Hydride, alkyl and carbyne derivatives of the unsaturated heterometallic anion [MoW Cp₂(μ-PCy₂)(μ-CO)]⁻

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Abstract

The heterometallic hydride [MoW Cp₂(μ-H)(μ-PCy₂)(CO)]⁻ was prepared in 30% yield through reaction of an equimolar mixture of [MoCp₂(CO)]₀ and [W₂Cp₂(CO)]₀ with a two-fold excess of PCH₂ in xylene solution, in a sealed tube at 453 K. The sodium salt of the title anion was then prepared from the latter hydride in a three-step process first involving dehydrogenation with HBF₄·OEt₂ in dichloromethane to give the cationic derivative [MoW Cp₂(μ-PCy₂)(CO)]⁺, then reaction of the latter with NaI in refluxing 1,2-dichloroethane to yield the iodide-bridged dicarbonyl complex [MoW Cp₂(μ-I)(μ-PCy₂)(CO)]⁻, and, finally, reaction of the latter with Na(Hg) in tetrahydrofuran solution. Reaction of this anion with (NH₄)₂P₂O₇ gave the hydride [MoW Cp₂(H)(μ-PCy₂)(CO)]⁻, which in solution displays an equilibrium mixture of two isomers, one with terminal carbonyls and the hydride ligand bridging the metal atoms (B), another one with a semibridging carbonyl and the hydride ligand terminally bound to the W atom (T). The prevalence of isomer T was higher than the observed ones in the corresponding homometallic analogues, and there was a clear thermodynamic preference of the hydride ligand for the W site, estimated in some 20 kJ/mol according to density functional theory (DFT) calculations. The title anion reacted selectively with benzyl chloride at room temperature, to give the agostic benzyl-bridged derivative [MoW Cp₂(μ-κ¹:κ²-CH₂Ph)(μ-PCy₂)(CO)]⁻, which displays specific κ¹-coordination to the W atom (Mo–W = 2.580(1) Å), while the analogous reaction with Mel gave a mixture of the related methyl-bridged complex [MoW Cp₂(μ-κ¹:κ²-CH₃)(μ-PCy₂)(CO)]⁻ and its methoxycarbyne-bridged isomer [MoW Cp₂(μ-CONMe)(μ-PCy₂)(μ-CO)]⁻ in a ratio of ca. 5:1, with the latter corresponding to a chemical behaviour intermediate between those of its homonuclear analogues. Photolysis of the above alkyl complexes with visible-UV light at room temperature resulted in fast decarbonylation followed by dehydrogenation, to give the corresponding carbyne-bridged derivatives [MoW Cp₂(μ-CR)(μ-PCy₂)(μ-CO)]⁻ (R = H, Ph) in good yield. This suggests that the cooperative action of Mo and W atoms greatly reduces the thermal barrier of the C–H bond cleavage steps required for dehydrogenation of the alkyl ligands in these substrates.

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1. Introduction

Mononuclear transition-metal carbonylates are classical reagents in organometallic chemistry. Due to their good nucleophilic properties, these anionic metal complexes react under mild conditions with a large variety of electrophilic molecules, whereby new bonds can be made between the metal atom and virtually any other element in the periodic table [1]. Even after many decades of extensive research, however, interesting new findings are just appearing in the field, as novel anions with unusual structures, electron counts, or metal atoms are being unveiled [2]. Compared to this state of facts, the chemistry of binuclear carbonylates has been much less developed, due to the scarce number of species available for reactivity studies. This is particularly so in the case of binuclear anions bearing metal-metal multiple bonds, of which only a few examples are known, and even fewer of them can be properly used in synthetic studies, these being essentially limited to the 32-electron complexes [M₂(CO)₆(μ-Ph₂PCH₂PPh₂)]⁻ [3], and [Fe₂(μ-PPH₂)(CO)₆]⁻ [4], with M=M bonds, and to the 30-electron complexes [M₂Cp₂(μ-PR₂)(μ-CO)]⁻ (M = Mo, R = Cy [5],...
Scheme 1. Reactivity of unsaturated homometallic anions.

Scheme 2. Synthesis of the heterometallic compound 1.
corresponding Mo2 and W2 analogues and related complexes [15,16], and need not to be discussed in detail. All these molecules display a transoid arrangement of their MCp(CO)2 fragments, which has been substantiated through X-ray studies in several cases [16,18]. As expected, compound 1 displays 31P (δp 178.9 ppm) and hydride (δH – 14.56 ppm, JHP = 30 Hz) resonances in positions intermediate with respect to its homometallic analogues, with one-bond P–W (197 Hz) and H–W (40 Hz) couplings comparable to those measured in the corresponding ditungsten complex (182 and 40 Hz, respectively). As for the carbonyl ligands of 1, the presence of Mo and W atoms in the same molecule removes all symmetry elements, so all of them become inequivalent, with the ones positioned cis to the P atom rendering 13C NMR resonances displaying measurable two-bond P–C couplings of ca. 20–30 Hz as expected [19,20].

2.2. Synthesis and structural characterization of the title anion and its heterometallic precursors

As noted above, the title anion could be efficiently prepared using the synthetic route previously developed for the related ditungsten analogue [7], a three-step process starting from the corresponding 34-electron hydride [Mo2Cp2(H)2(CO)2][BF4]2 (2). Spectroscopic data for 2 (Table 1 and Experimental section) are comparable to that of its ditungsten analogue [7] and related PPh2-bridged complexes [21]. In particular, we note the significant increase in the C–O stretches (relative to 1) as a result of the presence of a positive charge in the complex, while the increased one-bond P–W coupling (from 197 to 255 Hz) reflects the reduction in the number of ligands surrounding the W atom after dehydrogenation [20].

In the second step, the cationic complex 2 is reacted with an excess NaI in refluxing 1,2-dichloroethane solution, whereby iodide addition and decarbonylation takes place, to yield the iodide-bridged dicarboxyl complex [Mo2Cp2(I)2(CO)2][BF4]2 (3) almost quantitatively. As found for its ditungsten analogue, this 32-electron complex is quite air-sensitive and was used without further purification. Its IR spectrum displays two C–O stretching bands with relative intensities (weak and strong, in order of decreasing frequencies) characteristic of transoid Mo2(CO)2 oscillators [22]. This structural arrangement has been persistently found in all halide-bridged complexes of type [Mo2Cp2(μ-X)2(PPh2)(CO)2] prepared by us previously, and it has been substantiated crystallographically in the case of [Mo2Cp2(μ-Cl)(μ-PBu2)(CO)2]6. The 31P NMR resonance of 3 is substantially shielded with respect to 1 (125.8 vs. 178.9 ppm), as usually found in this family of neutral complexes, and the one-bond P–W coupling is substantially higher (307 vs. 197 Hz), thus reflecting the significant reduction in the coordination number around the W atom after decarbonylation.

In the last step, the iodide-bridged complex 3 is reduced with Na(Hg) in tetrahydrofuran solution, whereby the sodium salt of the targeted unsaturated anion Na[Mo2Cp2(μ-PCy2)(μ-CO)2][BF4]2 (4-Na) is formed in a quantitative way, along with NaI. This product is very air-sensitive and displays low solubility in tetrahydrofuran, thus precluding its analysis by NMR spectroscopy. Its IR spectrum displays a single and strong C–O stretch at very low frequency corresponding Mo2 and W2 analogues and related complexes [15,16], and need not to be discussed in detail. All these molecules display a transoid arrangement of their MCP(CO)2 fragments, which has been substantiated through X-ray studies in several cases [16,18]. As expected, compound 1 displays 31P (δp 178.9 ppm) and hydride (δH – 14.56 ppm, JHP = 30 Hz) resonances in positions intermediate with respect to its homometallic analogues, with one-bond P–W (197 Hz) and H–W (40 Hz) couplings comparable to those measured in the corresponding ditungsten complex (182 and 40 Hz, respectively). As for the carbonyl ligands of 1, the presence of Mo and W atoms in the same molecule removes all symmetry elements, so all of them become inequivalent, with the ones positioned cis to the P atom rendering 13C NMR resonances displaying measurable two-bond P–C couplings of ca. 20–30 Hz as expected [19,20].

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![Scheme 3. Synthesis of the unsaturated heterometallic anion 4.](image-url)
(1565 cm\(^{-1}\)), in a position intermediate with respect to those measured for the analogous Mo\(_2\) and W\(_2\) complexes (1580 and 1546 cm\(^{-1}\), respectively), which corresponds to the asymmetric stretch for the M\(_2(\mu\text{-CO})_2\) oscillator of these anions. The expected and weaker band corresponding to the symmetric stretch probably is too close to the latter band, to be observed separately.

We have shown previously that strong ion-pairing effects are present in the solutions of these unsaturated anions, which are in turn strongly dependent on their counter-ion [5a]; this is also the case for the heterometallic anion 4. For instance, the lithium salt Li\([\text{MoWCP}_{2}(\mu\text{-PCy}_2)(\mu\text{-CO})_2]\) (4-Li) could be analogously prepared by reacting 3 with Li(Hg) in tetrahydrofuran solution. Interestingly, as found for its Mo\(_2\) analogue, the IR spectrum of this salt now displays three C\(\equiv\)O stretches at 1642 (w), 1573 (m, sh) and 1552 (s) cm\(^{-1}\), with the latter two bands likely corresponding respectively to the symmetric and asymmetric stretches of the isolated anion (with unspecified cation-anion interactions), while the band at 1642 cm\(^{-1}\) can be attributed to the C\(\equiv\)O stretch of a tight ion pair involving the attachment of the Li\(^+\) cation to one of the bridging carbonyls [5a].

2.3. Formation and structural characterization of the hydride complex 5

The sodium salt of anion 4 reacts readily with the weak acid (NH\(_4\))PF\(_6\) in tetrahydrofuran solution to give the corresponding hydride \([\text{MoWCP}_{2}(\mu\text{-PCy}_2)(\mu\text{-CO})_2]\) (5), which can be isolated in good yield as a pure substance upon chromatographic workup. Protonation of 4 with strong acids such as HBF\(_4\)/OE\(_2\) led only to complex mixtures of unstable products. We note, however, that the protonation process leading to 5 is fully reversible, since 4-Na\(^+\) can be selectively regenerated upon stirring a tetrahydrofuran solution of 5 with Na(Hg) for a few minutes.

Complex 5 exists in solution as an equilibrium mixture of two isomers, one with terminal carbonyls and the hydride ligand bridging the metal atoms (5B), another one with a semibridging carbonyl and the hydride ligand terminally bound to the W atom (5T) (Scheme 4), as previously found for its ditungsten analogue (Scheme 1). These structural types have been characterized crystallographically for the dimolybdenum complexes \([\text{Mo}_{2}\text{Cp}_{2}(\mu\text{-PCy})_{2}(\mu\text{-CO})_2]\) (isomer B) [23], and \([\text{Mo}_{2}\text{Cp}_{2}(\mu\text{-PCy}_2)(\mu\text{-PBu}_3)(\mu\text{-CO})_2]\) (isomer T) [6]; the latter complexes, however, displayed in solution a single isomer in each case. In the case of 5, the isomer ratio T/B expectedly was solvent- and temperature-dependent but, interestingly, has a value outside the range spanned by its homometallic analogues (T/B ca. 0 and 0.33 in CD\(_2\)Cl\(_2\) solution at 193 K respectively for the Mo\(_2\) and W\(_2\) analogues), since under analogous conditions the terminal isomer 5T is the major species in solution (5T/5B = 2.5 at 183 K). This can be then considered as a genuine heterometallic effect of structural nature. Isomer 5T was also found to be favoured over isomer 5B on lowering the temperature, but disfavoured when using a less polar solvent as toluene-d\(_8\) (5T/5B = 0.6 at 183 K) (see the Experimental section). In any case, all of this means that the energetic difference between these two isomers in 5 is very small, in agreement with density functional theory (DFT) calculations [24] discussed below.

Spectroscopic data for isomers 5B and 5T are comparable to those of their homometallic analogues where applicable, and need not to be discussed in detail. The presence of the terminal isomer 5T at room temperature is denoted by the appearance of a C\(\equiv\)O stretch at 1762 cm\(^{-1}\) in the IR spectrum, indicative of the presence of a semibridging carbonyl ligand, in addition to the more energetic bands at 1869 (w, sh) and 1821 (vs) cm\(^{-1}\) expected for the stretches of antiparallel terminal carbonyls in the hydride-bridged isomer 5B. Separate NMR resonances could be observed for both isomers at low temperature (see the Experimental section), with the terminal isomer 5T reproducing the spectroscopic features of its ditungsten analogue: (a) a \(^{31}\)P NMR resonance more deshielded than isomer 5B (\(\delta_\text{C} = 232.8\) vs. 197.3 ppm); (b) a lower one-bond P\(\cdots\)W coupling (248 vs. 330 Hz), as expected from the higher coordination number at the W atom; (c) a less shielded hydride resonance (\(\delta_\text{H} = -1.46\) vs. \(-6.41\) ppm), indicative of its terminal coordination, with a high H\(\cdots\)W coupling of 70 Hz which denotes its attachment specifically at the W site (cf. \(\delta = -0.71\) ppm, \(J_{\text{HH}} = 99\) Hz for its W\(_2\) analogue); and (d) a strong deshielding of the W-bound carbonyl (\(\delta_\text{C} = 276.2\) ppm) indicative of its semibridging character (cf. 272.7 ppm in its W\(_2\) analogue). All these data provide conclusive evidence for a clear preference of the hydride ligand in 5 for terminal coordination specifically at the W site, a matter further analysed below.

2.3.1. DFT calculations on hydride 5

To gain more insight concerning the structures and relative stability of different isomers of compound 5 in solution we have performed DFT calculations on the observed isomers 5B and 5T, and also on a third isomer similar to the latter one, but with the hydride ligand terminally bound to the Mo atom, and the Mo-bound carbonyl involved in semibridging interaction with the W atom (5T-Mo) (Fig. 1 and Table 2, see the Experimental section and Figs. 1 and 2).

![Fig. 1. B3LYP-optimized structures for isomers 5B (upper, blue colour for Mo), 5T (lower, left) and 5T-Mo (lower, right), with H atoms (except hydride ligands) and Cy groups (except C\(_1\) atoms) omitted for clarity. Relative Gibbs free energies at 295 K were 0, +11 and +31 kJ mol\(^{-1}\) respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)](image-url)
Supplementary data). The latter isomer displays a structure essentially equivalent to that of 5T, but was computed to be some 20 kJ/mol less stable than 5T in the gas phase, which is consistent with the experimental fact that no significant amounts of such isomer are detected spectroscopically in solution, and with the general finding that W–H bonds are generally stronger than Mo–H bonds in comparable organometallic species [25]. Therefore we can conclude that the observed preference of the hydride ligand for terminal coordination at the W (instead of Mo) site is of thermodynamic origin.

Concerning the geometries computed for the observed isomers 5B and 5T, we notice that the structural parameters for these molecules at the B3LYP level are in good agreement with those determined crystallographically for the dimolybdenum hydrides \([\text{Mo}_2\text{Cp}_2(\mu-H)(\mu-\text{PCy}_2)(\text{CO})_2])\) and \([\text{Mo}_2\text{Cp}_2(\mu-\text{H})(\mu-\text{PBU}_3)(\text{CO})_2])\) respectively [6,22], although the computed distances involving the metal atoms are slightly higher than the experimental values in the \([\text{Mo}_2\text{Cp}_2(\mu-\text{H})(\mu-\text{PCy}_2)(\text{CO})_2])\) complexes, as commonly found at this level of calculation [24]. These structures in turn are comparable to those computed at the same level for isomers of type B and T for the above \(\text{PBU}_2\)-bridged complex, or for the ditungsten analogue of 5B, which we have analyzed previously in detail [7b,9]. Then, only a few comments are to be added: (a) The intermetallic separation in isomers 5B and 5T (ca. 2.54 Å) is very short and similar to each other, in line with our calculations (see the Experimental section) only marginally reduced the energetic difference between these isomers (to ca. 11 kJ/mol), but still did not reproduce the experimental prevalence of 5T in such solvent. This might suggest that interactions between the terminal isomer 5T and the dichloromethane molecules might be more specific than conventional dipole-dipole interactions, perhaps being of hydrogen-bond nature. Interestingly, hydrogen-bond interactions between the hydride complex \([\text{WCP}(\text{CO})_3\text{H}])\) and dichloromethane molecules have been computed to be of significant strength (ca. 9 kJ/mol) [27], enough to influence in our case the thermodynamic balance between isomers 5B and 5T in solution.

### 2.4. Reactions of anion 4 with alkyl halides

The sodium salt of anion 4 reacts slowly with excess Mel at room temperature in tetrahydrofuran solution, to give a mixture of the methyl-bridged complex \([\text{MoWCP}_2(\mu-\text{H})(\mu-\text{PCy}_2)(\text{CO})_2])\) and its methoxycarbonyl-bridged isomer \([\text{MoWCP}_2(\mu-\text{COMe})(\mu-\text{PCy}_2)(\mu-\text{CO})])\) (7), in a ratio of ca. 5:1 (Scheme 5). This corresponds to a chemical behaviour intermediate between those of its homometallic analogues, which in the same reaction instead yielded only the methyl derivative (Mo2) or mostly the methoxycarbonyl isomer (W2), as noted above (Scheme 1). Expectedly, the carbonyl complex 7 could be selectively prepared by using a stronger methylating reagent [5a], in this case methyl sulfate (see the Experimental section). In contrast, Na-\(4\) reacts selectively with benzyl chloride under the same conditions, to give the benzyl-bridged derivative \([\text{MoWCP}_2(\mu-\text{H})(\mu-\text{PCy}_2)(\mu-\text{CO})_2])\) (8) as the sole product, as found for the Mo2 and W2 related anions.

#### 2.4.1. Solid-state and solution structure of the agostic benzyl-bridged complex 8

The molecule of 8 in the crystal (Fig. 2 and Table 3) is built from two transoid MCP(CO) fragments bridged by a PCy2 group and an agostic methyl ligand which is \(\pi^1\)-bound to the tungsten atom (W–C = 2.26(2) Å) and \(\pi^2\)-bound to the Mo atom via a C–H bond (Mo–C = 2.40(2), Mo–H = 2.00(2) Å), whereby it formally contributes with three electrons to the dinitel metal site, which in turn leads to the proposal for 8 of an intermetallic double bond, according to the 18-electron rule. This is consistent with the intermetallic separation of 2.580(1) Å in 8, which is ca. 0.06 Å longer than the corresponding length of 2.528(2) Å in the 30-electron hydride \([\text{Mo}_2\text{Cp}_2(\mu-\text{H})(\mu-\text{PCy}_2)(\text{CO})_2])\) [23], although still some 0.08 Å shorter.
shorter than the figure expected for a double bond (cf. 2.666(1) Å in the 32-electron complex \([\text{Mo}_2\text{Cp}_2(\mu-\text{CtPh})(\mu-\text{PCy}_2)\text{(CO)}_2]\)) [28]. All of these structural data are generally very similar to those measured for the related homometallic complex \([\text{Mo}_2\text{Cp}_2(\mu-\text{x},\text{y}^2,\text{z}^2-\text{CH}_2\text{Ph})(\mu-\text{PCy}_2)\text{(CO)}_2]\) (\(\text{Mo-Mo} = 2.580(1)\) Å), a molecule for which the strength of the \(\eta^2\)-bonding interaction of the benzyl ligand has been estimated to be 89 kJ/mol, according to DFT calculations [29].

Spectroscopic data in solution for \(\mathbf{8}\) (Table 1 and Experimental section) are consistent with the structure found in the crystal, and also are comparable to those measured for its \(\text{Mo}_2\) and \(\text{W}_2\) analogues [29,7a], so a detailed discussion is not needed. The retention of chemical shift assignments for all H atoms of the methyl ligand [29] and all terminal Me groups bound to the W (yellow) atom (as found for the benzyl complex \(\mathbf{8}\)), and they seem to be derived from the chemical exchange of all H atoms of the methyl ligand [29].

We have shown previously that photolysis of the benzyl-bridged homometallic complexes \(\mathbf{[M}_2\text{Cp}_2(\mu-x,\text{y}^2,\text{z}^2-\text{CH}_2\text{Ph})(\mu-\text{PCy}_2)\text{(CO)}_2}\) (\(M = \text{Mo}, \text{W}\)) results in decarbonylation and dehydrogenation of the benzyl group, to give the corresponding benzylidyne-bridged derivatives [28,7a]. In contrast, photolysis of the related methyl-
bridged complex \([\text{Mo}_2\text{Cp}_2(\mu-\kappa^1:1^2:3\text{-CH}_3)(\mu-\text{PCy}_2)(\mu-\text{CO})_2]\) only resulted in decarbonylation of the dimetal substrate, to yield the 30-electron methyl-bridged derivative \([\text{Mo}_2\text{Cp}_2(\mu-\kappa^1:1^2:3\text{-CH}_3)(\mu-\text{PCy}_2)(\mu-\text{CO})]\) \([31]\). Recently, however, we found that the presence of the bulkier \(\text{PBu}_3\) group in these substrates somehow facilitates the dehydrogenation of bridging methyl ligands, so that the related complex \([\text{Mo}_2\text{Cp}_2(\mu-\kappa^1:1^2:3\text{-CH}_3)(\mu-\text{PBu}_3)(\mu-\text{CO})]\) could be transformed easily into the corresponding methylidyne-bridged derivative upon gentle heating at 353 K \([6]\). It was thus of interest to examine the influence of the heterometallic MoW site on the dehydrogenation processes of the alkyl ligands present in complexes 6 and 8.

Irradiation of toluene solutions of 6 with visible-UV light at 288 K resulted in decarbonylation and dehydrogenation to give the corresponding methylidyne-bridged complex \([\text{MoW}_2\text{Cp}_2(\mu-\text{CH})(\mu-\text{PCy}_2)(\mu-\text{CO})]\) \([9]\) as major product (Scheme 6), along with small amounts of compound 1, the latter obviously arising from some competing decomposition pathway. Since our previous studies on dehydrogenation reactions of the \(\text{PBu}_3\)-bridged alkyl complexes revealed that the \(\text{C}^\equiv\text{H}\) cleavage steps leading to dehydrogenation are thermal processes following photochemical decarbonylation \([6]\), then the formation of 9 at room temperature suggests that the cooperative action of Mo and W atoms in these substrates greatly reduces the thermal barrier of the \(\text{C}^\equiv\text{H}\) bond cleavage steps required for dehydrogenation of the methyl ligand. Unfortunately, we have no information concerning the photochemistry of the ditungsten complex \([\text{W}_2\text{Cp}_2(\mu-\kappa^1:1^2:3\text{-CH}_3)(\mu-\text{PCy}_2)(\mu-\text{CO})]\) \([7a]\), so more conclusive evidence for heterometallic effects in these dehydrogenation processes is not possible at this stage.

According to the mentioned studies on \(\text{Mo}_2\) substrates, the thermal barrier for the \(\text{C}^\equiv\text{H}\) bond cleavage steps leading to dehydrogenation are lower for the agostic benzyl ligands, when compared to the methyl ligands. Thus it was not surprising to find that photolysis of toluene solutions of the benzyl complex 8 at 288 K also resulted in easy dehydrogenation to yield the corresponding benzylidyne-bridged derivative \([\text{MoW}_2\text{Cp}_2(\mu-\text{CH})(\mu-\text{PCy}_2)(\mu-\text{CO})]\) \([10]\). In this case, however, small amounts of the bis(photophosphane) complex \([\text{MoW}_2\text{Cp}_2(\mu-\text{PCy}_2)(\mu-\text{CO})]\) \([11]\) were formed as a side product (Scheme 6). The latter was identified by comparison of its IR and \(^{31}\text{P}\) NMR data (Table 1) with those of related homometallic analogues \([\text{Mo}_2\text{Cp}_2(\mu-\text{PR}_3)(\mu-\text{CO})]\) \([M = \text{Mo}, \text{W}; R = \text{Cy, Ph}]\) \([15,32]\), and no attempts to fully characterize it were made.

2.5.1. Structural characterization of carbyne-bridged complexes 7, 9 and 10

Spectroscopic data for the carbyne-bridged complexes 7, 9 and 10 are comparable to each other and also to those of related homometallic \(\text{Mo}_2\) and \(\text{W}_2\) complexes \([5–7,28]\), then requiring no detailed discussion. We note that this family of 30-electron complexes has been structurally characterized in several cases \([8]\), whereby very short intermetallic lengths of ca. 2.47 Å have been found in all cases. This is consistent with the triple bond to be proposed for these molecules on the basis of the 18-electron rule, more precisely described as following from a \(\sigma^2\beta^1\) configuration, according to DFT calculations \([33]\).

All these molecules are built from MCP fragments bridged by three different ligands: phosphane, carbonyl and carbyne. The former gives rise to a strongly deshielded \(^{31}\text{P}\) NMR resonance at ca. 195 ppm, characteristic of 30-electron complexes, which also displays high one-bond \(\text{P}^\equiv\text{W}\) couplings of ca. 345 Hz denoting the low coordination number of the tungsten atom in these molecules. The carbyne ligand gives rise to diagnostic strongly deshielded \(^{13}\text{C}\) NMR resonances (ca. 350–375 ppm), while the methylidyne ligand in 9 also accounts for a highly deshielded \(^{1}\text{H}\) NMR resonance at 18.70 ppm (cf. 16.74 ppm for its crystallographically characterized \(\text{Mo}_2\) analogue) \([33]\). The bridging carbyne ligand in these complexes gives rise to a \(^{13}\text{C}\) resonance at ca. 300 ppm as expected, and the corresponding \(\text{C}^\equiv\text{O}\) stretch for compounds 9 and 10 is observed at ca. 1661 cm\(^{-1}\), a frequency which is reduced by some 10 cm\(^{-1}\) in the methoxycarbonyl complex 7 \((\text{v}_{\text{CO}} = 1653 \text{ cm}^{-1})\), a difference which can be attributed to the increased electron density at the dimetal site resulting from the \(\pi\)-bonding interaction present in the \(\text{C}^\equiv\text{O}\) bond of alkoxy carbonyl ligands \([33]\).

3. Conclusions

As found for its homometallic analogues, the heterometallic anion 4 displays multisite reactivity, with nucleophilic sites located at the dimetal centre and the \(\text{O}\) atoms of the bridging carboxyls, as the reaction with \(\text{Me}_2\) illus is. In this respect, anion 4 displays a chemical behaviour intermediate between those observed for the \(\text{Mo}_2\) and \(\text{W}_2\) analogues. The hydride derivative of 4 displays two isomers in solution, as found for the \(\text{W}_2\) system, yet two additional structural effects can be appreciated in the heterometallic system: (a) a clear thermodynamic preference of the hydride ligand for terminal coordination at the \(\text{W}\) site (vs. \(\text{Mo}\)), estimated in some 20 kJ/mol according to DFT calculations; and (b) a clear prevalence of the terminal isomer (\(\text{T}\)) vs. the hydride-bridged one (\(\text{B}\)), when compared to either of the \(\text{Mo}_2\) or \(\text{W}_2\) homometallic systems, which can be then considered as a genuine heterometallic effect. A defined structural preference is also observed for the agostic methyl and benzyl derivatives of 4, which specifically are \(\kappa^1\)-bound to the \(\text{W}\) atom, while one of the \(\text{C}^\equiv\text{H}\) bonds binds the \(\text{Mo}\) atom. The methyl ligand in the heterometallic complex is dehydrogenated much more easily than their \(\text{Mo}_2\) analogues, which suggests another genuine heterometallic effect, i.e. that the cooperative action of \(\text{Mo}\) and \(\text{W}\) atoms in these substrates greatly reduces the thermal barrier of the \(\text{C}^\equiv\text{H}\) bond cleavage steps required for such dehydrogenation.

4. Experimental

All reactions and manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques. Solvents were purified according to literature procedures \([34]\), and distilled under nitrogen prior to use. Petroleum ether refers to that fraction distilling in the range 338–343 K, and the xylene used actually was a mixture of the corresponding \(\alpha-\text{m-}\) and \(\beta\)-isomers. Complex
[W₂Cp₂(CO)₆] ([Cp = η⁵-C₅H₅]) was prepared as described previously [35]. All other reagents were obtained from the usual commercial suppliers and used as received. Photochemical experiments were performed using jacketed Schlenk tubes, cooled by tap water (ca. 288 K). A 400 W mercury lamp placed ca. 1 cm away from the Schlenk tube was used for all experiments. Chromatographic separations were carried out using jacketed columns refrigerated by tap water (ca. 288 K) or by a closed 2-propanol circuit kept at the desired temperature with a cryostat. Commercial aluminium oxide (activity I, 70–290 mesh) was degassed under vacuum prior to use. The latter was mixed under nitrogen with the appropriate amount of water to reach activity IV. IR stretching frequencies of CO ligands were measured in solution using CaF₂ windows, referred to as ν(CO), and are given in cm⁻¹. Nuclear magnetic resonance (NMR) spectra were routinely recorded at room temperature in CD₂Cl₂ solutions unless otherwise stated. Chemical shifts (δ) are given in ppm, relative to internal tetramethyliysilane (δH = 0 ppm, δC = 0 ppm) or external 85% aqueous H₃PO₄ solutions (δ31P). Coupling constants (J) are given in hertz.

4.1. Preparation of [MoWPc₂(µ-H)(µ-PCy₂)(CO)]₂ (1)

Neat PHCy₂ (500 µL, 2.280 mmol) was added to a xylene solution (3 mL) of complexes [MoWPc₂(CO)₆] (0.540 g, 1.102 mmol) and [W₂Cp₂(CO)₆] (0.730 g, 1.096 mmol) in a Schlenk tube equipped with a Young’s valve. After closing the valve, the solution was stirred at 453 K for 6 h to give an orange solution. The solvent was then removed under vacuum, the residue extracted with dichloromethane/petroleum ether (1/5) and the extracts were chromatographed through a silica gel column (230–400 mesh) at 253 K. Elution with dichloromethane/petroleum ether (1/5) gave an orange fraction yielding, after removal of solvents, the known complex [MoWPc₂(µ-H)(µ-PCy₂)(CO)]₂ as an orange solid (0.090 g, 13%). Elution with dichloromethane/petroleum ether (1/3) gave two more orange fractions analogously yielding, respectively, compound 1 (0.460 g, 29%) and the known complex [W₂Cp₂(µ-H)(µ-PCy₂)(CO)]₂ (0.080 g, 10%), as orange solids. Data for compound 1: Anal. Calc. for C₆₀H₅₃MoO₄W: C, 43.35; H, 4.62. Found: C, 43.08; H, 4.40.

4.2. Preparation of [MoWPc₂(µ-PCy₂)(CO)]₂ (2)

Neat HBF₄·OEt₂ (90 µL, 0.656 mmol) was added to a dichloromethane solution (20 mL) of compound 1 (0.350 g, 0.486 mmol), and the mixture was stirred at room temperature for 30 min to give a dark green solution which was filtered through diatomaceous earth. The solution was then removed from the filtrate under vacuum, and the residue was washed with diethyl ether (4 × 8 mL) to give a dark green powder containing essentially pure compound 2, which was used in the preparation of compound 3 without further purification. ¹H NMR (400.13 MHz, CD₂Cl₂): δ 6.03, 5.86 (2s, 2 × 5H, Cp), 2.52–0.53 (m, 22H, Cy).

4.3. Preparation of [MoWPc₂(µ-I)(µ-PCy₂)(CO)]₂ (3)

Solid Nal (0.300 g, 3.336 mmol) was added to a 1,2-dichloroethane solution (15 mL) of the crude compound 2 prepared as described in section 4.2 (ca. 0.486 mmol), and the mixture was refluxed for 90 min to give a green solution which was filtered using a canula. Removal of solvent from the filtrate gave a green solid containing essentially pure, air-sensitive compound 3, which was used in the preparation of compound 4 without further purification. ¹H NMR (300.13 MHz, C₆D₆): δ 5.01, 4.96 (2s, 2 × 5H, Cp), 2.40–1.07 (m, 22H, Cy).

4.4. Preparation of tetrahydrofuran suspensions of Na₄MoWPc₂(µ-PCy₂)(µ-ICO)₂ (4-Na)

Sodium amalgam (1 mL of a 0.5% amalgam, 3 mmol) was added to a tetrahydrofuran solution (15 mL) of the crude compound 3 prepared as described in section 4.3 (ca. 0.486 mmol), and the mixture was stirred for 20 min to give an orange suspension of the very air-sensitive compound 4-Na. This suspension was transferred with a cannula to an empty Schlenk tube to remove the excess amalgam, and was then ready for further use.

4.5. Preparation of [MoWPc₂(µ-H)(µ-PCy₂)(CO)]₂ (5)

Solid (NH₄)PF₆ (0.120 g, 0.736 mmol) was added to a tetrahydrofuran suspension (15 mL) of compound 4-Na (ca. 0.486 mmol) prepared as described in section 4.4, and the mixture was stirred for 5 min to give a purple solution. The solvent was then removed under vacuum, the residue extracted with dichloromethane/petroleum ether (1/5), and the extracts were filtered through diatomaceous earth. After removal of solvents from the filtrate, the residue was dissolved in dichloromethane/petroleum ether (1/5) and chromatographed on alumina at 253 K. Elution with dichloromethane/petroleum ether (1/3) gave a green band yielding, after removal of solvents, compound 5 as a purple solid (0.260 g, 80%). This compound was shown by NMR to display in solution two interconverting isomers (B and T, see text) with the equilibrium ST/T₅B ratio being solvent- and temperature-dependent, with ¹H NMR-measured ratios of 1.8 (CD₂Cl₂, 203 K), 2.5 (CD₂Cl₂, 183 K) and 0.6 (toluene-d₈, 183 K). Anal. Calc. for C₅₂H₅₃Cl₂MoO₂PW (5·CH₂Cl₂): C, 40.08; H, 4.71. Found: C, 39.71; H, 5.23. ¹H NMR (400.13 MHz, CD₂Cl₂, 293 K): δ 5.25, 5.18 (2s, 2 × 5H, Cp), 2.52–1.00 (m, 22H, Cy), 3.92 (s, br, 1H, M–H). ¹H NMR (400.13 MHz, CD₂Cl₂, 183 K): Isomer ST: δ 5.43, 5.31 (2s, 2 × 5H, Cp), 2.40–0.64 (m; J₁H₂p = 32, J₂H₂p = 70, W–H). Isomer SB: δ 5.24, 5.19 (2s, 2 × 5H, Cp), 2.40–0.64 (m; J₁H₂p = 3, J₂H₂p = 118, W–H). ¹C{¹H}NMR (100.63 MHz, CD₂Cl₂, 183 K): δ 276.2 (2s, WCO, ST), 251.0 (d, JCF = 7, MoCo, ST), 246.0 (d, JCF = 10, MoCo, 5B), 235.8 (s, WCO, 5B), 90.7 (d), 89.6 (2s, 2 × 5H, Cp), 2.32, 2.18 (m, J₁H₂p = 32, J₂H₂p = 70, W–H), 1.97 (m, J₁H₂p = 32, J₂H₂p = 70, W–H). Isomer SB: δ 5.24, 5.19 (2s, 2 × 5H, Cp), 2.40–0.64 (m; J₁H₂p = 3, J₂H₂p = 118, W–H).

4.6. Reaction of 4-Na with Mel

Neat Mel (40 µL, 0.643 mmol) was added to a tetrahydrofuran suspension (8 mL) of compound 4-Na (ca. 0.120 mmol) prepared as described in section 4.4, and the mixture was stirred at room temperature for 24 h to give a brown solution. The solvent was then removed under vacuum, the residue extracted with dichloromethane/petroleum ether (1/5), and the extracts were chromatographed on alumina at 253 K. Elution with dichloromethane/petroleum ether (1/3) gave a brown fraction yielding, after removal of solvents, complex [MoWPc₂(µ-ICO)(µ-PCy₂)(µ-ICO)] (6) as a brown solid (0.045 g, 55%). Elution with neat dichloromethane gave another brown fraction analogously yielding complex [MoWPc₂(µ-COMe)(µ-PCy₂)(µ-ICO)] (7) as a brown solid (0.010 g, 12%). Data for...
compound 6: Anal. Calc. for C_{23}H_{35}MoO_{2}PW: C, 44.27; H, 5.20. Found: C, 44.37; H, 5.59. ¹H NMR (400.13 MHz, CD_{2}Cl_{2}, 233 K): δ 5.29, 5.28 (2s, 2 × 5H, Cp), 2.28–2.16 (m, 22H, Cy), 0.87 (d, J_{HP} = 2, J_{HC} = 122, 3H, ï-CH_{3}). ¹³C(^{1}H) NMR (100.63 MHz, CD_{2}Cl_{2}, 233 K): δ 245.9 (d, J_{CP} = 12, MoOC), 241.4 (d, J_{CP} = 8, WCO), 88.5, 88.1 (2s, Cp), 47.0 [d, J_{CP} = 22, 2C(Cy)], 34.0, 33.9 [2d, J_{CP} = 3, C(Cy)], 32.7, 32.6 [2s, C(Cy)], 28.2 [d, J_{CP} = 12, 2C(Cy)], 28.0, 27.8 [2d, J_{CP} = 11, C(Cy)], 26.4, 26.3 [2s, C(Cy)], −44.6 (s, Ï-CH_{3}).

4.7. Preparation of [MoWO_{2}(μ-COMe)(μ-P_{2}Cy_{2})(μ-OC)] (7)

Neat Me_{2}SO_{4} (30 μL, 0.317 mmol) was added to a tetrahydrofuran suspension (4 mL) of compound 4-Na (ca. 0.060 mmol) prepared as described in section 4.4, and the mixture was stirred at room temperature for 18 h to give a brown solution. The solvent was then removed under vacuum, the residue extracted with dichloromethane/petroleum ether (1:5), and the extracts were chromatographed on alumina at 288 K. Elution with dichloromethane/petroleum ether (1:1) gave a purple fraction yielding, after removal of solvents, compound 8 as a brown solid (0.030 g, 0.040 mmol). Elution with dichloromethane/petroleum ether (1:7), and the extracts were chromatographed on alumina at 288 K. Elution with dichloromethane/petroleum ether (1:1) gave a brown fraction yielding, after removal of solvents, compound 9 as a red solid (0.020 g, 70%). Anal. Calc. for C_{24}H_{35}MoO_{2}PW: C, 44.47; H, 5.13. Found: C, 44.74; H, 5.55. ¹H NMR (400.13 MHz, CD_{2}Cl_{2}): δ 18.70 (s, J_{HP} = 20, 1H, Ï-CH_{3}), 5.84, 5.75 (2s, 2 × 5H, Cp), 1.83–0.63 (m, 19H, Cy), 0.48–0.33 (m, 3H, Cy). ¹³C(^{1}H) NMR (100.63 MHz, CD_{2}Cl_{2}): δ 369.4 (d, J_{CP} = 11, WCO), 296.6 (d, J_{CP} = 5, μ-CO), 94.6, 93.8 (2s, Cp), 42.6 [d, J_{CP} = 22, C(Cy)], 40.4 [d, J_{CP} = 20, C(Cy)], 34.1, 34.0, 33.7, 33.1 [4s, C(Cy)], 27.5 [d, J_{CP} = 11, C(Cy)], 27.4 [d, J_{CP} = 12, 3C(Cy)], 26.4, 26.1 [2s, C(Cy)].

4.10. Photolysis of the benzyl complex 8

A toluene solution (6 mL) of compound 8 (0.030 g, 0.040 mmol) was irradiated with visible-UV light at 288 K for 15 min, with a gentle nitrogen purge, to give a reddish brown solution containing complex [MoWO_{2}(μ-CPh)(μ-P_{2}Cy_{2})(μ-OC)] (10) as major product, along with smaller amounts of [MoWO_{2}(μ-P_{2}Cy_{2})_{2}(μ-OC)] (11). The solvent was then removed under vacuum, the residue extracted with dichloromethane/petroleum ether (1:7), and the extracts were chromatographed on alumina at 288 K. Elution with dichloromethane/petroleum ether (1:1) gave a brown fraction yielding, after removal of solvents, compound 10 as a brown solid (0.018 g, 62%). Elution with neat dichloromethane gave a pink fraction yielding analogously complex 9 as a pink solid (0.006 g, 17%). Data for compound 10: Anal. Calc. for C_{24}H_{35}MoO_{2}PW: C, 49.74; H, 5.15. Found: C, 49.52; H, 5.00. ¹H NMR (400.13 MHz, CD_{2}Cl_{2}): δ 7.12 [false t, J_{HH} = 8, 2H, H_{2}(Ph)], 6.99 [t, J_{HH} = 7, 1H, H_{2}(Ph)], 5.94, 5.87 (2s, 2 × 5H, Cp), 1.98–0.93 (m, 17H, Cy), 0.68–0.48 (m, 5H, Cy). ¹³C(^{1}H) NMR (100.63 MHz, CD_{2}Cl_{2}): δ 375.0 (d, J_{CP} = 11, μ-CPh), 302.4 (d, J_{CP} = 6, μ-CO), 166.5 [s, C(1)(Ph)], 127.8 [s, C(2)(Ph)], 124.1 [s, C(3)(Ph)], 121.0 [s, C(4)(Ph)], 96.0, 95.2 (2s, Cp), 43.6 [d, J_{CP} = 23, C(Cy)], 42.4 [d, J_{CP} = 21, C(Cy)], 34.2, 34.1, 33.6, 33.3 [4s, C(Cy)], 27.5 [d, J_{CP} = 12, C(Cy)], 27.5 [d, J_{CP} = 12, 3C(Cy)], 26.4, 26.3 [2s, C(Cy)].

4.11. X-ray data collection, structure determination and refinements for compound 8

X-ray intensity data were collected at ca. 140 K on an Oxford Diffraction Xcalibur Nova single crystal diffractometer, using Cu Kα radiation. Images were collected at a 63 mm fixed crystal-detector distance using the oscillation method, with 1° oscillation and variable exposure time per image. Data collection strategy was calculated with the program CrystAlis Pro CCD [36], and data reduction and cell refinement was performed with the program CrystAlis Pro RED [36]. An empirical absorption correction was applied using the SCALEE3 ABSPACK algorithm as implemented in the program CrystAlis Pro RED. Twinning was present in the crystal, but the twin law could not be found. Using the program suite WINGX [37], the structure was solved by Patterson interpretation and phase expansion using SHELXL2016 [38], and refined with full-matrix least squares on F² using SHELXL2016 to give the residuals shown in Table 4. All non-hydrogen atoms were refined anisotropically except for a few atoms which had to be refined anisotropically in combination with the instructions DELU and SIMU. A slight disorder was present in one Cp ligand, which could not be modelled. All hydrogen atoms were geometrically placed and refined using a riding model except for H(4), which was located on the Fourier maps and refined isotropically; in the latter case however, a restraint on the C(3)–H(4) and Mo(1)–H(4) bond lengths was necessary to obtain a satisfactory refinement of its position.
Table 4

Crystal data for compound 8.

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$^{a}$ $R_I = \sum |F_{o}|-|F_{c}|/\sum |F_{c}|$. $wR_2 = \sqrt{\sum (w(Fo^2)-w(Fc^2)/\sum w(Fo^2))/2}$. $w = 1/\left[\sigma^2(Fo^2)+[\sigma^2P]+bP\right]$ where $P = (Fo^2+2Fc^2)/3$.

4.12. DFT calculations

All DFT calculations were carried out using the G09W package [39], in which the hybrid method B3LYP was used with the Becke three-parameter exchange functional [40], and the Lee-Yang-Parr correlation functional [41]. A pruned numerical integration grid (99,590) was used for all the calculations via the keyword Int = Ultrafine. Effective core potentials and their associated double-$\zeta$ LANL2DZ basis set were used for Mo and W atoms [42]. The light elements (P, O, C and H) were described with the 6–31G* basis set [43]. Geometry optimizations were performed under no symmetry restrictions, using initial coordinates derived from the 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 effect of dichloromethane on the stability of isomers 5B and 5T in solution was modelled using the polarized-continuum-model (PCM) of Tomasi and co-workers [44], using the gas-phase optimized structures. The effect of dispersion forces on the relative stability of these isomers was estimated by using the empirical dispersion corrections developed by Grimme [45].

Declaration of interests

None.

Acknowledgment

This work is dedicated to the memory of the late Prof. Pascual Royo, in recognition for his outstanding contribution to Organometallic Chemistry in Spain. This research was funded by the MINECO of Spain and FEDER (Project CTQ2015-63726-P, and a grant to E.H.), and the Consejería de Educación de Asturias (Project GRUPIN14-011). We also thank the X-Ray unit of Universidad de Oviedo, Spain, for acquisition of diffraction data, and the CMC unit of Universidad de Oviedo for access to computing facilities.

Appendix A. Supplementary Data

An XYZ file containing the Cartesian coordinates for all computed species. CCDC 1901013 contains the supplementary crystallographic data for compound 8; these data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

References

The $\eta^2$-coordination of the Alkyl Ligand Likely Will Be Stronger Also at the W (Vs. Mo) Site: However, since the Strength of the $\eta^2$-coordination (Below Ca. 100 kJ/mol) Is Much Lower than the Strength of the $\kappa^1$-coordination (Around 200 kJ/mol), the Overall Thermodynamic Balance Will Be in Favour of $\kappa^1$-coordination to the W Atom.