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Chemistry of Highly Electrophilic Binuclear Cations. 2. Oxidation Reactions of $[W_2(\eta^5\text{-}C_5H_5)_2(CO)_4(\mu\text{-}Ph_2PCH_2PPh_2)]$ with $[FeCp_2][B\{3,5\text{-}C_6H_3(CF_3)_2\}_4]$

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Chemical oxidation of the title compound $[W_2Cp_2(CO)_4(\mu\text{-dppm})]$ ($Cp = \eta^5\text{-}C_5H_5$; dppm = $Ph_2PCH_2PPh_2$) with 1 equiv of $[FeCp_2](BAr'_4)$ ($Ar' = 3,5\text{-}C_6H_3(CF_3)_2$) leads to the tetracarbonyl radical $[W_2Cp_2(CO)_4(\mu\text{-dppm})](BAr'_4)$, which experiences spontaneous decarbonylation to give the 31-electron radical $[W_2Cp_2(\mu\text{-CO})(CO)_2(\mu\text{-dppm})](BAr'_4)$. Oxidation of $[W_2Cp_2(CO)_4(\mu\text{-dppm})]$ with 2 equiv of $[FeCp_2](BAr'_4)$ gives the tricarbonyl derivative $[W_2Cp_2(\mu\text{-CO})(CO)_2(\mu\text{-dppm})](BAr'_4)_2$. The same result is obtained when oxidizing the radical $[W_2Cp_2(\mu\text{-CO})(CO)_2(\mu\text{-dppm})](BAr'_4)$ with $[FeCp_2](BAr'_4)$. The triply bonded complex $[W_2Cp_2(\mu\text{-CO})(CO)_2(\mu\text{-dppm})](BAr'_4)_2$, which displays fluxional behavior in solution, reacts with $P(OMe)_3$ to give $[W_2Cp_2(\mu\text{-CO})(CO)\{P(OMe)_3\}(\mu\text{-dppm})](BAr'_4)_2$, the structure of which has been solved through a single-crystal X-ray diffraction study. Reaction of $[W_2Cp_2(\mu\text{-CO})(CO)_2(\mu\text{-dppm})](BAr'_4)_2$ with salts of halide ions X^- (X = Cl, Br, I) gives the corresponding halo derivatives $[W_2Cp_2(\mu\text{-X})(\mu\text{-CO})(CO)_2(\mu\text{-dppm})](BAr'_4)$. When X = I, a mixture of two isomers differing in the relative positions of the bridging halide and carbonyl is obtained. The same halide compounds were obtained in the reactions of paramagnetic $[W_2Cp_2(\mu\text{-CO})(CO)_2(\mu\text{-dppm})](BAr'_4)$ with halogens X_2. The tricarbonyl radical was found to react slowly with water to give the known hydroxycarbyne derivative $[W_2Cp_2(\mu\text{-COH})(CO)_2(\mu\text{-dppm})](BAr'_4)$.

Introduction

The combination of multiple metal−metal bonds with positive charges at binuclear transition-metal complexes enhances the Lewis acidity of the dimetal center, and this can promote novel transformations of interest in the fields of both pure and applied synthetic chemistry.[1] In the first part of this series, we used this strategy in order to generate highly reactive dimolybdenum or ditungsten cations. Thus, removal of two electrons from the neutral complexes $[M_2Cp_2(CO)_4(\mu\text{-dppm})]$ (M = Mo, W; $Cp = \eta^5\text{-}C_5H_5$; dppm = $Ph_2PCH_2PPh_2$) by reaction with $[FeCp_2]X$ (X = BF_4, PF_6) gave the extremely reactive dications $[M_2Cp_2(CO)_4(\mu\text{-dppm})]^{2+}$ (**A**). These cations, in the absence of other donor molecules, abstract fluoride from their counterions in solution, giving tetra- or tricarbonyl fluoro derivatives (Scheme 1),[1] thus limiting the study of their reactivity. An obvious way to avoid this problem is the use of a more inert and noncoordinating counterion. For this, we have chosen the tetraphenylborate derivative $[BAr'_4]^-$ ($Ar' = 3,5\text{-}C_6H_3(CF_3)_2$).[2] This anion has been shown to be a very efficient and inert counterion for reactive cations,[3] although some reactions, including η coordination,[4a] and

Scheme 1. Fluoride Abstraction Processes in the Oxidation Reactions of $[M_2Cp_2(CO)_4(\mu\text{-dppm})]$ with $[FeCp_2]X$ (X = BF_4, PF_6)

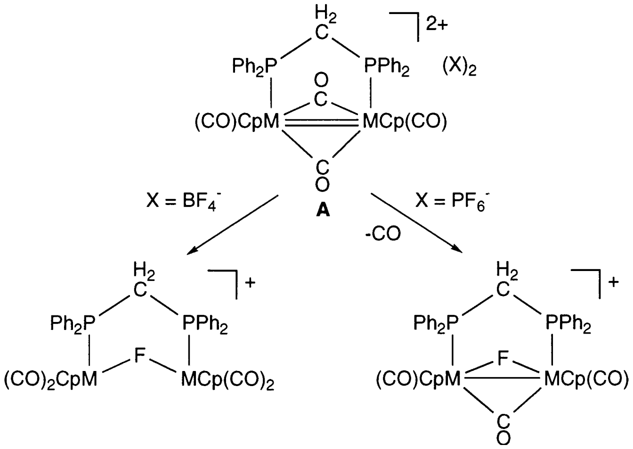

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Table 1. IR and $^{31}P\{^1H\}$ NMR Data for New Compounds

compd	ν_{st}(CO)[a]/cm^{-1}	δ(P) (J_{PW})[b]	J_{PP}
$[W_2Cp_2(\mu\text{-}CO)_2(CO)_2(\mu\text{-dppm})](PF_6)_2$	2024 (s), 1980 (w), 1864 (s), 1814 (vs)[c]		
$[W_2Cp_2(\mu\text{-}CO)_2(CO)_2(\mu\text{-dppm})](BAr'_4)$ (**2**)	1969 (vs), 1909 (w), 1747 (w), 1674 (m)		
$[W_2Cp_2(\mu\text{-}CO)(CO)_2(\mu\text{-dppm})](BAr'_4)$ (**3**)	1959 (vs), 1835 (m), 1676 (m)		
$[W_2Cp_2(\mu\text{-}CO)(CO)_2(\mu\text{-dppm})](BAr'_4)_2$ (**4**)	1991 (m), 1875 (m), 1842 (vs)	5.0 (br)[d]	
$[W_2Cp_2(CO)_2\{P(OMe)_3\}(\mu\text{-dppm})](BAr'_4)_2$ (**5**)	1890 (vs), 1798 (s)	110.1 (298)[e]	72
		25.3 (395)	44
		−13.1 (284)	72, 44
$[W_2(\mu\text{-}Cl)Cp_2(\mu\text{-}CO)(CO)_2(\mu\text{-dppm})](BAr'_4)$ (**6a**)	1974 (vs), 1912 (w), 1679 (m)	31.3 (214, −18)	83
$[W_2(\mu\text{-}Br)Cp_2(\mu\text{-}CO)(CO)_2(\mu\text{-dppm})](BAr'_4)$ (**6b**)	1973 (vs), 1912 (w), 1676 (m)	27.7 (216, −18)	83
$[W_2(\mu\text{-}I)Cp_2(\mu\text{-}CO)(CO)_2(\mu\text{-dppm})](BAr'_4)$ (**6c**)	1972 (vs), 1909 (w), 1672 (m)	22.8 (218, −15)[e,f]	81
$[W_2(\mu\text{-}I)Cp_2(\mu\text{-}CO)(CO)_2(\mu\text{-dppm})](BAr'_4)$ (**7c**)	1956 (vs), 1898 (w), 1669 (m)	5.7 (300, 2)[e,f]	63

[a] Recorded in CH_2Cl_2 solution. [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. [c] In Nujol mull.[1] [d] δ 11.6 (d, $J_{PP} = 33$, $J_{PW} = 311$) and −2.6 (d, $J_{PP} = 33$, $J_{PW} = 369$) at 213 K. [e] Recorded at 161.98 MHz. [f] Recorded at 253 K.

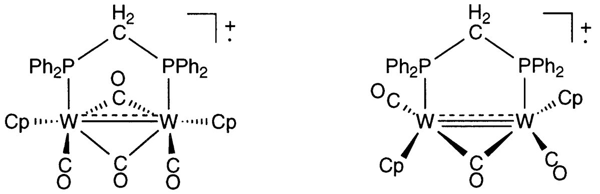
arylation,[4b] have been reported. In this paper we report our study on the oxidation reactions of $[W_2Cp_2(CO)_4(\mu\text{-dppm})]$ (**1**) with $[FeCp_2](BAr'_4)$. As will be shown, the use of the quite inert $[BAr'_4]^-$ anion not only solves the problem of fluoride abstraction, then allowing the formation of dipositive cations, but also stabilizes some of the paramagnetic intermediates in these reactions, thus allowing their detection and even the study of some of their reactions. The related reactions on the molybdenum substrate $[Mo_2Cp_2(CO)_4(\mu\text{-dppm})]$ were found to lead to substantially different results and will be discussed in a separate paper.

Results and Discussion

One-Electron Oxidation of Compound 1. The title compound reacts rapidly with 1 equiv of $[FeCp_2](BAr'_4)$ in dichloromethane at room temperature to give quantitatively the cationic tetracarbonyl radical $[W_2Cp_2(\mu\text{-}CO)_2(CO)_2(\mu\text{-dppm})](BAr'_4)$ (**2**). In solution, this species decarbonylates progressively to afford the corresponding tricarbonyl complex $[W_2Cp_2(\mu\text{-}CO)(CO)_2(\mu\text{-dppm})](BAr'_4)$ (**3**), which is also paramagnetic. Both complexes are only of limited stability and could not be isolated as pure solids. In relative terms, however, we can say that both radicals **2** and **3** are less reactive than the few metal−metal-bonded organometallic radicals previously known.[5]

The IR spectrum of **2** in dichloromethane solution is quite similar to that of the cation $[W_2Cp_2(\mu\text{-}CO)_2(CO)_2(\mu\text{-dppm})]^{2+}$ in the solid state (Table 1),[1] but with bands shifted to lower frequencies (ca. 50−70 cm^{-1} for terminal CO ligands and ca. 110 cm^{-1} for bridging CO), as expected due to reduction of positive charge at the dimetal center. This also suggests that the unpaired electron in **2** must be equally shared by both metal centers. The relative intensity of the two bands assigned to terminal C−O stretches (1969 (vs) and 1909 (w) cm^{-1})[6] reveals that those carbonyl ligands must be almost parallel to each other. On the other hand, from the relative intensities in the bands of the bridging CO groups it is deduced that the planes containing the corresponding W−C(O)−W atoms must define an angle somewhat bigger than 90°. The resulting geometry would be then not much different from that of the complex $[W_2Cp_2(\mu\text{-}F)(\mu\text{-}CO)(CO)_2(\mu\text{-dppm})](PF_6)$,[1] after replacement of fluoride by carbonyl at the bridging position (Chart 1).

Chart 1



2 **3**

The three C−O stretching bands found in the IR spectrum of radical **3** (Table 1) in dichloromethane solution support the formulation of this cation as a tricarbonyl complex. The lower band (1676 (m) cm^{-1}) has a frequency typical for bridging CO ligands. On the other hand, the relative intensity of the two higher bands suggests a pseudo cis disposition of the terminal carbonyls, with an angle of ca. 60−80° between them. In fact, the position and relative intensities of these bands are similar to those exhibited by the carbyne complex $[W_2Cp_2(\mu\text{-}COMe)(CO)_2(\mu\text{-dppm})](BF_4)$ (1946 (vs), 1842 (s) cm^{-1} in Me_2CO).[7] A similar geometry is thus assumed for **3**, after replacing the carbyne group in the above cation by a bridging carbonyl, which implies that all three CO ligands are roughly in the same plane (Chart 1).

Compounds **2** and **3** are 33- and 31-electron species, respectively. Thus, the corresponding formal intermetallic bond orders are 1.5 and 2.5, according to the EAN rule. While just a few 33-electron complexes have been isolated,[5] to our knowledge compound **3** represents the first 31-electron organometallic complex reported so far.

Two-Electron Oxidation of Compound 1. Reaction of **1** with 2 equiv of $[FeCp_2](BAr'_4)$ leads instantaneously at room temperature to a black solution con-

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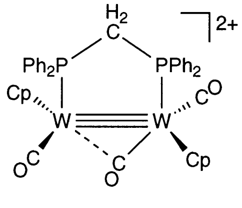
Chart 2



4

taining presumably the unsaturated cation $[W_2Cp_2(\mu\text{-}CO)_2(CO)_2(\mu\text{-}dppm)]^{2+}$ (**A** in Scheme 1). This highly unstable species loses CO rapidly, so that the only product that can be isolated in this process is the dark purple tricarbonyl complex $[W_2Cp_2(\mu\text{-}CO)(CO)_2(\mu\text{-}dppm)](BAr'_4)_2$ (**4**). This decarbonylation process seems to be reversible, as violet solutions of **4** became black when stirred under a CO atmosphere. Even under CO, the species present in these black solutions could not be isolated or even identified by IR spectroscopy, due to its rapid transformation into **4**. Prolonged treatment with CO gave finally the mononuclear species $[WCp(CO)_2(dppm)]^+$.[1.a]

The structure proposed for compound **4** (Chart 2) has been established on the basis of that found for the isoelectronic compound **5** (see later) and the available spectroscopic data. The IR spectrum of **4** shows three C−O stretching bands (Table 1). The frequency of one band (1842 cm^{-1}) is somewhat low for a terminal carbonyl and suggests the presence of semibridging interactions in the molecule, as found for compound **5** (see later).

NMR data for **4** are consistent with the IR information and also reveal that this species exhibits dynamic behavior in solution. Thus, the $^{31}P\{^1H\}$ NMR spectrum shows a broad resonance at room temperature centered at 5 ppm, which splits into two doublets of the same intensity when cooling the solution (δ 11.6, −2.6 ppm at 213 K). Both signals exhibit distinct one-bond couplings to the corresponding ^{183}W nuclei (311 and 369 Hz, respectively). Differences in the values of J_{PW} can be used as a diagnostic tool to assign NMR signals, as it is well established that one-bond coupling to metals increases as the coordination number decreases.[8] Indeed, when comparing the J_{PW} values in our starting product **1** with that for the unsaturated derivative $[W_2Cp_2(\mu\text{-}CO)_2(\mu\text{-}dppm)]$[9] (where there is one less ligand around the metals), we found that J_{PW} increases from ca. 340 Hz in **1** to 421 Hz in the unsaturated dicarbonyl, as expected. Following this, we can assign the resonance with the smaller coupling to that phosphorus atom coordinated to the metal center bearing two carbonyl ligands.

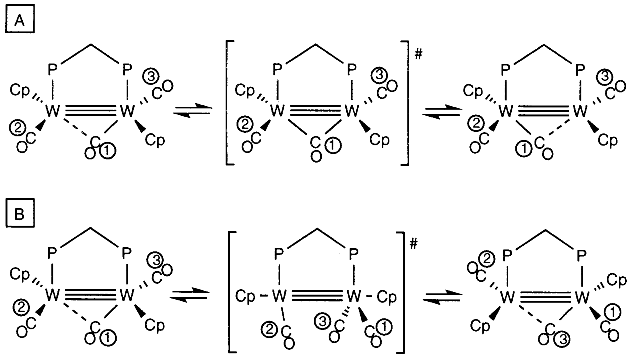


Figure 1. Fluxional processes proposed for compound **4** in solution (only the cation shown, with positive charge omitted for clarity; P−P = dppm).

Changes in the ^{31}P NMR spectra of **4** are consistent with those observed in the ^{13}C or ^1H NMR spectra. Thus, the $^{13}C\{^1H\}$ NMR spectrum at room temperature shows only one signal for the cyclopentadienyl or CO ligands, and the same situation is found in the ^1H NMR spectrum for the Cp groups. All this suggests the presence of a fluxional process equalizing the phosphorus, cyclopentadienyl, and carbonyl environments. Changes in the carbonyl resonances are especially informative. At room temperature, the three carbonyl ligands give rise to an extremely broad signal at ca. 232 ppm, which at 213 K has split into three resonances, two singlets (245.9 and 235.4 ppm), and a nonresolved multiplet (217.8 ppm). Comparison of these data with those of the $P(OMe)_3$ derivative **5** allows the assignment of the high-frequency resonance (245.9 ppm) to the semibridging carbonyl and the low-frequency resonance (217.8 ppm) to the monocarbonylic fragment. As will be later shown for compound **5**, its bridging ligand belongs to the type II linear semibridging carbonyls, in terms of the structural classification of semibridging carbonyls proposed by Crabtree and Lavin.[10] This coordination mode is characteristic of the triply bonded dimers $[M_2Cp_2(CO)_4]$ (M = Mo, W),[11] which are also fluxional. In fact, the same behavior was found for $[W_2Cp_2(\mu\text{-}CO)_2(\mu\text{-}dppm)]$.[9b] The process proposed to explain fluxionality in these systems[9b,12] involves an exchange of the semibridging carbonyls through the triple metal−metal bond. A similar process might be operative for **4** (A in Figure 1). This would equalize the chemical environments of the phosphorus atoms or cyclopentadienyl groups, but only the chemical environments of the terminal CO groups (2 and 3 in Figure 1) would be equalized. In the fast exchange limit, two signals would be observed in the $^{13}C\{^1H\}$ NMR spectrum for the CO ligands. However, as stated above, the $^{13}C\{^1H\}$ NMR spectrum of **4** at room temperature exhibits a single broad resonance; therefore, additional rearrangements must be operative in this system. A second fluxional process can be proposed for **4**, that being inspired in the dynamic behavior of dimanganese complexes with four-electron σ,π-CO bridges[13] (B in Figure 1). This second process implies an exchange of positions between the semibridging carbonyl and the terminal one bonded to the same metal atom. Such a process would equalize the environments of two CO groups (1 and 3 in Figure 1) but not those of cyclopentadienyl ligands or phospho-

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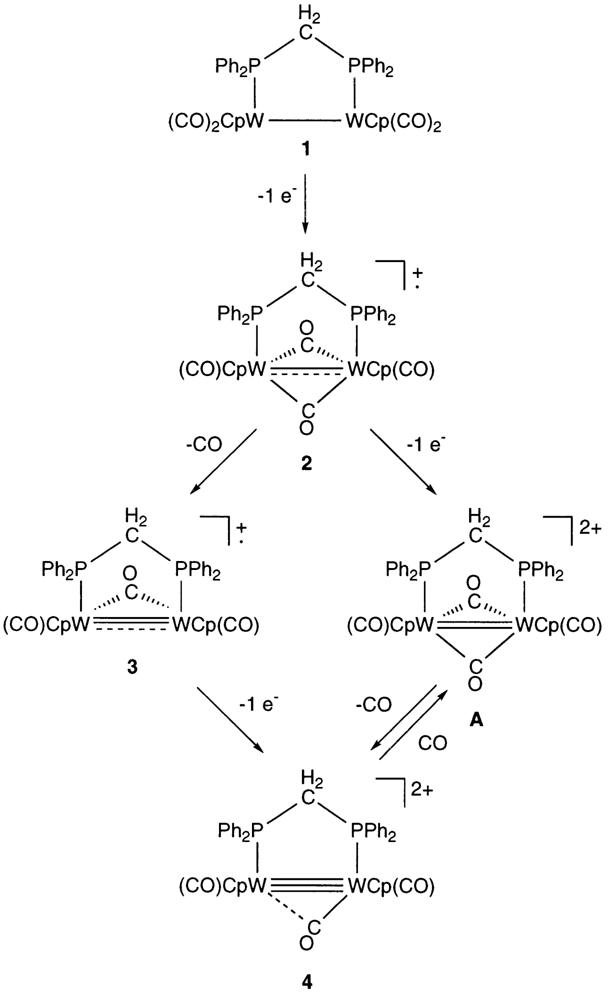
Scheme 2. Reaction Pathways in the Oxidation Reactions of $[W_2Cp_2(CO)_4(\mu\text{-dppm})]$ with $[FeCp_2](BAr'_4)$



rus atoms, which would remain inequivalent. In other words, this process alone cannot explain the experimental observations either. However, when the two processes represented in Figure 1 are combined, complete scrambling of the CO ligand results, and full agreement with all experimental observations is achieved.

Reaction Pathways in the Oxidation of Compound 1. As we have shown through the preceding sections, oxidation of **1** with 1 equiv of $[FeCp_2](BAr'_4)$ produces the tetracarbonyl radical **2**, which spontaneously experiences ejection of a CO molecule to yield the paramagnetic tricarbonyl **3**; if another 1 equiv of $[FeCp_2](BAr'_4)$ is present, **3** evolves to give the unsaturated tricarbonyl **4** (Scheme 2). As the structural differences between compounds **3** and **4** are noticeable, the existence of a chemical connection between these species was not evident. Nevertheless, we have verified through independent experiments that treatment of either **2** or **3** with 1 equiv of $[FeCp_2](BAr'_4)$ leads to the tricarbonyl **4**. In the case of reaction with **2**, the oxidation presumably proceeds without structural changes to give dication **A**, an extremely CO-labile complex. For radical **3**, removal of a second electron produces a significant structural rearrangement, as a bridging CO ligand cis to the diphosphine moves into a linear semibridging position trans to that phosphorus ligand.

There are two further points to comment on the above results. First, the stabilizing influence of the counterion on radicals **2** and **3** has to be noted. In fact, we must recall that the BF_4^- or PF_6^- salts of **2** were proposed in our previous study as the intermediates experiencing degradation to the mononuclear cations $[MCp(CO)_2(dppm)]^+$.[1a] Second, it is somewhat unexpected that the presumed tetracarbonyl **A**, a 32-electron complex now free from fluoride abstraction processes thanks to the stable counterion, evolves through a decarbonylation pathway to give the 30-electron complex **4**. This seems to be favored over intramolecular C−H or P−C oxidative additions, which are processes observed for the related 32-electron neutral compounds $[M_2Cp_2(\mu\text{-}L_2)(CO)_3]$ (L_2 = dppm, M = Mo, W).[14,15] No doubt the high positive charge in **A** makes the CO ligands more labile, while disfavoring oxidative additions in general. However, compound **4** combines the presence of a triple intermetallic bond and a high positive charge and should be a strong electrophile. This has been checked through some simple reactions such as those with tertiary phosphines or halide ions, as will be next discussed.

Reaction of Compound 4 with Tertiary Phosphines. Since **4** is a 30-electron cation, it could be anticipated that it should experience the addition of tertiary phosphines, giving perhaps a product more stable than tetracarbonyl **A**. First, we tried the reaction with PMe_3, but fragmentation of the dimetallic unit was observed, perhaps due to the cleavage of the Mo−P(dppm) bond by the highly basic PMe_3. We then tried the reaction with $P(OMe)_3$, a weaker and smaller donor.[16] Reaction of **4** with $P(OMe)_3$ occurs rapidly, even at low temperature, to give the dicarbonyl complex $[W_2Cp_2(\mu\text{-CO})(CO)\{P(OMe)_3\}(\mu\text{-dppm})](BAr'_4)_2$ (**5**) in high yield. The expected addition product $[W_2Cp_2(\mu\text{-CO})_2(CO)\{P(OMe)_3\}(\mu\text{-dppm})]^{2+}$ could not be detected under any of the experimental conditions examined.

The structure of **5** has been solved through an X-ray study (Table 2) and is depicted in Figure 2, while Table 3 lists the most relevant bond distances and angles. The cation exhibits a ditungsten core bridged by dppm and a carbonyl group. The coordination spheres are completed by cyclopentadienyl and terminal carbonyl (on W(1)) or trimethyl phosphite (on W(2)) ligands. The intermetallic distance, 2.599(1) Å, is comparable to those found for $[W_2Cp_2(\mu\text{-CO})_2(\mu\text{-dppm})]$ (2.5144(5) Å)[9b] and $[W_2(\mu\text{-CO})_2(CO)(\eta\text{-PhC}_2\text{Ph})\{\eta^5\text{-C}_5\text{Ph}_4(\text{C}_6\text{H}_4\text{Me-4})\}Cp]$ (2.586(1) Å)[17] and is consistent with the formulation of a triple W−W bond.

The bridging carbonyl in **5** deserves some comment. In the first place, we recall that **5** is isoelectronic with the triply bonded dimers $[M_2L_2(CO)_4]$[11,12] (M = Cr, Mo, W; L = Cp or related ligand) and with the compound $[W_2Cp_2(\mu\text{-CO})_2(\mu\text{-dppm})]$.[9] All these neutral complexes display linear semibridging carbonyls, a fact justified by theoretical calculations.[18] Curtis established the difference between the two types of bridging carbonyls

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Table 2. Crystal Data for Compound 5

mol formula	$C_{104}H_{65}B_2F_{48}O_5P_3W_2$
mol wt	2788.8
a, Å	13.226(3)
b, Å	15.715(3)
c, Å	28.727(7)
α, deg	76.34(3)
β, deg	78.87(2)
γ, deg	74.40(3)
V, Å^3	5534(5)
Z	2
cryst syst	triclinic
space group	$P\bar{1}$
linear abs coeff μ (cm^{-1})	22.9
calcd density (g cm^{-3})	1.67
diffractometer	CAD4, Enraf-Nonius
temp, K	295
radiation	Mo Kα (λ = 0.710 69 Å)
scan type	$\omega/2\theta$
scan range, deg	$0.8 + 0.345 \tan \theta$
θ limits, deg	1−25
octants collected	0−15; −17 to +18; −33 to +34
no. of data collected	20354
no. of unique data collected	19436
no. of unique data used for refinement	7592 $(F_o)^2 > 3\sigma(F_o)^2$
R(int)	0.03
decay of std rflns, %	<10
$R = \sum\|\|F_o\| - \|F_c\|\|/\sum\|F_o\|$	0.0720
$R_w = [\sum w(\|F_o\| - \|F_c\|)^2/\sum w(F_o)^2]^{1/2}$ [a]	0.0851
S	1.12
extinction param	49
no. of variables	1028
$\Delta\rho_{min}/\Delta\rho_{max}$, e Å^{-3})	−1.21/1.45

[a] $w = w'[1 - ((||F_o| - |F_c||)/6\sigma(F_o))^2]^2$ with $w' = 1/\sum rA_rT_r(X)$ with the three coefficients 6.30, −1.01, and 4.27 for a Chebyshev series, for which X is F_c/F_c(max).

Table 3. Selected Bond Distances (Å) and Angles (deg) for Compound 5

W(1)−W(2)	2.599(1)	W(2)−P(3)	2.474(5)
W(1)−P(1)	2.440(5)	W(2)−P(2)	2.550(2)
W(1)−C(6)	1.90(3)	C(6)−O(6)	1.17(2)
W(2)−C(1)	1.98(2)	C(1)−O(1)	1.16(2)
W(1)−C(1)	2.28(2)		
P(1)−W(1)−W(2)	98.3(1)	P(1)−W(1)−C(1)	107.6(4)
P(1)−W(1)−C(6)	98.4(7)	P(2)−W(2)−W(1)	89.2(1)
P(2)−W(2)−C(3)	81.7(2)	P(2)−W(2)−C(1)	117.1(5)
W(1)−C(1)−O(1)	118.6(15)	W(1)−C(6)−O(6)	168.4(22)
W(2)−W(1)−C(6)	75.1(7)	W(2)−W(1)−C(1)	47.3(5)
W(1)−W(2)−P(3)	120.0(1)	C(1)−W(1)−C(6)	118.6(8)
P(3)−W(2)−C(1)	74.3(5)	W(1)−W(2)−C(1)	58.0(5)
W(2)−C(1)−O(1)	166.5(16)	P(2)−W(2)−P(3)	81.7(2)

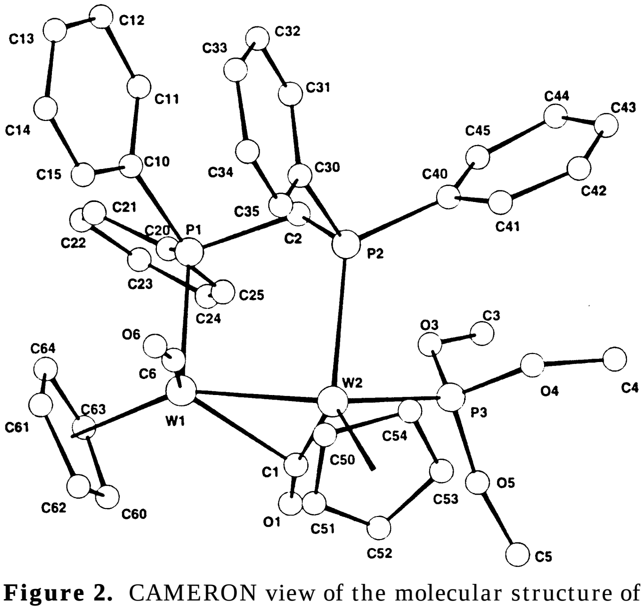
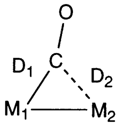


Figure 2. CAMERON view of the molecular structure of the cation in compound **5**.

Chart 3

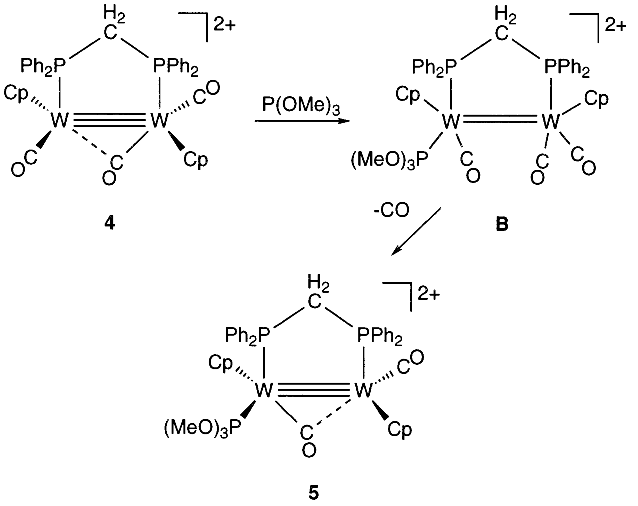


(bent or linear) by comparing the M_1−C−O angle with the asymmetry parameter $(D_2 - D_1)/D_1$ (see Chart 3).[12b] Application of this analysis to compound **5** (with M_1−C−O = 166.5(16)°, asymmetry parameter 0.15) confirms the linear semibridging description for the carbonyl ligand. In addition, Crabtree and Lavin established four types of linear semibridging carbonyls.[10] Clearly, structural data for **5** indicate a type II arrangement, characterized by the presence of short metal−metal bonds and weak π interactions between the semibridging CO and the second metal atom. The M_2−O distance for **5** (3.01 Å) is very large and excludes other descriptions of the carbonyl coordination as, for instance, the four-electron μ-η^1:η^2-CO mode. In comparison to the bridging carbonyls in $[W_2Cp_2(\mu\text{-CO})_2(\mu\text{-dppm})]$, the main difference concerns the D_2 distance, which falls from ca. 2.44 Å in $[W_2Cp_2(\mu\text{-CO})_2(\mu\text{-dppm})]$ to 2.28 Å in **5**. This suggests a stronger π interaction of the semibridging CO ligand with the M_2 atom in **5**. This interpretation agrees with the fact that the W≡W distance is somewhat longer than those found for other species with triple W−W bonds, while the contrary effect should have been expected for a molecule with two positive charges. Additionally, the presence of the phosphite ligand could have a cooperative effect because of the increased steric pressure on the dimetal center. This can be grasped from the fact that even the shorter W−P(dppm) distance (W(1)−P(1) = 2.440(5) Å) is slightly higher than those found for $[W_2Cp_2(\mu\text{-CO})_2(\mu\text{-dppm})]$ (average 2.409(2) Å).

Spectroscopic data in solution for compound **5** are consistent with the solid-state structure just discussed. The ^{31}P NMR spectrum exhibits three separated resonances for the inequivalent P atoms of dppm and $P(OMe)_3$. The P(2) atom of the bridging dppm is identified by its large coupling to the phosphite ligand and appears as a doublet of doublets at −13.1 ppm (Table 1). This resonance also exhibits a lower P−W coupling (284 Hz vs 395 Hz), as expected for a P atom bonded to the metal center with a higher coordination number.

The IR spectrum of **5** exhibits two well-separated bands at 1890 (vs) and 1798 (s) cm^{-1}, the low frequency of the latter being consistent with the presence of the semibridging carbonyl. In agreement with this, the ^{13}C NMR spectrum of **5** shows two resonances in the carbonyl region, a doublet at 250.2 ppm (J_{CP} = 43 Hz) and a doublet of triplets at 224.3 ppm (J_{CP} = 6 and 2 Hz). Because of the small P(3)−W(2)−C(1) angle (74.3(5)°), a high P−C coupling between the semibridging carbonyl and phosphite ligand is expected. Therefore, we can safely assign the resonance at 250.2 ppm to the semibridging CO, because of both its higher chemical shift and P−C coupling. The low P−C coupling for the terminal carbonyl is not unexpected, given the relatively large C(6)−W(1)−P(1) angle (98.4(7)°). It is

Scheme 3. Proposed Steps in the Formation of Compound 5

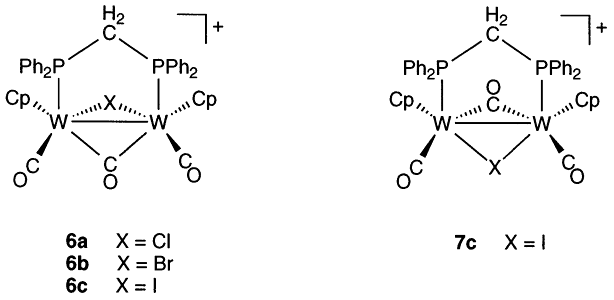


well established for complexes of the type $[MCpX(CO)_2(PR_3)]$ (M = Mo, W; X = halogen, alkyl, hydride, etc.) that $^2J_{PC}$ couplings usually follow the order $|J_{cis}| > |J_{trans}|$.[19,20]

Reaction of **4** with $P(OMe)_3$ to give **5** can be rationalized by considering the reaction pathway illustrated in Scheme 3. Initial addition of the phosphite ligand to the dimetallic center might first occur, yielding the intermediate species **B**, which would be isoelectronic with tetracarbonyl **A** and would also be unstable with respect to decarbonylation. Perhaps CO dissociation is even more favored for **5** than for **A**, due to the steric pressure imposed by the phosphite ligand.

Reaction of 4 with Halide Ions. We have previously shown that the insoluble salt $[W_2Cp_2(\mu\text{-}CO)_2(CO)_2(\mu\text{-dppm})](PF_6)_2$ reacts rapidly with halide ions to give the corresponding tricarbonyls $[W_2Cp_2(\mu\text{-}X)(\mu\text{-}CO)(CO)_2(\mu\text{-dppm})](PF_6)$.[1] It was thus expected that compound **4** would react with halide ions to give similar products. Indeed, reaction of soluble halide salts (such as $[AsPh_4]Cl$, $[NEt_4]Br$, and $[NBu_4]I$) with a solution of cation **4** in dichloromethane at room temperature leads as expected to the addition of the halide ion to the $W\equiv W$ bond, to give the corresponding tricarbonyl complexes $[W_2Cp_2(\mu\text{-}X)(\mu\text{-}CO)(CO)_2(\mu\text{-dppm})](BAr'_4)$ (X = Cl (**6a**), Br (**6b**), I (**6c** and **7c**)). The only remarkable difference in these reactions appears for X = I, for which two isomers (**6c** and **7c**) are formed. The amount of iodide ion available was found to have a modest effect on the relative amounts of isomers obtained. Thus, when the reaction is carried out with stoichiometric quantities of I^-, the ratio **6c**/**7c** was ca. 2/1, while when an excess of I^- isomer was used, **6c** was almost exclusively obtained. As will be shown later, isomer **7c** can be obtained almost selectively from radical **3** and I_2, and this can be related to the different geometries of **3** and **4**. We should note that isomers **6c** and **7c** cannot be interconverted, even with heating. Moreover, isomer **7c** was found to be quite unstable, and all attempts to isolate it resulted in its progressive decomposition. Despite this, the spectroscopic data available for this isomer allow a safe structural identification.

Chart 4



Spectroscopic data for compounds **6** are almost identical with those of the corresponding PF_6^- salts $[W_2Cp_2(\mu\text{-}X)(\mu\text{-}CO)(CO)_2(\mu\text{-dppm})](PF_6)$[1] and thus need no further comment. As verified by X-ray diffraction studies on the fluoro and chloro derivatives, these cations exhibit a bridging halide cis to the diphosphine ligand while the bridging carbonyl is located trans to that ligand (Chart 4).

The structure proposed for cation **7c** is similar to that of isomer **6c**, after exchanging the positions of the bridging CO and halide ligands (Chart 4). This proposal is firmly supported by IR and NMR spectroscopic data. Indeed, IR spectra for both isomers are quite similar (Table 1), although the C–O stretching frequencies are somewhat lower for **7c**. As the relative intensities of these peaks remain invariable, we conclude that the relative arrangement of the terminal CO ligands remains essentially unchanged. As a result, the molecule has a symmetry plane relating both metal fragments, in agreement with the single NMR resonances observed for each pair of phosphorus atoms, terminal carbonyl ligands (^{13}C), or cyclopentadienyl groups (^{13}C, ^1H). The $^{13}C\{^1H\}$ NMR resonances of both the bridging and terminal carbonyls exhibit coupling to phosphorus (J_{PC} = 6 Hz and $J_{PC} + J_{P'C}$ = 10 Hz, respectively), in agreement with their relative disposition cis to the diphosphine in both cases. In contrast, the bridging CO (trans to phosphorus) in the PF_6^- salt of **6c** showed no measurable P–C coupling.[1] The most definitive evidence of the geometry of **7c** comes from the analysis of P–W couplings. Although the $^{31}P\{^1H\}$ NMR spectrum of **7c** is relatively similar to that of **6c**, analysis of the ^{183}W satellites reveals a PW coupling substantially enhanced compared to that in **6c** (300 vs 218 Hz; Table 1). These changes can be rationalized by bearing in mind that, for octahedral geometries, the less the ligand trans to a phosphorus atom acts as a π acceptor, the larger its $^1J_{PM}$ value must be (as expected for a stronger P–M bond).[21] This general relationship holds for the four-legged piano-stool geometries common in the cyclopentadienyl derivatives of Mo and W. For isomer **7c**, the phosphorus atom is trans to I^-, and since the trans influence for I^- is much smaller than that for CO, the P–W bond must be stronger in **7c** than in **6c** (P atom trans to a CO ligand). Therefore, J_{PW} is expected to be higher for **7c** than for **6c**, as observed. We must note that the J_{PW} values found for **6c** and **7c** are close to the values found respectively for the cis and trans isomers

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of mononuclear methyl[22] or hydride[20] complexes of the type $[WCp(CO)_2X(PR_3)]$ ($X = H, CH_3$).

Chemical Behavior of the Paramagnetic Compound 3. A practical benefit of the stabilizing influence of the $[BAr'_4]^-$ anion is the possibility of preparing solutions of the paramagnetic compounds **2** or **3** that can be manipulated for short periods of time without substantial decomposition. Thus, the chemical behavior of these metal−metal-bonded radicals could be explored in some detail. This is of interest because little is known about the reactivity of metal−metal-bonded binuclear radicals apart from their electrochemistry,[23−25] due to the scarce number of examples which are stable enough to be isolated. We have recently reported the neutral metal−metal-bonded radical $[Mo_2Cp_2(\mu\text{-}PPh_2)(CO)_4]$,[5] which exhibits a wide chemistry involving several processes characteristic of mononuclear organometallic radicals such as atom transfer, ligand displacement, and metal−metal bond formation.

It was thus of interest to examine some reactions of the 31-electron radical **3**. Unfortunately, compound **3** turned out too unstable to become an useful synthetic intermediate. For instance, we carried out reactions of **3** with traditional radical traps such as halogens and NO. In the former reaction, addition of an halogen atom to the metal−metal bond occurs, giving the halogen-bridged compounds **6** and **7** already discussed. In the case of iodine, compound **7c** is the main isomer obtained in the absence of an excess of reagent (radio **7c**:**6c** = 3:1). This difference in the isomer distribution compared to that for the reaction of cation **4** and iodide (**6c** is then the major isomer formed) is obviously due to the different geometries exhibited by tricarbonyls **3** and **4**.

Reaction of compound **3** with NO (5% in N_2) leads to the disruption of the dimetallic unit, even at low temperature. When using a more diluted NO source (0.2% in N_2), a slow transformation occurs, yielding finally the previously known hydroxycarbyne complex $[W_2Cp_2(\mu\text{-}COH)(CO)_2(\mu\text{-}dppm)](BAr_4')$ (**8**).[26] A separate experiment showed that stirring a dichloromethane solution of **3** with a few drops of water gave the hydroxycarbyne derivative in about 30 min. Although proton abstraction from water seems to be an easy process for radical **3** at its bridging carbonyl, attempts to induce similar transformations through the reactions of **3** (or **2**) with reagents such as $HSnR_3$ ($R = {}^tBu$, Ph), H_2SiPh_2, and S_2Ph_2 were unsuccessful because no reaction was observed with these mild radical traps.

Concluding Remarks

Oxidation of compound **1** using the ferrocenium salt $[FeCp_2](BAr'_4)$ allows the isolation of binuclear cations having multiple intermetallic bonds which cannot be otherwise isolated. These includes the 33- and 31-electron paramagnetic species $[W_2Cp_2(CO)_x(\mu\text{-}dppm)]^+$ ($x = 4, 3$) or the highly electrophilic, triply bonded cation $[W_2Cp_2(CO)_3(\mu\text{-}dppm)]^{2+}$. The $[BAr'_4]^-$ counterion stabilizes these salts, thus largely diminishing their degradation to mononuclear species, and removes the fluoride abstraction problems encountered when using BF_4^- and PF_6^- counterions.

Experimental Section

General Comments. All reactions were carried out under an atmosphere of nitrogen. Solvents were purified according to standard procedures[27] and distilled under nitrogen prior to use. Petroleum ether refers to that fraction distilling in the range 65−70 °C. Compound $[W_2Cp_2(CO)_4(\mu\text{-}dppm)]$ (**1**)[9] was prepared as reported before. The reagent $[FeCp_2]BAr'_4$ was prepared according to the literature procedure.[28] All other reagents were purchased from the usual commercial suppliers and used as received. Low-temperature reactions were performed using jacketed Schlenk tubes, refrigerated by a closed 2-propanol circuit kept at the desired temperature with a cryostat. Filtrations were carried out using dry diatomaceous earth under nitrogen.

NMR spectra were recorded at 300.13 (^1H), 121.50 ($^{31}P\{^1H\}$), or 75.47 MHz ($^{13}C\{^1H\}$) 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 routinely recorded on solutions containing a small amount of tris(acetylacetonato)chromium(III) as a relaxation reagent.

Preparation of Solutions of $[W_2Cp_2(\mu\text{-}CO)_2(CO)_2(\mu\text{-}dppm)](BAr'_4)$ (2) and $[W_2Cp_2(\mu\text{-}CO)(CO)_2(\mu\text{-}dppm)](BAr'_4)$ (3). Solid compound **1** (0.033 g, 0.033 mmol) was added slowly to a well-stirred CH_2Cl_2 solution (8 mL) of $[FeCp_2](BAr'_4)$ (0.035 g, 0.033 mmol) to give instantaneously a green solution containing virtually pure compound **2**. After 20 min of stirring at room temperature, the color of the solution has changed to brown greenish, and the solution then contains compound **3** as the major species, according to the IR spectrum. Both compounds are quite unstable, and all manipulations of their solutions lead to their progressive decomposition.

Synthesis of $[W_2Cp_2(\mu\text{-}CO)(CO)_2(\mu\text{-}dppm)](BAr'_4)_2$ (4). Solid compound **1** (0.066 g, 0.066 mmol) was added slowly to a CH_2Cl_2 solution (16 mL) containing $[FeCp_2](BAr'_4)$ (0.140 g, 0.12 mmol), and the mixture was stirred for 30 s to give a black solution. Solvent was then removed under vacuum to give a purple residue which was washed with a mixture of diethyl ether and petroleum ether (1:1, 2 × 10 mL) and dried under vacuum to give 0.154 g (0.057 mmol, 86%) of virtually pure compound **4** as a black-purple oily residue. All attempts to get this complex as a crystalline solid resulted in its progressive decomposition. ^1H NMR (400.14 MHz, CD_2Cl_2, 243 K): δ 7.76 (s, 16H, Ar′), 7.56 (s, 8H, Ar′), 7.56−6.85 (m, 20H, C_6H_5), 5.72 (s, 10 H, C_5H_5) ppm. ^1H NMR (400.14 MHz, CD_2Cl_2, 213 K): δ 7.79 (s, 16H, Ar′), 7.56 (s, 8H, Ar′), 7.56−6.78 (m, 20H, C_6H_5), 5.74 (s, 5H, C_5H_5), 5.65 (s, 5H, C_5H_5) ppm. $^{13}C\{^1H\}$ NMR (50.32 MHz, CD_2Cl_2): δ 232.0 (br, CO), 163.0 (q, $J_{CB} = 50$, *i*-C(Ar′)), 136.1−117.7 (C_6H_5), 136.1 (s, *o*-C(Ar′)), 130.2 (q, $J_{CF} = 32$, *m*-C(Ar′)), 125.9 (q, $J_{CF} = 273$, CF_3), 118.8 (s, *p*-C(Ar′)), 100.2 (s, C_5H_5) ppm. $^{13}C\{^1H\}$ NMR (100.61 MHz, CD_2Cl_2, 213 K): δ 245.9 (s, CO), 235.4 (s, CO), 217.8 (s, CO), 162.2 (q, $J_{CB} = 50$, *i*-C(Ar′)), 138.5−125 (C_6H_5), 135.0 (s, *o*-C(Ar′)), 128.9 (q, J_{CF}

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= 32, *m*-C(Ar′)), 124.7 (q, $J_{CF} = 272$, CF_3), 117.9 (s, *p*-C(Ar′)), 99.9 (s, C_5H_5), 98.6 (s, C_5H_5), 63.0 (t, $J_{CP} = 37$, CH_2) ppm.

Synthesis of [W_2Cp_2(*μ*-CO)(CO){P(OMe)$_3$}(*μ*-dppm)](BAr′$_4$)$_2$ (5). Compound **4** (0.154 g, 0.057 mmol) was prepared "in situ" as described above. The complex was dissolved in 15 mL of CH_2Cl_2 and cooled to −15 °C. Then, $P(OMe)_3$ (8 *μ*L, 0.057 mmol) was added and the solution color changed from purple to black-violet. The solution was filtered and the solvent removed under vacuum to give a dark oily solid which was washed with toluene (3 × 5 mL). Recrystallization of this product from CH_2Cl_2/petroleum ether at − 20 °C gave compound **5** as dark red-purple crystals, which were separated from the solution, washed with petroleum ether, and dried under vacuum (0.115 g, 62%). Anal. Calcd for $C_{104}H_{65}B_2F_{48}O_5P_3W_2$: C, 44.79; H, 2.35. Found: C, 44.82; H, 2.23. ^1H NMR (400.13 MHz, CD_2Cl_2): *δ* 7.72 (s, 16H, Ar′), 7.56 (s, 8H, Ar′), 7.66−6.88 (m, 20 H, C_6H_5), 6.14 (s, 5H, C_5H_5), 6.09 (m, ABXZ, 2H, CH_2), 5.22 (d, $J_{HP} = 2$, 5H, C_5H_5), 3.69 (d, $J_{HP} = 11$, 9H, OCH_3) ppm. $^1H\{^{31}P\}$ NMR (400.13 MHz, CD_2Cl_2): *δ* 6.14 (s, 5H, C_5H_5), 6.12, 6.06 (AB, $J_{HH} = 14$, 2H, CH_2), 5.23 (s, 5H, C_5H_5), 3.70 (s, 9H, OCH_3) ppm. $^{13}C\{^1H\}$ NMR (100.61 MHz, CD_2Cl_2): *δ* 250.2 (d, $J_{CP} = 43$, CO), 224.3 (dt, $J_{CP} = 6, 2$, CO), 161.1 (q, $J_{CB} = 50$, *i*-C(Ar′)), 134.2 (s, *o*-C(Ar′)), 133.6−127.8 (C_6H_5), 128.3 (q, $J_{CF} = 32$, *m*-C(Ar′)), 123.9 (q, $J_{CF} = 272$, CF_3), 116.9 (s, *p*-C(Ar′)), 96.6 (s, C_5H_5), 95.1 (s, C_5H_5), 58.4 (t, $J_{CP} = 32$, CH_2), 57.2 (d, $J_{CP} = 12$, OCH_3) ppm.

Synthesis of [W_2Cp_2(*μ*-Cl)(*μ*-CO)(CO)$_2$(*μ*-dppm)](BAr′$_4$) (6a). Method A. Solid [$AsPh_4$]Cl (0.014 g, 0.03 mmol) was added to a solution of compound **4** (0.080 g, 0.033 mmol) in dichloromethane (5 mL), and the mixture was stirred for 10 min to give a orange-brown solution. Solvent was then removed under vacuum and the residue washed with 3:1 petroleum ether/toluene (3 × 3 mL), giving compound **6a** as a brown-orange microcrystalline powder (0.048 g, 86%).

Method B. A solution of Cl_2 in dichloromethane (2 mL of a ca. 0.008 M solution, 0.016 mmol) was added to a dichloromethane solution (5 mL) of compound **3** (0.050 g, 0.030 mmol). The reaction mixture turned instantaneously to orange-brown. After 3 min of stirring, solvent was removed under vacuum and the residue was washed with 3:1 petroleum ether/toluene (5 × 5 mL) and dried under vacuum to give compound **6a** as an orange powder (0.047 g, 85%). Anal. Calcd for $C_{70}H_{44}BClF_{24}O_3P_2W_2$: C, 45.08; H, 2.38. Found: C, 45.10; H, 2.43. ^1H NMR (300.13 MHz, CD_2Cl_2): *δ* 7.76 (s, 8H, Ar′), 7.56 (s, 4H, Ar′), 7.68−7.09 (m, 20 H, C_6H_5), 5.12 (s, 10H, C_5H_5), 4.51 (dt, $J_{HH} = 13$, $J_{HP} = 11$, 1H, CH_2), 3.06 (dt, $J_{HH} = 13$, $J_{HP} = 10$, 1H, CH_2) ppm.

Synthesis of [W_2Cp_2(*μ*-Br)(*μ*-CO)(CO)$_2$(*μ*-dppm)](BAr′$_4$) (6b). Method A. The procedure is completely analogous to that described for **6a**, except that [PPh_4]Br (0.010 g, 0.050 mmol) was used instead. The crude yellow-brown product was washed with 2:1 petroleum ether/toluene (5 × 5 mL) and dried under vacuum to give compound **6b** as a yellow-brown solid (0.049 g, 87%).

Method B. The procedure is analogous to that described for **6a**, except that a 0.02 M solution of Br_2 in dichloromethane (0.77 mL, 0.0154 mmol) was used instead. Workup as above gave compound **6b** as a yellow-brown solid (0.048 g, 85%). Anal. Calcd for $C_{70}H_{44}BBrF_{24}O_3P_2W_2$: C, 44.03; H, 2.32. Found: C, 44.05; H, 2.36. ^1H NMR (300.13 MHz, CD_2Cl_2): *δ* 7.72 (s, 8H, Ar′), 7.56 (s, 4H, Ar′), 7.47−7.17 (m, 20 H, C_6H_5), 5.13 (s, 10H, C_5H_5), 4.79 (dt, $J_{HH} = 13$, $J_{HP} = 11$, 1H, CH_2), 3.06 (dt, $J_{HH} = 13$, $J_{HP} = 10$, 1H, CH_2) ppm.

Synthesis of [W_2Cp_2(*μ*-I)(*μ*-CO)(CO)$_2$(*μ*-dppm)](BAr′$_4$) (6c). The procedure is completely analogous to that described for **6a** (method A), except that [NBu_4]I (0.020 g, 0.050 mmol) was used instead. The crude product was washed with 3:1 petroleum ether/toluene (4 × 10 mL) and dried under vacuum to give compound **6c** as a yellow powder (0.052 g, 89%). Anal. Calcd for $C_{70}H_{44}BF_{24}IO_3P_2W_2$: C, 41.46; H, 2.19. Found: C, 41.49; H, 2.23. ^1H NMR (400.13 MHz, CD_2Cl_2, 253 K): *δ* 7.70 (s, 8H, Ar′), 7.54 (s, 4H, Ar′), 7.46−7.20 (m, 20 H, C_6H_5), 5.18 (dt, $J_{HH} = 14$, $J_{HP} = 11$, 1H, CH_2), 5.15 (s, 10H, C_5H_5), 3.05 (dt, $J_{HH} = 14$, $J_{HP} = 10$, 1H, CH_2) ppm.

Synthesis of [W_2Cp_2(*μ*-I)(*μ*-CO)(CO)$_2$(*μ*-dppm)](BAr′$_4$) (7c). A 0.022 M solution of I_2 in dichloromethane (0.7 mL, 0.015 mmol) was added very slowly to a dichloromethane solution (5 mL) of compound **3** (0.050 g, 0.030 mmol), whereby the brown greenish solution turned green. Solvent was then removed under vacuum and the residue washed with petroleum ether to give a green solid shown (by NMR) to be a mixture of compounds **6c** and **7c**, in variable relative amounts, which could not be separated. Spectroscopic data for **7c** were then obtained from mixtures of **7c** and **6c**. ^1H NMR (400.13 MHz, CD_2Cl_2, 253 K): *δ* 5.15 (false t, $|J_{HP} + J_{HP'}| = 2$, 10H, C_5H_5), 4.05 (dt, $J_{HH} = 13$, $J_{HP} = 10$, 1H, CH_2) ppm. The resonance for the second methylene hydrogen was obscured by other signals present. $^{13}C\{^1H\}$ NMR (100.61 MHz, THF): *δ* 302.1 (t, $J_{CP} = 6$, *μ*-CO), 238.9 (AXX′, $|J_{CP} + J_{CP'}| = 10$, 2CO), 162.4 (q, $J_{CB} = 50$, *i*-C(Ar′)), 139.3−128.7 (C_6H_5), 135.0 (s, *o*-C(Ar′)), 129.3 (q, $J_{CF} = 30$, *m*-C(Ar′)), 125.1 (q, $J_{CF} = 272$, CF_3), 117.8 (s, *p*-C(Ar′)), 95.2 (s, C_5H_5) ppm. The resonance for the methylenic carbon could not be identified.

X-ray Structure Determination for Compound 5. Suitable crystals of **5** were obtained by slow diffusion of a concentrated dichloromethane solution of the complex into a layer of petroleum ether. The selected crystal was stuck on a glass fiber and mounted on a Enraf-Nonius CAD4 automatic diffractometer. Accurate cell dimensions and orientation matrix were obtained by least-squares refinements of 25 accurately centered reflections. No significant variations were observed in the intensities of two checked reflections during data collection. Complete crystallographic data and collection parameters are listed in Table 2. Data were corrected for Lorentz and polarization effects. Computations were performed by using the PC version of CRYSTALS.[29] Scattering factors and corrections for anomalous absorption were taken from ref 30. The structure was solved by direct methods (SHELXS),[31] completed by Fourier techniques, and refined by full-matrix least-squares. An empirical absorption correction (DIFABS)[32] was applied. All atoms of the cation were anisotropically refined. The main difficulty was the location of the CF_3 groups of the anions. The best solution was obtained by introducing 6 fluorine atoms with half occupancy, instead of 3, for 9 of the 16 CF_3 groups. Furthermore, applying restraints on the C−F bond lengths (1.34(2) Å) was necessary. Because of this disorder and in order to reduce the number of parameters to be refined, all atoms of the anions were left isotropic. The main bond lengths and bond angles are summarized in Table 3. The cationic entity is shown[33] in Figure 2.

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Supporting Information Available: Tables of fractional atomic coordinates, anisotropic thermal parameters, and bond lengths and angles and drawings of the two independent anions for compound **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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