Protonation Reactions on the Binuclear Complexes $[W_2Cp_2(CO)_n(\mu\text{-}L_2)]$ [$L_2 = Ph_2PCH_2PPh_2$, $Me_2PCH_2PMe_2$; $n = 2, 4$]. Chemical Behavior of Their Hydrido and Hydroxycarbyne Derivatives

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Reaction of the triply bonded dimers $[W_2Cp_2(CO)_2(\mu\text{-}L_2)]$ ($L_2 = Ph_2PCH_2PPh_2$, $Me_2PCH_2PMe_2$) with $HBF_4{\cdot}OEt_2$ and other strong acids leads to the unsaturated cationic hydrides $[W_2Cp_2(\mu\text{-}H)(CO)_2(\mu\text{-}L_2)]^+$. In contrast with this, reaction of $HBF_4{\cdot}OEt_2$ with the singly bonded dimers $[W_2Cp_2(CO)_4(\mu\text{-}L_2)]$ leads, depending on L_2 and reaction conditions, to either hydroxycarbyne cations $[W_2(\mu\text{-}COH)Cp_2(CO)_2(\mu\text{-}L_2)]^+$ or hydridoderivatives $[W_2Cp_2(\mu\text{-}H)(CO)_n(\mu\text{-}L_2)]^+$ ($n = 2$ or 4). The relative amounts of the above products in the reaction mixtures depend both on the nature of L_2 and reaction conditions. From these data and the results of additional experiments it is concluded that, when $L_2 = Ph_2PCH_2PPh_2$, protonation gives initially the hydroxycarbyne complex, which can experience afterward a solvent-assisted transformation into the corresponding hydrido derivatives, possibly through an H−C(cyclopentadienyl) activation step. When $L_2 = Me_2PCH_2PMe_2$, the above *O*-protonation competes with direct proton attack at the intermetallic bond, the latter process being dominant under most of the reaction conditions. The structure of the new complexes as well as the dynamic behavior of some of them is discussed with the aid of IR and variable-temperature NMR spectroscopy.

Introduction

Protonation is a fundamental acid−base reaction in chemistry. In the context of organometallic compounds containing metal−metal bonds, it is known that the latter often behave as nucleophilic centers, so that they can be protonated to afford hydrido-bridged complexes.[1] As expected, the donor and steric properties of the ligands around the dimetal center can dramatically influence these reactions. For instance, the dimer $[Fe_2(\mu\text{-}SMe)_2(CO)_2L_2]$ is readily protonated at the intermetallic bond when $L = PMe_2Ph$ but not when $L = PMePh_2$.[2] Sometimes, depending on the nature of the coordinated ligands, protonation can alternatively occur at the latter sites, and in this way a wide variety of products can be obtained.[3,4] Coordinated carbon monoxide is not, however, a frequent site of protonation. In fact, the few precedents reported so far all involve protonation of bridging CO ligands in anionic carbonyl clusters such as $[M_3H(CO)_{10}]^-$ (M = Fe, Ru, Os),[5] $[Fe_4H(CO)_{13}]^-$,[6] or $[Co_3(CO)_{10}]^-$.[7] This results in the formation of hydroxycarbyne clusters, which are without exception thermally unstable and could be characterized only at low temperature. Due to the scarce number of examples of hydroxycarbyne complexes available and their low stability, the chemistry of this ligand has been very little explored. In this paper we report our studies on the protonation reactions of the metal−metal bonded complexes $[W_2Cp_2(CO)_4(\mu\text{-}L_2)]$ (**1**) [$L_2 = Ph_2PCH_2PPh_2$ (dppm), $Me_2PCH_2PMe_2$ (dmpm); $Cp = \eta^5\text{-}C_5H_5$].[8] We have found that, depending on the substrate and reaction conditions, protonation can occur at the metal−metal bond to give hydrido derivatives or, alternatively, at a terminal CO ligand to give the unsaturated hydroxycarbyne complexes $[W_2(\mu\text{-}COH)Cp_2(CO)_2(\mu\text{-}L_2)]^+$ (**5**). Compounds **5** are stable at room temperature, both in solution and in the solid state, thus facilitating the study of their reactivity.

In the context of the present work, it was also of interest to examine the behavior of the triply metal−metal bonded complexes $[W_2Cp_2(CO)_2(\mu\text{-}L_2)]$ (**2**). When compared to their saturated precursors **1**, we could anticipate two relevant differences concerning their

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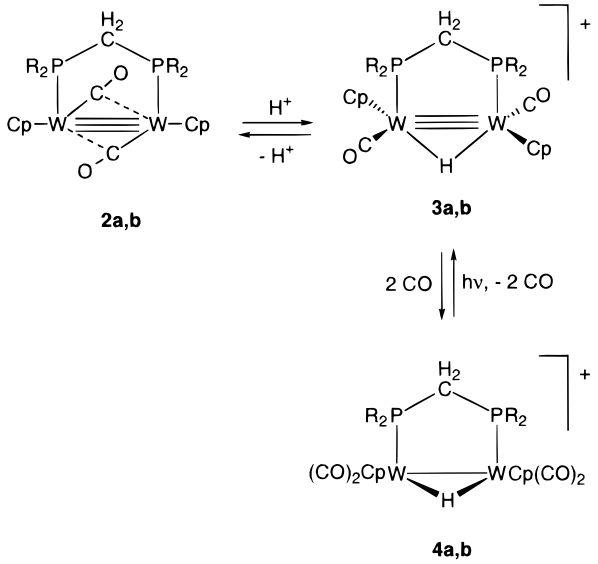
Table 1. IR and $^{31}P\{^1H\}$ NMR Data for New Compounds

compd	$\nu_{st}(CO)^a/cm^{-1}$	δ P(J_{PW})^b	J_{PP}
$[W_2Cp_2(\mu\text{-H})(CO)_2(\mu\text{-dppm})]BF_4$ (**3a**)	1915 (m), 1865 (m), 1811 (vs)^c	19.1 (334, 27)	42
$[W_2Cp_2(\mu\text{-H})(CO)_2(\mu\text{-dmpm})]BF_4$ (**3b**)	1886 (s), 1800 (vs)	−12.7 (338, − 24)^d	33
$[W_2Cp_2(\mu\text{-H})(CO)_4(\mu\text{-dppm})]BF_4$ (**4a**)	1976 (vs), 1953 (s), 1891 (m), 1877 (s)^{e,f}	15.9 (250, 2, isomer *B*)^d	48
		22.9 (237, 3, isomer *A*)^d	56
$[W_2Cp_2(\mu\text{-H})(CO)_4(\mu\text{-dmpm})]BF_4$ (**4b**)	1970 (vs), 1943 (s), 1878 (s)^f	−19.2 (218, 3, isomer *B*)	52
		−12.5 (220, 4, isomer *A*)	52
$[W_2(\mu\text{-COH})Cp_2(CO)_2(\mu\text{-dppm})]BF_4$ (**5a**)	1975 (w, sh), 1943 (s), 1891 (m), 1853 (vs)	18.4 (br, 405)	
$[W_2(\mu\text{-COH})Cp_2(CO)_2(\mu\text{-dmpm})]BF_4$ (**5b**)	*g*	−10.2 (br)^d	
$[W_2(\mu\text{-COMe})Cp_2(CO)_2(\mu\text{-dppm})]BF_4$ (**7**)	1942 (vs), 1931 (sh), 1838 (vs)	18.0 (br, 400)^h	

^{a} Recorded in dichloromethane solution unless otherwise stated. ^{b} Recorded at 121.50 MHz and 291 K in CD_2Cl_2 solution, unless otherwise stated; δ in ppm relative to external 85% aqueous H_3PO_4; *J* in hertz. PP and PW coupling constants in compounds **3** were obtained from the ^{183}W "satellite" lines (see ref 8b). ^{c} 1917 (m), 1775 (vs) cm^{-1} in acetone. ^{d} Recorded at 81.02 MHz. ^{e} Recorded in tetrahydrofuran. ^{f} Isomers *A* and *B*. ^{g} ν(CO) bands could not be unambiguously assigned (see text). ^{h} Recorded in acetone-d_6.

protonation reactions. In first place, compounds **2** display linear semibridging carbonyls,[8b] which is expected to increase electron density at the oxygen atoms, thus favoring hydroxycarbyne formation. On the other hand, compounds **2** are formally electron deficient, so that protonation at the dimetal center is not expected to be their preferred reaction pathway. In fact, simple protonation on complexes having multiple metal−metal bonds is a relatively rare reaction. More often, protonation on multiply bonded organometallic species involves coordination of both the proton and the counterion to the dimetal center.[9] Our results indicate that compounds **2** are protonated to afford the corresponding hydrido derivatives without coordination of the counterion present. However, no hydroxycarbyne intermediates have been detected in these reactions. Part of the work described in this paper has been previously reported.[10]

Scheme 1



Results and Discusion

Protonation Reactions on Compounds 2. The starting substrates $[W_2Cp_2(CO)_2(\mu\text{-}L_2)]$ (**2a,b**) [L_2 = dppm (**a**), dmpm (**b**)] are the decarbonylation products of the neutral complexes $[W_2Cp_2(CO)_4(\mu\text{-}L_2)]$ (**1a**,**b**) and formally contain a triple metal−metal bond.[8b] Addition of equimolar quantities of a variety of acids HX (X^- = BF_4^-, CF_3COO^-, Cl^-) to dichloromethane solutions of compounds **2** cooled at −40 °C leads instantaneously in all cases to the formation of the unsaturated cations $[W_2Cp_2(\mu\text{-H})(CO)_2(\mu\text{-}L_2)]^+$ (**3a**,**b**) in very high yield (Scheme 1). IR and NMR data for these cations are virtually identical whatever the counterion present, so we conclude that no specific cation−anion interaction is present in the solutions of these complexes. Therefore, we will concentrate our discussion on the data for the BF_4^- salts. We also note that the PF_6^- salt of cation **3a** has been prepared previously by us through an entirely different synthetic route.[11] Since the donor ability of anions CF_3COO^- and Cl^- is significant, it is surprising in these cases that simple protonation of the W≡W unit occurs rather than the oxidative addition of HX on the triple bond. In fact, although complexes having bridging hydride ligands across triple metal−metal bonds are not themselves rare (however most of the examples are found in the area of rhenium polyhydrides), they are really scarce in the organometallic family.[12] We can recall for example the complexes $[M_2Cp^*_2(\mu\text{-H})_2(\mu\text{-CO})]$ (M = Ru,[13a] Os),[13b] $[Ru_2Cp^*_2(\mu\text{-H})_4]$,[13c] or $[Ir_2Cp^*_2(\mu\text{-H})_3]^+$,[13d] but none of them have been prepared through protonation reactions. Recently, protonation of the double Ir−Ir bond present in $[Ir_2Cp^*_2(\mu\text{-CO})_2]$ has been reported, but even poorly coordinating anions such as BF_4^- or OTf^- were found to interact with the resulting cationic hydride.[14]

The IR spectrum of cations **3** in acetone exhibits two bands with medium and strong intensities (in order of decreasing frequencies), which is indicative of a *transoid* arrangement of the $W_2(CO)_2$ moiety.[15] In dichloromethane, however, all dppm-bridged cations **3a** exhibit a third medium band of intermediate frequency (Table 1 and Experimental Section). As the corresponding NMR spectra did not change significantly when changing solvent or lowering the temperature to −90 °C, it is reasonable to exclude the possibility that more than one

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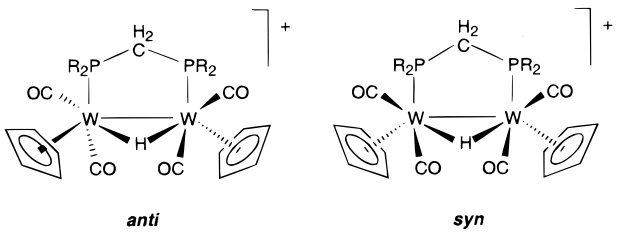
isomer is present in these solutions. Moreover the above effect is independent of the counterion present, so we rather trust that a weak, nonspecific cation−anion interaction is responsible for the appearance of the extra IR band, it being detected only in the poorly solvating dichloromethane solvent.

The NMR data are consistent with an approximate C_2 symmetry for the cations **3**, which makes both phosphorus atoms, cyclopentadienyl rings, and methylenic protons equivalent. The hydrido ligand gives rise to an unusually deshielded NMR resonance (ca. −2 ppm) which exhibits a low coupling to the P atoms (8 Hz) and large coupling to the W atoms (ca. 105 Hz). The latter is indicative of a strongly bound hydrido atom, while the reduced H−P coupling suggests a trans relative disposition of H and P nuclei (cis couplings between μ-H and P atoms in related species have been found around 20 Hz;[16a] on the other hand, trans P−H couplings are expected to be much lower than cis P−H couplings in "piano-stool" [MCpL$_4$] group 6 cyclopentadienyl complexes).[16b] Finally, the strong deshielding of the hydrido atom can be attributed to the large magnetic anisotropy of the triple metal−metal bond, which is expected to cause this effect on atoms placed in the intermetallic region and close to the metal atoms.[17] As an example, the bridging hydrido atom in [W$_2$(μ-H)(H)$_4$(μ-PMe$_2$)(PMe$_3$)$_5$] gives rise to a resonance at −2.26 ppm).[18]

The unsaturated complexes **3** react quantitative and instantaneously with CO at room temperature to give the corresponding saturated hydrides [W$_2$Cp$_2$(μ-H)(CO)$_4$(μ-L$_2$)]$^+$ (**4a**,**b**). IR and NMR data (Table 1 and Experimental Section) indicate that compounds **4** are isostructural with the molybdenum cation [Mo$_2$Cp$_2$(μ-H)(CO)$_4$(μ-dppm)]$^+$ previously prepared by us.[19] The above carbonylation is reversible, so that compounds **3** can be regenerated by photochemical treatment of the tetracarbonylic products (Scheme 1).

In solution, complexes **4** exist as an equimolar mixture of two isomers (labeled *A* and *B* in Table 1). Full assignment of the NMR resonances (^{1}H, ^{31}P, ^{13}C, see Experimental Section) was made with the aid of ^{31}P-decoupling experiments. The main spectroscopic difference between isomers concerns the methylenic protons. In isomer *A*, they appear as chemically equivalent and very weakly coupled to the hydrido ligand ($^4J_{HH}$ = 1 Hz), while for isomer *B* they are not equivalent and display quite different couplings to that bridging atom ($^4J_{HH}$ = 5 or 0 Hz). This situation is analogous to that found for the above-mentioned Mo$_2$ complex[19] and needs then no further comments. On the basis of this analogy, we identify isomer *A* as the one having the Cp rings on opposite sides of the average plane defined by the W and P atoms (anti isomer) and isomer *B* as the one present in the crystalline Mo$_2$ complex (syn isomer, Chart 1).

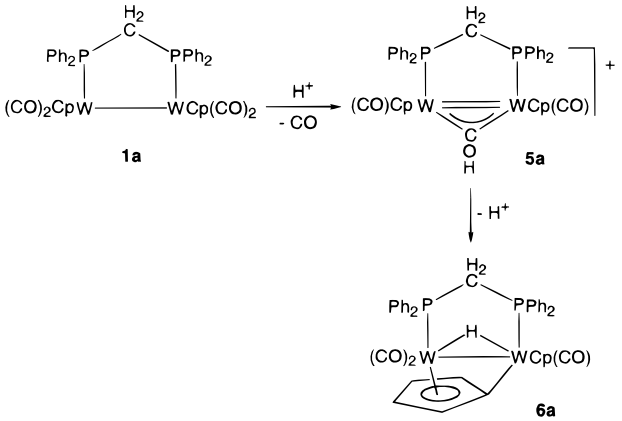
Chart 1



In agreement with this, freshly prepared solutions of solid **4a** contain isomer *B* as a major species, but an equimolar mixture of isomers is reached after ca. 2 h. In both isomers, the hydrido ligand is placed in a cis disposition relative to the P atom, as revealed by the large H−P couplings (ca. 30 Hz).[19] The disappearance of the multiple W−W bond (relative to the parent dicarbonyls **3**) takes the corresponding resonances to the normal, highly shielded region (ca. −20 ppm), while largely reducing the H−W coupling (from 105 to ca. 50 Hz). The latter is indicative of a significant weakening of the W−H interaction upon carbonylation of compounds **3**.

Protonation Reactions on Compounds 1. As stated in the Introduction, the result of these reactions is strongly dependent on experimental conditions and starting substrates. When protonation of the dppm-bridged compound **1a** is carried out by using HBF$_4$·OEt$_2$ in dichloromethane at −40 °C, the hydroxycarbyne complex [W$_2$(μ-COH)Cp$_2$(CO)$_2$(μ-dppm)]BF$_4$ (**5a**) is formed almost quantitatively (Scheme 2). The same reaction on

Scheme 2



the dmpm complex **1b** gives a mixture of **5b**, **3b**, and **4b**, their relative amounts depending on the reaction temperature. Best results for the formation of hydroxycarbyne **5b** are obtained at −75 °C, thus yielding (by NMR) ca. 60% of **5b**, along with smaller amounts of the hydrides **4b** and **3b**. Unfortunately it was not possible to isolate **5b** from the corresponding reaction mixtures due to its low stability. Although the ν(CO) bands of this compound could not be identified unambiguously in the IR spectra of the reaction mixtures (due to overlapping with the bands of the hydrido derivatives), the NMR data allow us to establish that **5b** is isostructural to the dppm complex **5a**.

By contrast with the above results, addition of 1 equiv of HBF$_4$·OEt$_2$ to a toluene solution of **1b** at −40 °C leads to nearly quantitative precipitation of the hydrido

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complex **4b**. The same reaction, when carried out on compound **1a**, gives a precipitate being mostly the dicarbonyl **3a** along with small amounts of **4a**. As mentioned above, species **3** and **4** can be interconverted quantitatively, and this provides in fact the most convenient synthetic route to the tetracarbonyl complex **4a** (see Experimental Section).

To understand the critical role of solvent in all the above protonation reactions, the reverse processes (i.e., deprotonation) must be considered. In the first place, the hydrido derivatives **3** and **4** have been found to be stable in donor solvents such as THF or acetone. This is obviously an expected stabilizing effect of the diphosphine ligand as compared with related unsubstituted carbonyl hydrides (for example, the related cation $[W_2(\mu\text{-}\eta\text{:}^5\eta^5\text{-}C_{10}H_8)(CO)_6(\mu\text{-H})]^+$ is rapidly deprotonated by the above solvents).[20] In fact, deprotonation of hydrides **3** and **4** requires the use of medium to strong bases (2,6-lutidine for dppm derivatives, NaH for the dmpm complexes). By contrast, the hydroxycarbyne complexes **5** are unstable in donor solvents such as THF or Et_2O, where they are rapidly transformed into a mixture of the corresponding hydrides **3** (major) and **4** (minor). Neat deprotonation of **5a** can be accomplished with DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) in CH_2Cl_2 at −40 °C. Under these conditions, the known cyclopentadienylidene complex $[W_2(\mu\text{-H})(\mu\text{-}\eta^1,\eta^5\text{-}C_5H_4)Cp(CO)_3(\mu\text{-dppm})]$ (**6a**)[8b] is quantitatively and instantaneously formed (Scheme 2). Protonation of the latter with $HBF_4\cdot OEt_2$ or dry HCl in dichloromethane gives in turn the dicarbonyl **3a** along with a small amount of **4a**. The ratio **3a**:**4a** in the final product is quite similar to that observed after protonation of **1a** with $HBF_4\cdot OEt_2$ in toluene. This gives support to the hypothesis that both the hydroxycarbyne **5** and the cyclopentadienylidene complexes **6** are intermediates in the formation of hydrides **3** and **4**, a matter that will be addressed later on.

We should note that all hydroxycarbyne complexes previously reported[5−7] have been obtained through protonation of anionic species having bridging carbonyl ligands. Thus, the observed *O*-protonation of compounds **1** constitutes to our knowledge the first example of protonation on neutral carbonylic compounds and also in the absence of bridging CO ligands (compounds **1** are isostructural to their dimolybdenum analogues, the crystal structure of which has revealed the presence of only terminal CO ligands).[21] Another remarkable aspect of this protonation reaction is that it provides the first example of species supporting μ-COH ligands that are thermally stable at room temperature. This might be of relevance with respect to the possible role played by the μ-COH ligand in carbon monoxide reduction processes[22] or in the modeling of chemisorbed species involved in related heterogeneous reactions.[23]

Structure of Hydroxycarbyne Complexes. Spectroscopic data in solution for complexes **5** revealed that these species do not exhibit a simple dynamic behavior. It was therefore important to have precise structural information on these molecules, but all attempts to obtain X-ray quality single crystals were unsuccessful. It could be anticipated that, as species capable of experiencing *O*-protonation at a carbonyl ligand, compounds **1** might be similarly reactive to alkyl carbocations.[24] Indeed, compound **1a** reacts with $(Me_3O)BF_4$ to give the methoxycarbyne complex **7** (Chart 2), which is

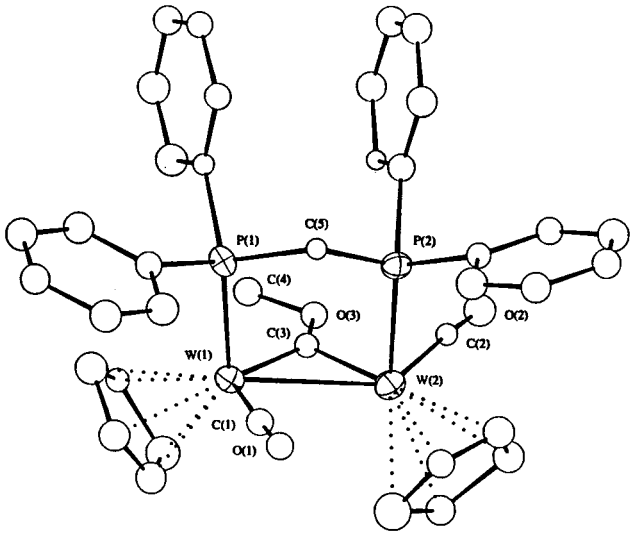
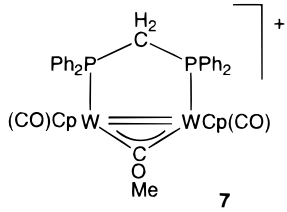


Figure 1. Molecular structure of the cation in compound **7**.[10] Selected interatomic distances [Å] and angles [deg]: W(1)−W(2) 2.781(3), W(1)−C(1) 1.82(6), W(2)−C(2) 2.02(5), W(1)−C(3) 1.95(5), W(2)−C(3) 1.99(5), C(3)−O(3) 1.42(5), O(3)−C(4) 1.42(6), C(1)−W(1)−C(3) 119.8(23), C(2)−W(2)−C(3) 75.2(20), W(1)−W(2)−P(2) 90.6(4), W(2)−W(1)−P(1) 94.7(3), C(1)−W(1)−P(1) 82.3(18), C(2)−W(2)−P(2) 90.7(14), C(3)−O(3)−C(4) 120.3(39).

Chart 2



7

isostructural with the hydroxycarbyne complexes **5** (see later). Single crystals suitable for X-ray diffraction studies could be obtained for **7**, and the structure of the cation is shown in Figure 1.[10] This dimer exhibits a rather symmetrical methoxycarbyne ligand bridging the metal atoms, and according to the 18-electron rule, a double metal−metal bond should be formulated. In agreement with this, the intermetallic separation in **7** [2.781(3) Å] is very close to that found in the related 32-electron complex $[W_2(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(PMe_3)(\eta\text{-}C_5H_5)\{\eta^5\text{-}2,8\text{-}C_2B_9H_8\text{-}10\text{-}(CH_2R)\text{-}2,8\text{-}Me_2\}]$ [2.798(1) Å][25] and about 0.25 Å shorter than those found for related saturated species.[8b]

As for the carbyne ligand, the methoxy group lies in the plane defined by the tungsten and carbyne [C(3)] atoms, pointing away from the closest carbonyl ligand, so as to minimize steric repulsions. This structural effect

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is also present in the few structures available on dinuclear complexes having μ-COR ligands[26,27] and presumably has a thermodynamic origin, as some multiple character in the O−C(carbyne) bond is thus retained.[27−30] Unfortunately, the quality of our X-ray study does not allow us to discuss at a fine level the C−O distances found for complex **7**. We just note that the C−O−C angle of 120.3(39)° is in agreement with the above interpretation, it being identical to the value found for [*cis*-(Cp)(CO)Fe(μ-COEt)(μ-CO)Mn(CO)(η^5-Cp′)] (Cp′= C_5H_4Me),[27] and well inside the general range found in other polynuclear species having alkoxycarbyne ligands bridging two or more metals [ca. 116−123°].[29]

Overall, the coordination environments of both tungsten atoms in compound **7** are quite different. For W(1), the carbonyl ligand is placed trans to the carbyne group, while for W(2) the corresponding carbonyl is placed cis to the bridging carbyne. All these ligands lie roughly in the same plane, with the diphosphine bridge placed nearly perpendicular to it. The origin of this dissymmetry seems to be the need to minimize the steric repulsions between methoxycarbyne and carbonyl ligands.

Solution Structure and Dynamics of Carbyne Complexes. The dicarbonylic nature of compound **7** is evidenced in the IR spectrum in acetone, which shows two strong bands at 1946 (vs) and 1842 (s) cm^{-1}. However, the IR spectrum in CH_2Cl_2 exhibits an additional shoulder at 1931 cm^{-1}. As the NMR data (discussed below) indicates the presence of only one species in solution, we trust that the appearance of this extra ν(CO) band can be attributed to the presence of ion pairs in dichloromethane, as proposed for the unsaturated hydrides **3**.

The presence of the μ-COMe ligand in **7** is denoted by a ^{13}C NMR resonance at 368.5 ppm, in the typical region of alkoxycarbyne bridging ligands,[26,27,30] and a resonance at 72.0 ppm due to the OCH_3 group.[26,31] At room temperature only one signal for the cyclopentadienyl and CO ligands is observed, respectively, which suggests the presence of a dynamic process equalizing the chemical environments of both metal atoms. As similar observations were made for the hydroxycarbyne complex **5a**, we decided to carry out variable-temperature NMR measurements (^{13}C, ^{31}P, ^{1}H) on both complexes. From these we conclude that both **7** and **5a** experience a fluxional process equalizing the phosphorus, cyclopentadienyl, and carbonyl environments. In addition, the hydroxycarbyne complex **5a** experiences a faster isomerization process (Figure 2). The corresponding free energies of activation have been estimated[32] from coalescence data (^{31}P and ^{1}H) and are collected in Table 2. The interested reader is referred to the Supporting Information for details of the study. Here we just note that the above rearrangements imply

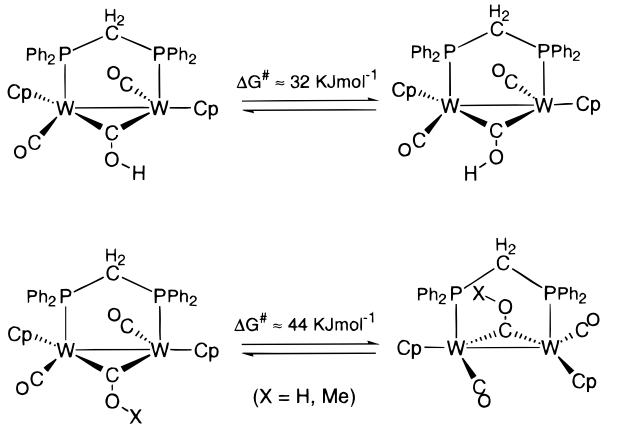

Figure 2. Dynamic processes proposed for compounds **5a** and **7** in solution.

Table 2. Coalescence Data for NMR Spectra of Complexes 5a and 7

compd	signal	T_c/K	$\Delta\nu$/Hz[a]	$\Delta G^{\#}$/kJ mol^{-1}
5a	P	248(±2)	1310(±2)	44.0(±0.5)
	P	178(±5)	845(±5)	32.0(±1)[b]
7	P	258(±2)	1120(±2)	44.5(±0.5)
	H(Cp)	210(±0.5)	25(±0.5)	43.8(±0.2)

[a] Chemical shift differences ($\Delta\nu$) changed with temperature; the values quoted are those corresponding to temperatures ca. 20 K below coalescence. [b] Average value.

at some stage the rotation of the COH or COMe moieties around the CO bond, a known process.[29,30,33]

The dmpm-bridged hydroxycarbyne complex **5b** presumably displays a dynamic behavior similar to that observed for **5a**. However, we have not studied this point in detail due to our inability to isolate **5b** as a pure solid. We just note that the hydroxycarbyne ligand in **5b** displays characteristic resonances at 12.4 ppm (^1H) and 358.7 ppm (^{13}C),[5,7] while the $^{31}P\{^1H\}$ NMR spectrum exhibits a broad resonance at room temperature (δ = −10.2 ppm), which splits into two doublets on cooling the solution (δ = −14.5, −3.1 ppm at 210 K).

Reaction Pathways for the Protonation Reactions of Compounds 1. Through the preceding sections, we have shown that the nature of products (hydride versus hydroxycarbyne derivatives) resulting from protonation of compounds **1** with $HBF_4{\cdot}OEt_2$ is critically dependent upon reaction conditions (particularly solvent and, to a lesser extent, temperature) and the nature of the diphosphine bridges. The ligand dmpm seems to favor hydride formation (as compared with dppm), while hydroxycarbyne formation is favored by the poorly coordinating solvent CH_2Cl_2 (as compared with toluene or tetrahydrofuran). When hydrides are formed, a mixture of tetracarbonyls **4** and dicarbonyls **3** is obtained, with the latter being by far the major hydride formed in the case of the dppm complex, but the minor one in the case of the dmpm substrate. All these results can be rationalized in a unified way by considering the reaction pathways illustrated in Scheme 3.

Initial H^+ attack on compounds **1** might occur at either the metal−metal bond or a terminal carbonyl ligand. The former process would yield tetracarbonyls

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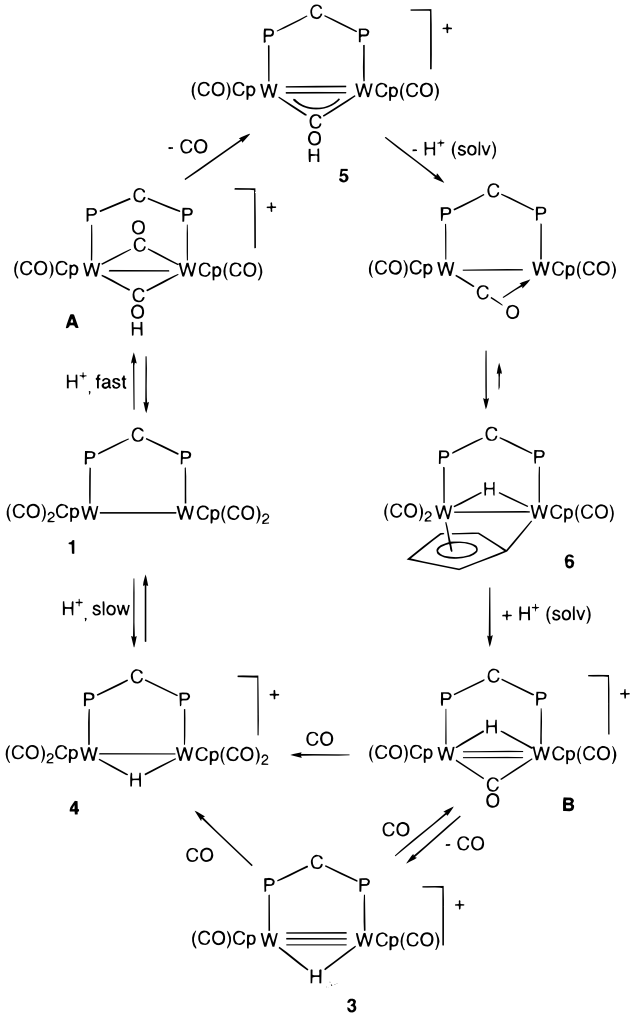
Scheme 3. Reaction Pathways Proposed for the Protonation Reactions of Compounds 1: P−C−P = dppm or dmpm; Solv = Solvent; Anion Is BF_4^-



4, which are thermodynamically stable (relative to **3** or **5**) and are not decomposed by donor solvents. As compound **4a** is at most a minor species in all final reaction mixtures, we conclude that, under the reaction conditions studied, direct H^+ attack at the intermetallic bond is a relatively slow process for the dppm substrate. We propose that in this case *O*-protonation at a terminal carbonyl is the fastest and dominant process under all conditions, to yield initially a tricarbonyl hydroxycarbyne intermediate **A**, not detected, which rapidly would lose a carbonyl group to give the hydroxycarbyne **5a**. The latter is then the kinetic product of the reaction and is itself stable in dichloromethane solution in the absence of donor molecules such as tetrahydrofuran or diethyl ether (small amounts of the latter are however invariably present, due to the acid used). These solvents have been shown (through independent experiments) to transform compound **5a** into the corresponding hydrides **3a** (major) and **4a** (minor). The same has been accomplished through neat deprotonation (to give the hydrido cyclopentadienylidene complex **6a**) followed by reprotonation. Thus we propose that, when protonation of compound **1a** is carried out in toluene, the hydroxycarbynes **A** and **5a** are also initially formed, but are rapidly deprotonated by solvent. In the case of dicarbonyl **5a** this gives the cyclopentadienylidene **6a** (the corresponding C−H cleavage has been studied in detail previously by us),[8] which in turn is protonated by solvent to afford the hydride **3a** after loss of carbon monoxide. A reactive unsaturated hydride $[W_2Cp_2(\mu\text{-H})(\mu\text{-CO})(CO)_2(\mu\text{-dppm})]^+$ (**B**) might be involved in that process. Finally, part of the evolved CO could itself react with these hydrides, thus accounting for the small amounts of tetracarbonyl **4a** detected in the final reaction mixtures. Under this view, the unsaturated hydride **3a** is properly the thermodynamic product of the protonation reactions of complex **1a**.

We have attempted to check the correctness of the proposed reaction pathway by using DSO_3CF_3 on **1a** instead of $HBF_4{\cdot}OEt_2$. Unfortunately, although reactions proceed analogously, we have not succeeded in introducing significant amounts of deuterium at the hydroxycarbyne ligand in complex **5a**. Apparently, the OH group of the ligand rapidly exchanges its proton with traces of water invariably introduced during manipulation of the solutions. We have succeeded, however, in deuterating complex **6a**. ^1H and ^2H NMR spectra of the product (mainly the dicarbonyl **3a**) indicate that deuterium is specifically incorporated to the Cp ligand; that is, protonation occurs at the cyclopentadienylidene C−W bond (eq 1). The above results imply that, as far as the proposed reaction pathway is correct, the hydrido ligand present in the final products of protonation of complex **1a** would not come mainly from the acid used in the reaction but rather from the cyclopentadienyl ligands in the starting substrate.

$$\mathbf{6a} + DSO_3CF_3 \rightarrow [W_2Cp(C_5H_4D)(\mu\text{-H})(CO)_2(\mu\text{-dppm})]SO_3CF_3 + CO \quad (1)$$

As for the protonation reactions on the dmpm-bridged compound **1b**, the point to be addressed is the influence of this ligand (compared to dppm) in favor of hydride formation. We have shown above that **3b** and **4b** are more difficult to deprotonate than their dppm-bridged analogues, so here we can find a thermodynamic effect consistent with the experimental findings. Additionally, it can be argued that, due to the smaller size of dmpm when compared to the relatively bulky dppm ligand, the intermetallic bond should be sterically more accessible for **1b**, thus allowing for the direct protonation at that site to be somewhat faster and therefore more competitive against *O*-protonation at the carbonyl ligand. From the limited data available, we deduce that both processes compete with each other when using dichloromethane as solvent, with *O*-protonation being dominant the lower the temperature used. When using toluene as solvent, the tetracarbonyl hydride **4b** is the major product detected, with only trace amounts of the unsaturated **3b** being present. Therefore we infer that no significant amounts of hydroxycarbyne **5b** are formed under the latter conditions, even at an intermediate step. We rather think that solvent might reduce, via deprotonation, the presence of significant amounts of the hydroxycarbyne intermediate **A**, thus favoring (by defect) the proton attack at the intermetallic bond.

In summary, we conclude that *O*-protonation at a carbonyl ligand is the dominant process occurring during reaction of $HBF_4{\cdot}OEt_2$ with the dppm-bridged

substrate **1a** to yield the hydroxycarbyne **5a**, which, under the influence of certain solvents such as tetrahydrofuran, diethyl ether, or even the modest donor toluene, rearranges to hydride products through a process that possibly involves, inter alia, an intramolecular H−C(cyclopentadienyl) activation step. For the dmpm-bridged substrate **1b**, the above reactions compete with direct protonation at the intermetallic bond only when using dichloromethane as solvent; otherwise the latter process becomes totally dominant. The size and basicity of the diphosphine ligands as well as the donor properties of the solvents used seem to be the relevant factors governing the course of these protonation reactions.

Experimental Section

General Comments. All reactions were carried out under an atmosphere of nitrogen. Solvents were purified according to standard procedures[34] and distilled under nitrogen prior to use. Compounds **1a**,**b** and **2a**,**b** were prepared as described previously.[8b] All reagents were purchased from the usual commercial suppliers and used as received. Filtrations were carried out using dry diatomaceous earth under nitrogen. Photochemical experiments and low-temperature reactions were performed using jacketed Pyrex Schlenk tubes, refrigerated by a closed 2-propanol circuit kept at the desired temperature with a cryostat. A 400 W mercury lamp (Applied Photophysics), placed ca. 1 cm away from the Schlenk tube, was used for photochemical experiments.

NMR spectra were recorded at 400.13 (^{1}H), 161.98 (^{31}P{^{1}H}), or 100.61 (^{13}C{^{1}H}) MHz in CD_2Cl_2 solution at room temperature, unless otherwise indicated. Chemical shifts (δ) are given in ppm, relative to internal TMS (^{1}H, ^{13}C) or external 85% H_3PO_4 aqueous solution (^{31}P) with positive values for frequencies higher than that of the reference. Coupling constants (J) are given in hertz. ^{13}C{^{1}H} NMR spectra were routinely recorded on solutions containing a small amount of tris(acetylacetonato)chromium(III) as a relaxation reagent.

Synthesis of $[W_2Cp_2(\mu\text{-H})(CO)_2(\mu\text{-dppm})]BF_4$ (3a-BF_4). Method A. Compound **2a** (0.1 g, 0.107 mmol) in dichloromethane (10 mL) was stirred with $HBF_4{\cdot}OEt_2$ (13 μL of a 85% solution in Et_2O, 0.11 mmol) at −30 °C for 5 min to give a brown solution. Solvent was then removed under vacuum, and the residue washed with toluene (5 × 3 mL), extracted with dichloromethane, and filtered. Removal of solvent from the filtrate gave compound **3a** (0.095 g, 87%) as a brown-orange solid.

Method B. A tetrahydrofuran solution (15 mL) of compound **4a** (0.050 g, 0.046 mmol) was irradiated with UV−visible light at −10 °C for 30 min while nitrogen was bubbled gently through the solution. The resulting brown solution was then filtered and solvent removed under vacuum to give compound **3a** as a brown-orange solid (0.041 g, 86%). Satisfactory microanalytical data could not be obtained for this air-sensitive complex. ^{1}H NMR (300.13 MHz): δ 7.85−7.15 (m, 20H, Ph), 5.66 (t, J_{HP} = 11, 2H, CH_2), 5.10 (d, J_{HP} = 1, 10H, Cp), −2.59 (t, J_{HP} = 8, J_{HW} = 103, 1H, μ-H) ppm. ^{13}C{^{1}H} NMR (75.47 MHz): δ 225.5 (s, CO), 138.3−125.5 (Ph), 91.9 (s, Cp), 56.7 (t, J_{CP} = 32, CH_2).

Synthesis of $[W_2Cp_2(\mu\text{-H})(CO)_2(\mu\text{-dppm})]CF_3CO_2$ (3a-CF_3CO_2). The procedure is entirely analogous to that described for **3a-BF_4** except that 8 μL (0.107 mol) of CF_3CO_2H was used. ν(CO) (CH_2Cl_2): 1914 (m), 1870 (m), 1809 (vs) cm^{-1}. ^{1}H NMR (300.13 MHz): δ 7.65−7.20 (m, 20H, Ph), 5.65 (t, J_{HP} = 11, 2H, CH_2), 5.10 (s, 10H, Cp), −2.64 (t, J_{HP} = 8, J_{HW} = 102, 1H, μ-H). ^{31}P{^{1}H} NMR (121.50 MHz): δ 18.5 (s, μ-dppm).

Synthesis of $[W_2Cp_2(\mu\text{-H})(CO)_2(\mu\text{-dppm})]Cl$ (3a-Cl). The procedure is completely analogous to that described for **3a-BF_4** except that a stream of dry HCl(g) generated in situ from solid NaCl and 98% H_2SO_4 was bubbled gently through the solution. ν(CO) (CH_2Cl_2): 1915 (m), 1866 (m), 1810 (vs) cm^{-1}. ^{1}H NMR: δ 7.50−7.10 (m, 20H, Ph), 5.69 (t, J_{HP} = 11, 2H, CH_2), 5.14 (s, 10H, Cp), −2.50 (t, J_{HP} = 8, J_{HW} = 103, 1H, μ-H). ^{31}P{^{1}H} NMR: δ 18.9 (s, J_{PP} = 43, J_{PW} = 337, 27, μ-dppm). ^{13}C{^{1}H} NMR (75.47 MHz): δ 225.3 (s, CO), 135.8−131.9 (Ph), 93.0 (s, Cp), 59.0 (t, J_{CP} = 32, CH_2).

Synthesis of $[W_2Cp_2(\mu\text{-H})(CO)_2(\mu\text{-dmpm})]BF_4$ (3b). Method A. A tetrahydrofuran solution (10 mL) of compound **2b** (0.049 g, 0.066 mmol) was stirred at 0 °C with the stoichiometric amount (8 μL) of $HBF_4{\cdot}OEt_2$ (85% in Et_2O) for 1 min. The red-brown solution was filtered and the solvent removed under vacuum. The solid obtained was washed with toluene (3 × 5 mL) to give compound **3b** as a reddish solid (0.034 g, 75%).

Method B. The procedure is completely analogous to that described for **3a-BF_4** (method B), except that compound **4b** (0.050 g, 0.06 mmol) was irradiated for 1 h. Compound **3b** was thus obtained as a reddish solid (0.042 g, 90%). Satisfactory microanalytical data could not be obtained for this air-sensitive complex. ^{1}H NMR (200.13 MHz): δ 5.34 (s, 10H, Cp), 4.42 (t, J_{HP} = 12, 2H, CH_2), 1.99 [AA′(XX′)$_3$, $|J_{HP} + J_{HP'}|$ = 9, 6H, CH_3], 1.76 [AA′(XX′)$_3$, $|J_{HP} + J_{HP'}|$ = 9, 6H, CH_3], −1.97 [t, J_{HP} = 7, J_{HW} = 109, μ-H, 1H]. ^{13}C{^{1}H} NMR (50.32 MHz): δ 226.8 (s, CO), 90.4 (s, Cp), 59.6 (t, J_{CP} = 36, CH_2), 24.2 (AXX′, $|J_{CP} + J_{CP'}|$ = 42, CH_3), 21.4 (AXX′, $|J_{CP} + J_{CP'}|$ = 35, CH_3).

Synthesis of $[W_2Cp_2(\mu\text{-H})(CO)_4(\mu\text{-dppm})]BF_4$ (4a). Carbon monoxide was gently bubbled through a dichloromethane solution (10 mL) containing 0.1 g (0.097 mmol) of compound **3a** for 1 min. The brown solution turned to violet almost instantaneously, and compound **4a** was formed quantitatively. Anal. Calcd for $C_{39}H_{33}BF_4O_4P_2W_2$: C, 41.05; H, 2.90. Found: C, 41.27; H, 3.03. ^{1}H NMR: δ 5.34 (s, 10H, Cp, isomer *B*), 5.12 (s, 10 H, Cp, isomer *A*), 4.96 (dtd, J_{HH} = 13, J_{HP} = 12, J_{HH} = 5, 1H, CH_2, isomer *B*), 4.04 (td, J_{HP} = 11, J_{HH} = 1, 2H, CH_2, isomer *A*), 4.02 (dt, J_{HH} = 13, J_{HP} = 10, 1H, CH_2, isomer *B*), −20.79 (td, J_{HP} = 27, J_{HH} = 5, J_{HW} = 47, 1H, μ-H, isomer *B*), −20.85 (tt, J_{HP} = 31, J_{HH} = 1, J_{HW} = 45, 1H, μ-H, isomer *A*) ppm. ^{13}C{^{1}H} NMR (50.32 MHz): δ 232.2 (AXX′, $|J_{CP} + J_{CP'}|$ = 21, CO, isomer *B*), 227.8 (AXX′, $|J_{CP} + J_{CP'}|$ = 23, CO, isomer *A*), 226.7 (s, CO, isomer *B*), 225.2 (s, CO, isomer *A*), 138.3−125.6 (Ph), 93.1 (s, Cp, isomer *A*), 92.2 (s, Cp, isomer *B*), 44.6, 44.2 (2t, J_{CP} = 27, 25, CH_2, isomers *A* and *B*) ppm. The assignments were confirmed with the aid of ^{31}P decoupling experiments.

Synthesis of $[W_2Cp_2(\mu\text{-H})(CO)_4(\mu\text{-dmpm})]BF_4$ (4b). A toluene solution (15 mL) of compound **1b** (0.1 g, 0.134 mmol) cooled at −40 °C was treated with the equivalent amount of $HBF_4{\cdot}OEt_2$ (16 μL of a 85% Et_2O solution) to give a red-violet oily solid instantaneously. The solution was syringed off, and the residue stirred in a mixture of dichloromethane (0.5 mL) and petroleum ether (20 mL) for 24 h. The solution was then discarded and the residue washed with toluene (3 × 5 mL) to yield compound **4b** as a red powder (0.080 g, 72%). Anal. Calcd for $C_{19}H_{25}BF_4O_4P_2W_2$: C, 27.37; H, 3.00. Found: C, 27.41; H, 3.02. ^{1}H NMR: δ 5.61 (s, 10H, Cp, isomer *B*), 5.59 (s, 10H, Cp, isomer *A*), 2.99 (td, J_{HP} = 11, J_{HH} = 1, 2H, CH_2, isomer *A*), 2.93, 2.87 (ABXP$_2$, J_{AB} = 15, J_{AP} = J_{BP} = 9, J_{BX} = 2, 2H, CH_2, isomer *B*), 1.87−1.80 (m, 24H, CH_3, isomers *A* and *B*), −18.86 (td, J_{HP} = 26, J_{HH} = 2, J_{HW} = 51, 1H, μ-H, isomer *B*), −21.49 (tt, J_{HP} = 29, J_{HH} = 1, J_{HW} = 47, 1H, μ-H, isomer *A*) ppm. ^{13}C{^{1}H} NMR (50.32 MHz): δ 234.8 (AXX′, $|J_{CP} + J_{CP'}|$ = 24, CO, isomer *B*), 233.0 (AXX′, $|J_{CP} + J_{CP'}|$ = 24, CO, isomer *A*), 226.5 (s, CO, isomer *A*), 225.8 (s, CO, isomer *B*), 91.8 (s, Cp, isomer *A*), 90.8 (s, Cp, isomer *B*), 40.2 (t, J_{CP} = 32, CH_2, isomer *B*), 39.7 (t, J_{CP} = 30, CH_2, isomer *A*), 22.8−20.1 (m, CH_3, isomers *A* and *B*) ppm. The assignments were confirmed with the aid of ^{31}P decoupling experiments.

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Synthesis of $[W_2(\mu\text{-COH})Cp_2(CO)_2(\mu\text{-dppm})]BF_4$ (5a). A dichloromethane solution (30 mL) of compound **1a** (0.1 g, 0.1 mmol) was stirred with $HBF_4{\cdot}OEt_2$ (12 μL, 85% in Et_2O) for 45 min at −40 °C to give a brown solution. Solvent was then removed under vacuum and the residue washed with toluene (3 × 5 mL) and petroleum ether (2 × 5 mL) to give compound **5a** (0.094 g, 89%) as a brown powder. Anal. Calcd for $C_{38}H_{33}BF_4O_3P_2W_2$: C, 43.26; H, 3.13. Found: C, 43.30; H, 3.15. ^{1}H NMR (200.13 MHz): δ 12.96 (sa, 1H, μ-COH), 7.5−7.0 (m, 20H, Ph), 5.30 (t, J_{HP} = 1, 10H, Cp), 4.88 (t, J_{HP} = 11, 2H, CH_2) ppm. $^{31}P\{^1H\}$ NMR (121.50 MHz, 198 K): δ 23.9 (d, J_{PP} = 48, J_{PW} = 414, 1P, μ-dppm), 13.2 (d, J_{PP} = 48, J_{PW} = 394, 1P, μ-dppm). $^{31}P\{^1H\}$ NMR (121.50 MHz, 172 K): δ 27.9 (br, μ-dppm, isomer *D*), 20.8 (br, μ-dppm, isomer *C*), 13.5 (s br, μ-dppm, isomers *C* and *D*). $^{13}C\{^1H\}$ NMR (50.32 MHz): δ 356.9 (s, μ-COH), 240.4 (s br, 2CO), 134.8−129.0 (Ph), 94.6 (s, Cp), 64.4 (t, J_{CP} = 31, CH_2) ppm. $^{13}C\{^1H\}$ NMR (75.47 MHz, 198 K): δ 357.8 (s, J_{CW} = 121, μ-COH), 251.5 (s, CO), 229.9 (s, CO), 134.4−128.5 (Ph), 96.4 (s, Cp), 92.6 (s, Cp), 63.4 (t, J_{CP} = 31, CH_2) ppm.

Protonation Reaction of 1b in Dichloromethane. A dichloromethane solution (15 mL) of compound **1b** (0.1 g, 0.134 mmol) was stirred with 1 equiv of $HBF_4{\cdot}OEt_2$ (16 μL, 85% in Et_2O) at −75 °C. The reaction was instantaneous and gave a mixture containing compound **5b** as a major species (ca. 60% by NMR) along with smaller amounts of **3b** and **4b**. All attempts to separate these compounds resulted in decomposition of the mixture. Spectroscopic data for **5b**: ^{1}H NMR (200.13 MHz): δ 12.38 (s br, μ-COH), 5.49 (s, 10H, Cp) ppm. $^{31}P\{^1H\}$ NMR (81.02 MHz): δ −10.2 (br, μ-dmpm) ppm. $^{31}P\{^1H\}$ NMR (210 K): δ −3.1 (d, J_{PP} = 38, μ-dmpm), −14.5 (d, J_{PP} = 38, μ-dmpm). $^{13}C\{^1H\}$ NMR (50.32 MHz): δ 358.7 (s br, μ-COH), 238.5 (m, CO), 93.2 (s, Cp), 65.8 (t, J_{CP} = 33, CH_2) ppm. Other resonances for this compound were obscured by those from the other products present in the reaction mixture.

Synthesis of $[W_2(\mu\text{-COMe})Cp_2(CO)_2(\mu\text{-dppm})]BF_4$ (7). Solid $[Me_3O]BF_4$ (0.01 g, 0.07 mmol) was added to a dichloromethane solution (10 mL) containing compound **1a** (0.05 g, 0.05 mmol) at room temperature, and the mixture was stirred for 2.30 h to give a brownish-green solution, which was filtered. Solvent was then removed from the filtrate under vacuum and the residue washed with toluene (3 × 5 mL) to give compound **7** as a brown powder (0.036 g, 65%). Suitable crystals for the X-ray study were grown by slow diffusion of a concentrated acetone solution of the complex into a layer of toluene at − 20 °C.[10] Anal. Calcd for $C_{39}H_{35}BF_4O_3P_2W_2$: C, 43.82; H, 3.28. Found: C, 43.88; H, 3.30. ^{1}H NMR (300.13 MHz, acetone-d_6): δ 7.35−7.27 (m, 20H, Ph), 5.58 (s, 10H, Cp), 5.27 (t, J_{HP} = 11, 2H, CH_2), 4.94 (s, 3H, CH_3) ppm. ^{1}H NMR (acetone-d_6, 188 K): δ 7.40−7.10 (m, 20H, Ph), 5.68 (s br, 5H, Cp), 5.61 (s br, 6H, Cp and CH_2), 4.87 (s br, 4H, CH_3 and CH_2). $^{31}P\{^1H\}$ NMR (acetone-d_6, 200 K): δ 19.3 (d, J_{PP} = 48, J_{PW} = 409, 1P, μ-dppm), 13.4 (d, J_{PP} = 48, J_{PW} = 388, 1P, μ-dppm). $^{13}C\{^1H\}$ NMR (acetone-d_6): δ 368.5 (s, μ-COMe), 239.0 (br, 2CO), 136.1−129.0 (Ph), 94.9 (Cp), 72.0 (s, CH_3), 61.8 (t, J_{CP} = 32, CH_2) ppm.

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Supporting Information Available: Details of the variable-temperature NMR study on complexes **5a** and **7**, with an explanatory figure (4 pages). See any current masthead page for ordering information and Internet access instructions.

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