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Reactivity of the Carbyne Complexes $[W_2(\mu\text{-COR})(\eta^5\text{-}C_5H_5)_2(CO)_2(\mu\text{-}Ph_2PCH_2PPh_2)]^+$ (R = H, Me) toward Diazomethane

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Reaction of $[W_2(\mu\text{-COH})Cp_2(CO)_2(\mu\text{-dppm})]BF_4$ ($Cp = \eta^5\text{-}C_5H_5$; $dppm = Ph_2PCH_2PPh_2$) with CH_2N_2 in the presence of CuCl at −75 °C leads to the methoxycarbyne cluster $[CuW_2Cl(\mu_3\text{-COMe})Cp_2(CO)_2(\mu\text{-dppm})]BF_4$. Copper(I) chloride can be cleanly removed from the latter upon addition of PPh_3, thus giving the methoxycarbyne complex $[W_2(\mu\text{-COMe})Cp_2(CO)_2(\mu\text{-dppm})]BF_4$. In the absence of CuCl, either the hydroxy or the methoxycarbyne ditungsten cations react with CH_2N_2 to give a mixture of the μ-methylene, μ-alkenyl compound $[W_2(\mu\text{-}CH_2)\{\mu\text{-}\eta^1{:}\eta^2\text{-C(OMe)}{=}CH_2\}Cp_2(CO)_2(\mu\text{-dppm})]BF_4$, which has been characterized through an X-ray study, and the μ-alkyne, μ-alkenyl species $[W_2\{\mu\text{-}\eta^1{:}\eta^2\text{-C(OMe)CH}\}\{\mu\text{-}\eta^1{:}\eta^2\text{-C(OMe)}CH_2\}Cp_2(CO)(\mu\text{-dppm})]BF_4$, the latter being the result of the addition of four molecules of CH_2N_2 to the starting hydroxycarbyne compound. The influence of experimental conditions on the above reactions has been analyzed through separate experiments. For example, the use of tetrahydrofuran as solvent almost suppresses the formation of the alkyne product, whereas the use of a noncoordinating anion such us $[B\{3,5\text{-}C_6H_3(CF_3)_2\}_4]^-$ instead of BF_4^- as counterion precludes the reaction to occur beyond the methoxycarbyne compound. The solution structures of the new compounds are analyzed in the light of the IR and NMR spectra, and plausible reaction pathways are proposed in order to explain the formation of the reaction products.

Introduction

The formation of C−C bonds at transition metal centers is a fundamental process that attracts considerable attention, not only because it can lead to new and useful synthesis of organic compounds but also because complexes experiencing these processes can act as models for the surface species involved in heterogeneously catalyzed related reactions.[1] In this context, metal complexes containing coordinated hydrocarbons susceptible to transformation through C−C coupling reactions are of interest as molecular models for processes such as the Fischer−Tropsch synthesis.[2] Among the most attractive candidates for modeling the elemental steps involved in the latter we note several di- and polynuclear complexes containing μ-carbyne,[3] μ-methylene,[4] methyl,[5] μ-alkenyl,[6] or μ-alkylidene[7] ligands, all of which have been found to experience coupling to other hydrocarbon groups.

The Fischer−Tropsch reaction involves the transformation of CO at the metallic surface into surface-bound methyne, methylene, or even methyl groups.[8] There is general agreement that the final products (mainly linear aliphatic alkanes and alkenes) are formed through

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[1] Somarjai, G. A. *Introduction to Surface Chemistry and Catalysis*; Wiley-Interscience: New York, 1994.

[2] (a) Muetterties, E. L.; Stein, J. *Chem. Rev.* **1979**, *19*, 479. (b) Rofer De Poorter, C. K. *Chem. Rev.* **1981**, *81*, 447. (c) Beanan, L. R.; Keister, J. B. *Organometallics* **1985**, *4*, 1713. (d) Maitlis, P. M. *J. Organomet. Chem.* **1995**, *500*, 239. (e) Maitlis, P. M.; Long, H. C.; Quyoum, R.; Turner, M. L.; Wang, Z.-Q. *J. Chem. Soc., Chem. Commun.* **1996**, 1.

[3] (a) García, M. E.; Jeffery, J. C.; Sherwood, P.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1988**, 2443. (b) García, M. E.; Jeffery, J. C.; Sherwood, P.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1988**, 2431. (c) García, M. E.; Tran-Huy, N. H.; Jeffery, J. C.; Sherwood, P.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1987**, 2201. (d) Delgado, E.; Hein, J.; Jeffery, J. C.; Ratermann, A. L.; Stone, F. G. A.; Farrugia, L. J. *J. Chem. Soc., Dalton Trans.* **1987**, 1191.

[4] (a) Royo, E.; Royo, P.; Cuenca, T.; Galakhov, M. *Organometallics* **2000**, *19*, 5559. (b) Nishioka, T.; Isobe, K.; Kinoshita, I.; Ozawa, Y.; Vázquez de Miguel, A.; Nakai, T.; Miyajima, S. *Organometallics* **1998**, *17*, 1637. (c) Akita, M.; Hua, R.; Knox, S. A. R.; Moro-oka, Y.; Nakanishi, S.; Yates, M. I. *J. Organomet. Chem.* **1998**, *569*, 71. (d) Wang, Z.-Q.; Martínez, J.; Maitlis, P. M. *Inorg. Chim. Acta* **1998**, *280*, 62.

[5] (a) Torkelson, J. R.; McDonald, R.; Cowie, M. *J. Am. Chem. Soc.* **1998**, *120*, 4047. (b) Beringhelli, T.; D'Alfonso, G.; Panigati, M.; Porta, F.; Mercandelli, P.; Moret, M.; Sironi, A. *J. Am. Chem. Soc.* **1999**, *121*, 2307.

[6] (a) Glushove, D.; Hogarth, G.; Lavender, M. H. *J. Organomet. Chem.* **1997**, *528*, 3. (b) Brady, L. A.; Dyke, A. F.; Garner, S. E.; Guerchais, V.; Knox, S. A. R.; Maher, J. P.; Nicholls, S. M.; Orpen, A. G. *J. Chem. Soc., Chem. Commun.* **1992**, 310.

[7] Nucciarone, D.; Taylor, N. J.; Carty, A. J.; Tiripicchio, A.; Tiripicchio Camellini, M.; Sappa, E. *Organometallics* **1988**, *7*, 118, and references therein.

[8] Kamisnsky, M. P.; Winograd, N.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1986**, *108*, 1315.

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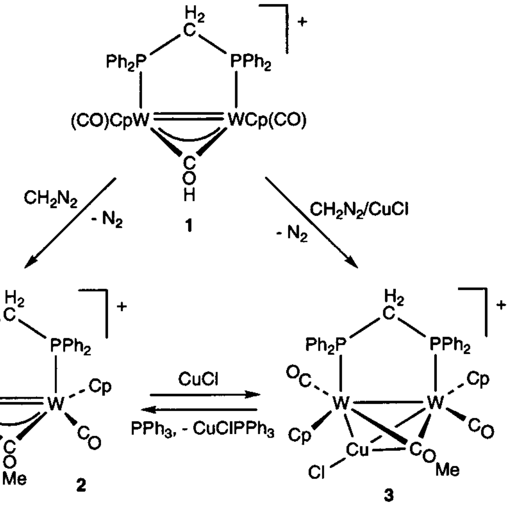
stepwise polymerization of methylene groups.[1] For this reason, the controlled addition of methylene groups to metal complexes is a process of interest. Although diazocompounds have been extensively used as a source of alkylidene ligands in organometallic chemistry,[9] there are only a few examples of controlled and stepwise addition of methylene groups to a single metal complex by using diazomethane.[3c,10]

Recently we reported the synthesis of the thermally stable hydroxy and alkoxycarbyne complexes [$W_2(\mu$-COR)$Cp_2(CO)_2(\mu$-dppm)]$^+$ [R = H (**1**), Me (**2**); Cp = η^5-C_5H_5; dppm = $Ph_2PCH_2PPh_2$].[11] These complexes reacted with BH_3·THF to yield the methylidyne-borane complex [$W_2(\mu$-$CHBH_3)Cp_2(CO)_2(\mu$-dppm)]$^+$. The latter transformation completed an unusual CO to CH reduction via the hydroxycarbyne intermediate **1**, a significant observation in the general context of the Fischer–Tropsch synthesis. Apart from the carbyne atom as a reaction center, compounds **1** and **2** have formal double metal–metal bonds, so they seemed very suitable substrates to explore stepwise addition reactions of methylene groups. In this paper we describe the reactivity of compounds **1** and **2** toward diazomethane under different conditions, which allows some control over the products. These result from several transformations induced by methylene groups, such as insertion of CH_2 into O–H bonds or coupling to carbyne or carbonyl ligands.

Results and Discussion

Reaction of Compounds 1 and 2 with CH_2N_2 in the Presence of CuCl. Copper(I) chloride is well known to catalyze the decomposition of CH_2N_2, thus releasing the methylene fragment.[13] For this reason, we first carried out the reaction of the carbyne complexes **1** and **2** with CH_2N_2 in the presence of CuCl. Surprisingly, however, the product was the same in both cases. Thus, the reaction of either **1** or **2** in CH_2Cl_2 with an excess of an ethereal solution of CH_2N_2 at low temperature (−75 °C), in the presence of stoichiometric amounts of CuCl, leads to the trimetallic cluster [$CuW_2Cl(\mu_3$-COMe)$Cp_2(CO)_2(\mu$-dppm)]$^+$ (**3**) in very good yield. Copper(I) chloride is easily removed from the latter cluster by treatment with a base such as PPh_3 at room temperature, whereby the methoxycarbyne **2** is obtained in excellent yield along with [CuCl(PPh_3)]$_4$ (Scheme 1). As expected, **3** can be obtained by treating **2** with CuCl at room temperature, this reaction being illustrative of the donor ability of the methoxycarbyne ligand in **2** and its potential in the synthesis of heterometallic clusters.[12] The addition of group 11 metal halides to carbyne complexes has been previously observed.[14] Thus it is perhaps surprising that the hydroxycarbyne complex **1** does not react with CuCl even after long stirring times.

Scheme 1. Chemical Transformations between Carbyne Complexes



In all, the above results reveal the way by which compound **1** is transformed into **3**. It is evident that the hydroxycarbyne **1** experiences an insertion reaction of CH_2 into the O–H bond, thus giving the methoxycarbyne **2**. The latter then reacts with the Lewis acid CuCl to yield the acid–base adduct **3**. Although compound **2** was originally prepared through *O*-methylation at a terminal CO ligand on the complex [$W_2Cp_2(CO)_4(\mu$-dppm)],[11] the above reactions (conversion of **1** into **3** followed by treatment with PPh_3) offer an alternative, more efficient, preparative route to the methoxycarbyne **2**. The presence of CuCl is critical in this synthesis, as we will discuss later, because this precludes further additions of CH_2N_2.

The arrangement of terminal ligands and bridging diphosphine in **3** does not differ greatly from that of **2**.[11] Its IR spectrum exhibits in the ν_{st}(CO) region two bands and a shoulder with relative intensities similar to those of **2**, but shifted to slightly higher frequencies. The $^{31}P\{^1H\}$ NMR spectrum at 238 K shows two doublets (11.6 and 6.1 ppm, J_{PP} = 44 Hz), thus indicating that addition of the CuCl fragment to **2** proceeds with retention of the chemical inequivalence of the two phosphorus atoms and hence the tungsten atoms. By contrast, the ^{13}C resonance of the carbyne ligand (332.7 ppm at 238 K) is strongly shifted (by ca. 40 ppm) upfield with respect to that of **2**. This shielding effect is characteristic when changing the coordination mode of the carbyne ligands from μ_2 to μ_3.[12a,c] Overall, the above data justify the formulation of compound **3** as a triangular cluster CuW_2, with the methoxycarbyne ligand bridging the three metallic atoms.

In solution, compound **3** seems to experience a dynamic process equalizing the chemical environment of

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(9) For reviews see: (a) Herrmann, W. A. *Adv. Organomet. Chem.* **1982**, *20*, 159. (b) J. E. Hahn. *Prog. Inorg. Chem.* **1984**, *31*, 205.

(10) (a) Trepanier, S. J.; Sterenberg, B. T.; McDonald, R.; Cowie, M. *J. Am. Chem. Soc.* **1999**, *121*, 2613. (b) Dell'Anna, M. M., Trepanier, S. J.; McDonald, R.; Cowie, M. *Organometallics* **2001**, *20*, 88. (c) Akita, M.; Hua, R.; Knox, S. A. R.; Moro-oka, Y.; Nakanishi, S.; Yates, M. I. *J. Chem. Soc., Chem. Commun.* **1997**, 51. (d) Holmgren, J. S.; Shapley, J. R.; Wilson, S. R.; Pennington, W. T. *J. Am. Chem. Soc.* **1986**, *108*, 508. (e) Nucciarone, D.; Taylor, N. J.; Carty, A. J. *Organometallics* **1984**, *3*, 177. (f) Nucciarone, D.; MacLaughlin, S. A.; Taylor, N. J.; Carty, A. J. *Organometallics* **1988**, *7*, 106.

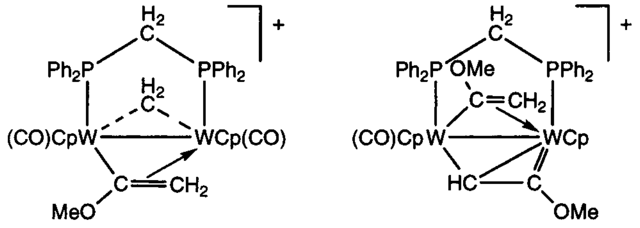
(11) (a) Alvarez, M. A.; Bois, C.; García, M. E.; Riera, V.; Ruiz, M. A. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 102. (b) Alvarez, M. A.; García, M. E.; Riera, V.; Ruiz, M. A. *Organometallics* **1999**, *18*, 634.

(12) (a) Stone, F. G. A. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 89. (b) Kreissl, F. R. In *Carbyne Complexes*; Fischer, H., Hofmann, P., Kreissl, F. R., Schrock, R. R., Schubert, U., Weiss, K., Eds.; VCH: Weinheim, Germany, 1988; p 100. (c) Stone, F. G. A. *Adv. Organomet. Chem.* **1990**, *31*, 53.

(13) (a) Hoel, E. L.; Ansell, G. B.; Leta, S. *Organometallics* **1984**, *3*, 1633, and references therein. (b) Casey, C.; Austin, E. A. *Organometallics* **1986**, *5*, 584.

(14) (a) Clark, G. R.; Cochrane, C. M.; Marsden, K.; Roper, W. R.; Wright, L. J. *J. Organomet. Chem.* **1986**, *315*, 211. (b) Jeffery, J. C.; Ruiz, M. A.; Stone, F. G. A. *J. Organomet. Chem.* **1988**, *355*, 231.

Chart 1



4 5

both tungsten atoms. This is indicated by the fact that the ^{31}P resonances broaden severely when raising the temperature, although coalescence is not yet reached at 293 K. In agreement with this, the ^{1}H NMR spectrum at that temperature exhibits a single resonance for the cyclopentadienyl groups. All these observations are indicative of the presence of a dynamic process similar to that found for **2**, which we have discussed in detail previously[11] and needs then not be reproduced here.

Reaction of Compounds 1 and 2 with CH_2N_2 in the Absence of CuCl. When copper(I) chloride is not present, the reaction between CH_2N_2 and either **1** or **2** becomes more dependent on experimental conditions. Thus, addition of an excess of an ethereal solution of CH_2N_2 to a dichloromethane solution of compound **1** or **2** cooled at −75 °C leads in both cases to a mixture containing the alkyne alkenyl complex $[W_2\{\mu\text{-}\eta^1{:}\eta^2\text{-C(OMe)CH}\}\{\mu\text{-}\eta^1{:}\eta^2\text{-C(OMe)CH}_2\}Cp_2(CO)(\mu\text{-dppm})](BF_4)$ (**5**) as major product, along with significant amounts of the alkenyl methylene compound $[W_2(\mu\text{-CH}_2)\{\mu\text{-}\eta^1{:}\eta^2\text{-C(OMe)CH}_2\}Cp_2(CO)_2(\mu\text{-dppm})](BF_4)$ (**4**) (Chart 1). In contrast with this, the methylene complex **4** becomes the major product formed when the addition of CH_2N_2 is carried out on a THF solution of compound **2** (this reaction cannot be tested on the hydroxycarbyne complex **1** because this compound is unstable in donor solvents).[11] The temperature has no significant influence on the relative amounts of **4** and **5**, although we have noticed that when the reaction is performed at higher temperatures, a variety of other uncharacterized products start to appear. The relative amount of CH_2N_2 has little effect either. For example, reaction of **1** with a slight excess of diazomethane in CH_2Cl_2 gives expectedly **2** as the major compound, with small amounts of complexes **4** and **5**. However, the ratio **4**:**5** in that mixture is roughly the same (ca. 1:2) as that obtained when using a large excess of reagent. Finally, we must note that treatment of a pure sample of **4** with excess of diazomethane leads to no reaction, an observation implying that **4** is not an intermediate in the formation of **5**.

Unfortunately, we have not been able to isolate compound **5** from the corresponding reaction mixture as a pure solid, and all attempts to obtain X-ray quality single crystals have been unsuccessful. Nevertheless, the NMR and IR data allow us to establish quite precisely the structure of **5** in solution, as we will discuss later. The structure of **4** has been determined through an X-ray study. A view of the cation is shown in Figure 1, and selected bond lengths and angles are listed in Table 2. The ditungsten center is bridged by dppm, a roughly symmetrical methylene ligand, and a methoxyvinyl group. The coordination spheres are completed by terminal cyclopentadienyl and carbonyl ligands, arranged *trans* to each other. The methylene group lies nearly in the average plane defined by the Cp centroids and CO ligands, with the diphosphine bridge placed almost perpendicular to it and the μ-vinyl ligand placed *trans* to the dppm bridge. The relative position of the bridging groups in this cation is analogous to those found for the bridging ligands in the isoelectronic complexes $[W_2(\mu\text{-X})Cp(\mu\text{-CO})(CO)_2(\mu\text{-dppm})]^+$ (X = F, Cl).[15] According to the 18-electron rule, a single metal−metal bond should be formulated for this cation, in agreement with the intermetallic distance, 2.965(1) Å, which is very close to those measured in the above-mentioned halide complexes.[15]

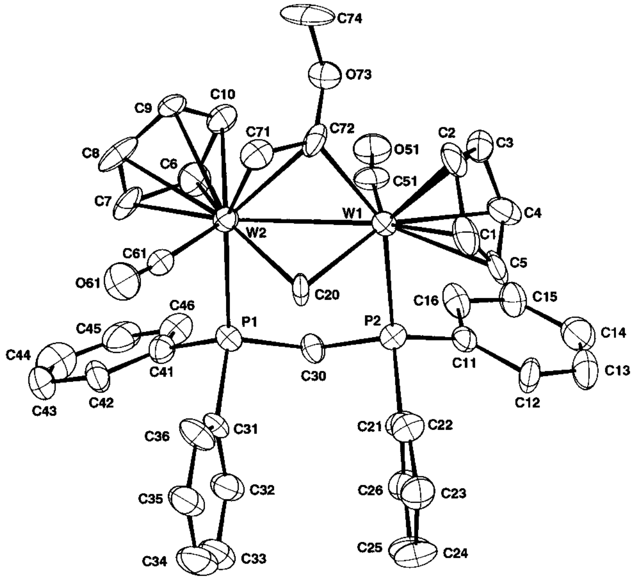


Figure 1. CAMERON drawing of the molecular structure of the cation in compound **4**. Ellipsoids represent 30% probability.

The tungsten atoms of the cation are not equivalent, and the methylene group is *trans* to the carbonyl ligand on W(1) but *cis* with respect to the carbonyl on W(2). Despite this, this methylene ligand bridges symmetrically the dimetallic unit (W−C distances 2.19(2) and 2.22(2) Å). The intrinsically asymmetric bridging alkenyl ligand in **4** displays some unexpected interatomic lengths. An inspection of the corresponding figures in related Mo[16] or W[17] alkenyl complexes reveals the following general trends: (a) the bridgehead carbon atom displays similar M−C lengths, in the range 2.10−2.20 Å, the shortest one being frequently that corresponding formally to the π interaction; (b) the second carbon atom, π bonded to the metal, exhibits longer C−M lengths, in the range 2.20−2.30 Å; (c) the C−C bond length within the alkenyl group, in the range

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[15] (a) Alvarez, M. A.; García, G.; García, M. E.; Riera, V.; Ruiz, M. A.; Bois, C.; Jeannin, Y. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1156. (b) Alvarez, M. A.; García, G.; García, M. E.; Riera, V.; Ruiz, M. A.; Lanfranchi, M.; Tiripicchio, A. *Organometallics* **1999**, *18*, 4509.

[16] (a) Conole, G.; Hill, K. A.; McPartlin, M.; Mays, M. J.; Morris, M. J. *J. Chem. Soc., Chem. Commun.* **1989**, 688. (b) Doel, G. R.; Feasey, N. D.; Knox, S. A. R.; Orpen, A. G.; Webster, J. *J. Chem. Soc., Chem. Commun.* **1986**, 542. (c) Adams, H.; Biebricher, A.; Gay, S. R.; Hamilton, T.; McHugh, P. E.; Morris, M. J.; Mays, M. J. *J. Chem. Soc., Dalton Trans.* **2000**, 2983. (d) Bamber, M.; Froom, S. F. T.; Green, M.; Schulz, M.; Werner, H. *J. Organomet. Chem.* **1992**, *434*, C19.

[17] (a) Finnimore, S. R.; Knox, S. A. R.; Taylor, G. E. *J. Chem. Soc., Dalton Trans.* **1982**, 1783. (b) Ahmed, K. J.; Chisholm, M. H.; Folting, K.; Huffmann, J. C. *J. Chem. Soc., Chem. Commun.* **1985**, 152. (c) Mays, M. J.; Reinisch, P. F.; Solan, G. A.; McPartlin, M.; Powell, H. R. *J. Chem. Soc., Dalton Trans.* **1995**, 1597.

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}
$[W_2(\mu\text{-COH})Cp_2(CO)_2(\mu\text{-dppm})](TFPB)$ (**1′**)	1892 (m), 1857 (mf)	18.3 (br)	
$[W_2(\mu\text{-COMe})Cp_2(CO)_2(\mu\text{-dppm})](TFPB)$ (**2′**)	1952 (vs), 1838 (s)	17.7^c	
$[CuW_2Cl(\mu_3\text{-COMe})Cp_2(CO)_2(\mu\text{-dppm})](BF_4)$ (**3**)	1961 (s), 1927 (sh, w), 1846 (vs)	12.5 (br), 7.0 (v br)^{d,e}	
$[W_2(\mu\text{-}CH_2)\{\mu\text{-C(OMe)}CH_2\}Cp_2(CO)_2(\mu\text{-dppm})](BF_4)$ (**4**)	1955 (vs), 1875 (s br)	11.1 (248), 6.2 (218)^d	56
$[W_2\{\mu\text{-C(OMe)CH}\}\{\mu\text{-C(OMe)}CH_2\}Cp_2(CO)(\mu\text{-dppm})](BF_4)$ (**5**)	1879 (vs)	10.6, 9.6	81

^{a} Recorded in CH_2Cl_2 solution. ^{b} Recorded at 121.50 MHz and 291 K in acetone-d_6 solution, unless otherwise stated; δ in ppm relative to external 85% aqueous H_3PO_4; J in hertz. ^{c} Recorded at room temperature in CH_2Cl_2/D_2O. ^{d} Recorded at 161.98 MHz. $^e\delta = 11.6$ (400), 6.1 (350), $J_{PP} = 44$, when recorded at 238 K.

Table 2. Crystal Data for Compound 4·1/2CH_2Cl_2

mol formula (**4**·1/2CH_2Cl_2)	$C_{41.5}H_{40}BClF_4O_3P_2W_2$
mol wt	1138.68
a, Å	10.714(3)
b, Å	15.405(3)
c, Å	24.875(7)
α, deg	90
β, deg	90.27(2)
γ, deg	90
V, Å^3	4116(2)
Z	4
cryst syst	monoclinic
space group	$P2_1/c$
systematic absences	$h0l$, $l = 2n+1$, $0k0$, $k = 2n+1$
cryst shape/color	parallelepiped/red
linear abs coeff μ (cm^{-1})	59.03
density calcd (g cm^{-3})	1.837
diffractometer	CAD4−Enraf-Nonius
temp, K	293
radiation	Mo Kα ($\lambda = 0.71069$ Å)
scan type	$\omega/2\theta$
scan range, deg	$0.8 + 0.345 \tan\theta$
θ limits, deg	1−25
octants collected	0, 12; 0, 18; −29, 29
no. of data collected	7964
no. of unique data collected	7231
no. of unique data used for refinement	3768 $(F_o)^2 > 3\sigma(F_o)^2$
R (int)	0.075
decay of standards reflns %	<1
$R = \sum\|\|F_o\| - \|F_c\|\|/\sum\|F_o\|$	0.046
$R_w = \sum_w(\|F_o\| - \|F_c\|)^2/\sum_w(F_o)^2$	0.053, $w = 1.0$
abs corr	DIFABS (min = 0.94, max = 1.10)
no. of variables	506
$\Delta\rho_{min}/\Delta\rho_{max}$ (e/Å^3)	−1.64/1.70

Table 3. Selected Bond Distances (Å) and Angles (deg) for Compound 4

W(1)−W(2)	2.965(1)	W(2)−C(71)	2.39(2)
W(1)−P(2)	2.480(5)	W(2)−P(1)	2.546(5)
W(1)−C(20)	2.19(2)	W(2)−C(20)	2.22(2)
W(1)−C(72)	2.17(2)	W(2)−C(72)	2.43(2)
W(1)−C(51)	1.94(2)	W(2)−C(61)	1.96(2)
C(71)−C(72)	1.48(3)	C(72)−O(73)	1.29(2)
C(74)−O(73)	1.46(2)		
P(1)−W(2)−C(72)	135.6(4)	P(2)−W(1)−C(72)	146.5(5)
P(1)−W(2)−C(71)	147.9(5)	P(2)−W(1)−W(2)	92.8(1)
P(1)−W(2)−W(1)	89.6(1)	C(20)−W(1)−C(51)	122.2(7)
C(20)−W(2)−C(61)	78.9(7)	W(1)−C(20)−W(2)	84.5(6)

1.40−1.45 Å, is intermediate between that corresponding to a single and a double bond. Thus, the description of the metal to ligand interaction in terms of a σ bond (C to M) and a π bond (C═C to M) is generally satisfactory. Under this view, it is expected that an increase of the π bond strength should cause a C−C elongation and vice versa. This is actually observed, for example, for the dimolybdenum complex $[Mo_2Cp_2(\mu\text{-SPh})(\mu\text{-}\eta^1\text{:}\eta^2\text{-C(Me)═CHMe})(CO)_2]$, which displays quite long Mo−C (π type) distances of ca. 2.37 Å, which is consistent with a short C−C distance (1.384(11) Å).[18a] A similar effect is found in the complexes $[Mo_2Cp_2Cl(\mu\text{-}\eta^1\text{:}\eta^2\text{-CHCHPh})(CO)_4]$[18b] or $[Mo_2Cp_2(\mu\text{-}\eta^1\text{:}\eta^2\text{-C(Me)CHMe})(\mu\text{-}PMe_2)(CO)_3]$.[18c] The unusual feature in the bridging alkenyl ligand in **4** is that the quite large π-type W−C lengths (W(2)−C(71) = 2.39(2), W(2)−C(72) = 2.43(2) Å) are indicative of a relatively weak π interaction, but do not correlate with the C(71)−C(72) length of 1.48(3) Å, almost corresponding to a single bond. At present, we cannot offer a rationale for this geometric feature.

The spectroscopic data in solution for **4** are consistent with its solid-state structure. The inequivalent carbonyl ligands give rise to two strong ν_{st}(CO) bands at 1955 (vs) and 1875 (s, br) cm^{-1} in the IR spectrum in dichloromethane and to two ^{13}C NMR resonances in the region of terminal carbonyls. In the ^{1}H NMR spectrum, the inequivalent protons of the μ-CH_2 ligand appear as doublets of triplets at 3.02 and 4.44 ppm, and the corresponding carbon atom gives rise to a triplet at 89.9 ppm in the ^{13}C NMR spectrum. These data are not unusual for a methylene bridging ligand.[9] The μ-alkenyl ligand also gives rise to $^{13}C\{^1H\}$ and ^{1}H NMR resonances in the expected regions.[19−21] A typical set of two weakly coupled resonances in the ^{1}H spectrum is observed for the geminal CH_2 group,[3c] while the two metal-bonded carbon atoms of the alkenyl group give resonances at 192.1(C_α) and 68.1 (CH_2) ppm.

The structure proposed for compound **5** is depicted in Chart 1 and is in full agreement with all spectroscopic data available. The monocarbonylic nature of **5** is deduced from the presence of a single band in the ν_{st}(CO) region of the IR spectrum (1879 cm^{-1} in CH_2Cl_2) and a doublet at 228.1 ppm in the ^{13}C NMR spectrum, a chemical shift consistent with its terminal nature. The presence of a methoxyvinyl ligand similar to that found for **4** is deduced from the appearance of characteristic NMR resonances. This ligand gives rise to two P-coupled resonances in the ^{13}C NMR spectrum, at 188.3 (C_α) and 77.0 (CH_2) ppm, these chemical shifts being similar to those for **4**. The presence of this alkenyl ligand is also deduced from the appearance of two weakly coupled resonances at 0.75 and 3.33 ppm ($J_{HH} = 4$ Hz), similar to those found for **4** and other vinyl ligands.[19,20]

The NMR data for **5** clearly show that, in addition to the alkenyl group, the molecule contains a second

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(18) (a) Schollhammer, P.; Pétillon, F. Y.; Poder-Guillou, S.; Talarmin, J.; Muir, K. W.; Yufit, D. S. *J. Organomet. Chem.* **1996**, *513*, 181. (b) Acum, G. A.; Mays, M. J.; Raithby, P. R.; Solan, G. A. *J. Organomet. Chem.* **1995**, *492*, 65. (c) Conole, G.; Henrick, K.; McPartlin, M.; Horton, A. D.; Mays, M. J. *New J. Chem.* **1988**, *12*, 559.

(19) (a) Raithby, P. R.; Rosales, M. J. *Adv. Inorg. Chem. Radiochem.* **1985**, *29*, 168. (b) Sappa, E.; Tiripicchio, A.; Braunstein, P. *Coord. Chem. Rev.* **1985**, *65*, 219. (c) Holton, J.; Lappert, M. F.; Pearce, R.; Yarrow, P. I. W. *Chem. Rev.* **1983**, *83*, 135.

(20) Evans, J.; McNulty, G. S. *J. Chem. Soc., Dalton Trans.* **1984**, 79.

(21) Fong, R. H.; Hersh, W. H. *J. Am. Chem. Soc.* **1987**, *109*, 2843.

hydrocarbon ligand which can be unambiguously identified as a bonded methoxyacetylene molecule. The metal-bonded carbon atoms give ^{13}C resonances at 253.6 (*C*OMe) and 147.3 (*C*H) ppm. The large chemical shift difference between these resonances suggests a very asymmetric coordination of the alkyne to the dimetallic unit, while the quite high chemical shift of the internal resonance suggests substantial multiple-bond character in the corresponding W−C interaction. Similar high ^{13}C chemical shifts (ca. 260 ppm) have been recently described for *both* carbon atoms of the bridging alkyne ligand in the molybdenum cations $[Mo_2Cp_2(\mu\text{-SMe})_3(RCCH)]^+$.[22] Actually, the chemical shifts found for the alkyne group in **5** are similar to those exhibited by the bridging aminoalkyne ligand in the clusters $[M_3(CO)_9(\mu_3\text{-S})(\mu_3\text{-MeC}_2NMe_2)]$ (M = Fe, Ru, Os).[23] Structural data for aminoalkyne ligands bridging either trimetallic clusters[23] or dinuclear compounds[24,25] support a view of these ligands as bis-carbene (one terminal, one bridging) donor groups, which is consistent with the corresponding ^{13}C chemical shifts and is also supported on MO calculations[26] and reactivity.[25,27] In summary, we believe that the methoxyalkyne ligand in **5** is very similar to a dialkylaminoalkyne group and is thus bonded as a terminal alkylidene through the internal carbon atom, thus effectively replacing the lost carbonyl group, and as a bridging alkylidene through the terminal (CH) carbon atom.

Role of Cation−Anion Interactions in the Reactivity of the Carbyne Complexes. The results discussed above seem to prove that there are independent pathways for the generation of either **4** or **5** from the carbyne complexes and diazomethane. As we have found strong differences in the relative amounts of **4** and **5** when changing the donor properties of the reaction solvent (from CH_2Cl_2 to tetrahydrofuran), we suspected that interactions between the cation **2** and its counterion and/or the solvent might influence the course of the reaction. We must note that cation−anion interactions occur for salt **2** in poorly solvating solvents, as deduced from IR data.[11] Thus, a change in the solvent modifies not only any cation−solvent interaction but also any cation−anion interaction being present.

To study the role of the counterion in the above reactions, we have prepared the hydroxycarbyne (**1′**) and methoxycarbyne (**2′**) cations as salts of the TFPB anion (TFPB = $[B\{3,5\text{-}C_6H_3(CF_3)_2\}_4]^-$). The latter is a rather inert, noncoordinating anion that has been found to be useful in the stabilization of highly reactive cationic species.[28] Compound **1′** was prepared similarly to **1**,[11] but using $H(TFPB)\cdot 2Et_2O$[28b] instead of $HBF_4\cdot OEt_2$. No attempts to isolate this new salt were made. Spectroscopic data for **1′** (Table 1) are similar to those of **1**, but now the IR spectrum for **1′** in dichloromethane solution displays just two strong bands in the $\nu_{st}(CO)$ region, instead of the four ones exhibited by **1**. This indicates that the cation−anion interaction likely responsible for the observed splitting of the $\nu_{st}(CO)$ bands in **1**[11] is eliminated when replacing BF_4^- for the less coordinating $TFPB^-$, as expected.

Compound **2′** was prepared by reaction of a dichloromethane solution of **1′** and CH_2N_2 (in Et_2O). However, even when using a large excess of CH_2N_2, the major organometallic product formed is still **2′**, along with large amounts of polymethylene as a white insoluble solid. The IR spectrum of **2′** in dichloromethane solution displays just two $\nu_{st}(CO)$ bands instead of the three bands observed for **2**.[11] This again indicates that the anion/cation interaction present in **2** has been largely eliminated after replacement of BF_4^- by $TFPB^-$. In all, however, the use of the TFPB ion in the diazomethane reactions under discussion is not useful for elucidating the reaction pathways in operation: it allows the hydroxy to methoxycarbyne transformation, but makes the latter complex an efficient catalyst for the decomposition of diazomethane, which in turn precludes the formation of significant amounts of products (like **4** or **5**) incorporating more methylene units. Decomposition of diazomethane catalyzed by transition metal complexes is not an unusual reaction.[29]

Reaction Pathways in the Formation of Compounds 4 and 5. The results discussed above reveal that the reactions of the carbyne complexes **1** and **2** with diazomethane are not simple processes, as they involve the addition of up to four methylene groups to the starting substrates. The surroundings of the carbyne cation are also important, so that changing the solvent or the counterion has a strong influence on the distribution of products. Although the information obtained is not complete enough so as to define all elemental steps involved, we can get a general picture of the reaction pathways under operation (Scheme 2).

In the first place, it is clear that the initial step is the formal insertion of methylene into the O−H bond of the hydroxycarbyne ligand in **1**, thus yielding the methoxycarbyne **2**. The fact that the same distribution of products is obtained starting from **1** or **2** supports this view. On the other hand, the insertion of methylene into O−H bonds is well documented.[3c,30] Compound **2** has two reactive sites for further methylene addition, the W−W bond and the W−C(carbyne) bond, both of them with double-bond character. These type of methylene additions are well known, the first one being the classical metallacyclopropanation process[9a] and the second one leading to bridging alkenyl $CR{=}CH_2$ ligands.[3c,d] In fact, compound **4** is the result of both types of methylene addition to the methoxycarbyne complex **2**, but we cannot tell in which order this double addition is actually occurring. By recalling that the methoxyvinyl ligand is present in both **4** and **5**, we propose that methylene addition to the bridging carbyne occurs first to give the alkenyl intermediate **A**, which is still

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[22] Schollhammer, P.; Cabon, N.; Capon, J. F.; Pétillon, F. Y.; Talarmin, J. *Organometallics* **2001**, *20*, 1242.

[23] Adams, R. D.; Chen, G.; Tanner, J. F.; Yin, J. *Organometallics* **1990**, *9*, 595.

[24] Adams, R. D.; Chen, G.; Yin, J. *Organometallics* **1991**, *10*, 1278.

[25] Cabrera, E.; Daran, J. C.; Jeannin, Y.; Kristiansson, O. *J. Organomet. Chem.* **1986**, *310*, 367.

[26] Nomikon, Z.; Halet, J. F.; Hoffmann, R.; Tanner, J.; Adams, R. D. *Organometallics* **1990**, *9*, 588.

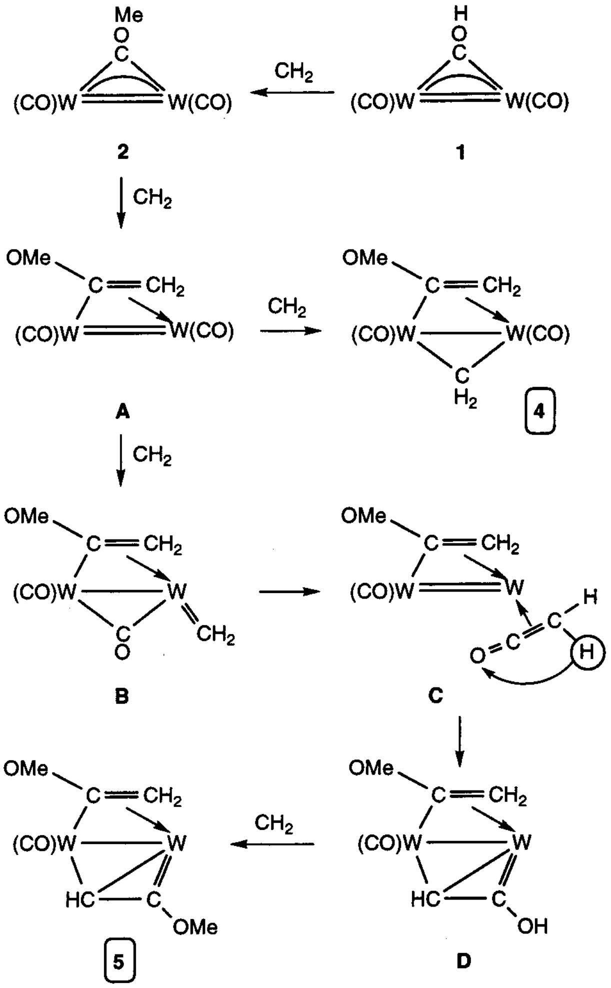
[27] Cabrera, E.; Daran, J. C.; Jeannin, Y. *Organometallics* **1988**, *7*, 2010.

[28] (a) Nishida, H.; Takada, N.; Yoshhimura, M.; Sonoda, T.; Kobayashi, H. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 2600. (b) Brookhart, M.; Grant, B.; Volpe, A. F., Jr. *Organometallics* **1992**, *11*, 3920. (c) Butts, M. D.; Scott, B. L.; Kubas, G. J. *J. Am. Chem. Soc.* **1996**, *118*, 4746. (d) Heinekey, D. M.; Radzewich, C. E. *Organometallics* **1998**, *17*, 51, and references therein.

[29] Hamilton, D. H.; Shapley, J. R. *Organometallics* **2000**, *19*, 761.

[30] Hayashi, T.; Kato, T.; Kaneko, T.; Asai, T.; Ogoshi, H. *J. Organomet. Chem.* **1994**, *473*, 323.

Scheme 2. Proposed Pathways for the Reactions of Diazomethane with Compound 1 [W−W = $W_2Cp_2(\mu\text{-dppm})$]



unsaturated. Further methylene addition to the double W−W bond would yield complex **4**, thus completing one of the reaction pathways. Alternatively, the methylene addition can give a terminal methylene group, with displacement of a terminal CO to a bridging position, then yielding a new intermediate **B**. Precedents for this type of addition to a doubly bonded binuclear center can also be found on related complexes. For example, ^tBuNC adds to the doubly bonded $[Mo_2Cp'_2(\mu\text{-}CH_2PPh_2)(\mu\text{-}PPh_2)(CO)_2]$ to give $[Mo_2Cp'_2(\mu\text{-}CH_2PPh_2)(\mu\text{-}PPh_2)(\mu\text{-}CO)(CO)(CN^tBu)]$ ($Cp' = \eta^5\text{-}C_5H_4Me$).[31] Intermediate **B** has now methylene and carbonyl groups which can couple to each other to give a bonded ketene group, also a known process.[10d,32] An H migration in the unsaturated ketene intermediate **C** to give the hydroxy acetylene species **D** is then proposed, thus providing the two extra electrons needed for electronic saturation of the molecule. This is the elemental step for which we have not found clear precedents in the literature. We note, however, that the *reverse* process has been proposed in order to explain the formation of the ketene complex $[Ru_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}CO)(CO)_2\{\mu\text{-}C(O)CH_2\}]$.[33] Finally, a further insertion of methylene into the O−H bond in intermediate **D** gives the alkyne product **5**.

To obtain further support for our proposal on the formation of compounds **4** and **5**, we carried out the reaction of **1** with an excess of CD_2N_2 in CH_2Cl_2 at −65 °C. This led to a mixture of compounds **4** and **5** deuterated as expected, i.e., containing a $\mu\text{-}C(OCHD_2)\text{-}CD_2$ vinyl group. This itself implies that there is no H-exchange involving the hydroxycarbyne ligand. The most important observation was, however, that the **4**:**5** ratio was then 1:1, to be compared with a 1:2 ratio when using the normal, nondeuterated reagent. This kinetic isotope effect in the formation of **5** is in agreement with the transformation **C**/**D** proposed (Scheme 2), the latter requiring the cleavage of a C−H bond.

In summary, by combining rational elemental steps we can give a satisfactory explanation for the formation of compounds **4** and **5**. Yet, some speculation is unavoidable and some questions remain to be answered, for example, the precise role of the solvent and the counterion, both of which can almost suppress the formation of some of the methylene derivatives of the carbyne complexes **1** and **2**.

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. Petroleum ether refers to that fraction distilling in the range 60−65 °C. Compound **1**,[11] $H(TFPB)\cdot 2Et_2O$,[28b] CuCl,[35] and diethyl ether solutions of CH_2N_2[36] were prepared according to literature procedures. Diethyl ether solutions of CD_2N_2 were prepared analogously, but using $NaOD/D_2O$ solutions and EtOD instead of the nondeuterated reagents. All other reagents were purchased from the usual commercial suppliers and used as received. Filtrations were carried out using dry diatomaceous earth under nitrogen. 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.

NMR spectra were recorded at 400.13 (^1H), 161.98 ($^{31}P\{^1H\}$), or 100.61 ($^{13}C\{^1H\}$) MHz in acetone-d_6 solution at room temperature, unless otherwise indicated. Chemical shifts (δ) are given in ppm, relative to internal TMS (^1H, ^{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. $^{13}C\{^1H\}$ NMR spectra were recorded on solutions containing a small amount of tris(acetylacetonato)chromium(III) as a relaxation reagent. The assignments of the ^{13}C resonances were routinely verified through standard DEPT experiments.

Preparation of Solutions of Compound 1′. A dichloromethane solution (30 mL) of compound $[W_2Cp_2(CO)_4(\mu\text{-dppm})]$ (0.1 g, 0.1 mmol) was stirred with $H(TFPB)\cdot 2Et_2O$ (100 mg, 0.1 mmol) for 45 min at −40 °C to give a brown solution. Solvent was then removed under vacuum and the residue

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[31] García, G.; García, M. E.; Melón, S.; Riera, V.; Ruiz, M. A.; Villafañe, F. *Organometallics* **1997**, *16*, 624.

[32] (a) Gao, Y.; Jennings, M. C.; Puddephatt, R. J. *Organometallics* **2001**, *20*, 1882. (b) Morrison, E. D.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1985**, *107*, 3541. (c) Yang, Y.-L.; Wang, L. J.-J.; Lin, Y.-Ch.; Huang, S.-L.; Chen, M.-C.; Lee, G.-H.; Wang, Y. *Organometallics* **1997**, *16*, 1573. (d) Geoffroy, G. L.; Bassner, S. L. *Adv. Organomet. Chem.* **1988**, *28*, 1, and references therein. (e) Lin, Y. C.; Calabrese, J. C.; Wreford, S. S. *J. Am. Chem. Soc.* **1983**, *105*, 1679.

[33] Doherty, N. M.; Filders, M. J.; Forrow, N. J.; Knox, S. A. R.; Macpherson, K. A.; Orpen, A. G. *J. Chem. Soc., Chem. Commun.* **1986**, 1335.

[34] Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*; Pergamon Press: Oxford, U.K., 1988.

[35] Brauer, G. *Handbuch der Präparativen Anorganischen Chemie*; Ferdinand Enke Verlag: Stuttgart, Germany, 1978; Vol. 2, p 972.

[36] Vogel, A. I. *Textbook of Practical Organic Chemistry,* 4th ed.; Longmans: London, U.K., 1978; p 291.

washed with petroleum ether (2 × 5 mL) to give compound **1′** as an oily solid. The latter was redissolved in CH_2Cl_2 and was then ready for further use.

Preparation of Solutions of Compound 2′. A diethyl ether solution of CH_2N_2 (5 mL, ca. 3 mmol) was added to a dichloromethane solution (8 mL) of compound **1′** (0.165 g, 0.09 mmol) at −65 °C. The mixture was stirred for 45 min, and solvent was then removed under vacuum. The oily residue was extracted with CH_2Cl_2 (3 × 5 mL) and filtered. Removal of solvent from the filtrate under vacuum gave a residue containing compound **2′** as the major species present. Attempts to further purify this product were unsuccessful due to its progressive decomposition upon manipulation.

Preparation of [CuW$_2$Cl(μ_3-COMe)Cp$_2$(CO)$_2$(μ-dppm)](BF$_4$) (3). A diethyl ether solution of CH_2N_2 (5 mL, ca. 3 mmol) and 0.01 g (0.09 mmol) of CuCl were added to a dichloromethane solution (15 mL) containing compound **1** (0.094 g, 0.09 mmol) at − 75 °C. The mixture was stirred for 45 min and allowed to reach room temperature slowly. Solvent was then removed under vacuum and the residue extracted with CH_2Cl_2 (3 × 5 mL) and filtered. Removal of solvent from the filtrate under vacuum yielded compound **3** as a brown microcrystalline powder (0.087 g, 83%). Anal. Calcd for $C_{39}BClCuF_4H_{35}O_3P_2W_2$: C, 40.10; H, 3.00. Found: C, 40.18; H, 3.05. ^{1}H NMR (200.13 MHz): δ 7.80−7.10 (m, 20H, Ph), 5.60 (s, 10H, Cp), 5.17 (t, J_{HP} = 11, 2H, CH$_2$), 4.91 (s, 3H, OCH$_3$). ^{31}P{^{1}H} NMR (238 K): δ 11.6 (d, J_{PP} = 44, J_{PW} = 400, 1P, μ-dppm), 6.1 (d, J_{PP} = 44, J_{PW} = 350, 1P, μ-dppm). ^{13}C{^{1}H} NMR (238 K): δ 332.7 (s, μ_3-COMe), 247.8 (s, CO), 220.7 (s br, CO), 140.1−126.5 (Ph), 99.8 (s, Cp), 92.6 (s, Cp), 73.1 (s, OCH$_3$), 48.9 (t, J_{CP} = 31, CH$_2$).

Preparation of [W$_2$(μ-COMe)Cp$_2$(CO)$_2$(μ-dppm)](BF$_4$) (2). Solid PPh$_3$ (0.020 g, 0.078 mmol) was added to a dichloromethane solution (8 mL) of compound **3** (0.087 g, 0.075 mmol) at room temperature. The mixture was stirred for 10 min and the solvent removed under vacuum. The residue was washed with toluene (5 × 5 mL), extracted with CH_2Cl_2, and filtered. Removal of solvent from the filtrate under vacuum yielded compound **3** as a dark brown powder (0.075 g, 83%).

Preparation of [W$_2$(μ-CH$_2$){μ-η^1:η^2-C(OMe)CH$_2$}(CO)$_2$Cp$_2$(μ-dppm)]BF$_4$ (4). A diethyl ether solution of CH_2N_2 (5 mL, ca 3 mmol) was added to a tetrahydrofuran solution (12 mL) of compound **2** (0.01 g, 0.09 mmol) cooled at 0 °C. The mixture was stirred for 30 min, and solvent was then removed under vacuum. The residue was extracted with CH_2Cl_2 (3 × 5 mL) and filtered. Removal of solvent from the filtrate under vacuum gave a solid containing compound **4** as major product. Recrystallization at room temperature from CH_2Cl_2/diethyl ether/petroleum ether yielded compound **4** (0.053 g, 52%) as orange crystals. Suitable crystals for the X-ray study were grown by slow diffusion of a concentrated CH_2Cl_2 solution of a pure sample of the complex into a layer of petroleum ether at room temperature. Anal. Calcd for $C_{41}H_{39}BF_4O_3P_2W_2$: C, 44.92; H, 3.59. Found: C, 45.21; H, 3.70. ^{1}H NMR (300.13 MHz): δ 7.62−6.98 (m, 20H, Ph), 5.86 (td, J_{HP} = 13, J_{HH} = 12, 1H, PCH$_2$), 5.12 (d, J_{HP} = 3, 5H, Cp), 4.95 (d, J_{HP} = 1.5, 5H, Cp), 4.44 (td, J_{HP} = 26, J_{HH} = 12, 1H, μ-CH$_2$), 3.89 (dt, J_{HP} = 14, 11, J_{HH} = 11, 1H, PCH$_2$), 3.85 [d, J_{HH} = 4, 1H, C═CH$_2$], 3.70 (s, 3H, OMe), 3.02 (q, J_{HP} = J_{HH} = 12, 1H, μ-CH$_2$), 2.36 [dd, J_{HH} = 4, J_{HP} = 1, 1H, C═CH$_2$] ppm. ^{13}C{^{1}H} NMR (50.32 MHz): δ 229.0 (d, J_{CP} = 7, CO), 218.0 (d, J_{CP} = 6, CO), 192.1 [d, J_{CP} = 9, μ-*C*(OMe)═CH$_2$], 138.5−128.1 (Ph), 94.2 (s, Cp), 89.9 (t, J_{CP} = 8, μ-CH$_2$), 88.4 (s, Cp), 68.1 [dd, J_{CP} = 9, 3, μ-C(OMe)═*C*H$_2$], 60.8 (s, OMe), 41.8 (dd, J_{CP} = 19, 23, PCH$_2$) ppm.

Preparation of [W$_2${μ-η^1:η^2-C(OMe)CH}{μ-η^1:η^2-C(OMe)CH$_2$}Cp$_2$(CO)(μ-dppm)]BF$_4$ (5). A diethyl ether solution of CH_2N_2 (5 mL, ca. 3 mmol) was added to a dichloromethane solution (12 mL) of compound **2** (0.01 g, 0.09 mmol) at −65 °C. The solution was stirred for 45 min and allowed to reach room temperature slowly. Solvent was then removed under vacuum, and the residue washed with toluene (5 × 5 mL), extracted with CH_2Cl_2, and filtered. Removal of solvent from the filtrate under vacuum gave a solid containing complex **5** as major species. Attempts to further purify this product were unsuccessful. ^{1}H NMR: δ 7.96 (s, 1H, CH), 7.94−7.01 (m, 20H, Ph), 5.24 (s, 5H, Cp), 5.16 (s, 5H, Cp), 3.80 (s, 3H, OMe), 3.67 (br q, J_{HH} ≅ J_{HP} ≅ 13, 1H, PCH$_2$), 3.64 (s, 3H, OMe), 3.33 [d, J_{HH} = 4, 1H, μ-C(OMe)═C*H$_2$*], 2.63 [dt, J_{HP} = 10, J_{HH} = 14, 1H, PCH$_2$], 0.75 [d, J_{HH} = 4, 1H, μ-C(OMe)═C*H$_2$*] ppm. ^{13}C-{^{1}H} NMR: δ 253.6 [t, J_{CP} = 4, J_{CW} = 135, μ-*C*(OMe)≡CH), 228.1 [d, J_{CP} = 8, WCO], 188.3 [t, J_{CP} = 4.5, μ-*C*(OMe)═CH$_2$], 147.3 (s, μ-C(OMe)≡*C*H), 143.0−129.0 (Ph), 98.7, 94.1 (2 × s, 2 x Cp), 77.0 [t, J_{CP} = 5, μ-C(OMe)═*C*H$_2$], 61.8, 60.2 (2 × s, 2 × OMe), 23.4 [dd, J_{CP} = 29, 24, PCH$_2$] ppm.

X-ray Structure Determination for Compound 4·1/2CH$_2$Cl$_2$. A selected crystal was set up on an automatic diffractometer. Unit cell dimensions with estimated standard deviations were obtained from least-squares refinements of the setting angles of 25 well-centered reflections. Two standard reflections were monitored periodically; they showed no change during data collection. Corrections were made for Lorentz and polarization effects. Empirical absorption correction (Difabs)[37] was applied. An extinction correction was unnecessary.

Computations were performed by using the PC version of CRYSTALS.[38] Atomic form factors for neutral atoms were taken from ref 39. Real and imaginary parts of anomalous dispersion were taken into account. The structures were solved by direct methods (SHELXS)[40] and successive Fourier maps. Hydrogen atoms could not be found on difference maps and were not introduced in the calculations. Other atoms were anisotropically refined. Full matrix least-squares refinements were carried out by minimizing the function $\sum_w(|F_o| - |F_c|)^2$ where F_o and F_c are the observed and calculated structure factors. Models reached convergence with $R = \sum(|F_o| - |F_c|)/\sum|F_o|$ and $R_w = [\sum_w(|F_o| - |F_c|)^2/\sum_w(F_o)^2]^{1/2}$ having values listed in Table 2; each reflection was assigned a weight unity. Criteria for a satisfactory complete analysis were the ratios of rms shift to standard deviations being less than 0.2 and no significant features in the last difference map. The asymmetric unit contains a half molecule of CH$_2$Cl$_2$. Figure 1 represents a CAMERON[41] view of the cation, with the numbering scheme.

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Supporting Information Available: Tables of fractional atomic coordinates, anisotropic thermal parameters, and bond lengths and angles for compound **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(37) Walker, N.; Stuart, D. *Acta Crystallogr., A* **1983**, *39*, 158.
(38) Watkin, D. J.; Carruthers, J. R.; Betteridge, P. W. *CRYSTALS*, An Advanced Crystallographic Computer Program; Chemical Crystallography Laboratory: Oxford, U.K., 1988.
(39) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. IV.
(40) Sheldrick, G. M. *SHELXS 86, Program for Crystal Structure Solution*; University of Göttingen: Göttingen, 1986.
(41) Pearce, L. J.; Watkin, D. J. *CAMERON*; Chemical Crystallography Laboratory: Oxford, U.K., 1989.