Chemistry of Highly Electrophilic Binuclear Cations. 1. Oxidation Reactions of $[M_2(\eta^5\text{-}C_5H_5)_2(CO)_4(\mu\text{-}Ph_2PCH_2PPh_2)]$ (M = Mo, W) with $[FeCp_2]X$ (X = BF_4, PF_6)

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Oxidation of the title compounds with 2 equiv of $[FeCp_2]BF_4$ in dichloromethane leads to the tetracarbonylic fluoro complexes $[M_2Cp_2(\mu\text{-}F)(CO)_4(\mu\text{-}dppm)]BF_4$ in high yields (dppm = $Ph_2PCH_2PPh_2$). By contrast, the analogous reaction with $[FeCp_2]PF_6$ gives the tricarbonylic fluoro derivatives $[M_2Cp_2(\mu\text{-}F)(\mu\text{-}CO)(CO)_2(\mu\text{-}dppm)]PF_6$. Separate experiments revealed that the latter cations cannot be obtained through decarbonylation of the former fluoro complexes. By carrying out the $[FeCp_2]PF_6$ oxidations in the presence of halide ions X^- (X = Cl, Br, I), the corresponding halo derivatives $[M_2Cp_2(\mu\text{-}X)(\mu\text{-}CO)(CO)_2(\mu\text{-}dppm)]PF_6$ are formed in good yields. All above species are derived from the unsaturated dications $[M_2Cp_2(\mu\text{-}CO)_2(CO)_2(\mu\text{-}dppm)]^{2+}$, which are the initial products of the removal of two electrons from the title compounds. Despite its high reactivity, the tungsten dication can be isolated as a solid, thanks to its low solubility in dichloromethane, and has been shown to react with other donor molecules such as acetate ions or methanol, to give tricarbonylic derivatives $[W_2Cp_2(\mu\text{-}Y)(\mu\text{-}CO)(CO)_2(\mu\text{-}dppm)]PF_6$ (Y = O_2CMe, OMe), which display structures comparable to those of the corresponding halogeno complexes. The structure of both tungsten fluoro complexes has been determined by X-ray diffraction methods, that on the tetracarbonylic compound revealing the presence of a weak H-bonding interaction between the BF_4^- counterion and a methylenic hydrogen in the diphosphine ligand. The reaction pathways likely operative in the oxidation of the title compounds are analyzed in light of the experimental findings and the critical role played by the BF_4^- or PF_6^- counterions.

Introduction

Organometallic transition metal dimers with formal metal−metal bond orders of 2 or higher constitute a very interesting group of species, mainly due to their high reactivity toward a great variety of molecules under mild conditions.[1] Electrophilicity is perhaps their most characteristic property, and this is expected to be enhanced when the molecule carries a neat positive charge. Examples of this type of cation are however very scarce, they being generally synthesized through redox reactions,[2] and their chemistry has been therefore little explored. Further interest in these species comes from the fact that they are expected to behave as transition metal-based Lewis acids. In fact, mononuclear complexes having this chemical behavior are being extensively studied because of their proven or potential catalytic applications in a number of organic reactions. For example, there is a large number of mononuclear transition metal complexes that act as Lewis acid catalysts in different aldol additions and cycloaddition reactions.[3,4] Perhaps the most prominent example is provided by the dicyclopentadienyl group 4 metal−alkyl complexes, which are excellent catalysts for alkene polymerization.[5] The latter process is one of high

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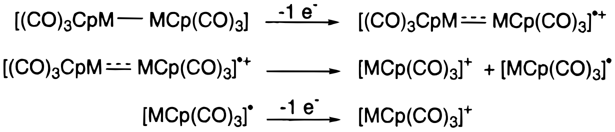
Scheme 1. Mechanism for the Oxidation Reactions of $[M_2Cp_2(CO)_6]$ (M = Mo, W)[12]



$$[(CO)_3CpM{-}MCp(CO)_3] \xrightarrow{-1\,e^-} [(CO)_3CpM{\cdots}MCp(CO)_3]^{\bullet+}$$

$$[(CO)_3CpM{\cdots}MCp(CO)_3]^{\bullet+} \longrightarrow [MCp(CO)_3]^+ + [MCp(CO)_3]^\bullet$$

$$[MCp(CO)_3]^\bullet \xrightarrow{-1\,e^-} [MCp(CO)_3]^+$$

industrial importance, and the search for new types of complexes displaying improved catalytic performance still continues.[6] Although most of the current research is concentrated on mononuclear complexes, multiply bonded binuclear cations meet in principle the requirements for this sort of catalytic activity, that is, Lewis acidity and coordinative unsaturation.[3,5,6] As an example, the dication $[Ru_2H_2(CO)_4(\mu\text{-}L_4)]^{2+}$ (L_4 = tetradentate P-donor ligand) has been found to be a good precatalyst for the hydroformilation of 1-alkenes.[7] Thus, exploring and understanding the chemistry of binuclear unsaturated cations not only is a matter of academic interest but also can lead to some useful applications.

Removal of one or more electrons from a singly metal−metal bonded dimetallic complex is the most straightforward route for multiply metal−metal bonded cations. Very often, however, the reactivity of the product is so high that the system further evolves so as to reduce the electronic unsaturation generated. Typical secondary processes are solvent coordination or ligand rearrangements.[8,9] The latter processes can be sometimes avoided by the use of bridging ligands which increase the stability of the unsaturated cation. This is the case, for example, of the 33-electron dimers $[W_2(\mu\text{-}PPh_2)_2(CO)_6(PPh_2H)_2]^+$ [10] and $[Mo_2(\mu\text{-}C_5H_4PPh_2)_2(CO)_4]^+$,[11] where the diphenylphosphido or cyclopentadienyl(diphenyl)phosphine bridging ligands no doubt play a determinant stabilizing role. The latter complex is prepared through oxidation of neutral dimer $[Mo_2(\mu\text{-}C_5H_4PPh_2)_2(CO)_4]$, but removal of two electrons leads to decomposition. For comparison, the oxidation of the unbridged hexacarbonyls $[M_2Cp_2(CO)_6]$ (M = Mo, W), studied by electrochemical methods,[12] leads to the disruption of the dimetallic unit even at the monocation step (Scheme 1).

In this paper we report our full studies on the chemical oxidation of the dppm-bridged complexes $[M_2Cp_2(CO)_4(\mu\text{-dppm})]$ (**1a,b**) [M = Mo (**a**),[13] W (**b**);[14] Cp = η^5-C_5H_5; dppm = $Ph_2PCH_2PPh_2$] using the BF_4^- and PF_6^- salts of the ferricenium cation $[FeCp_2]^+$, a well-known and "innocent" one-electron-oxidizing species in organometallic chemistry.[15] This cation has been previously used in the selective oxidation of compounds containing metal−metal bonds.[8,16] Although the mentioned counteranions can be classified as "noncoordinating" species, there are however examples where they can act as ligands.[17−19] In fact, our preliminary studies on the reaction of **1b** with $[FeCp_2]PF_6$ showed that the unsaturated species initially formed, $[W_2Cp_2(\mu\text{-}CO)_2(CO)_2(\mu\text{-dppm})][PF_6]_2$ (**2b**), was able to abstract a fluoride ion from the counterion.[20] As will be next discussed, the oxidation products of compounds **1a,b** are highly electrophilic and interact in different ways with their counterions to give fluoro derivatives unless a competitor ligand is present, in which case coordination of the latter preferentially occurs.

Results and Discussion

Oxidation of Compounds 1 with $[FeCp_2]BF_4$. Compounds **1a,b** react rapidly with 2 equiv of $[FeCp_2]BF_4$ in dichloromethane at temperatures of ca. −25 °C to give with good yield the fluoro derivatives $[M_2Cp_2(\mu\text{-}F)(CO)_4(\mu\text{-dppm})]BF_4$ (**3a,b**). The reaction conditions are critical. Thus, the use of lower temperatures or 1 equiv of oxidant leads to the formation of the mononuclear cations $[MCp(CO)_2(dppm)]^+$. The molybdenum cation has been previously detected by us,[13b] and the tungsten one can be identified by comparison of its IR and NMR spectra[21] with those of the molybdenum analogue[13] and related species.[8b,16a,22] On the other hand, if the reaction on **1a** is carried out at room temperature, we have observed that a mixture of the corresponding complexes **3a** and some tricarbonyl $[Mo_2Cp_2(\mu\text{-}F)(\mu\text{-}CO)(CO)_2(\mu\text{-dppm})]PF_6$ (**4a**, see later) is obtained. These observations have mechanistic implications, as will be discussed later on.

The structure of the dichloromethane solvate of the tungsten compound **3b** has been determined by an X-ray study. A view of structure of **3b** is shown in the Figure 1 together with the atom-numbering system. Selected bond distances and angles are given in Table 2. The cation is made up of two *cis*-$W(CO)_2Cp$ fragments joined by symmetrical dppm and fluoride bridges. The local geometry around each metal atom is of the usual four legged "piano stool" type. The overall conformation of the molecule is of the *syn* type, with the Cp ligands

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[21] ν(CO)(CH_2Cl_2): 1978 (vs), 1915 (s) cm^{-1}. $^{31}P\{^1H\}$ (CD_2Cl_2) δ −32.5 (s, J_{PW} = 206).

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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	$J_{PP}{}^c$
$[W_2Cp_2(\mu\text{-}CO)_2(CO)_2(\mu\text{-dppm})](PF_6)_2$ (**2b**)	2024 (s), 1980 (w), 1864 (s), 1814 (vs)^d		
$[Mo_2Cp_2(\mu\text{-}F)(CO)_4(\mu\text{-dppm})]BF_4$ (**3a**)	1983 (vs), 1906 (m), 1886 (s)	54.3^{e,f}	
$[W_2Cp_2(\mu\text{-}F)(CO)_4(\mu\text{-dppm})]BF_4$ (**3b**)	1973 (vs), 1960 (sh), 1893 (m), 1868 (m)	38.0 (308)^g	
$[Mo_2Cp_2(\mu\text{-}F)(\mu\text{-}CO)(CO)_2(\mu\text{-dppm})]PF_6$ (**4a**)	1980 (vs), 1920 (w), 1726 (s)	48.7^h	
$[W_2Cp_2(\mu\text{-}F)(\mu\text{-}CO)(CO)_2(\mu\text{-dppm})]PF_6$ (**4b**)	1969 (vs), 1907 (w), 1681 (s)	55.1 (257, −59)^{i,j}	99
$[Mo_2Cp_2(\mu\text{-}Cl)(\mu\text{-}CO)(CO)_2(\mu\text{-dppm})]PF_6$ (**5a**)	1982 (vs), 1918 (w), 1723 (s)	46.0^{e,i}	
$[W_2Cp_2(\mu\text{-}Cl)(\mu\text{-}CO)(CO)_2(\mu\text{-dppm})]PF_6$ (**5b**)	1973 (vs), 1911 (w), 1678 (m)	31.1 (214, −17)	83
$[Mo_2Cp_2(\mu\text{-}Br)(\mu\text{-}CO)(CO)_2(\mu\text{-dppm})]PF_6$ (**6a**)	1980 (vs), 1905 (w), 1719 (s)	45.5^i	
$[W_2Cp_2(\mu\text{-}Br)(\mu\text{-}CO)(CO)_2(\mu\text{-dppm})]PF_6$ (**6b**)	1971 (vs), 1907 (w), 1674 (m)	27.9 (215, −18)^e	83
$[Mo_2Cp_2(\mu\text{-}I)(\mu\text{-}CO)(CO)_2(\mu\text{-dppm})]PF_6$ (**7a**)	1980 (vs), 1905 (m), 1714 (m)	45.2^i	
$[W_2Cp_2(\mu\text{-}I)(\mu\text{-}CO)(CO)_2(\mu\text{-dppm})]PF_6$ (**7b**)	1971 (vs), 1908 (w), 1671 (m)	22.3 (218, −18)	80
$[W_2Cp_2(\mu\text{-}O_2CCH_3)(\mu\text{-}CO)(CO)_2(\mu\text{-dppm})]PF_6$ (**8**)	1975 (vs), 1888 (w), 1663 (m)^k	37.9 (235, −20)^e	114
$[W_2Cp_2(\mu\text{-}OCH_3)(\mu\text{-}CO)(CO)_2(\mu\text{-dppm})]PF_6$ (**9**)	1963 (vs), 1896 (w), 1674 (m)	39.1 (214, −17)^e	96

[a] Recorded in CH_2Cl_2 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. [c] PP and PW coupling constants are obtained from the ^{183}W "satellite" lines (see ref 10b). [d] In Nujol mull. $\nu_{st}(PF)$ 846 (vs, br) cm^{-1}. [e] Recorded at 81.02 MHz. [f] $J_{PF} = 44$ Hz. [g] Recorded at 161.98 MHz, $J_{PF} = 56$ Hz, isomer *syn*. [h] Recorded at 233 K; $J_{PF} = 22$ Hz. [i] Recorded in acetone-d_6. [j] $J_{PF} = 29$ Hz. [k] $\nu_{asym}(OCO)$: 1556 (m) cm^{-1} in CH_2Cl_2; 1543 (m) cm^{-1} in Nujol mull.

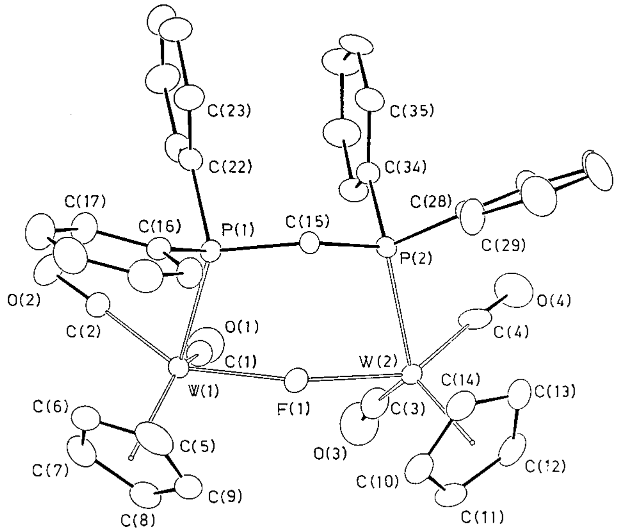


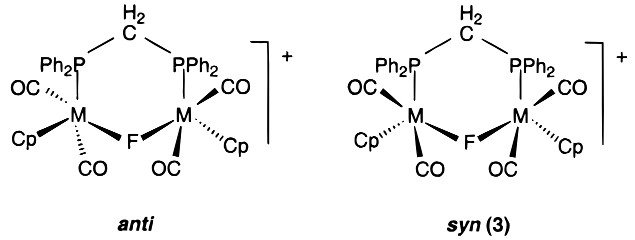
Figure 1. ORTEP view of the structure of the complex **3b** together with the atomic numbering scheme. The ellipsoids for the atoms are drawn at the 30% probability level.

Table 2. Selected Bond Distances (Å) and Angles (deg) for Compound 3b

W(2)−F(1)	2.127(6)	W(1)−F(1)	2.125(6)
W(2)−P(2)	2.489(2)	W(1)−P(1)	2.481(2)
W(2)−C(3)	1.965(11)	W(1)−C(1)	1.979(10)
W(2)−C(4)	1.972(11)	W(1)−C(2)	1.940(10)
P(2)−C(15)	1.857(9)	P(1)−C(15)	1.845(10)
P(1)−C(15)−P(2)	120.2(5)	W(1)−F(1)−W(2)	155.8(3)
P(1)−W(1)−F(1)	79.8(1)	P(2)−W(2)−F(1)	77.2(2)
P(1)−W(1)−C(2)	80.2(3)	P(2)−W(2)−C(4)	81.0(3)
F(1)−W(1)−C(1)	86.3(3)	F(1)−W(2)−C(3)	85.5(4)
C(1)−W(1)−C(2)	74.9(4)	C(3)−W(2)−C(4)	74.8(4)

placed on the same side of the average plane defined by the W and P atoms (Chart 1), as found for the hydridocomplex $[Mo_2Cp_2(\mu\text{-}H)(CO)_4(\mu\text{-dppm})]^+$.[13] On the basis of the EAN rule, the bond order for the cation in **3b** must be 0, in agreement with the long intermetallic separation of 4.158(1) Å. This allows the fluoride anion to display a large W−F−W angle of 155.8(3)°. Although comparable carbonylic fluoro compounds are not available, the tendency of the fluoride ligand to adopt a linear bridging mode in classical coordination complexes is well-known, thus maximizing its donor ability though π-donation.

Chart 1



The six-membered ring formed by the two bridges with the two W atoms adopts a twist-boat conformation, with the methylenic carbon on the same side of the fluoride bridge. The F(5) atom of the tetrafluoborate ion is involved in three weak interactions with the H(152) methylenic proton [H(152)···F(5) = 2.50(1) Å], with the H(21) of a phenyl group [H(21)···F(5) = 2.49(1) Å] and with the H(14) from a Cp ring [H(14)···F(5) = 2.41(2) Å]. These interactions, slightly shorter than the sum of van der Waals radii (2.60 Å),[23] could be retained in solution, as will be discussed next. Although we are not aware of any previously reported H-bonding interactions involving the methylenic group of the dppm ligand, we can quote the complex $[Ru_2Cp_2(\mu\text{-}CH_2)(\mu\text{-}CO)(CO)(CF_2{=}CFCF_3)]$,[24] where a significantly shorter H···F separation (2.23 Å) was found between a methylenic proton and a F atom in the coordinated olefin.

Spectroscopic data for compounds **3a,b** indicate that both species are isostructural and also that the solid-state structure found for **3b** is retained in solution. The *syn* geometry of the molecule (Chart 1) is revealed by the appearance of nonequivalent methylenic protons in the ^1H NMR spectra. For both compounds, the more shielded methylenic resonance exhibits a large coupling to the bridging fluoride ($^4J_{FH}$ = 10−13 Hz) and is significantly broader than the other one. For comparison, $^4J_{HF}$ = 3.7 Hz for the *trans* ethylimido fluoro complex $[W(F)(NEt)(dppe)_2]BF_4$.[25] We interpret the unusual broadening effect as derived from the presence in solution of some H-bonding interaction between this proton and the tetrafluoroborate counterion, as found

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Table 3. $^{19}F\{^1H\}$ NMR Data for New Compounds

	δ/ppm (J_{FP})[a]	
compd	anion	μ-F
3a	−150.6 (s)	−645.3 (t, 44)
3b	−152.2 (s)	−674.8 (t, 56)[b]
4a	−72.6 (d, J_{FP} = 715)	−480.1 (t, 22)
4b[c]	−71.7 (d, J_{FP} = 710)	−523.8 (t, 29)

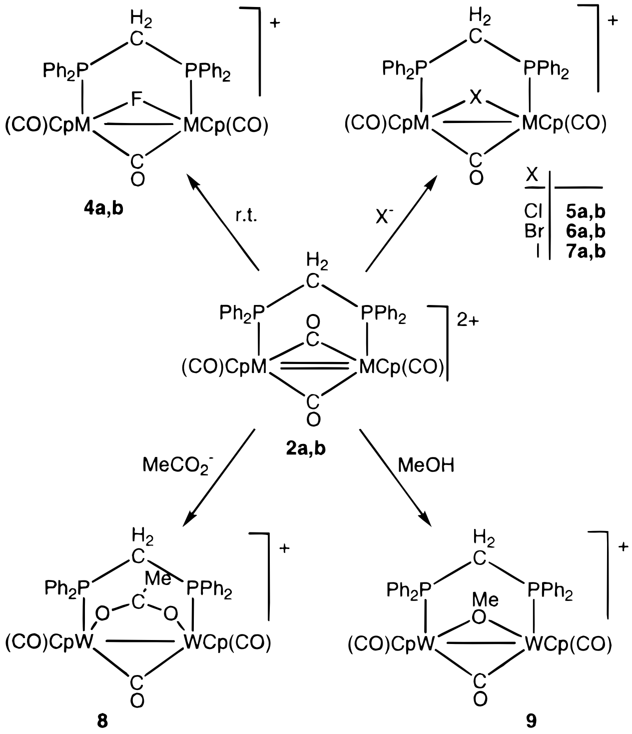
[a] Measured at 188.30 MHz in CD_2Cl_2 solutions at 291 K unless otherwise indicated; chemical shifts relative to $CFCl_3$; coupling constants in hertz. [b] J_{FW} = 51. [c] Measured in acetone-d_6.

in the solid state. On the other hand, the large F−H coupling detected is indicative of a strong binding of the fluorine ligand. This might also contribute to the strong shielding observed for this ligand in the ^{19}F NMR spectra of compounds **3**. The observed chemical shifts (ca. −645 and −675 ppm, Table 3) are among the lowest ones reported for transition metal fluoro complexes.

Compounds **3** are structurally related to the molybdenum cations $[Mo_2Cp_2(\mu\text{-}X)(CO)_4(\mu\text{-dppm})]^+$ (X = H, I), prepared through reaction of H^+ or I_2 on compound **1a**.[13] However, the latter cations display two isomers in solution (*syn* and *anti*, Chart 1). On the basis of the size and electronegativity of F (as compared with H or I) there would be no apparent reason for the existence of a single, *syn* isomer in the case of fluoro complexes **3**. When examining by ^{31}P NMR spectroscopy at −30 °C the crude reaction mixture in the case of **3b**, we noted, in addition to the resonance of the final product, the presence of a doublet at 26.8 ppm (J_{PF} = 44 Hz, intensity ca. 10% relative to the main resonance), which irreversibly disappears on leaving the solution at room temperature for a couple of minutes. In agreement with this, small changes were also detected in the IR spectra of the corresponding reaction mixtures. For example, a crude solution of the tungsten compound, just after being prepared from **1b** and $[FeCp_2]BF_4$ at −30 °C, exhibits just three CO-stretching bands at 1973 (vs), 1892 (m), and 1868 (m) cm^{-1}, but after a few minutes a fourth band at 1960 (m, sh) cm^{-1} is clearly appreciated, while the two bands at lower frequency invert their relative intensities. We interpret all the above observations by assuming that the reaction of compounds **1** with $[FeCp_2]BF_4$ initially generates both *syn* and *anti* isomers, but the latter rapidly transform into the former ones. The reason for the higher stability of the *syn* isomers for complexes **3** is not clear, but might be due to a more favorable H-interaction with the tetrafluoroborate counterion. As has been discussed for the solid structure of **3b**, the *syn* geometry allows one of the methylenic protons to point away from the molecule, thus facilitating such an interaction. For an *anti* geometry, however, the NMR data on the above-mentioned cations $[Mo_2Cp_2(\mu\text{-}X)(CO)_4(\mu\text{-dppm})]^+$ (chemical equivalence of methylenic protons, low couplings to bridging hydrido atom)[13b] suggest that both methylenic protons might be less exposed to the molecular surroundings.

Oxidation of Compounds 1 with $[FeCp_2]PF_6$. The result of the title reaction has been found to be strongly dependent not only on experimental conditions but also on the dimetal substrate. Two equivalents of oxidant is also required, otherwise the side reaction yielding the mononuclear cations $[MCp(CO)_2(dppm)]^+$ becomes competitive, as found in the oxidations using $[FeCp_2]BF_4$. For this reason, compounds **1** were usually added to a solution containing the ferricenium cation, so that defect of oxidant was avoided during reaction. Temperature is also a critical parameter in the reactions of the tungsten substrate **1b** in dichloromethane using 2 equiv of oxidant. At low temperatures (ca. −60 °C) the mononuclear cation is preferentially formed. On the other hand, when the reaction is carried out at room temperature, the tricarbonyl fluoro derivative $[W_2Cp_2(\mu\text{-}F)(\mu\text{-}CO)(CO)_2(\mu\text{-dppm})]$ (**4b**) is obtained in high yield (we note here that a small amount of tetracarbonylic **3b** is detected in the latter reaction when working at elevated concentrations of reactants). Finally, by working in the range −20 to −10 °C, clean and nearly quantitative precipitation of $[W_2Cp_2(\mu\text{-}CO)_2(CO)_2(\mu\text{-dppm})](PF_6)_2$ (**2b**) occurs. The molybdenum substrate **1a** behaves in a similar way, except that the corresponding dication **2a** cannot be isolated or even detected.

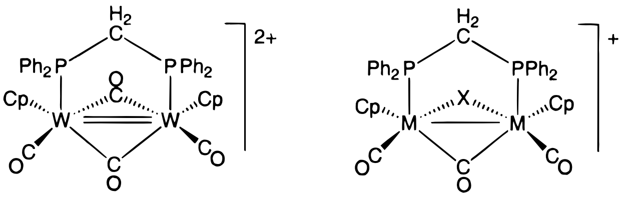
Scheme 2. Reactivity of Compounds 2 as PF_6^- Salts



The unsaturated dication **2b** is stable only in the solid state. It can be stored at −10 °C for several weeks or handled at room temperature for short periods of time. However, fast cation−anion reaction occurs in solution even at low temperatures (for example, acetone at −40 °C) to give cleanly the tricarbonyl fluoro derivate **4b** (Scheme 2). Obviously then, isolation of **2b** is possible just because of its very low solubility in dichloromethane. This circumstance is apparently not met for the dimolybdenum analogue **2a** and, hence, our inability to even detect that complex in the reactions under discussion. However, the formation of the fluoro complex **4a** and related halogeno derivatives (see later) strongly suggests that cation **2a** is also the initial product of the oxidation of **1a** with $[FeCp_2]PF_6$.

The structure proposed for compound **2b** in just based on its IR spectrum. The latter gives no indication of PF_6^- interaction with the cation. Thus, a single and strong

Chart 2



2b **4-9**

P–F stretch is found at 854 cm^{-1}, as expected for a free PF$_6^-$ ion.[19] It is known that coordination of this anion, by the lowering of local symmetry implied, causes the splitting of this band (for example, [MoCp(FPF$_5$)(CO)$_3$] exhibits P–F stretching bands at 879, 810, and 739 cm^{-1}).[19] Moreover, should PF$_6^-$ coordination to the cation be present in **2b**, the ν_{st}(CO) bands of the latter would shift to values comparable to those of the tetracarbonylic fluoro derivatives **3**, a circumstance not met either. In fact, the CO stretching bands of **2a** are much higher in frequency than those of **3** or **4**, in agreement with the presence of a higher positive charge in the molecule. These bands are grouped in two sets, which we assign to terminal C–O stretches (2024 (s), 1980 (w) cm^{-1}) and bridging ones (1864 (s), 1814 (vs) cm^{-1}). From their relative intensities[26] it can be deduced that the terminal carbonyls are almost parallel to each other (as found for compounds **4**), while the bridging CO groups must define an angle somewhat larger than 90°. The implied geometry would be then not much different from the tricarbonylfluoro complex **4b** (to be discussed next) after replacement of fluoride by carbonyl at the bridging position (Chart 2). From our limited data, however, we cannot rule out that semibridging carbonyls (instead of fully bridging ones) might actually be present in compound **2b**.

The structure of the tricarbonylic fluoro complex **4b** has been determined by an X-ray study. A view of the structure of the cation of **4b** is shown in Figure 2 together with the atom-numbering system. Selected bond distances and angles are given in Table 4. The structure of the cation is very similar to that of its analogous chlorocomplex **5b**.[20] Apart from the expected differences in the structural parameters involving the halide bridge, all other bond distances and angles are similar, except for the intermetallic distance, which falls from 3.040(3) Å (for **5b**) to 2.945(1) Å (for **4b**). These values are not themselves unusual for cyclopentadienylic cations having single metal–metal bonds (for example, 3.001(2) Å for [Mo$_2$Cp$_2$(μ-CH$_2$PPh$_2$)(μ-I)(μ-PPh$_2$)(CO)$_2$]$^+$ or 3.008(2) Å for [Mo$_2$Cp$_2$(μ-S^{t}Bu)$_2$(CO)$_4$]$^{2+}$).[27,28] However, the ca. 0.1 Å shortening in the W–W length from **5b** to **4b** cannot be exclusively a geometrical consequence of the necessarily shorter W–F lengths (relative to W–Cl ones), as, for example, the resulting W–F–W angle (89.1(2)°) is already quite acute if we recall the general tendency of fluoride for linear bridges. Unfortunately, organometallic complexes having bridging fluorides across metal–metal bonds are rare, so structural comparisons are not possible. In fact, we are aware of just one other related fluorocarbonylic complex structurally characterized. In [Mn$_3$(μ_2-F)(μ_3-OEt)$_2$(CO)$_9$] the fluoro ligand bridges two manganese atoms separated by only 2.829(7) Å (Mn–F–Mn = 93(1)°).[29] However, the presence of a metal–metal bond in this trimetallic 52-valence-electron compound is doubtful.

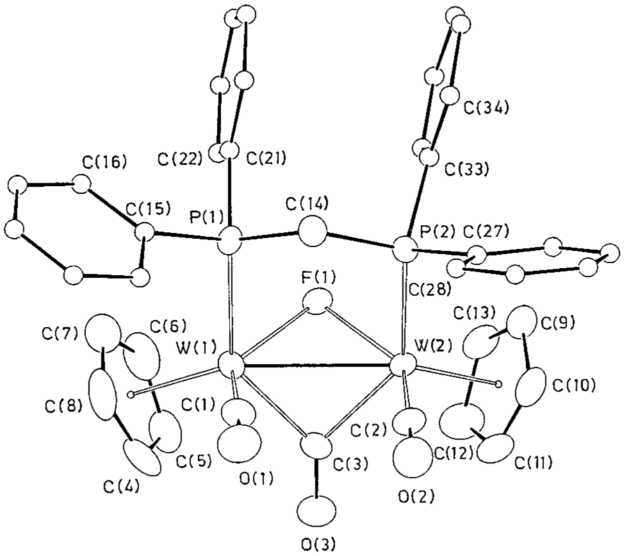


Figure 2. ORTEP view of the structure of the complex **4b** together with the atomic numbering scheme. The ellipsoids for the atoms are drawn at the 30% probability level.

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

W(1)–W(2)	2.945(1)		
W(2)–P(2)	2.510(3)	W(1)–P(1)	2.506(3)
W(2)–F(1)	2.091(5)	W(1)–F(1)	2.107(5)
W(2)–C(2)	1.953(11)	W(1)–C(1)	1.934(11)
W(2)–C(3)	2.128(11)	W(1)–C(3)	2.127(10)
P(1)–C(14)	1.815(9)	P(2)–C(14)	1.821(9)
P(1)–W(1)–F(1)	77.9(1)	P(2)–W(2)–F(1)	82.7(1)
F(1)–W(1)–C(3)	73.8(3)	F(1)–W(2)–C(3)	74.1(3)
C(1)–W(1)–C(3)	86.3(4)	C(2)–W(2)–C(3)	87.6(4)
P(1)–W(1)–C(1)	85.7(3)	P(2)–W(2)–C(2)	83.5(3)
W(2)–W(1)–P(1)	90.8(1)	W(1)–W(2)–P(2)	90.7(1)
W(2)–W(1)–F(1)	45.2(1)	W(1)–W(2)–F(1)	45.7(1)
W(2)–W(1)–C(1)	86.4(4)	W(1)–W(2)–C(2)	93.2(3)
W(2)–W(1)–C(3)	46.2(3)	W(1)–W(2)–C(3)	46.2(3)
W(1)–C(3)–W(2)	87.6(4)	W(1)–F(1)–W(2)	89.1(2)
P(1)–C(14)–P(2)	112.7(5)		

The geometry around the tungsten atoms in **4b** is of the "four-legged piano stool" type, with the bridging CO *trans* to the dppm bridge and the bridging halide *trans* to the terminal carbonyls. The overall structure of the cation is again of the *syn* type, so that the terminal carbonyls are almost parallel to each other. Although the bridging dppm ligand adopts a nearly eclipsed conformation, as found for **3b**, the methylenic carbon now points away from the fluoride bridge.

Spectroscopic data in solution for the fluoro complexes **4** are consistent with the solid-state structure of **4b**. The nearly parallel positioning of the terminal carbonyls gives rise to strong and weak (in order of decreasing frequency) C–O stretching bands, as predicted.[26] On the

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[29] Abel, E. W.; Towle, I. D. H.; Cameron, T. S.; Cordes, R. E. *J. Chem. Soc., Dalton Trans.* **1979**, 1943.

other hand, the bridging carbonyl gives rise to the expected low-frequency C−O stretch (ca. 1700 cm^{-1}) and highly deshielded ^{13}C NMR resonance (ca. 300 ppm), which in the molybdenum complex exhibits coupling to the bridging fluorine nucleus. Lack of symmetry relating both sides of the M_2P_2 pseudoplane is indicated by the appearance of nonequivalent methylenic protons, which now show no coupling to the bridging fluorine. The latter gives in turn a highly shielded ^{19}F NMR resonance (Table 3). Noticeably, no F−W coupling is detectable for the tungsten complex **4b** (to be compared with a value of 51 Hz for the tetracarbonyl **3b**). We regard this fact as accidental, perhaps due to a mutual cancellation of the one-bond and two-bond contributions (usually of opposite signs) to the tungsten−fluorine coupling in complex **4b** (this possibility is obviously to be excluded for the tetracarbonyl **3b**, which lacks a W−W bond). A final unusual spectroscopic detail concerns the ^{31}P shielding of complexes **4**. Phosphorus chemical shifts for molybdenum complexes are usually higher than those for the corresponding tungsten complexes. Indeed, this is the case for all compounds here reported, the difference being around 15−20 ppm. In contrast, the chemical shift of **4b** is ca. 7 ppm *higher* than that of its molybdenum analogue **4a**. At present we cannot offer a satisfactory explanation for this anomaly.

The formation of the fluoro derivatives **4** implies a fluoride abstraction from PF_6^- by the unsaturated dications **2**. Although several examples of mononuclear complexes experiencing such a process have been described,[30] precedents involving binuclear complexes seem to be restricted to the F$^-$ abstraction observed in the oxidation of $[Fe_2(\mu\text{-SMe})_2(CO)_4(PMe_3)_2]$ with $AgPF_6$.[31] Attempts to detect intermediate species in the transformation **2b**/**4b**, which also requires CO elimination, were however unsuccessful. ^{31}P or ^{19}F NMR monitoring of the reaction mixtures did not show new resonances, so we could not determine the fate of the “reacted” PF_6^-, which presumably is evolved as PF_5.

Halide and Related Derivatives of Compounds 2. From the preceding sections it is clear that the unsaturated cations **2** are highly acidic species able to extract a fluoride anion from its own counterion. Cations **2** are also good oxidants, and we have found a number of reagents that just promote electron transfer to give back the parent neutral dimers **1**. This occurs, for example, in the reactions of **2b** with KOH, LiC≡CPh, H_2O, or RSH. However, the high acidity of cations **2** (as PF_6^- salts) can be put to good synthetic use by reacting them with bases more resistant to oxidation. This is the case of the halide anions and some oxygen donors as the acetate of methoxide anions. In this way, the compounds of general formula $[M_2Cp_2(\mu\text{-X})(\mu\text{-CO})(CO)_2(\mu\text{-dppm})]PF_6$ [X = Cl (**5**), Br (**6**), I (**7**), O_2CMe (**8**), OMe (**9**)] have been obtained in good yield (Scheme 2). The synthetic procedure is simple. For molybdenum derivatives, the neutral complex **1a** is oxidized with $[FeCp_2]PF_6$ in the presence of X$^-$. For tungsten derivatives, a suspension of compound **2b** in dichloromethane is reacted with the appropriate X$^-$ salt. In the case of the methoxycomplex **9**, the use of NaOMe caused substantial electron transfer (i.e., formation of **1b**), and dry MeOH proved to be a much more convenient source of the methoxide ion. Thus, rather than a simple cation−anion reaction, coordination of methanol to unsaturated **2b** followed by proton ejection from the resulting dicationic intermediate seems to be a more likely reaction pathway in this reaction.

Spectroscopic data in solution for complexes **5**−**9** (Table 1 and Experimental Section) indicate that these species have the same structure as the fluoro derivatives **4** and need then no further comments in general. We just note that ^{31}P chemical shifts increase with the electronegativity of the donor X (I < Br < Cl < O < F). The C−O stretching frequencies are much less sensitive to the nature of X and cannot be correlated in this way. In the case of compound **8**, the presence of the acetate ligand is denoted by a ^{1}H resonance at 1.15 ppm and a ^{13}C resonance at 188.8 ppm. The latter is in the region observed for other organometallic dimers having bridging acetate groups.[32a,b] The coordination mode of the bridging acetate group through both oxygen atoms (μ-η^2) rather than coordination through a single oxygen atom (μ-η^1) is derived from the solid-state IR spectrum of **8**. This exhibits a strong band at 1543 cm^{-1} (Nujol mull), which can be assigned to the asymmetric O−C−O stretch of the ligand.[33] This value is similar to those observed for other carbonylic complexes containing an $M_2(\mu\text{-}\eta^2\text{-}O_2CMe)$ moiety,[32] whereas a μ-η^1 coordination of the ligand would give rise to a C−O stretch some 100 cm^{-1} higher in fequency.[32c]

Reaction Pathways in the Oxidation of Compounds 1. Through the preceding sections, we have shown that the nature of products resulting from oxidation of compounds **1** with $[FeCp_2]X$ (X = BF_4, PF_6) is strongly dependent on the nature of reactants and experimental conditions, particularly stoichiometry and temperature. The use of a defect of oxidant (less than 2 equiv) or very low temperatures leads to the mononuclear cations $[MCp(CO)_2(dppm)]^+$. Fluoride abstraction from X$^-$ finally occurs in all cases, with BF_4^- promoting the formation of tetracarbonylic derivatives **3** and PF_6^- favoring that of the tricarbonyls **4**. From separate experiments we have found that **3** and **4** cannot be interconverted. In fact, compounds **3** could not be transformed into **4** by either thermal or photochemical decarbonylation, and compounds **4** were found in turn to be unreactive toward CO at room temperature. Therefore, we conclude that compounds **3** and **4** are formed though different reaction pathways. Attempts to gain complementary information from CV experiments were unsuccessful, the cyclic voltammograms being too complex and irreversible to be interpreted. Despite this, we can rationalize the experimental findings by considering the reaction pathways illustrated in Scheme 3.

In the first place, our data indicate that reaction of compounds **1** with $[FeCp_2]^+$ occurs in all cases through

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[31] Mathieu, R.; Poilblanc, R.; Lemoine, P.; Gross, M. *J. Organomet. Chem.* **1979**, *165*, 243.

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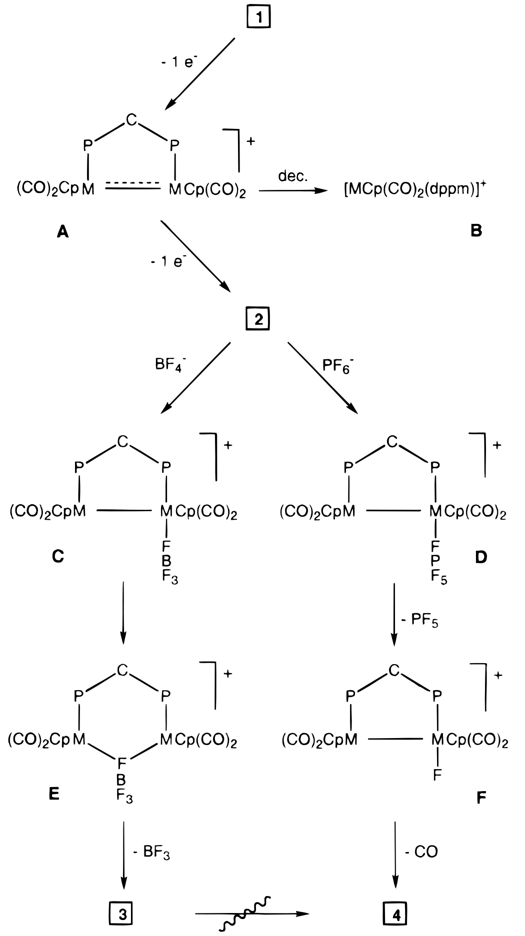
[33] Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed.; Wiley: New York, 1986; p 231.

Scheme 3. Reaction Pathways Proposed for the Oxidation of Compounds 1 with $[FeCp_2]X$ ($X^- = BF_4^-, PF_6^-$; P−P = dppm)



one-electron steps. Removal of the first electron would give the 33-electron radical **A**. Although we have not been able to isolate this intermediate, we note that if compounds **1** are reacted with 1 equiv of $[FeCp_2]X$ at ca. −60 °C, a deep green solution is formed. The latter turns to yellow in a few minutes at that temperature, or instantaneously if warmed, and the IR spectrum shows then the C−O bands of the corresponding mononuclear cations $[MCp(CO)_2(dppm)]^+$ (**B**). We note here that the 33-electron radical $[W_2(\mu\text{-}PPh_2)_2(CO)_6(PPh_2H)_2]^+$ also exhibits a green color.[10]

It seems clear, then, that radical **A** is the main precursor of the mononuclear species **B**, possibly through a process similar to that proposed for $[M_2Cp_2(CO)_6]$ (Scheme 1).[12] If a second equivalent of $[FeCp_2]^+$ is present, radical **A** can be further oxidized to give the unsaturated dications **2**. This second step is slower than the former and competes with the decomposition leading to **B**, being dominant at temperatures above ca. −30 °C. However, the unsaturated cations **2** are only stable for the combination M = W, X = PF_6^- due to its low solubility in dichloromethane. For the other combinations, or at higher temperatures in any case, cations **2** react with the corresponding counterion X, but different reaction pathways must then appear for either BF_4^- or PF_6^-.

It is reasonable to assume that either anion would coordinate to cations **2** through one of their fluorine atoms to give intermediates **C** and **D**, respectively. Examples of this type of complexes are well established.[19] Clearly, intermediates **C** and **D** must be in turn precursors of compounds **3** and **4**, respectively. Both processes require F^- abstraction from either BF_4^- or PF_6^-, but this must occur at a different step. At this point we can just put forward a somewhat speculative explanation for this difference. We propose that, being sterically more demanding, the bonded hexafluorophosphate tends to lose first a PF_5 molecule to give intermediates **F**. Loss of CO from the latter, possibly induced by the labilizing effect of the terminal fluoro ligand, would give finally the tricarbonyls **4**. By contrast, the smaller sized tetrafluoroborate ligand might survive enough in the coordination sphere of the metals so as to move into a coordinatively more sensible bridging position (**E**) before boron trifluoride elimination. Loss of BF_3 from the latter intermediate would then give the tetracarbonyls **3**.

Although somewhat speculative, the reaction pathways just proposed are consistent with the experimental finding that the unsaturated cations **2** invariably give tricarbonylic products in the presence of halide ions. Because of the presence of bridging carbonyls in compound **2**, initial attack of halide on these substrates is expected to occur at a single metal center, thus giving an intermediate similar to **F**, which afterward would experience an analogous decarbonylation to yield complexes **5**−**7**.

In summary we have shown that, in addition to experimental conditions, the nature of the counterions has a critical role in the fate of the highly electrophilic unsaturated cations **2**. It can be anticipated that the use of $[FeCp_2]^+$ salts having "weakly coordinating" anions different from BF_4^- or PF_6^- might have a dramatic influence on the course of the oxidation reactions of compounds **1**. Studies in that direction are currently in progress in our laboratory.

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 65−70 °C. The compounds $[Mo_2Cp_2(CO)_4(\mu\text{-dppm})]$[13] and $[W_2Cp_2(CO)_4(\mu\text{-dppm})]$[14b] were prepared as reported before. Reagents $[FeCp_2]PF_6$ and $[FeCp_2]BF_4$ were prepared according to literature procedures.[15] 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), 188.31 ($^{19}F\{^1H\}$), 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 $CFCl_3$ (^{19}F) 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 (Hz). $^{13}C\{^1H\}$ NMR spectra were routinely recorded on solutions containing a small amount of tris(acetylacetonato)chromium(III) as a relaxation reagent.

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Synthesis of [$W_2Cp_2(CO)_4(\mu$-dppm)]$(PF_6)_2$ (2b). Compound **1b** (0.066 g, 0.06 mmol) was added slowly to a dichloromethane solution (16 mL) containing [$FeCp_2$]PF_6 (0.040 g, 0.12 mmol) at −15 °C, whereupon a black-violet microcrystalline powder precipitated immediately. The solution was syringed off, and the solid was washed with dichloromethane (2 × 6 mL) at −10 °C and dried in vacuo, yielding 0.075 g (0.058 mmol, 88%) of compound **2**. Satisfactory microanalytical data could not be obtained for this air-sensitive complex, which is also unstable in solution (see Results and Discussion section).

Synthesis of [$Mo_2Cp_2(\mu$-F)$(CO)_4(\mu$-dppm)]BF_4 (3a). Compound **1a** (0.049 g, 0.06 mmol) was added slowly to a dichloromethane solution (10 mL) containing [$FeCp_2$]BF_4 (0.033 g, 0.12 mmol) at −30 °C, and the mixture was stirred for 5 min to give a violet solution. Solvent was then removed under vacuum, and the residue was washed with toluene (2 × 4 mL) and petroleum ether (3 × 3 mL) and then extracted with a mixture of CH_2Cl_2/toluene (1:1) and filtered. Removal of solvents from the filtrate gave compound **3a** (0.048 g, 87%) as a violet solid. Anal. Calcd for $C_{39}H_{32}BF_5Mo_2O_4P_2$: C, 50.67; H, 3.49. Found: C, 50.65; H, 3.46. ^{1}H NMR (200.13 MHz, CD_2Cl_2): δ 7.70−7.05 (m, 20H, Ph), 5.25 (s, 10H, Cp), 3.64 (dt, J_{HH} = 13, J_{HP} = 9, 1H, CH_2), 2.96 (tt, br, J_{HP} = 17, J_{HH} = 13, J_{HF} = 13, 1H, CH_2).

Synthesis of [$W_2Cp_2(\mu$-F)$(CO)_4(\mu$-dppm)]BF_4 (3b). The procedure is completely analogous to that described for **3a** but using compound **1b** (0.049 g, 0.06 mmol) instead. In this way, compound **3b** is isolated as a violet powder (0.070 g, 90%). Single crystals suitable for the X-ray diffraction study were grown by slow diffusion of a concentrated dichloromethane solution of the complex into a layer of toluene at −20 °C. They were shown (by NMR and X-ray) to contain one molecule of dichloromethane per molecule of complex. Anal. Calcd for $C_{40}H_{34}BCl_2F_5O_4P_2W_2$ (**3b**·CH_2Cl_2): C, 40.55; H, 2.89. Found: C, 40.60; H, 2.81. ^{1}H NMR (400.13 MHz, CD_2Cl_2): δ 7.65−7.02 (m, 20H, Ph), 5.43 (s, 10H, Cp), 3.69 (dt, J_{HH} = 13, J_{HP} = 10, 1H, CH_2), 2.25 (m br, CH_2, 1H). ^{1}H{^{31}P} NMR (400.13 MHz, CD_2Cl_2): δ 3.69 (d, J_{HH} = 13, 1H, CH_2), 2.26 (dd br, J_{HH} = 13, J_{HF} = 10, 1H, CH_2). ^{19}F NMR (CD_2Cl_2): δ − 152.2 (s, BF_4^-), −674.8 [dt, J_{FP} = 56, J_{FH} = 10, μ-F). ^{13}C{^{1}H,^{31}P} NMR (100.61 MHz, CD_2Cl_2): δ 246.2 (s, CO), 246.0 (d, J_{CF} = 19, CO), 132.0−129.3 (Ph), 95.8 (s, Cp), 16.9 (s, CH_2).

Synthesis of [$Mo_2Cp_2(\mu$-F)$(\mu$-CO)$(CO)_2(\mu$-dppm)]PF_6 (4a). Compound **1a** (0.049 g,0.06 mmol) was added slowly to a dichloromethane solution (20 mL) containing [$FeCp_2$]PF_6 (0.040 g, 0.12 mmol) at room temperature, and the mixture was stirred for 15 min to give a green solution. Solvent was then removed under vacuum, and the residue was washed with toluene (4 × 4 mL), extracted with dichloromethane, and filtered. Removal of the solvent from the filtrate under vacuum yielded compound **4a** (0.048 g, 85%) as a green solid. Anal. Calcd for $C_{38}H_{32}F_7Mo_2O_3P_3$: C, 47.82; H, 3.38. Found: C, 48.05; H, 3.40. ^{1}H NMR (CD_2Cl_2, 233 K): δ 7.48−6.88 (m, 20H, Ph), 5.11 (s, 10H, Cp), 3.02 (dt, J_{HH} = 11, J_{HP} = 10, 1H, CH_2), 2.70 [dt, J_{HH} = 11, J_{HP} = 6, 1H, CH_2). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 297.4 (d, J_{CF} = 11, μ-CO), 245.5 (s br, CO), 137.2−124.5 (Ph), 96.1 (s, Cp), 22.7 (t, J_{CP} = 16, CH_2).

Synthesis of [$W_2Cp_2(\mu$-F)$(\mu$-CO)$(CO)_2(\mu$-dppm)]PF_6 (4b). The procedure is completely analogous to that described for **4a** except that compound **1b** (0.066 g, 0.06 mmol) was used instead. In this way, compound **4b** was isolated as a green powder (0.064 g, 85%). The crystals used in the X-ray study were grown by slow diffusion of a concentrated dichloromethane solution of the complex into a layer of petroleum ether. Anal. Calcd for $C_{38}H_{32}F_7O_3P_3W_2$: C, 40.38; H, 2.85. Found: C, 40.43; H, 2.84. IR (Nujol mull): ν_{st}(CO) 1973 (vs), 1913 (m), 1674 (vs); ν(PF) 854 (vs br) cm^{-1}. ^{1}H NMR (acetone-d_6): δ 7.75−7.06 (m, 20H, Ph), 5.40 (s, 10H, Cp), 3.98 (dt, J_{HH} = 13, J_{HP} = 12, 1H, CH_2), 3.38 (dt, J_{HH} = 13, J_{HP} 10, 1H, CH_2). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 304.1 (s, μ-CO), 232.9 (s br, J_{CW} = 164, CO), 134.8−128.3 (Ph), 94.8 (s, Cp), 27.4 (t, J_{CP} = 21, CH_2).

Synthesis of [$Mo_2(\mu$-Cl)$Cp_2(\mu$-CO)$(CO)_2(\mu$-dppm)]PF_6 (5a). A dichloromethane solution (10 mL) containing 0.049 g (0.06 mmol) of **1a** and 0.025 g (0.06 mmol) of [$AsPh_4$]Cl was added very slowly to another solution containing 0.040 g (0.12 mmol) of [$FeCp_2$]PF_6 in 10 mL of dichloromethane. The mixture was stirred at room temperature for 15 min and then the solvent removed under vacuum. The residue was afterward washed with petroleum ether (4 × 4 mL), extracted with a mixture of toluene/THF (1:1), and filtered. Removal of solvents under vacuum gave compound **5a** as a greenish solid (0.055 g, 95%). Anal. Calcd for $C_{38}H_{32}ClF_6Mo_2O_3P_3$: C, 47.01; H, 3.32. Found: C, 46.98; H, 3.30. ^{1}H NMR (200.13 MHz, acetone-d_6): δ 7.67−7.01 (m, 20H, Ph), 5.32 (s, 10H, Cp), 4.45 (dt, J_{HH} = 13, J_{HP} = 12, 1H, CH_2), 3.15 (dt, J_{HH} = 13, J_{HP} = 10, 1H, CH_2). ^{13}C{^{1}H} NMR (50.32 MHz, acetone-d_6): δ 295.8 (s, μ-CO), 242.6 (AXX′, $|J_{CP} + J_{CP'}|$ = 16, CO), 138.5−126.1 (Ph), 96.3 (s, Cp); the CH_2 resonance for this complex was obscured by those from the solvent.

Synthesis of [$W_2(\mu$-Cl)$Cp_2(\mu$-CO)$(CO)_2(\mu$-dppm)]PF_6 (5b). Solid [$AsPh_4$]Cl (0.016 g, 0.038 mml) was added to a suspension of compound **2** (0.050 g (0.038 mmol) in dichloromethane (3 mL) at −30 °C, and the mixture was stirred for 3 min to give a brown-orange solution, which was afterward allowed to reach room temperature for 30 min. Solvent was then removed under vacuum, and the residue was washed with petroleum ether (3 × 3 mL), extracted with EtOH, and filtered. Removal of solvent from the filtrate under vacuum gave compound **5b** as a brown-orange solid (0.038 g, 86%). Anal. Calcd for $C_{38}H_{32}ClF_6O_3P_3W_2$: C, 39.80; H, 2.81. Found: C, 39.79; H, 2.81. ^{1}H NMR (CD_2Cl_2): δ 7.95−7.15 (m, 20H, Ph), 5.15 (s, 10H, Cp), 4.50 (dt, J_{HH} = 13, J_{HP} = 11, 1H, CH_2), 3.06 (dt, J_{HH} = 13, J_{HP} = 10, 1H, CH_2). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 294.5 (s, μ-CO), 229.0 (s, CO), 137.5−127.1 (m, Ph), 94.0 (s, Cp), 36.0 (t, J_{CP} = 24, CH_2).

Synthesis of [$Mo_2(\mu$-Br)$Cp_2(\mu$-CO)$(CO)_2(\mu$-dppm)]PF_6 (6a). The procedure is completely analogous to that described for **5a**, except that [PPh_4]Br (0.025 g, 0.06 mmol) was used instead, and the extraction was carried out using a toluene/THF (2:1) mixture. In this way, compound **6a** (0.054 g, 90%) was obtained as an orange solid. Anal. Calcd for $C_{38}H_{32}BrF_6Mo_2O_3P_3$: C, 44.95; H, 3.18. Found: C, 44.93; H, 3.15. ^{1}H NMR (acetone-d_6): δ 7.70−7.16 (m, 20H, Ph), 5.31 (s, 10H, Cp), 4.73 (dt, J_{HH} = 13, J_{HP} = 12, 1H, CH_2), 3.15 (dt, J_{HH} = 13, J_{HP} = 10, 1H, CH_2). ^{13}C{^{1}H} NMR (acetone-d_6): δ 294.3 (s, μ-CO), 240.1 (s br, CO), 138.5−127.0 (m, Ph), 95.8 (s, Cp), 31.3 (t, J_{CP} = 21, CH_2).

Synthesis of [$W_2(\mu$-Br)$Cp_2(\mu$-CO)$(CO)_2(\mu$-dppm)]PF_6 (6b). The procedure is completely analogous to that described for **5b**, except that [PPh_4]Br (0.016 g, 0.038 mmol) was used instead. The brown-yellow reaction mixture was stirred with water several times (5 × 5 mL) and the organic phase then filtered through $MgSO_4$ and diatomaceous earth. Solvent was removed under vacuum from the filtrate, and the residue was washed with toluene (3 × 3 mL) and dried under vacuum, to give compound **6b** as a brown powder (0.038 g, 84%). Anal. Calcd for $C_{38}H_{32}BrF_6O_3P_3W_2$: C, 38.32; H, 2.71. Found: C, 38.32; H, 2.71. ^{1}H NMR (CD_2Cl_2): δ 7.96−7.17 (m, 20H, Ph), 5.19 (s, 10H, Cp), 4.88 (dt, J_{HH} = 13, J_{HP} = 11, 1H, CH_2), 3.06 (dt, J_{HH} = 13, J_{HP} = 10, 1H, CH_2). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 290.8 (s, μ-CO), 226.5 (AXX′, $|J_{CP} + J_{CP'}|$ = 8, CO), 136.0−128.5 (m, Ph), 92.6 (s, Cp), 37.7 (t, J_{CP} = 24, CH_2).

Synthesis of [$Mo_2Cp_2(\mu$-I)$(\mu$-CO)$(CO)_2(\mu$-dppm)]PF_6 (7a). The procedure is completely analogous to that described for **5a**, except that [N^tBu_4]I (0.022 g, 0.06 mmol) was used instead. Compound **7a** (0.053 g, 84%) was thus obtained as a brown powder. Anal. Calcd for $C_{38}H_{32}F_6IMo_2O_3P_3$: C, 42.96; H, 3.03. Found: C, 42.94; H, 3.11. ^{1}H NMR (acetone-d_6): δ 7.70−7.14 (m, 20H, Ph), 5.30 (s, 10H, Cp), 5.13 (dt, J_{HH} = 14, J_{HP} = 12, 1H, CH_2), 3.16 [dt, J_{HH} = 14, J_{HP} = 10, 1H, CH_2].

Synthesis of [$W_2Cp_2(\mu$-I)(μ-CO)(CO)$_2$(μ-dppm)]PF_6 (7b). The procedure is completely analogous to that described for **5b**, except that [N^tBu_4]I (0.014 g (0.038 mmol) was used instead. Solvent was removed under vacuum from the reaction mixture, and the residue was extracted with a toluene/THF (3:1) mixture (5 × 4 mL) and filtered. Removal of solvent from the filtrate under vacuum gave compound **7b** as a brown-orange solid, which was washed with petroleum ether (3 × 3 mL) (0.041 g, 85%). Anal. Calcd for $C_{38}H_{32}F_6IO_3P_3W_2$: C, 36.86; H, 2.60. Found: C, 36.86; H, 2.61. ^{1}H NMR (400.13 MHz, CD_2Cl_2): δ 7.62−7.11 (m, 20H, Ph), 5.24 (dt, $J_{HH} = 14$, $J_{HP} = 11$, 1H, CH_2), 5.20 (s, 10H, Cp), 3.06 (dt, $J_{HH} = 14$, $J_{HP} = 10$, 1H, CH_2). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 316.2 (s, μ-CO), 222.4 (AXX′, $|J_{CP} + J_{CP'}| = 9$, CO), 138.2−129.1 (Ph), 91.9 (s, Cp), 40.6 (t, $J_{CP} = 25$, CH_2).

Synthesis of [$W_2Cp_2(\mu$-$O_2CMe)(\mu$-CO)(CO)$_2$(μ-dppm)]PF_6 (8). Solid Na[$MeCO_2$] (0.010 g, 0,12 mmol) was added to a suspension of compound **2** (0.050 g, 0.038 mmol) in dichloromethane (3 mL) at −15 °C, and the mixture was stirred for 1 h to give a dark orange solution, which was filtered. Solvent was then removed under vacuum from the filtrate and the residue washed with petroleum ether (3 × 3 mL) to give compound **8** as a brown orange powder (0.039 g, 88%). Anal. Calcd for $C_{40}H_{35}F_6O_5P_3W_2$: C, 41.05; H, 3.01. Found: C, 40.99; H, 3.07. ^{1}H NMR (400.13 MHz, acetone-d_6): δ 7.70−7.14 (m, 20H, Ph), 5.54 (dt, $J_{HH} = 15$, $J_{HP} = 10$, 1H, CH_2), 5.37 (s, 10H, Cp), 4.13 (dt, $J_{HH} = 15$, $J_{HP} = 11$, 1H, CH_2), 1.15 (s, 3H, Me). $^{13}C\{^1H\}$ NMR (100.61 MHz, CD_2Cl_2): δ 300.1 (s br, μ-CO), 232.6 (s, $J_{CW} = 142$, CO), 188.8 [s, μ-OO*C*Me], 136.3−128.8 (Ph), 96.1 (s, Cp), 42.4 (t, $J_{CP} = 26$, CH_2), 21.5 (s, Me).

Synthesis of [$W_2Cp_2(\mu$-OMe)(μ-CO)(CO)$_2$(μ-dppm)]PF_6 (9). Dry MeOH (0.5 mL) was added to a suspension of compound **2** (0.050 g, 0.038 mmol) in dichloromethane (3 mL) at −30 °C, and the mixture stirred for 5 min to give a brown-yellow solution. Solvents were then removed under vacuum, and the residue was washed with toluene (2 × 5 mL), extracted with dichloromethane, and filtered. Removal of solvent from the filtrate under vacuum gave compound **9** as a brown-orange solid, which was washed with petroleum ether (3 × 3 mL) (0.037 g, 85%). Anal. Calcd for $C_{39}H_{35}F_6O_4P_3W_2$: C, 41.01; H, 3.09. Found: C, 40.66; H, 3.03. ^{1}H NMR (200.13 MHz, CD_2Cl_2): δ 7.55−6.94 (m, 20H, Ph), 5.09 (s, 10H, Cp), 4.00 (s, 3H, OMe), 3.69 (dt, $J_{HH} = 13$, $J_{HP} = 11$, 1H, CH_2), 2.84 (dt, $J_{HH} = 13$, $J_{HP} = 9$, 1H, CH_2). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 302.3 (br, μ-CO), 231.0 (s, CO), 134.0−127.3 (Ph), 92.2 (s, Cp), 80.6 (s, OMe), 27.8 (t, $J_{CP} = 22$, CH_2).

Crystal Structure Determinations of Complexes 3b·CH_2Cl_2 and 4b. Selected crystallographic data for both compounds are listed in Table 5. Data were collected at room temperature on a Philips PW 1100 single-crystal diffractometer using graphite-monochromated Mo Kα radiation. All reflections with θ in the range 3−27° (**3b**·CH_2Cl_2) and 3−24° (**4b**) were measured. The intensities were corrected for Lorentz and polarization effects. A correction for absorption was applied (maximum and minimum values for the transmission factors were 1.000 and 0.706 (**3b**·CH_2Cl_2) and 1.000 and 0.740 (**4b**)).[35] Only the observed reflections were used in the structure solution and refinement.

Both structures were solved by Patterson and Fourier methods and refined by full-matrix least-squares first with isotropic and then with anisotropic thermal parameters in the last cycles for all the non hydrogen atoms excepting the C and Cl atoms of the CH_2Cl_2 solvate molecules for **3b** and the phenyl carbon atoms of dppm for **4b**. All hydrogen atoms were placed at their calculated positions (C−H = 0.96 Å) and refined "riding" on the corresponding carbon atoms. The final cycles of refinement were carried out on the basis of 493 (**3b**·CH_2Cl_2) and 360 (**4b**) variables; after the last cycles, no parameters shifted by more than 0.2 (**3b**·CH_2Cl_2) and 0.8 (**4b**) esd. The highest remaining peak in the final difference map was equivalent to about 1.8 (**3b**·CH_2Cl_2) and 0.6 (**4b**) e/Å^3. A weighting scheme $w = K[s^2(F_o) + gF_o{}^2]^{-1}$ was used in the last cycles of refinement with $K = 1.096$ and $g = 0.0009$ (**3b**·CH_2Cl_2) and $K = 0.199$ and $g = 0.0022$ (**4b**) at convergence. Final R and R_w values were 0.0397 and 0.0482 (**3b**·CH_2Cl_2) and 0.0281 and 0.0338 (**4b**), respectively. Atomic scattering factors, corrected for anomalous dispersion, were taken from ref 36. The SHELX-76 and SHELXS-86 systems of computer programs were used.[37] All calculations were carried out on the GOULD POWERNODE 6040 of the Centro di Studio per la Strutturistica Diffrattometrica del CNR, Parma.

Table 5. Experimental Data for the X-ray Diffraction Studies

	3b·CH_2Cl_2	**4b**
mol formula	$C_{40}H_{34}BCl_2F_5O_4P_2W_2$	$C_{38}H_{32}F_7O_3P_3W_2$
mol wt	1185.06	1130.28
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$
radiation (λ, Å)	graphite-monochromated (Mo Kα, 0.71073)	
a, Å	11.256(2)	10.961(2)
b, Å	19.221(3)	18.787(3)
c, Å	11.092(2)	18.055(3)
α, deg	97.86(1)	90
β, deg	114.38(1)	91.85(1)
γ, deg	101.43(1)	90
V, Å^3	2077.2(7)	3716(1)
Z	2	4
F(000)	1136	2160
cryst size, mm	0.12 × 0.21 × 0.30	0.15 × 0.24 × 0.35
μ(Cu Kα), cm^{-1}	58.01	63.88
diffractometer	Philips PW 1100	Philips PW 1100
scan type	$\theta/2\theta$	$\theta/2\theta$
scan speed, deg/min	3−12	3−12
θ range, deg	3−27	3−24
std reflctn	one measd after 100 reflctns	
no. of reflctns measd	$\pm h, \pm k, l$	$\pm h, k, l$
total no. of unique data	9058	5863
unique obsd data [$I > 2\sigma(I)$]	6137	3066
R^a	0.0397	0.0281
$R_w{}^b$	0.0482	0.0338

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum_w(|F_o| - |F_c|)^2/\sum_w(F_o)^2]^{1/2}$.

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Supporting Information Available: Tables of atomic coordinates, anisotropic thermal parameters, and bond lengths and angles for compounds **3b** and **4b**. This material is available free of charge via the Internet at http://pubs.acs.org. Tables of observed and calculated structure factors may be obtained from the authors.

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