}C_7H_8)M(CO)_3$ (M = Cr, Mo) in reflux with THF, the anions **2a**$^-$ and **2b**$^-$ were obtained in good yield (99 and 91%, respectively, with respect to $(\eta^6\text{-}C_7H_8)M(CO)_3$).[9] Nevertheless, the synthesis of $(\eta^6\text{-}C_7H_8)Cr(CO)_3$ itself is slow (it needs about 20 h of reflux); in addition the substitution reaction of $(\eta^6\text{-}C_7H_8)Cr(CO)_3$ with $Li(C_5H_4PPh_2)$ needs a three-day period of reflux to reach completeness. Moreover, the product [Li][**2a**] was formed along with a pyrophoric compound whose separation is awkward and decreases its yield (60%). These constraints prompted us to use the complex $(CH_3CH_2CN)_3Cr(CO)_3$ as the starting material. In our hands, the preparation of this complex following the published procedure[10] also gave a modest yield (60%), but its reaction *in toluene* with a suspension of $Li(C_5H_4PPh_2)$ very conveniently affords [Li][**2a**], which precipitated in high purity and good yield [99% with respect to $(CH_3CH_2CN)_3Cr(CO)_3$].

The preparation of **2c**$^-$, starting from the cycloheptatrienyl complex $(\eta^6\text{-}C_7H_8)W(CO)_3$, has also been tested. In addition to the slowness of the preparation of this starting material, its reaction with $Li(C_5H_4PPh_2)$ in THF reflux is accompanied by decomposition. Therefore a second method of preparation was preferred using $(CH_3CN)_3W(CO)_3$ as the starting material.[11] As in the case of the chromium compound, the use of suspensions in toluene of the reactants $(CH_3CN)_3W(CO)_3$ and $Li(C_5H_4PPh_2)$ affords easily a precipitate of the product [Li][**2c**] in high purity and good yield with respect to $(CH_3CN)_3W(CO)_3$ (97%).

The lithium salts [Li][**2a**], [Li][**2b**] and [Li][**2c**] were identified in $^{31}P\{^1H\}$ NMR by signals at chemical shifts (**2a**$^-$,

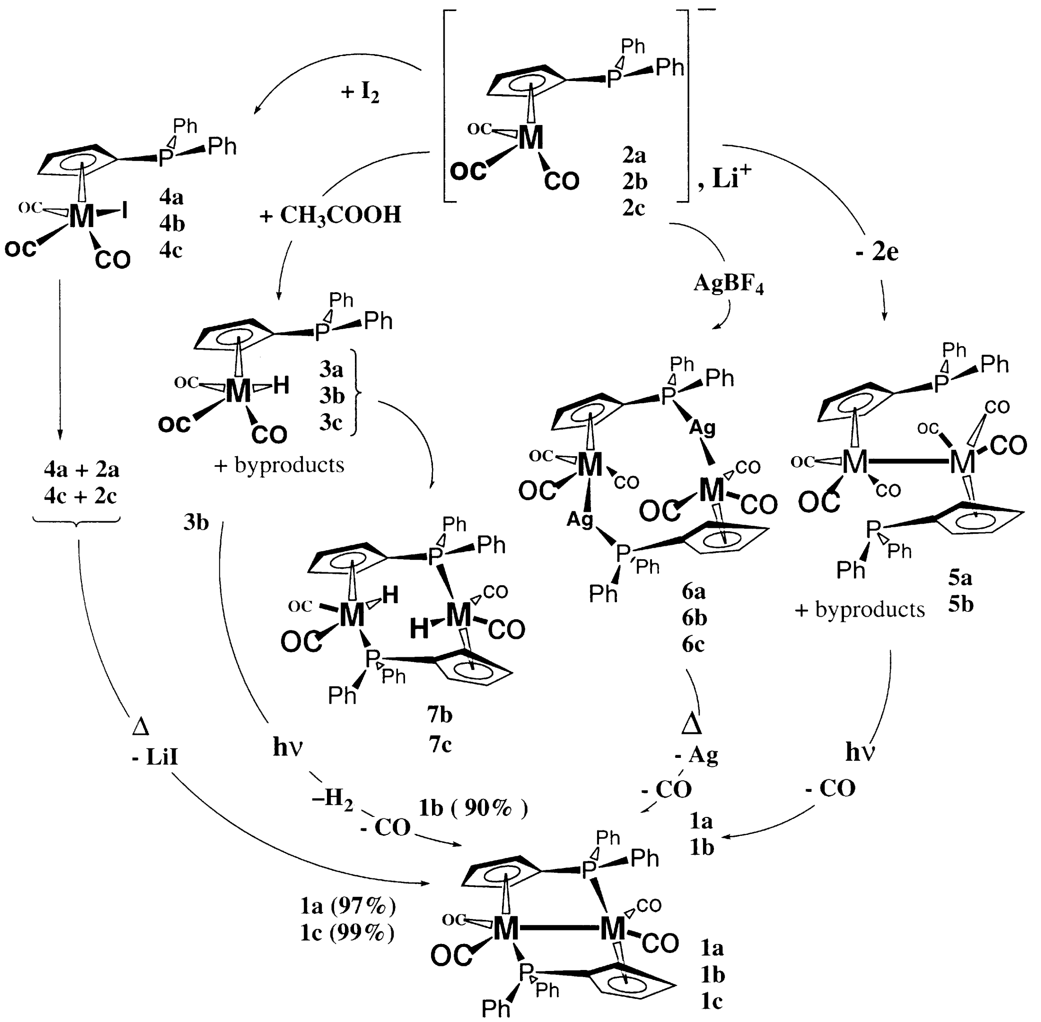


Fig. 1 The four synthetic reaction paths affording the bridged homobimetallic derivatives $[(\mu\text{-}\eta^5\text{-}C_5H_4PPh_2)M(CO)_2]_2$ [M = Cr (**1a**), Mo (**1b**), W (**1c**)]

δ – 17.0(s); **2b**$^-$, δ – 18.2 (s); **2c**$^-$, δ – 17.2 (s + d, $^2J_{P\text{-}W} = 41$ Hz) in [$^2H_6$]benzene, consistent with a non-coordinated phosphorus arm and in the infrared, surprisingly, by four C—O stretching bands. The occurrence of four bands instead of the three normally expected for tricarbonyl compounds has been attributed to the formation of a species in which an interaction occurs between the CO groups and a lithium cation.[12]

The new hydrido complexes $(\eta^5\text{-}C_5H_4PPh_2)M(CO)_3H$ [M = Cr (**3a**), Mo (**3b**), W (**3c**)] were readily prepared by adding one equivalent of glacial acetic acid to toluene solutions of the lithium salts [Li][**2**]. The solutions (from orange for chromium to yellow for the tungsten derivatives) instantaneously turned red (from bright red for chromium to orange red for the tungsten derivatives) together with the formation of a light precipitate of lithium acetate. The hydrido complexes were identified in $^{31}P\{^1H\}$ NMR spectra by singlets at chemical shifts consistent with a dangling phosphino group (**3a**, δ – 19.8; **3b**, δ – 19.5; **3c**, δ – 19.8), in ^1H NMR spectra by their hydride signals at high field [**3a**, δ – 5.39(s); **3b**, δ – 5.26(s); **3c**, δ – 7.28 (s + d, $^1J_{H\text{-}W} = 36$ Hz)] and in infrared by two bands that compare quite well with those of their parent compounds $(\eta^5\text{-}C_5H_5)M(CO)_3H$. The formation of byproducts was also observed and will be discussed further. The three complexes **3a**–**3c** have been obtained as crystalline solids by concentrating and cooling their solutions in toluene (or THF) to –18 °C.

The transformation of the preceding anionic compounds **2a**$^-$–**2c**$^-$ into the iodo derivatives $(\eta^5\text{-}C_5H_4PPh_2)M(CO)_3I$, (**4a**–**4c**) has been easily performed, by simply adding iodine to a toluene solution of **2a**$^-$–**2c**$^-$. The three new complexes **4a**–**4c** were easily identified, namely in $^{31}P\{^1H\}$ NMR spectra, which show singlets at δ –14.0 and –12.8 in [$^2H_6$]acetone, respectively, for **4a** and **4b** and at –16.1 (s + d, $J_{P\text{-}W} = 71$ Hz) in [$^2H_6$]benzene for **4c**, fully consistent with a pendant phosphorus atom.

Electro- and photo-chemical processes leading to the bridged dinuclear complexes 1a and 1b: method A

The transformation of the mononuclear anionic complexes **2a**$^-$–**2c**$^-$, into the dinuclear neutral complexes **1a**–**1c** can be regarded as the succession of two processes, the oxidative coupling of the anions, then the substitution of a carbonyl ligand bonded to one of the metal centers by the phosphino group bonded to the other metal center. We have already reported our observations in the case of the *molybdenum* complexes.[6] We mention that in this case, the primary formation of a dimetallic neutral species $[(\eta^5\text{-}C_5H_4PPh_2)Mo(CO)_3]_2$ (*M*—*M*), **5b** (Fig. 1), resulted directly from the electrochemical oxidation of the mononuclear anionic complexes **2b**$^-$.

We have attempted to apply the same processes to the *chromium* compounds. An oxidative electrolysis of **2a**$^-$ was performed at 0 mV on a platinum-gauze electrode in acetone with 0.1 M Et_4NBF_4. Noticeably, as in the case of the molybdenum compounds, a phenomenum of saturation of the electrode occurred, limiting the number of electrons exchanged per mole of **2a**$^-$ during the exhaustive electrolysis. Therefore, for purposes of electron counting and electrosynthesis, an electrolytic cell without a frit was used. After the electrolysis, the acetone solution showed complicated infrared and

$^{31}P\{^1H\}$NMR spectra, from which the bridged complex **1a** was easily identified. Additionally, a peak at δ — 19.0 suggests the presence of a complex bearing a dangling phosphine arm. To this signal observed in the $^{31}P\{^1H\}$ NMR spectra, one can associate, in respect of the concomitant intensity variations during various essays, two bands in the infrared spectra at 1978 and 1908 cm^{-1}. These data were finally assigned to the metal–metal bonded complex **5a** resulting probably from the dimerization of the electrogenerated radical $\{(\eta^5-C_5H_4PPh_2)Cr(CO)_3\}$.[13] Attempts to transform **5a** into **1a** failed, leading to the precipitation of an unidentified green powder.

We have also tried to use the considered two-phase electro-photochemical process to get the *tungsten* compound **1c**. In this case the electrolysis, performed at 600 mV, also on a platinium-gauze electrode in acetone with 0.1 M Et_4NBF_4, stopped after the consumption of only 0.5 Faraday mol^{-1}. The absence in the infrared spectra of any band in the 2000–1800 cm^{-1} region where **5b** was characterized and the presence in the $^{31}P\{^1H\}$ NMR spectra of peaks without the characteristic satellites due to the coupling with ^{183}W show that the expected products, **5c** and **1c**, do not form. Considering this result, we thought it useless to perform further photochemical experiments.

An attempt to oxidize the anion by silver tetrafluoroborate: method B

A further possibility to get the dimeric complexes **1a**–**1c** is chemically to oxidize the anionic complexes $\mathbf{2a}^-$–$\mathbf{2c}^-$. Considering the value of the oxidation potential of $\mathbf{2b}^-$ ($E_p = 100$ mV), it is advisable to use ferrocenium as an oxidizing reagent; unfortunately we were unable to get a clean reaction. For this reason, we extended the investigation using silver cation as the oxidant.

As already reported in the case of the molybdenum compounds,[5] when 1 equiv of silver tetrafluoroborate crystals was added to a toluene solution of one of anions $\mathbf{2a}^-$–$\mathbf{2c}^-$, a grey precipitate of lithium tetrafluoroborate appeared, which was easily removed. In each case one can obtain from the resulting solution, in moderate yield, yellow crystals of the crown-like complexes $[(\mu-\eta^5-C_5H_4PPh_2)M(CO)_3Ag]_2$ [M = Cr (**6a**), Mo (**6b**), W (**6c**)]. These complexes have been fully characterized by elemental analysis, MS, IR and NMR spectroscopies and their crystal structures have been solved.[14] The scheme shown in Fig. 1 is based on the results of this study.

As far as the synthesis of the complexes **1a**–**1c** is concerned, it was effectively possible to observe their formation by heating at reflux the toluene solutions of their respective silver derivatives **6a**–**6c**. But these reactions are non-selective and unidentified products form through a decomposition process.

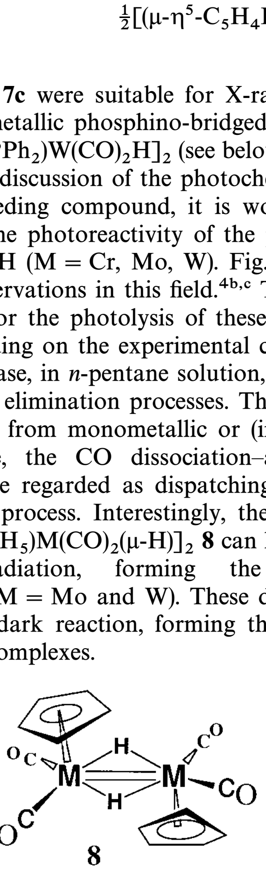
Synthesis of the hydrido complexes $(\eta^5-C_5H_4PPh_2)M(CO)_3H$ [M = Cr (3a), Mo (3b), W (3c)] and $[(\mu-\eta^5-C_5H_4PPh_2)M(CO)_2H]_2$ [M = Mo (7b), W (7c)]: some observations on the photochemical dehydrogenation processes: method C

The hydrido complexes $(\eta^5-C_5H_4PPh_2)M(CO)_3H$ [M = Cr (**3a**), Mo (**3b**), W (**3c**)] were expected to be the direct precursors of the dimeric compounds **1a**–**1c** and lead to efficient pathways for their dehydrogenation and decarbonylation reactions. The preparation of these hydrido compounds was attempted from the lithium salt [Li][**2**] through reaction with acetic acid. In the case of the *chromium* complex, the reaction in toluene at room temperature affords mainly the monometallic hydrido complex **3a**, but the formation of small quantities of **1a** suggests also a spontaneous multistep transformation of **3a** into **1a**. In the case of the *molybdenum* complex the reaction of [Li][**2b**] with acetic acid affords similarly the hydrido complex $(\eta^5-C_5H_4PPh_2)Mo(CO)_3H$, **3b**, but in addition gives noticeable amounts of a compound **7b** that was characterized in ^1H NMR spectra by a high-field signal at δ — 5.29 and in $^{31}P\{^1H\}$ NMR spectra by a singlet at δ 59.37, suggesting the coordination of the phosphine arm. In the *tungsten* case, analogous mixtures were obtained, from which the hydrido complex $(\eta^5-C_5H_4PPh_2)W(CO)_3H$, **3c**, was easily identified by its IR and ^1H NMR spectra. Moreover, by slow evaporation of an acetone solution of **3c**, crystals of the compound **7c** were obtained, suggesting the occurrence of a substitution process, even in absence of irradiation:

$$\underset{\mathbf{3c}}{(\eta^5-C_5H_4PPh_2)W(CO)_3H} \xrightarrow{\Delta,\ -CO} \underset{\mathbf{7c}}{\tfrac{1}{2}[(\mu-\eta^5-C_5H_4PPh_2)W(CO)_2H]_2}$$

The crystals of **7c** were suitable for X-ray analysis which confirmed the dimetallic phosphino-bridged molecular structure $[(\mu-\eta^5-C_5H_4PPh_2)W(CO)_2H]_2$ (see below).

To support the discussion of the photochemical transformation of the preceding compound, it is worth summarizing some aspects of the photoreactivity of the parent complexes $(\eta^5-C_5H_5)M(CO)_3H$ (M = Cr, Mo, W). Fig. 2 recalls part of the published observations in this field.[4b,c] The various pathways postulated for the photolysis of these complexes differ essentially, depending on the experimental conditions (in CO matrice, in gas phase, in *n*-pentane solution,...), in the nature of the dihydrogen elimination processes. They are postulated to occur either (i) from monometallic or (ii) from bimetallic species. Therefore, the CO dissociation–association equilibrium (iii) can be regarded as dispatching the system into one or the other process. Interestingly, the hydrido-bridged complexes $[(\eta^5-C_5H_5)M(CO)_2(\mu-H)]_2$ **8** can lose H_2 reversibly upon UV irradiation, forming the dimers $[(\eta^5-C_5H_5)M(CO)_2]_2$ (M = Mo and W). These dimers are known to add CO in a dark reaction, forming the saturated $[(\eta^5-C_5H_5)M(CO)_3]_2$ complexes.



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Concerning the presently studied hydrido complexes **3a**–**3c**, the presence of a pendant ligand PPh_2 led us to anticipate photoprocesses notably different from those described in Fig. 2. Because of the spontaneous decarbonylation of **3b** into **7b** (or of **3c** into **7c**), it was not expected to be easy to get significant data for the separate pathways. Therefore we restricted

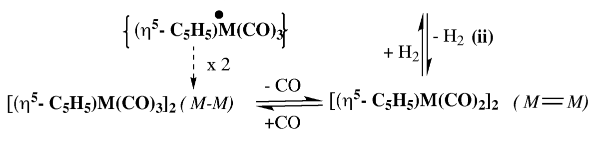

Fig. 2 Photoreactivity in the parent series of non-bridged cyclopentadienyl hydrido tricarbonyl complexes $(\eta^5-C_5H_5)M(CO)_3H$ (M = Mo and W) as summarized from references 4

ourself to preliminary experiments. Thus the solutions containing *both* **3b** and **7b** (or **3c** and **7c**) have been irradiated with a UV high-pressure lamp. The mixture of *molybdenum* complexes transformed *in toto* into complex **1b**, affording no additional observations. In contrast, in the case of the *tungsten* complexes, monitoring by infrared spectroscopy of the progress of the photoreaction showed the characteristic C—O stretching bands of the complexes **1c** and **5c** [this compound being identified by its bands at 1963(s) and 1906(s) cm^{-1}, similar to those of **5b** at 1959 and 1913 cm^{-1}]. The appearance of **5c** shows that the irradiation of **3c** induces a dehydrogenation process, which ends with the formation of a metal–metal bonded complex:[15]

$$\underset{\mathbf{3c}}{(\eta^5\text{-}C_5H_4PPh_2)W(CO)_3H} \xrightarrow{h\nu,\ -H_2} \underset{\mathbf{5c}}{\tfrac{1}{2}[(\eta^5\text{-}C_5H_4PPh_2)W(CO)_3]_2\ (W{-}W)}$$

Finally in the case of the *chromium* compounds, the irradiation of **3a** (in fact of a mixture containing in addition small amounts of **1a**) afforded a light green powder. This green product, which apparently from its ponderal analysis, does not contain the diphenylphosphinocyclopentadienyl ligand, was not considered for further studies. To sum up, as regards the efficiency, the preparation of compounds **1a**–**1c** by the irradiation of the hydrido complexes (method C) appears limited to the previously described case of the molybdenum compound **1b**, which was obtained with high yield (90%).[6]

The X-ray molecular structure of $[(\mu,\eta^5\text{-}C_5H_4PPh_2)W(CO)_2H]_2$, 7c

The noticeable stability of the dihydrido complex **7c** with respect to the dehydrogenation process led us to try to obtain a better understanding of its structure. Therefore an X-ray crystallographic investigation of a suitable crystal of **7c** was carried out.

The molecular geometry and atomic numbering scheme of **7c** are shown in Fig. 3 and selected bond lengths and angles are given in Table 2. In a perspective view the most prominent features are the dinuclear nature of the complex and the head-to-tail disposition of the bridging ligands. The geometry of each $(\eta^5\text{-}C_5H_4\text{—})W(CO)_2(Ph_2P\text{—})H$ moiety conforms to the 'four-legged piano stool' description with the four 'legs' including one phosphine, two carbonyl ligands and the hydride ligand. The two carbonyl groups are in cisoïd positions. Those two moieties are related by centrosymmetry and, in particular, the two M—H bonds occupy transoïd positions with respect to the molecular center of symmetry. The metal–metal distance, 4.5408(6) Å, is long enough to prevent any metal–metal interaction.

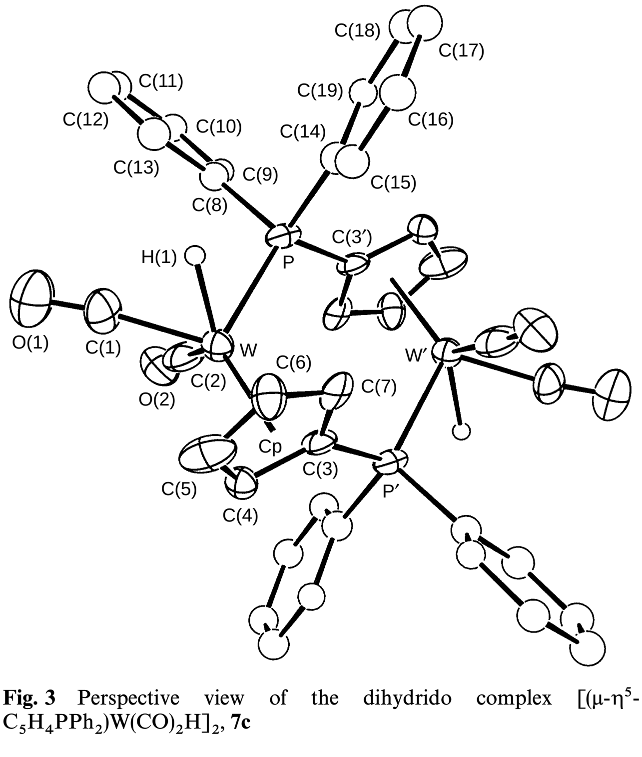

Fig. 3 Perspective view of the dihydrido complex $[(\mu\text{-}\eta^5\text{-}C_5H_4PPh_2)W(CO)_2H]_2$, **7c**

Table 2 Selected bond lengths (Å) and angles (deg) with e.s.d.s in parentheses for the complex $[(\mu\text{-}\eta^5\text{-}C_5H_4PPh_2)W(CO)_2H]_2$ **(7c)**

W···W′	4.5408(6)		
W—P	2.413(2)	W—C(1)	1.923(10)
W—Cp	2.004(8)	W—C(2)	1.942(10)
W—H(1)	1.65(5)		
W—C(3)	2.294(7)	C(3)—C(4)	1.443(10)
W—C(4)	2.323(7)	C(4)—C(5)	1.421(12)
W—C(5)	2.358(9)	C(5)—C(6)	1.372(13)
W—C(6)	2.367(8)	C(6)—C(7)	1.400(11)
W—C(7)	2.312(8)	C(7)—C(3)	1.360(10)
C(1)—O(1)	1.145(13)	C(2)—O(2)	1.195(12)
P—W—Cp	125.4(2)	Cp—W—C(2)	125.6(4)
P—W—C(1)	103.2(3)	Cp—W—H(1)	119(2)
P—W—C(2)	79.4(3)	C(1)—W—C(2)	77.7(4)
P—W—H(1)	66(2)	C(1)—W—H(1)	61(2)
Cp—W—C(1)	127.5(4)	C(2)—W—H(1)	116(2)

′ denotes the $1 - x, -y, 1 - z$ symmetry operation. Cp is the centroid of the C(3)C(4)C(5)C(6)C(7) cyclopentadienyl ring.

There have been numerous studies of the cyclopentadienyl complexes that adopt a 'four-legged piano stool' geometry but, among the hydrido-substituted complexes of the type $(\eta^5\text{-}C_5R_5)M(CO)_2LH$, whose structures are similar to the fragment $(\eta^5\text{-}C_5H_4\text{—})W(CO)_2(Ph_2P\text{—})H$ of **7c**, only the structure of the chromium derivative $(\eta^5\text{-}C_5H_5)Cr(CO)_2(PPh_2Cy)H$ (Cy = cyclohexyl)[16] and of the molybdenum derivatives $(\eta^5\text{-}C_5Me_5)Mo(CO)_2(CNBu^t)H$ [17] and $(\eta^5\text{-}C_5Me_5)Mo(CO)_3H$ [18] have been reported. In the former molybdenum compound a Mo—H distance of 1.63(4) Å was observed while the neutron diffraction study of the latter affords 1.789(7) Å. Our determination of a W—H distance of 1.65(5) Å is coherent with the former observation as the covalent radius of tungsten is only 0.01 Å longer than that of molybdenum; nevertheless the lower precision of our result precludes any comparison with the latter neutron diffraction determination.

To our knowledge, **7c** is the first reported structure of a tungsten derivative of the type $(\eta^5\text{-}C_5R_5)M(CO)_2LH$, and this limits therefore the comparisons that can be made. The average W—CO distance of 1.93 Å in **7c** appears, as expected, some 0.05 Å shorter than the values generally observed in $[(\eta^5\text{-}C_5R_4R')W(CO)_3]$ complexes (R = R′ = Me; R = H, R′ = various groups).[19] Concerning the C—O distances, it would be unwise, in view of their e.s.d.s, to try a precise comparison; we will just consider that they lie in the normal range. The angles between the 'legs' and the (Cp)—W axis and also between them indicate no significant deviations worth mention.

Considering the dehydrogenation processes in **7c**, it is worth noticing the transoïd geometry of the hydrido ligands. Such a mutual position could well be a considerable endergonic hindrance to a reductive elimination process of dihydrogen and it was surprising that both complexes **3c** and **7c** disappear when they are irradiated. Nevertheless, the existence of a facile pathway to the cisoïd isomer, based on the *cis–trans* rearrangement observed[20] in the related monometallic hydride $(\eta^5\text{-}C_5H_5)W(CO)_2(PMe_3)H$, is not excluded and could provide a reasonable explanation of the observations reported above in the description of "method C".

Formation of metal–metal bonds by reaction of the lithium salts [Li][2] with the corresponding iodo complexes (η^5-$C_5H_4PPh_2$)M(CO)$_3$I [M = Cr (4a), Mo (4b), W (4c)]: method D

Such syntheses of some dinuclear metal–metal bonded complexes of molybdenum and tungsten, bridged by one or two heterodifunctional ligands $C_5H_4PPh_2$, have already been reported.[21] Following this method, *THF was used as solvent.* Thus, by heating at reflux solutions of **2b**$^-$ with one equivalent of (η^5-C_5H_5)M(CO)$_3$I (M = Mo, W) for 16 h, the monobridged (CO)$_3$Mo(μ-η^5-$C_5H_4PPh_2$)M(η^5-C_5H_5) (M = Mo, W) were obtained but in low yield. Following this process using **2b**$^-$ with one equivalent of **4b**, the dibridged complex **1b** was obtained, *also in a low yield* (32%). Overall this method appears to be non-selective and all products need to be purified by column chromatography.

We have used the above principle to synthesize the three complexes **1a**–**1c**, *in toluene solution.* First, iodo complexes **4a**–**4c** were obtained with a good yield from solutions of anionic complexes **2a**$^-$–**2c**$^-$ with one equivalent of iodine. **4a**–**4c** were added to the corresponding anionic species **2a**$^-$–**2c**$^-$ and the resulting toluene solutions were refluxed during 16 h for the chromium and molybdenum complexes and 24 h for the tungsten complex. This method appears quite selective, the three complexes **1a**, **1b** and **1c** are obtained as crystalline powders without purification, with excellent yields of 95, 95 and 99%, respectively.

Experimental

General methods and materials

All reactions of water- or air-sensitive compounds were conducted under a dry argon atmosphere using Schlenck techniques. Solvents were purified as follows: toluene, diethyl ether and tetrahydrofuran were distilled under nitrogen over Na/benzophenone. Dichloromethane was distilled over CaH_2. Starting materials (η^6-C_7H_8)M(CO)$_3$ (M = Cr, Mo),[9] $(CH_3CH_2CN)_3Cr(CO)_3$ [10] and $(CH_3CN)_3W(CO)_3$,[11] as well as the cyclopentadienide Li($C_5H_4PPh_2$),[22] were prepared as described in the literature.

All irradiations were performed by a 500-watt, high-pressure, water-cooled, mercury lamp with a Hanau power supply. Infrared spectra were obtained on a 1725 X Perkin Elmer FT-IR spectrometer. ^1H, ^{13}C and ^{31}P NMR spectra were recorded using 80-, 200-, or 250-MHz Bruker instruments. Mass spectra were recorded on a Nermag R10 instrument. Elemental analyses (%) were performed by the Microanalytical Laboratory of the Coordination Chemistry Laboratory (Toulouse, France).

Syntheses

Only the selected methods of preparation of compounds **1** are described hereafter in detail.

[(μ-η^5-$C_5H_4PPh_2$)Cr(CO)$_2$]$_2$, 1a. Method D: To an orange solution of 1.44 mmol of **2a**$^-$ in 20 mL of toluene was added a red solution of 1.44 mmol of **4a** in 20 mL of toluene. The resulting violet solution was refluxed for 16 h, then cooled to room temperature. After concentration and filtration, dark metallic crystals were obtained, giving 0.977 g of **1a** (95% yield). ^1H NMR (200 MHz, C_6D_6): δ 7.90 and 7.75 (2m, 8H, *ortho*), 7.13 (m, 12H, *meta* and *para*), 4.64 (s, 2H, C_5H_4), 4.38 (s, 2H, C_5H_4), 3.81 (s, 2H, C_5H_4), 3.34 (s, 2H, C_5H_4); ^1H NMR (200 MHz, [$^2H_6$]acetone): δ 8.05 and 7.70 (2m, 8H, *ortho*), 7.65 (m, 12H, *meta* and *para*), 5.15 (s, 2H, C_5H_4), 4.48 (s, 2H, C_5H_4), 3.58 (m, 2H, C_5H_4), 3.41 (s, 2H, C_5H_4); ^{31}P {^1H} NMR (32.40 MHz, C_6D_6): δ 83.6 (s); ^{31}P {^1H} NMR (81.015 MHz, [$^2H_6$]acetone): δ 88.5 (s); IR (CH_2Cl_2, ν_{CO}): 1940 (vs), 1889 (vs), 1864 (w), 1842 (s) cm^{-1}; IR (toluene, ν_{CO}): 1941 (vs), 1890 (vs), 1864 (w), 1844 (s) cm^{-1}; MS (DCI/NH_3), *m/z* 714 [MH^+] showing an isotopic pattern characteristic for a dichromium compound. Anal. calcd for $Cr_2C_{38}H_{28}O_4P_2$: C, 63.87; H, 3.95. Found: C, 63.45; H, 3.69.

Li[(η^5-$C_5H_4PPh_2$)Cr(CO)$_3$], [Li][2a]. First method: To a yellow solution of 1.20 g (4.68 mmol) of Li($C_5H_4PPh_2$) in 130 mL of THF was added 1.07 g of (η^6-C_7H_8)Cr(CO)$_3$ (4.68 mmol). The resulting red solution was refluxed for 3 days, giving an orange solution that was cooled to room temperature. The solvent was removed *in vacuo* to give a brown yellow residue, which was washed with pentane to give 1.82 g of [Li][**2a**] as a beige solid (99% yield). Second method: To a heterogeneous yellow solution of 0.128 g (0.5 mmol) of Li($C_5H_4PPh_2$) in 15 mL of toluene was added a green solution of 0.150 g (0.5 mmol) of $(CH_3CH_2CN)_3Cr(CO)_3$ in 15 mL of toluene. The heterogeneous mixture was heated and when the reflux temperature was obtained the solution became homogeneous. A white precipitate rapidly appeared. The new mixture was cooled to room temperature and the suspension was filtered and washed with pentane. [Li][**2a**] was obtained as 0.160 g of a dried white product (82% yield). ^1H NMR (200 MHz, C_6D_6): δ 7.84 (2m, 4H, *ortho*), 7.66 to 7.08 (m, 6H, *meta* and *para*), 5.02 (s, 4H, C_5H_4); ^{31}P {^1H} NMR (32.40 MHz, C_6D_6): δ −17.0 (s); IR (THF, ν_{CO}): 1903 (vs), 1811 (vs), 1788 (s), 1725 (s) cm^{-1}. Anal. calcd for $LiCrC_{20}H_{14}O_3P$: C, 61.24; H, 3.57. Found: C, 60.82; H, 4.28.

(η^5-$C_5H_4PPh_2$)Cr(CO)$_3$H, 3a. To a dark orange solution of 0.12 g (0.31 mmol) of [Li][**2a**] in 30 mL of toluene was added 18 μL of glacial acetic acid (0.31 mmol, one equivalent). The solution, which had turned bright red, was stirred for 10 min. After filtration and elimination of CH_3COOLi, the solution was concentrated and cooled to −18 °C. A red solid precipitated and the suspension was filtered. **3a** was obtained as 0.11 g of a dried red powder (92% yield). ^1H NMR (200 MHz, C_6D_6): δ 7.70 and 7.45 (2m, 4H, *ortho*), 7.20 (m, 6H, *meta* and *para*), 4.98 (s, 2H, C_5H_4), 4.74 (s, 2H, C_5H_4), −5.39 (s, hydride); ^{31}P {^1H} NMR (32.40 MHz, C_6D_6): δ −19.8 (s); IR (toluene, ν_{CO}): 2012 (vs), 1927 (vs) cm^{-1}. Anal. calcd for $CrC_{20}H_{15}O_3P$: C, 62.18; H, 3.91. Found: C, 62.34; H, 3.79.

[(η^5-$C_5H_4PPh_2$)Cr(CO)$_3$I], 4a. To an orange solution of 1.78 mmol of **2a**$^-$ in 40 mL of toluene was added 0.451 g of I_2 (1.78 mmol). The resulting red solution was stirred for 10 min. After filtration, the solution was concentrated and cooled to −18 °C. An orange solid precipitated, and the suspension was filtered. **4a** was obtained as 0.738 g of a dried orange powder (81% yield). ^1H NMR (200 MHz, C_6D_6): δ 7.98 to 7.30 (m, 10H, *ortho*, *meta* and *para*), 5.82 (s, 2H, C_5H_4), 5.38 (s, 2H, C_5H_4); ^{31}P {^1H} NMR (32.40 MHz, C_6D_6): δ −16.1 (s); ^{31}P {^1H} NMR (81.015 MHz, [$^2H_6$]acetone): δ −14.0 (s); IR (toluene, ν_{CO}): 2029 (vs), 1975 (vs) with a shoulder at 1955 (s) cm^{-1}. Anal. calcd for $CrC_{20}H_{14}O_3PI$: C, 46.90; H, 2.76. Found: C, 46.77; H, 2.81.

[(μ-η^5-$C_5H_4PPh_2$)Mo(CO)$_2$]$_2$, 1b. Method A: The hydride **3b** (in fact a mixture also containing **7b** can be used) was dissolved in 30 mL of toluene and the solution was irradiated with a low-pressure Hg lamp for 5 h. The red solution was then concentrated and cooled to −18 °C. A red solid precipitated and the suspension was filtered. The product was washed with pentane and dried under vacuum. **1b** was obtained as 0.17 g of a dried red powder (99% yield). Method B: After linear voltametry of Li[(η^5-$C_5H_4PPh_2$)Mo(CO)$_3$], [Li][**2b**], on a platinum-gauze electrode in acetone with 0.1 M Et_4NBF_4 electrolyte, electrolysis at 100 mV was performed. The bright orange solution turned progressively dark red when one electron/mol of **2b**$^-$ was exchanged. The supporting electrolyte was eliminated through two cycles of evaporation to dryness and redissolution in different solvents, from acetone to THF in which Et_4NBF_4 is not soluble, and then from THF to toluene. The $^{31}P\ \{^1H\}$ NMR (32,40 MHz, C_6D_6) spectrum shows the presence of $[(\eta^5\text{-}C_5H_4PPh_2)Mo(CO)_3]_2$, **5b**, at δ −17.0 (s), of **1b** at δ 68.1 (s) and of unidentified species at δ 62.5 (s); in IR (THF, ν_{CO}) the bands at 1959(s), 1913 (s) cm^{-1} were assigned to **5b** (main product) by comparison with $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$ for which ν_{CO} are at 1960(s), 1914 (s) cm^{-1} in CCl_4. The red solution was irradiated with a high-pressure Hg vapor lamp for 3 h. It was then concentrated, filtered, and cooled to −18 °C. The precipitate was washed with pentane and dried under vacuum. A dried red powder of **1b** was obtained with a 40 to 50% yield for electrolysis and irradiation. Method D: To an orange solution of 1 mmol of $\mathbf{2b}^-$ in 50 mL of toluene was added a red solution of 1 mmol of **4b** in 50 mL of toluene. The dark solution was refluxed for 16 h and then cooled to room temperature. After concentration and filtration, 0.761 g of **1b** were obtained (95% yield). ^1H NMR (200 MHz, C_6D_6): δ 7.90 and 7.75 (2m, 8H, *ortho*), 7.13 (m, 12H, *meta* and *para*), 4.89 (s, 2H, C_5H_4), 4.42 (s, 2H, C_5H_4), 3.73 (s, 2H, C_5H_4), 3.15 (s, 2H, C_5H_4); $^{31}P\ \{^1H\}$ NMR (32.40 MHz, C_6D_6): δ 68.2 (s); $^{13}C\ \{^1H\}$ NMR (50.323 MHz, C_6D_6): δ 244.5 (d, $^1J_{CP} = 27$ Hz, 2CO), 232.3 (s, 2CO), 140.4 (d, $^1J_{CP} = 41$ Hz, 4C, *ipso*), 134.3 and 133.4 (2s, 4C, *para*), 135.2 and 132.2 (2d, $^1J_{CP} = 10$ Hz, 8C, *ortho*), 131.6 and 130.7 (2s, 8C, *meta*), 94.1 and 88.2 (2s, $4C_3$ of C_5H_4P), 91.8 and 88.6 (2d, $^1J_{CP} = 11$ Hz, $4C_2$ of C_5H_4P), 53.6 (d, $^1J_{CP} = 41$ Hz, $2C_1$ of C_5H_4P); IR (THF, ν_{CO}): 1941 (vs), 1896 (vs), 1865 (w), 1843 (s) cm^{-1}; IR (toluene, ν_{CO}): 1943 (vs), 1898 (vs), 1868 (w), 1846 (s) cm^{-1}; MS (DCI/NH_3), *m/z* 802 $[MH^+]$ showing an isotopic pattern characteristic for a dimolybdenum compound. Anal. calcd for $Mo_2C_{38}H_{28}O_4P_2$: C, 56.87; H, 3.52. Found: C, 57.0; H, 3.56.

$Li[(\eta^5\text{-}C_5H_4PPh_2)Mo(CO)_3]$, [Li][2b]. To a yellow solution of 2.40 g (9.37 mmol) of $Li(C_5H_4PPh_2)$ in 275 mL of THF was added 2.55 g of $(\eta^6\text{-}C_7H_8)Mo(CO)_3$ (9.37 mmol). The red solution was refluxed for 3 h and the resulting yellow solution was cooled to room temperature. The solvent was removed *in vacuo* to give a brown yellow residue, which was washed with pentane to give 3.72 g of [Li][**2b**] as a beige solid (91% yield). ^1H NMR (200 MHz, C_6D_6): δ 7.70 and 7.46 (2m, 4H, *ortho*), 7.14 (m, 6H, *meta* and *para*), 5.50 (br s, 4H, C_5H_4); $^{31}P\ \{^1H\}$ NMR (32.40 MHz, C_6D_6): δ −18.2 (s); IR (THF, ν_{CO}): 1909 (vs), 1813 (vs), 1790 (s), 1724 (s) cm^{-1}; IR (KBr, ν_{CO}): 1980 (s), 1901 (vs), 1789 (vs), 1763 (s) cm^{-1}. Anal. calcd for $LiMoC_{20}H_{14}O_3P$: C, 55.1; H, 3.2. Found: C, 52.2; H, 3.9.

$(\eta^5\text{-}C_5H_4PPh_2)Mo(CO)_3H$, 3b and $[(\mu\text{-}\eta^5\text{-}C_5H_4PPh_2)Mo(CO)_2H]_2$, 7b. An orange solution of 0.21 g (0.48 mmol) of [Li][**2b**] in 30 mL of toluene was treated with 28 μL of glacial acetic acid (0.48 mmol, one equivalent). The bright orange solution was stirred for 10 min. After filtration and elimination of CH_3COOLi, the solution was concentrated and cooled to −18 °C. An orange solid precipitated and the suspension was filtered. A dried orange powder (0.18 g) was obtained. Spectroscopic analyses showed that the monometallic hydride compound **3b** and the dimetallic dihydride compound **7b** were present in an approximate ratio of 6 : 1. ^1H NMR (200 MHz, C_6D_6): δ 7.70 and 7.45 (2m, 32H, *ortho*), 7.20 (m, 48H, *meta* and *para*), 4.98 (s, 24H, C_5H_4 of **3b**) and 4.74 (s, 8H, C_5H_4 of **7b**), −5.26 (s, 6H, hydride of **3b**) and −5.29 (s, 2H, hydrides of **7b**); $^{31}P\ \{^1H\}$ NMR (32.40 MHz, C_6D_6): δ −19.5 (s, **3b**) and 59.4 (s, **7b**); IR (toluene, ν_{CO}): 2024 (s), 1937 (s) cm^{-1}. Anal. calcd for 6 $MoC_{20}H_{15}O_3P$ and 1 $Mo_2C_{36}H_{30}O_4P_2$: C, 53.4; H, 3.4. Found: C, 54.1; H, 3.9.

$(\eta^5\text{-}C_5H_4PPh_2)Mo(CO)_3I$, 4b. To an orange solution of 1 mmol of $\mathbf{2b}^-$ in 30 mL of THF was added 0.254 g of I_2 (1 mmol). The red solution was stirred for 10 min. After filtration, the solution was concentrated and cooled to −18 °C. An orange solid precipitated and the suspension was filtered. **4b** was obtained as 0.500 mg of a dried orange product (90% yield). ^1H NMR (200 MHz, $[^2H_6]$acetone): δ 7.57 to 7.45 (m, 10H, *ortho*, *meta* and *para*), 6.24 (m, 2H, C_5H_4), 5.81 (m, 2H, C_5H_4); $^{31}P\ \{^1H\}$ NMR (81.015 MHz, $[^2H_6]$acetone): δ −12.8 (s); IR (THF, ν_{CO}): 2039 (vs), 1964 (vs) cm^{-1}. Anal. calcd for $MoC_{20}H_{14}O_3PI$: C, 43.19; H, 2.54. Found: C, 43.01; H, 2.65.

$[(\mu\text{-}\eta^5\text{-}C_5H_4PPh_2)W(CO)_2]_2$, 1c. Method D: To a solution of 0.120 g of [Li][**2c**] (0.23 mmol) in 15 mL of toluene was added a red solution of 0.147 g of **4c** (0.23 mmol) in 15 mL of toluene. The solution was refluxed for 16 h. and then cooled to room temperature. After concentration and filtration, a red powder was obtained, giving 0.224 g of **1c** (99% yield). Red crystals of **1c** were obtained by slow diffusion of diethyl ether in a saturated dichloromethane solution. ^1H NMR (200 MHz, C_6D_6): δ 7.92 and 7.41 (2m, 8H, *ortho*), 7.23 to 7.09 (m, 12H, *meta* and *para*), 4.64 (s, 2H, C_5H_4), 4.38 (s, 2H, C_5H_4), 3.81 (s, 2H, C_5H_4), 3.34 (s, 2H, C_5H_4); ^1H NMR (200 MHz, $[^2H_6]$acetone): δ 8.08 and 7.81 (2m, 8H, *ortho*), 7.67 to 7.30 (m, 12H, *meta* and *para*), 5.45 (s, 2H, C_5H_4), 5.00 (s, 2H, C_5H_4), 4.19 (s, 2H, C_5H_4), 3.89 (s, 2H, C_5H_4); $^{31}P\ \{^1H\}$ NMR (32.40 MHz, C_6D_6): δ 35.0 (s + d, $J_{P\text{-}W} = 328$ Hz); IR (CH_2Cl_2, ν_{CO}): 1940 (vs), 1889 (vs), 1864 (w), 1842 (s) cm^{-1}; IR (toluene, ν_{CO}): 1938 (vs), 1892 (vs), 1863 (w), 1838 (s) cm^{-1}; IR (THF, ν_{CO}): 1936 (vs), 1890 (vs), 1862 (w), 1835 (s) cm^{-1}; MS (DCI/NH_3), *m/z* 978 $[MH^+]$ showing an isotopic pattern characteristic for a ditungsten compound. Anal. calcd for $W_2C_{38}H_{28}O_4P_2$: C, 46.65; H, 2.89. Found: C, 46.20; H, 3.00.

$Li[(\eta^5\text{-}C_5H_4PPh_2)W(CO)_3]$, [Li][2c]. To a yellow solution of 0.835 g (3.26 mmol) of $Li(C_5H_4PPh_2)$ in 50 mL of toluene was added a solution of 1.275 g of $(CH_3CN)_3W(CO)_3$ (3.26 mmol) in 50 mL of toluene. The heterogeneous mixture was heated and when the reflux temperature was obtained, the solution became homogeneous. After 15 min a beige precipitate appeared. The new mixture was cooled to room temperature and the suspension was filtered. [Li][**2c**] was obtained as 1.655 g of a dried white powder (97% yield). ^1H NMR (200 MHz, $[^2H_6]$acetone): δ 7.56 to 7.48 (m, 4H, *ortho*), 7.45 to 7.38 (m, 6H, *meta* and *para*), 5.25 (s, $J_{H\text{-}P} = 2.3$ Hz, 2H, C_5H_4), 5.04 (s, $J_{H\text{-}P} = 1.9$ Hz, 2H, C_5H_4); $^{31}P\ \{^1H\}$ NMR (32.40 MHz, C_6D_6): δ −17.2 (s + d, $^2J_{P\text{-}W} = 41$ Hz); IR (THF, ν_{CO}): 1903 (vs), 1808 (vs), 1786 (s), 1724 (s) cm^{-1}. Anal. calcd for $LiWC_{20}H_{14}O_3P$: C, 45.84; H, 2.69. Found: C, 46.12; H, 3.27.

$(\eta^5\text{-}C_5H_4PPh_2)W(CO)_3H$, 3c. To a yellow solution of 0.290 g (0.55 mmol) of [Li][**2c**] in 30 mL of THF was added 30 μL of glacial acetic acid (0.55 mmol). The resulting red solution was stirred for 10 min. After filtration and elimination of CH_3COOLi, the solution was concentrated and cooled to −18 °C. An orange solid precipitated, and the suspension was filtered. **3c** was obtained as 0.275 g of a dried orange powder (96% yield). ^1H NMR (200 MHz, $[^2H_6]$acetone): δ 7.57 to 7.37 (m, 10H, C_6H_5), 6.03 (s, 2H, C_5H_4), 5.75 (s, 2H, C_5H_4), −7.23 (s + d, hydride, $J_{H\text{-}W} = 36$ Hz); ^1H NMR (200 MHz, $CDCl_3$): δ 7.45 to 7.25 (m, 10H, C_6H_5), 5.59 (s, 2H, C_5H_4), 5.40 (s, 2H, C_5H_4), −7.28 (s + d, hydride, $^1J_{H\text{-}W} = 36$ Hz); $^{31}P\ \{^1H\}$ NMR (32.40 MHz, C_6D_6): δ − 19.8 (s + d, $^2J_{P\text{-}W} = 63$ Hz); IR (THF, ν_{CO}): 2019 (vs), 1926 (vs) cm^{-1}. Anal. calcd for $WC_{20}H_{15}O_3P$: C, 62.18; H, 3.91. Found: C, 62.34; H, 3.79.

$(\eta^5\text{-}C_5H_4PPh_2)W(CO)_3I$, 4c. To a yellow solution of 0.315 g (0.60 mmol) of [Li][**2c**] in 30 mL of THF was added 0.152 g of I_2 (0.60 mmol). The resulting red solution was stirred for 10 min. After filtration, the solution was concentrated and cooled to −18 °C. An orange solid precipitated and the suspension was filtered. **4c** was obtained as 0.314 g of a dried orange powder (81% yield). ^1H NMR (200 MHz, C_6D_6): δ 7.40 and

Table 3 Crystal Data for $[(\mu\text{-}\eta^5\text{-}C_5H_4PPh_2)W(CO)_2H]_2$ **7c**

Chemical formula	$C_{38}H_{30}O_4P_2W_2$
FW	980.3
Crystal system	Orthorhombic
Space group	*Pbca* (no.61)
a/Å	12.042(1)
b/Å	16.535(2)
c/Å	16.871(2)
U/Å^3	3359(1)
F(000)	1872
Z	4
ρ_{calc}/g cm^{-3}	1.938
Radiation	MoKα ($\lambda = 0.71073$ Å)
μ(MoKα)/mm^{-1}	6.70
T_{min}–T_{max}	0.922–1.000
2θ range/deg	3–46
Scan mode	$\omega - 2\theta$
No. of data collected	2328 (all unique)
No. of observed data	1193 $[F_o^2 > 3\sigma(F_o^2)]$
No. of variable params	128
S	1.093
w	$[\sigma^2(F_o) + 0.0011F_o^2]^{-1}$
$(\Delta/\sigma)_{max}$	0.008
$R = \Sigma[(\lvert F_o\rvert - \lvert F_c\rvert)/\Sigma\lvert F_o\rvert$	0.030
$Rw = [\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\Sigma w\lvert F_o\rvert^2]^{1/2}$	0.034
$(\Delta/\rho)_{max, min}$/e Å^{-3}	0.55, −0.53

7.31 (2m, 4H, *ortho*), 7.17 to 7.12 (m, 6H, *meta* and *para*), 5.07 (quint., 2H, C_5H_4), 4.87 (t, 2H, C_5H_4); $^{31}P\ \{^1H\}$ NMR (32.40 MHz, C_6D_6): δ −16.1 (s + d, $^2J_{P\text{-}W} = 71$ Hz); IR (THF, ν_{CO}): 2033 (vs), 1951 (vs) cm^{-1}. Anal. calcd for $WC_{20}H_{14}O_3PI$: C, 37.30; H, 2.19. Found: C, 37.52; H, 2.24.

Formation of the complex $[(\mu\text{-}\eta^5\text{-}C_5H_4PPh_2)W(CO)_2H]_2$, 7c. In the ^1H NMR tube of a **3c** solution in $[^2H_6]$acetone, orange crystals of **7c** were obtained by slow concentration $[^2H_6]$acetone. MS (DCI/NH_3), m/z 980 [MH^+] showing an isotopic pattern characteristic for a ditungsten compound. Anal. calcd for $W_2C_{38}H_{30}O_4P_2$: C, 46.56; H, 3.08. Found: C, 46.42; H, 3.01.

Table 4 Atomic coordinates for **7c**

Atom	x/a	y/b	z/c
W	0.51845(2)	0.12256(2)	0.44077(2)
H(1)	0.4614(62)	0.1285(41)	0.3522(21)
P	0.3671(2)	0.0294(1)	0.4198(1)
C(1)	0.4576(7)	0.2245(6)	0.4072(6)
O(1)	0.4262(7)	0.2885(5)	0.3940(5)
C(2)	0.4224(8)	0.1510(6)	0.5289(6)
O(2)	0.3677(6)	0.1747(4)	0.5832(4)
C(3)	0.6529(6)	0.0465(4)	0.5018(4)
C(4)	0.6857(6)	0.1301(4)	0.5089(5)
C(5)	0.7071(7)	0.1596(7)	0.4313(5)
C(6)	0.6919(7)	0.0962(5)	0.3800(5)
C(7)	0.6581(5)	0.0283(5)	0.4233(4)
C(8)	0.2335(4)	0.0803(3)	0.4119(3)
C(9)	0.1480(4)	0.0638(3)	0.4654(3)
C(10)	0.0452(4)	0.1015(3)	0.4567(3)
C(11)	0.0277(4)	0.1557(3)	0.3946(3)
C(12)	0.1131(4)	0.1722(3)	0.3411(3)
C(13)	0.2160(4)	0.1345(3)	0.3498(3)
C(14)	0.3631(4)	−0.0301(4)	0.3289(3)
C(15)	0.4514(4)	−0.0297(4)	0.2754(3)
C(16)	0.4450(4)	−0.0748(4)	0.2057(3)
C(17)	0.3502(4)	−0.1204(4)	0.1895(3)
C(18)	0.2618(4)	−0.1209(4)	0.2430(3)
C(19)	0.2683(4)	−0.0757(4)	0.3127(3)

X-Ray crystallography for 7c

Diffraction data were collected on an Enraf-Nonius CAD-4 diffractometer at room temperature using MoKα graphite-monochromated radiation ($\lambda = 0.71073$ Å). Accurate unit cell parameters were obtained from least-squares refinement of 25 reflections in the 11–15° θ range. The intensities were corrected for Lorentz and polarization effects and for a slight (−6.3%) linear decay.[23] Empirical absorption corrections[24] were made from ψ scans. The structure was solved by Patterson techniques.[25a] Relevant crystallographic data for **7c** are listed in Table 3. Full-matrix least-squares refinement[25b] minimizing $\Sigma w(\lvert F_c\rvert - \lvert F_c\rvert)^2$ was performed with non-hydrogen atoms anisotropic but those of phenyl rings refined as isotropic rigid groups. The hydride ligand H(1) was located on a difference-Fourier map. Its position agreed with that obtained by seeking sites of potential energy minima.[26] It was refined isotropically. All other H atoms were introduced in calculated positions. Final atomic coordinates are given in Table 4.

CCDC reference number 440/002.

Conclusions

The possibility to obtain in very good yields a series of bridged metal–metal bonded complexes now opens opportunities to study comparatively the structures and physical properties in that series. Chemical properties, in particular the electrochemical behavior, are currently extended from the case of the molydenum complex[5] to the chromium and tungsten ones.

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