# **Oxidative Additions of Coordinated Ligands at Unsaturated Molybdenum and Tungsten Diphosphine-Bridged Carbonyl Dimers. 3. Decarbonylation Reactions of** $[MoW(\eta^{5}-C_{5}H_{5})_{2}(CO)_{4}(\mu-Ph_{2}PCH_{2}PPh_{2})]$

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Decarbonylation of the heterometallic title complex [MoWCp<sub>2</sub>(CO)<sub>4</sub>( $\mu$ -dppm)] (Cp =  $\eta^5$ - $C_5H_5$ ; dppm = Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>) in refluxing tetrahydrofuran leads to the phosphido complex  $[MoWCp_2(\mu-CH_2PPh_2)(\mu-PPh_2)(CO)_2]$ , presumably *via* the tricarbonylic species  $[MoWCp_2(\mu-CH_2PPh_2)(\mu-PPh_2)(CO)_2]$  $CH_2PPh_2)(\mu$ -PPh\_2)( $\mu$ -CO)(CO)<sub>2</sub>]. The latter is an unstable compound which can be generated upon reaction of the former with CO and also contains the phosphinomethyl ligand C-bonded to the tungsten atom. In contrast, photolytic decarbonylation of the title complex at -10 °C leads reversibly to the hydrido compound [MoW( $\mu$ - $\eta^1$ : $\eta^5$ -C<sub>5</sub>H<sub>4</sub>)Cp( $\mu$ -H)(CO)<sub>3</sub>( $\mu$ -dppm)], in which the cyclopentadienylidene ligand is specifically  $\eta^5$ -bonded to tungsten and  $\eta^1$ -bonded to molybdenum. Further photolysis of this complex at 10 °C leads to the triply bonded dimer  $[MoWCp_2(CO)_2(\mu-dppm)]$  with concomitant regeneration of a H–C (cyclopentadienyl) bond. The latter species reacts with 'BuCN to give  $[MoWCp_2(\mu-\eta^1:\eta^2-CN^tBu)(CO)_2(\mu-dppm)]$ , in which the isocyanide ligand is specifically  $\eta^1$ -bonded to tungsten and  $\eta^2$ -bonded to molybdenum. In order to account for the metal selectivity observed in the above species, two different intermediates, having either  $\mu$ - $\eta^1$ -CO or  $\mu$ - $\eta^1$ : $\eta^2$ -CO ligands, are thought to be involved in the decarbonylation reactions of the title compound.

### Introduction

In the previous parts of this series<sup>1,2</sup> we have shown that the unsaturated species generated through ejection of carbon monoxide from the single-metal-metalbonded dimers  $[M_2Cp_2(CO)_4(\mu\text{-dppm})]$  (Cp =  $\eta^5$ -C<sub>5</sub>H<sub>5</sub>; dppm =  $Ph_2PCH_2PPh_2$ ; M = W,<sup>1</sup> Mo<sup>2</sup>) are able to activate C-H or P-C (sp<sup>3</sup>) bonds in the coordinated cyclopentadienyl or diphosphine ligands, respectively. The results are strongly dependent on the metal. Thus, when M = Mo, only P–C bond activation is observed, which leads irreversibly to the phosphido-phosphinomethyl complex  $[Mo_2Cp_2(\mu-CH_2PPh_2)(\mu-PPh_2)(CO)_2]$ . In contrast, when M = W a reversible C-H bond activation occurs, which gives the hydrido cyclopentadienylidene compound  $[W_2(\mu-\eta^1:\eta^5-C_5H_4)Cp(\mu-H)(CO)_3(\mu-dppm)]$ . From the above studies we could not give a fully satisfactory explanation for this striking difference in the chemical behavior of the dimolybdenum and ditungsten systems. Thus, while the behavior of the dimolybdenum system could be in part due to the low thermodynamic stability of the cyclopentadienylidene ligand when bonded to this metal,<sup>3</sup> it was not clear why the P-C cleavage of the backbone of the dppm ligand occurs readily in the



dimolybdenum complex but is almost absent in the ditungsten analogue under all decarbonylation conditions examined (thermal or photochemical). Because of the fact that both  $P-C^4$  and  $C-H^5$  bond cleavage reactions are relevant processes in the chemistry of organometallic compounds, we were interested in gaining more insight about the influence of the metal on these activation processes. We therefore decided to study the decarbonylation reactions of the mixed-metal dimer [MoWCp<sub>2</sub>(CO)<sub>4</sub>( $\mu$ -dppm)] (1).

#### **Results and Discussion**

Synthesis and Structure of [MoWCp<sub>2</sub>(CO)<sub>4</sub>(µdppm)] (1). As found for its homonuclear analogues,

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compd	$v_{ m st}( m CO)^{a}/ m cm^{-1}$	$\delta$ (P) (assignt, $J_{\rm PW})^b$	$J_{\mathrm{PP}}$
$[MoWCp_2(CO)_4(\mu-dppm)] (1)$	1913 (m), 1877 (vs)	47.7 (MoP), 10.7 (WP) {isomer A}	108 <sup>c</sup>
	1840 (w), 1819 (m)	34.9 (MoP), -1.7 (WP) {isomer B}	75 <sup>c</sup>
$[MoWCp_2(\mu-CH_2PPh_2)(\mu-PPh_2)(CO)_2] (2)$	1828 (m, sh), 1790 (s) <sup>d</sup>	71.7 (µ-P, 227), 39.6 (MoP, 28)	$14^{e}$
$[MoWCp_2(\mu-CH_2PPh_2)(O)(\mu-PPh_2)(CO)] (3)$	1776 (s) $^{d,f}$	176.3 (u-P, 275), 25.7 (MoP, 66)	$4^{e}$
$[MoWCp_2(\mu-CH_2PPh_2)(\mu-PPh_2)(\mu-CO)(CO)_2] (4)$	1938 (vs), 1878 (w), 1656 (m)	51.6 (µ-P, 200), 53.8 (MoP)	$7^g$
$[MoW(\mu - \eta^{1}: \eta^{5}-C_{5}H_{4})Cp(\mu - H)(CO)_{3}(\mu - dppm)]$ (5)	1930 (vs), 1852 (s), 1793 (m)	72.5 (MoP), 22.2 (WP, 294)	70 <sup>h</sup>
$[MoWCp_2(CO)_2(\mu - dppm)] (6)$	1735 (vs)	54.9 (MoP), 28.7 (WP, 425)	<b>74</b> g
$[MoWCp_2(\mu-\eta^1:\eta^2-CN^tBu)(CO)_2(\mu-dppm)] $ (7)	1824 (s), 1787 (vs) <sup>i</sup>	51.7 (MoP), 8.12 (WP, 394)	83

<sup>*a*</sup> Recorded in THF solution, unless otherwise stated. <sup>*b*</sup> Recorded at 161.97 MHz and 291 K in toluene- $d_8$  solution, unless otherwise stated.  $\delta$  is given in ppm relative to external 85% aqueous H<sub>3</sub>PO<sub>4</sub> and *J* in hertz. <sup>*c*</sup> In acetone- $d_6$  solution at 248 K. <sup>*d*</sup> Dichloromethane solution. <sup>*e*</sup> C<sub>6</sub>D<sub>6</sub> solution. <sup>*f*</sup>  $v_{st}$ (W–O) 931 cm<sup>-1</sup> in Nujol mull. <sup>*g*</sup> CD<sub>2</sub>Cl<sub>2</sub> solution. <sup>*h*</sup> 253 K. <sup>*i*</sup>  $v_{st}$ (CN) 1629 (w) cm<sup>-1</sup>.



compound **1** can be synthesized in good yield by addition of dppm to the triply bonded dimer [MoWCp<sub>2</sub>(CO)<sub>4</sub>]. Spectroscopic data for **1** (Table 1 and Experimental Section) are strongly related to those of the homonuclear dimers, thus indicating a close structural relationship. As expected,<sup>1,2</sup> two isomers are observed in solution, their ratio (*ca.* 1:1 in Me<sub>2</sub>CO-*d*<sub>6</sub> at 248 K) being midway between those observed for the dimolybdenum and ditungsten complexes. The structures of these isomers have been previously discussed<sup>1,2</sup> and need no further comments.

**Thermal Decarbonylation of Compound 1.** Complex **1** is readily decarbonylated in refluxing tetrahydrofuran to give the unsaturated, air-sensitive complex [MoWCp<sub>2</sub>( $\mu$ -CH<sub>2</sub>PPh<sub>2</sub>)( $\mu$ -PPh<sub>2</sub>)(CO)<sub>2</sub>] **(2**) in good yield, along with trace amounts of the oxo compound [MoWCp<sub>2</sub>-( $\mu$ -CH<sub>2</sub>PPh<sub>2</sub>)(O)( $\mu$ -PPh<sub>2</sub>)(CO)] **(3**). The latter is formed due to the presence of trace amouts of atmospheric oxygen in the reaction medium and during manipulation of the reaction mixture. Thus, complex **3** is the major species formed when solutions of **2** are exposed to air, although extensive decomposition also occurs.

Spectroscopic data for **2** and **3**, which will be discussed later on, clearly show that these complexes are obtained as single isomers in each case, with the carbon atom of the phosphinomethyl ligand specifically bonded to the tungsten atom (Chart 2). The oxo ligand in **3** is also bonded to the tungsten atom, as expected in view of the structures of its homonuclear analogues  $[M_2Cp_2(\mu-CH_2-PPh_2)(O)(\mu-PPh_2)(CO)]$  (M = Mo,<sup>6</sup> W<sup>1</sup>).

Complex **2** reacts readily with CO (1 atm) to give the electron-precise species  $[MoWCp_2(\mu-CH_2PPh_2)(\mu-PPh_2)-(\mu-CO)(CO)_2]$  (**4**). The latter compound, however, could not be isolated as a pure solid because it starts to decarbonylate when the CO atmosphere is removed so as to give back the parent dicarbonyl **2**. Thus, compound **4** is assumed to be an intermediate species in the thermal formation of **2**. In fact, IR monitoring of the thermolytic reaction leading to dicarbonyl **2** shows the presence of weak  $\nu_{st}(CO)$  bands that can be assigned to complex **4**. On the other hand, NMR data for **4** (see





Chart 3

We must note that the dimolybdenum analogue of complex **2** failed to give a CO adduct stable enough to be detected spectroscopically under the usual experimental conditions.<sup>2</sup> Thus, it seems that complexes of the type **4** give up CO more easily as we replace tungsten for molybdenum atoms, as is usually observed in the chemistry of carbonylic complexes of these elements.

**Photochemical Decarbonylation of Compound 1.** Complex **1** easily loses a single CO molecule when irradiated with visible–UV light in THF solution at –10 °C to give cleanly the hydrido cyclopentadienylidene complex [MoW( $\mu$ - $\eta^1$ : $\eta^5$ -C<sub>5</sub>H<sub>4</sub>)Cp( $\mu$ -H)(CO)<sub>3</sub>( $\mu$ -dppm)] (**5**). Complex **5** is thermally unstable and decomposes readily above 0 °C. When further irradiated at 10 °C, it rapidly gives the triply metal–metal bonded dicarbonyl [MoW-Cp<sub>2</sub>(CO)<sub>2</sub>( $\mu$ -dppm)] (**6**) in good yield. As expected, the latter can be obtained through direct irradiation of **1** at 10 °C, a process that can be reversed by just bubbling CO through a solution of compound **6**.

Complex **6** is isostructural with its ditungsten<sup>1</sup> and dimolybdenum<sup>2</sup> analogues and also displays fluxional behavior in solution, so that the linear semibridging carbonyls exchange their positions between molybdenum and tungsten atoms. This is clearly indicated in the <sup>13</sup>C NMR spectrum by the presence of a single carbonyl resonance at 248.4 ppm (to be compared with 254.2 and 240.7 ppm for the corresponding dimolybdenum and ditungsten complexes, respectively). This dynamic behavior has been also observed in the triply bonded heterometallic complex [MoWCp<sub>2</sub>(CO)<sub>4</sub>]<sup>7</sup> and requires only a modest energy of activation.

As found for **2**, the cyclopentadienylidene complex **5** is obtained as a single isomer. NMR data (see later) allow us to establish clearly that the  $C_5H_4$  group is specifically  $\eta^5$ -bonded to tungsten and  $\eta^1$ -bonded to molybdenum (Chart 4). This is just opposite to what we would have expected on the basis of our previous

<sup>(7)</sup> Curtis, M. D.; Fotinos, M. A.; Messerle, L.; Sattelberger, A. P. *Inorg. Chem.* **1983**, *22*, 1559.



studies on the structure of heterometallic species  $[M_2M'-(\mu-\eta^1:\eta^5-C_5H_4)Cp_2(CO)_6]$  (M, M' = Mo, W), which revealed a clear preference of the  $C_5H_4$  ligand to form  $\sigma$  bonds to tungsten rather than to molybdenum atoms.<sup>3</sup> The above data suggested to us that the structure exhibited by compound **5** might be not only dictated by the strength of the  $\sigma$  bond between the  $C_5H_4$  ligand and the Mo or W atoms but also influenced by the nature of its precursors.

In order to trace back the origin of the stereospecific formation of **5**, we examined the reaction of the dicarbonyl species **6** with <sup>t</sup>BuCN. In the case of the ditungsten analogue of **6**, this has been shown<sup>1</sup> to proceed through a  $\mu$ - $\eta^1$ : $\eta^2$ -<sup>t</sup>BuCN complex, which then experiences C–H bond oxidative addition to yield a hydrido cyclopentadienylidene complex analogous to **5**. Indeed, <sup>t</sup>BuCN readily reacts with **6** to yield the isocyanidebridged complex [MoWCp<sub>2</sub>( $\mu$ - $\eta^1$ : $\eta^2$ -CN<sup>t</sup>Bu)(CO)<sub>2</sub>( $\mu$ -dppm)] (7). This product, however, does not experience any detectable C–H activation process at room temperature, thus resembling the behavior of its dimolybdenum analogue.<sup>2</sup>

Once more, NMR data indicate that complex **7** is formed as a single isomer, out of the two possible ones. From these data we conclude that the isocyanide ligand is  $\sigma$ -bonded to tungsten and  $\pi$ -bonded to molybdenum. This is not surprising itself, as W–C  $\sigma$  bonds are usually stronger than Mo–C ones.<sup>8</sup> However, this structural feature might be at the origin of the failure of **7** to experience C–H (cyclopentadienyl) bond oxidative addition. Were such a process to occur for **7**, we would expect this to render the cyclopentadienylidene ligand in its less favorable disposition: that is,  $\sigma$ -bonded to molybdenum instead of tungsten (Scheme 1).

Complex 7 can be taken as a model for the tricarbonylic intermediate presumably formed after ejection of the first CO molecule in compound **1** (see later).<sup>1,2</sup> Thus, the anomalous presence of the cyclopentadienylidene ligand specifically  $\sigma$ -bonded to molybdenum in complex **5** would be the result of the specific coordination ( $\sigma$  to Scheme 1. Expected Specificity in the C–H Bond Cleavage Process (Not Observed) of Complex 7<sup>a</sup>



 $^{a} P-C-P = Ph_{2}PCH_{2}PPh_{2}$ 

tungsten and  $\pi$  to molybdenum) of a bridging carbonyl ligand in the tricarbonylic precursor of **5**.

Structural Characterization of New Complexes. With the exception of 4, all heterometallic complexes 1-7 have dimolybdenum and/or ditungsten counterparts. Therefore, the structural characterization of these heterometallic species is straightforward by comparison of their IR and NMR (<sup>1</sup>H, <sup>31</sup>P, <sup>13</sup>C) data with those of the corresponding homonuclear compounds<sup>1,2</sup> and needs then no detailed comments. Typically,  $v_{st}(CO)$  frequencies in the heterometallic complexes (Table 1) are intermediate between those observed in the corresponding homometallic species. As for NMR chemical shifts, they are mostly dictated by the identity of the metal to which the nucleus under observation is bonded. For example,  $\delta_{\rm P}$  values for compound **6** measured in CD<sub>2</sub>Cl<sub>2</sub> at 248 K are 54.9 and 28.7 ppm ( $J_{PP} =$ 108 Hz), very close to the values found respectively for the corresponding dimolybdenum (57.9 ppm) and ditungsten (27.2 ppm,  $J_{PP} = 112$  Hz) analogues. Thus, the assignments of the NMR resonances in the heterometallic species 1-7 are quite obvious in general. Of relevance in the present context are only the data which allow us to identify the coordination position of ligands when two isomers are possible.

For compounds **2** and **3**, the disposition of the phosphinomethyl ligand P-bonded to molybdenum is denoted by the similarity of their <sup>31</sup>P chemical shifts (Table 1) to those of the dimolybdenum analogues<sup>2,6</sup> and the reduced value of the corresponding P–W couplings (30–60 Hz), almost an order of magnitude lower than one-bond couplings measured in related ditungsten complexes.<sup>1</sup> The oxo ligand in **3** can be safely placed on tungsten by exclusion, because the single carbonyl of the molecule exhibits chemical shifts and P–C couplings (to both phosphorus atoms) almost identical with those of the dimolybdenum analogue.<sup>6</sup>

<sup>(8)</sup> Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; p 100.

#### Mo and W Diphosphine-Bridged CO Dimers

As was said before, compound 4 has no homometallic counterpart. In spite of this, the spectroscopic data for **4** allow a precise definition of its structure. First, the phosphorus atoms of the phosphinomethyl and phosphido groups are weakly coupled ( $J_{PP} = 7$  Hz), as was found for 2 and 3, which seems characteristic of a transoid disposition of these bridging ligands, so as to define an almost flat five-atom ring.<sup>1,2,6</sup> The IR and <sup>13</sup>C NMR spectra denote the presence of two terminal and one bridging carbonyl (Table 1 and Experimental Section). The relative intensity of the high-energy  $v_{st}(CO)$ bands (strong and weak, in order of decreasing frequency) is indicative of the presence of a *cisoid*  $M_2(CO)_2$ oscillator,<sup>9</sup> as found in the isoelectronic complexes [W<sub>2</sub>- $Cp_2(\mu-X)(\mu-CO)(CO)_2(\mu-dppm)$ ] PF<sub>6</sub> (X = halogen).<sup>10</sup> Therefore, the bridging CO must be located in a transoid disposition with respect to the terminal carbonyls (Chart 3).

The dppm ligand in **5** displays two <sup>31</sup>P NMR resonances at 72.5 and 22.2 ppm ( $J_{PW} = 294$  Hz), so that the latter corresponds to the phosphorus atom bonded to tungsten. The unique cyclopentadienyl ligand in the molecule gives rise to a doublet ( $J_{HP} = 1$  Hz) in the <sup>1</sup>H NMR spectrum. On selective <sup>31</sup>P decoupling of the 72.5 ppm signal, this cyclopentadienyl resonance becomes a singlet, which proves that this ligand is bonded to the molybdenum atom. Then, the cyclopentadienylidene ligand must be  $\eta^5$ -bonded to tungsten and  $\eta^1$ -bonded to molybdenum (Chart 4).

In the case of the isocyanide compound **7**, the coordination of the bridging isocyanide as  $\eta^1$ -bonded to tungsten and  $\eta^2$ -bonded to molybdenum is based on the NMR chemical shift of its carbon atom (214.2 ppm), very similar to that measured for the corresponding ditungsten complex (212.3)<sup>1</sup> and substantially lower than that for the dimolybdenum analogue (223.1 ppm).<sup>2</sup>

**Reaction Pathways in the Decarbonylation of Complex 1.** The results discussed above indicate that decarbonylation of the heterometallic complex 1 can lead to either P-C cleavage (complex 2) or C-H cleavage (complex 5) products, in addition to the triply bonded dicarbonyl 6. Therefore, this behavior has common characteristics with both the molybdenum and tungsten homometallic systems and can be understood by considering similar reaction pathways,<sup>1,2</sup> slightly modified as shown in Scheme 2. The transformations 1/6 and 1/5, which are the dominant processes at low temperatures (photochemical decarbonylations), have been discussed in detail for the homometallic systems. Here it should only be noted that the bridging carbonyl in intermediate **A** is assumed to be  $\sigma$ -bonded to tungsten and  $\pi$ -bonded to molybdenum, as found for the isocyanide-bridged complex 7. In this way, the C-H bond oxidative addition of the cyclopentadienyl ligand is expected to render, via the agostic intermediate **B**, a cyclopentadienylidene ligand  $\sigma$ -bonded to molybdenum, as found for 5. Finally, because of the reversibility of these low-temperature transformations, the nature of the photochemical products (5 or 6) is just governed by the extent of decarbonylation induced in the system.

The heterometallic system, however, offers two new pieces of information concerning the processes occurring

Scheme 2. Proposed Reaction Pathways in the Decarbonylation Reactions of Compound 1<sup>a</sup>



 $^{a}P-C-P = Ph_{2}PCH_{2}PPh_{2}.$ 

during high-temperature (thermolytic) decarbonylation. First, we have been able to detect and characterize complex 4, which is most likely the immediate precursor of the dicarbonylic product 2. We have also shown that the phosphinomethyl ligand in 4 is C-bonded to the tungsten atom. As a result, it is unlikely that complex 4 can be derived directly from intermediate A, because this should expectedly render, after P-C bond oxidative addition, a phosphinomethyl complex having this ligand C-bonded to molybdenum rather than to tungsten, as observed in the C-H oxidative addition leading to 5. As an alternative explanation, it could be thought that, at high temperatures, intermediate A might be able to experience at some extent an isomerization process so that the bridging CO group would be  $\sigma$ -bonded to molybdenum and  $\pi$ -bonded to tungsten, which then could allow the formation of 4. However, we consider this possibility as rather unlikely in light of the dynamic information available on fluxional homometallic complexes having four-electron CO groups. Thus, in the case of  $[Mn_2(\mu - \eta^1: \eta^2 - CO)(CO)_4(\mu - dppm)_2]^{11}$  and  $[Mn_2(\mu - \eta^2: \eta^2: CO)(CO)_4(\mu - dppm)_2]^{11}$  $\eta^{1}:\eta^{2}-CO(CO)_{5}L(\mu-dppm)$ ] (L = CO,<sup>12a</sup> PR<sub>3</sub><sup>12b</sup>), NMR experiments have shown that the bridging CO ligand exchanges its position only with terminal carbonyls in the metal atom to which it is  $\sigma$ -bonded.

In order to explain the structure shown by the P-C cleavage products **4** and **2**, we then propose that, at high temperatures, the unsaturated tricarbonylic intermediate **C** is formed, having a two-electron bridging CO group. P-C bond oxidative addition for this species could now equally occur on tungsten or molybdenum centers, so that the process would then occur so as to give the most stable product.

While we do not have direct evidence for the formation of intermediate C, there is at least a precedent of this sort of species as products of decarbonylation in metal-

<sup>(9)</sup> Braterman, P. S. *Metal Carbonyl Spectra*; Academic Press: London, U.K., 1975.

<sup>(10)</sup> Alvarez, M. A.; García, M. E.; Riera, V.; Ruiz, M. A.; Bois, C.; Jeannin, Y. Angew. Chem., Int. Ed. Engl. **1993**, *32*, 1156.

<sup>(11)</sup> Marsella, J. A.; Caulton, K. G. *Organometallics* 1982, *1*, 274.
(12) (a) Liu, X. Y.; Riera, V.; Ruiz, M. A. *Organometallics* 1994, *13*, 2925. (b) Liu, X. Y.; Riera, V.; Ruiz, M. A. Unpublished results.

metal-bonded carbonyl dimers. Thus, different studies have shown that photochemical decarbonylation of [Fe2- $Cp_2(CO)_4$  may yield two independent isomeric products, the unsaturated  $[Fe_2Cp_2(\mu-CO)_3]^{13}$  and the electron-precise  $[Fe_2Cp_2(\mu-\eta^{1}:\eta^{2}-CO)(CO)_2]$ .<sup>14,15</sup> The latter is the most stable isomer and can be isolated as a solid,<sup>15</sup> but the unsaturated isomer is the most stable in the case of the pentamethylcyclopentadienyl system.<sup>16</sup> The above information suggests that, in the case of our heterometallic system, intermediates A and C might not differ much in energy, although the electron-precise A is expected to be more stable. However, even after accepting the involvement of intermediate C in the formation of compounds 4 and 2, we cannot yet make a reasonable proposal about the question of whether A and **C** are independent primary products of the decarbonylation of 1 or, alternatively, one precedes the other.

It is interesting to compare the relative efficiencies of the pathways leading to P-C cleavage products in compound 1 and its homometallic analogues. For the ditungsten system, P-C bond cleavage of the backbone of the dppm ligand is only observed at high temperatures and as a very low-efficiency process.<sup>1</sup> In contrast, the dimolybdenum system experiences such a process with very high efficiency at 70 °C and remains somewhat active even at 0 °C (photochemical decarbonylation).<sup>2</sup> The heterometallic system behaves in an intermediate way, so that the P-C cleavage process is dominant at high temperatures but is fully suppressed during low-temperature (photochemical) decarbonylations. Clearly, the above facts do not have a thermodynamic origin (relative reluctance of the P-C bond to oxidatively add to tungsten atoms) as, in fact, the P-Cbond oxidative addition in the heterometallic complex occurs on the tungsten atom. Thus, we conclude that the relative efficiency of the P-C cleavage process occurring in these dimetallic complexes has a kinetic origin. Replacement of tungsten for molybdenum atoms seems to decrease the relevant energy barriers so as to increase the rate of oxidative addition of this bond.

## **Concluding Remarks**

Depending on reaction conditions (thermolytic or photolytic), decarbonylation of the heterometallic dimer 1 can result in the oxidative addition of C-H (cyclopentadienyl) or P-C (dppm backbone) bonds to the dimetal center. In contrast to what might have been deduced only on the basis of the behavior of the dimolybdenum or tungsten analogues of 1, both processes can occur at either molybdenum or tungsten centers. The presence of tungsten atoms stabilizes the products arising from the C-H cleavage, in agreement with previous findings,<sup>3</sup> while the presence of molybdenum atoms seems to reduce the temperature threshold for the P-C cleavage of the backbone of the dppm

ligand. On the basis of the stereochemistry of the heterometallic products derived from 1, it is proposed that two different intermediates, having a bridging CO ligand in either a  $\mu$ - $\eta^1$  or  $\mu$ - $\eta^1$ : $\eta^2$  coordination mode, are possibly involved in these decarbonylation reactions.

#### **Experimental Section**

General Comments. The general experimental techniques and manipulation procedures are described in ref 1a. [MoWCp<sub>2</sub>- $(CO)_4$ <sup>7</sup> and dppm<sup>17</sup> were prepared by literature methods. NMR spectra were recorded at 291 K and 300.13 (1H), 121.5  $({}^{31}P{}^{1}H{})$ , or 75.47 MHz  $({}^{13}C{}^{1}H{})$  unless otherwise stated. Chemical shifts are given in ppm, relative to internal TMS (<sup>1</sup>H, <sup>13</sup>C) or external 85%  $H_3PO_4$  aqueous solution (<sup>31</sup>P). Coupling constants (J) are given in hertz. Compound 2 is highly air-sensitive, whereas 4 and 5 are thermally unstable, so that satisfactory elemental analyses could not be obtained in these cases.

Preparation of [MoWCp2(CO)4(µ-dppm)] (1). A dichloromethane solution (20 mL) of [MoWCp<sub>2</sub>(CO)<sub>4</sub>] (0.521 g, 1 mmol) was treated with dppm (0.384 g, 1 mmol) and the mixture was stirred at room temperature for 10 min. Solvent was then removed under vacuum; the residue was dissolved in a minimum of toluene, and this solution was chromatographed on a tap-water-refrigerated alumina column (activity III,  $30 \times 2.5$  cm) prepared in petroleum ether. Elution with petroleum ether gave a minor fraction containing some [MoWCp<sub>2</sub>(CO)<sub>6</sub>]. Elution with toluene gave a red-orange fraction, which was taken to dryness under vacuum. Crystallization of the residue from toluene/petroleum ether at -20°C yielded complex 1 as dark brown crystals (0.679 g, 75%). Anal. Calcd for C<sub>39</sub>H<sub>32</sub>O<sub>4</sub>P<sub>2</sub>MoW (1): C, 51.54; H, 3.56. Found: C, 51.87; H, 3.78. <sup>1</sup>H NMR (400.13 MHz, Me<sub>2</sub>CO-d<sub>6</sub>, 248 K):  $\delta$  8.18–7.04 (Ph), 5.82 (ddd,  $J_{\rm HH} =$  17,  $J_{\rm HP} =$  12, 4, 1H, CH<sub>2</sub>, isomer A), 5.56 (ddd,  $J_{HH} = 17$ ,  $J_{HP} = 16$ , 9, 1H, CH<sub>2</sub>, isomer A), 5.48 (s, 5H, Cp, isomer B), 5.33 (s, 5H, Cp, isomer B), 5.17 (m, 1H, CH<sub>2</sub>, isomer B), 4.70 (m, 1H, CH<sub>2</sub>, isomer B), 4.60 (s, 5H, Cp, isomer A), 4.54 (s, 5H, Cp, isomer A). Ratio A:B ca. 1:1.

Preparation of [MoWCp<sub>2</sub>(µ-CH<sub>2</sub>PPh<sub>2</sub>)(µ-PPh<sub>2</sub>)(CO)<sub>2</sub>] (2). A tetrahydrofuran (THF) solution (15 mL) of compound 1 (0.045 g, 0.05 mmol) was refluxed for 4 h to give a dark brown solution. The solvent was then removed under vacuum; the residue was dissolved in toluene, and this solution was chromatographed at 10 °C on an alumina column (activity III,  $20 \times 2.5$  cm) prepared in petroleum ether. Elution with the latter solvent gave a fraction containing a small amount of  $[MoWCp_2(CO)_6]$ . Elution with toluene gave a greenish-brown fraction followed by a minor violet fraction. Removal of solvent under vacuum from the main fraction yielded complex 2 as an air-sensitive brown powder (0.027 g, 65%). <sup>1</sup>H NMR (200.13 MHz, toluene-*d*<sub>8</sub>):  $\delta$  7.80–6.80 (20H, Ph), 4.81 (d, *J*<sub>HP</sub> = 0.5, 5H, WCp), 4.77 (s, 5H, MoCp), 3.23 (dd, J<sub>HH</sub> = 11, J<sub>HP</sub> = 6, 1H, CH<sub>2</sub>), 2.06 (ddd,  $J_{\rm HH} = 11$ ,  $J_{\rm HP} = 17$ , 2, 1H, CH<sub>2</sub>). <sup>13</sup>C-{<sup>1</sup>H} NMR (100.61 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  229.7 (dd,  $J_{PC} = 14$ , 10, MoCO), 224.2 (dd,  $J_{PC} = 7$ , 5,  $J_{WC} = 210$ , WCO), 148.7–128.0 (Ph), 89.9, 89.7 (2 × s, Cp), -5.74 (d,  $J_{CP} = 8$ ,  $J_{CW} = 50$ , WCH<sub>2</sub>). Removal of solvent under vacuum from the violet fraction yielded the oxo compound 3 as a dark gray powder in variable amounts (usually less than 5%). Anal. Calcd for C<sub>36</sub>H<sub>32</sub>O<sub>2</sub>P<sub>2</sub>-MoW (3): C, 51.43; H, 3.34. Found: C, 51.05; H, 3.15. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  7.90–6.90 (20H, Ph), 5.27 (s, 5H, WCp), 4.71 (s, 5H, MoCp), 3.33 (td, J<sub>HH</sub> = 12, J<sub>HP</sub> = 12, 5, 1H, CH<sub>2</sub>), 2.43 (dd,  $J_{\rm HH} = 12$ ,  $J_{\rm HP} = 8$ , 1H, CH<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (100.61 MHz,  $C_6D_6$ ):  $\delta$  234.2 (dd,  $J_{PC} = 11$ , 5, MoCO), 147.0–128.0 (Ph), 106.9 (s, WCp), 87.9 (s, MoCp), -2.20 (d,  $J_{CP} = 10$ , WCH<sub>2</sub>).

Preparation of [MoWCp<sub>2</sub>(µ-CH<sub>2</sub>PPh<sub>2</sub>)(µ-PPh<sub>2</sub>)(µ-CO)-(CO)<sub>2</sub>] (4). Essentially pure complex 4 (by IR and <sup>31</sup>P NMR spectroscopy) is rapidly formed when CO (1 atm) is gently

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results

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bubbled at room temperature through THF or CH<sub>2</sub>Cl<sub>2</sub> solutions of complex **2** for about 30 s. Removal of solvent under vacuum from these solutions gave almost quantitative back-conversion of **4** into **2**. NMR data for **4** were then obtained by carrying out the above carbonylation process in the deuterated solvent, inside the NMR tube. <sup>1</sup>H NMR (400.13 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  7.7–7.0 (20H, Ph), 4.95 (s, 5H, Cp), 4.57 (s, 5H, Cp), 1.74 (t, *J*<sub>HH</sub> = *J*<sub>HP</sub> = 12, 1H, CH<sub>2</sub>), 1.43 (dd, *J*<sub>HH</sub> = 12, *J*<sub>HP</sub> = 14, 1H, CH<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (100.61 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 213 K):  $\delta$  308.3 (d, *J*<sub>PC</sub> = 24,  $\mu$ -CO), 250.1 (t, *J*<sub>PC</sub> = 13, MoCO), 237.4 (s, WCO), 149.0–127.1 (Ph), 94.1, 91.0 (2 × s, Cp), -20.0 (d, *J*<sub>CP</sub> = 7, CH<sub>2</sub>).

**Preparation of [MoW**( $\mu$ - $\eta^1$ : $\eta^5$ -C<sub>5</sub>H<sub>4</sub>)Cp( $\mu$ -H)(CO)<sub>3</sub>( $\mu$ -dppm)] (5). A THF solution (15 mL) of compound 1 (0.045 g) was irradiated with visible–UV light at –10 °C for 1 h while nitrogen was bubbled through the solution gently. This solution was then filtered at the same temperature, the solvent was removed under vacuum, and the residue washed with petroleum ether to give almost pure compound 5 as a brown solid. This species is unstable at room temperature in solution or even in the solid state. For NMR studies, the solid compound was dissolved at –10 °C in toluene- $d_8$ . <sup>1</sup>H NMR (400.13 MHz, toluene- $d_8$ , 253 K):  $\delta$  6.16 (br, 1H, C<sub>5</sub>H<sub>4</sub>), 4.99 (br, 1H, C<sub>5</sub>H<sub>4</sub>), 4.85 (d,  $J_{HP} = 1$ , 5H, MoCp), 4.63 (m, 1H, C<sub>5</sub>H<sub>4</sub>), 4.30 (m, 1H, C<sub>5</sub>H<sub>4</sub>), 4.14 (dt,  $J_{HH} = 13$ ,  $J_{HP} = 10$ , 1H, CH<sub>2</sub>), 3.94 (q, br,  $J_{HP} \approx J_{HP} \approx 11$ , 1H, CH<sub>2</sub>), –14.36 (ddd,  $J_{HP} = 38$ , 29,  $J_{HH} = 1$ , 1H,  $\mu$ -H).

**Preparation of [MoWCp<sub>2</sub>(CO)<sub>2</sub>(\mu-dppm)] (6).** Compound 1 (0.045 g, 0.05 mmol) was photolyzed as described for 5, but at 10 °C for 2 h, to yield a greenish mixture. Solvent was then removed under vacuum; the residue was dissolved in dichloromethane/petroleum ether (1:1), and this solution was chromatographed at 10 °C on an alumina column (activity III, 20 × 2.5 cm) prepared in petroleum ether. Elution with

the same solvent mixture gave a very minor orange fraction containing trace amounts of  $[MoWCp_2(CO)_6]$ , followed by a green fraction. Removal of solvents under vacuum from the latter yielded complex **6** as a black-green air-sensitive solid (0.026 g, 62%). Anal. Calcd for  $C_{37}H_{32}O_2P_2MoW$  (**6**): C, 52.11; H, 3.79. Found: C, 51.75; H, 3.66. <sup>1</sup>H NMR (CD\_2Cl\_2):  $\delta$  7.60–7.20 (20H, Ph), 5.73 (t,  $J_{HP}$  = 10, 2H, CH<sub>2</sub>), 4.57 (d,  $J_{HP}$  = 1, 5H, Cp), 4.54 (d,  $J_{HP}$  = 1, 5H, Cp),  $^{13}C\{^{1}H\}$  NMR (100.61 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  248.4 (d,  $J_{PC}$  = 5, CO), 139.6–125.5 (Ph), 89.4, 87.9 (2  $\times$  s, Cp), 67.4 (dd,  $J_{CP}$  = 22, 5, CH<sub>2</sub>).

Preparation of [MoWCp<sub>2</sub>(CO)<sub>2</sub>( $\mu$ - $\eta^{1}$ : $\eta^{2}$ -CN<sup>t</sup>Bu)( $\mu$ -dppm)] (7). <sup>t</sup>BuCN (6  $\mu$ L, 0.05 mmol) was added to a THF solution (15 mL) of compound 6 (0.043 g, 0.05 mmol), and the mixture was stirred at room temperature for 15 min to give a red-brown solution. Solvent was then removed under vacuum and the residue washed with petroleum ether ( $2 \times 5$  mL) and extracted with THF (15 mL). The filtered solution was then concentrated under vacuum; petroleum ether was added, and this mixture was stored overnight at -20 °C. In this way, redbrown crystals of 7 were obtained (0.037 g, 78%). Anal. Calcd for C<sub>42</sub>H<sub>41</sub>O<sub>2</sub>NP<sub>2</sub>MoW (7): C, 53.90; H, 4.42; N, 1.50. Found: C, 53.61; H, 4.27; N, 1.40. <sup>1</sup>H NMR (toluene- $d_8$ ):  $\delta$  8.45–6.86 (20H, Ph), 5.96 (m, 1H, CH<sub>2</sub>), 5.64 (m, 1H, CH<sub>2</sub>), 4.58 (d, J<sub>HP</sub> = 1, 5H, Cp), 4.22 (s, 5H, Cp), 1.39 (s, 9H, Me). <sup>13</sup>C{<sup>1</sup>H} NMR (toluene- $d_8$ ):  $\delta$  260.2 (br, MoCO), 227.8 (d,  $J_{PC} = 9$ , WCO), 214.2 (br, WCN), 145.0-120.0 (Ph), 93.6, 88.8 (2 × s, Cp), 79.1 (br, CH<sub>2</sub>), 56.4 (s, CMe<sub>3</sub>), 31.5 (s, Me).

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