Chemistry of Dinuclear Fulvalene Complexes: Dihydrides, Zwitterions, and Ring-Slippage Complexes Derived from $FvM_2(CO)_6$ (M = Mo, W)

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Reduction of the metal-metal-bonded complex $FvW_2(CO)_6$ generated the dianion $FvW_2(CO)_6^{2-}$. An X-ray crystallographic analysis of $[Et_4N^+]_2[FvW_2(CO)_6]^{2-}$ (monoclinic space group $P2_1/c$, a = 7.687(2) Å, b = 13.752(4) Å, c = 16.297(5) Å, $\beta = 94.80(2)^\circ$, V = 1716.8(8)Å³, Z = 4) showed the dianion to contain a planar Fv ring system bonded to the two metal centers in an anti fashion. The dianion reacted with a number of electrophiles to yield the neutral species $FvW_2(CO)_6E_2$ (E = H, Me, Et, σ -C₃H₅, CH₂Ph). The pK_a values for the two consecutive deprotonations of $FvW_2(CO)_6H_2$ were determined as 14.0 and 16.6 by equilibrium measurements in acetonitrile. Thermolysis and photolysis of FvW₂(CO)₆H₂ yielded FvW₂- $(CO)_6$ and H₂. Unlike $Cp_2W_2(CO)_6$, $FvW_2(CO)_6$ underwent protonation at the W-W bond by HBF₄·Et₂O in acetonitrile. Reactions of FvW₂(CO)₆ and FvMo₂(CO)₆ with PMe₃ and Me₂- PCH_2PMe_2 (dmpm) resulted in generation of the dinuclear zwitterions $FvM_2(CO)_5(PMe_3)_2$ and FvM₂(CO)₅)(dmpm), respectively. An X-ray crystallographic analysis of FvMo₂(CO)₅ (orthorhombic space group $P2_{1}2_{1}2_{1}$, a = 9.1049(8) Å, b = 12.2598(14) Å, c = 20.1606(18) Å, V = 2250.4(7) Å³, Z = 4) showed an *anti* coordination of the Mo(CO)₃⁻ and Mo(CO)₂(dmpm)⁺ moieties at a planar Fv ligand. Electrophiles added at the anionic part of the zwitterions, whereas LiAlH₄ effected reduction of coordinated CO to CH₃ at the cationic center of FvMo₂- $(CO)_5(PMe_3)_2$. Excess PMe₃ caused the conversion of $FvMo_2(CO)_5(PMe_3)_2$ and $FvMo_2(CO)_5$)-(dmpm) to Mo(CO)₃(PMe₃)₃ along with FvMo(CO)₂(PMe₃)₂ and FvMo(CO)₂(dmpm), respectively. These reactions constitute the first ring-slippage reactions that have been observed in fulvalene metal complexes. When treated with $M_0(CO)_3(NCMe)_3$, $FvM_0(CO)_2(PMe_3)_2$ cleanly regenerated $FvMo_2(CO)_5(PMe_3)_2$.

Introduction

Dinuclear organotransition-metal complexes have attracted special attention among organometallic chemists.² The reason for the interest in such systems stems in part from the suggestion that polynuclear species may act as suitable models for the interaction of organic molecules with surfaces.^{3a} Organometallic compounds that incorporate two or more reactive metal sites in close proximity might provide access to reaction pathways not available to mononuclear systems as a result of cooperative electronic and/or steric effects.³ In order to achieve true polynuclear reactivity, it is important that fragmentation of the polynuclear framework is avoided. Despite the fact that a wide variety of bidentate, metal-metal bridging ligands have been designed with this in mind, fragmentation reactions are frequently seen-presumably resulting from relatively weak metal-ligand bonds. For example, dissociation energies for tertiary phosphine-metal bonds fall in the range 30-40 kcal/mol.⁴ The cyclopentadienyl (η^5 -C₅H₅, Cp) ligand is among the more strongly bonded ligands in organometallic systems, with bond strengths to metals typically estimated at 90-100 kcal/mol.^{4,5} Therefore, dinuclear systems containing two Cp moieties connected to each other appear to be attractive bridging ligands. On the basis of this strategy, Cp's connected by methylene and other linkages have been used.⁶ Earlier work^{7a,b} provided ready access to dinuclear fulvalene (η^5 : η^5 -C₁₀H₈, henceforth to be abbreviated Fv) complexes, in which the Cp moieties are directly attached to each other without intervening bridging groups. The high-

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yield syntheses have facilitated the exploration of the chemistry of such species in detail.⁷

There are at least two important reasons that suggest that Fv-bridged dinuclear systems might exhibit properties quite different from those of Cp analogues, and even of analogues based on Cp rings connected by intervening linkages. First, in the metal-metal-bonded complexes that lend themselves as obvious starting materials for this type of chemistry, the Fv ligands are forced to bend away from planarity in order to accommodate the metal-metal bonds. The distance between the ring centroids in a planar Fv ligand is ca. 4.0 Å.⁸ In comparison, the Ru-Ru distance in FvRu₂(CO)₄ is 2.821 Å and the Fv ligand is distorted from planarity by a 28.5° dihedral angle between the two Cp ring planes.^{7a} This bending of the Fv ligand is thought to weaken the metal-metal bonds, leading in turn to unique reactivity.^{7e} Second, the conjugated π system of the Fv ligand provides a mechanism for electronic communication between the metal centers regardless of whether there is a metal-metal bond present or not, and of whether the metals are oriented syn or anti with respect to the bridging ligand. The Hückel MO diagram of fulvalene⁹ shows that the first and third lowest energy levels in the π -electron system provide significant bonding interactions between the two ring π systems. The presence of significant electronic communication is supported by the report that FvRh₂(CO)₂(PPh₃)₂ underwent a reversible, two-electron oxidation at 0.01 V vs SCE, whereas CpRh(CO)(PPh₃) underwent a one-electron oxidation at 0.43 V.^{10a} The large difference in oxidation potentials suggests that special stabilization is provided to the cation in the former case. Additional evidence for electronic communication through the Fv ligand was provided by the observation^{10b} that the radical cation $FvFe_2(HMB)_2^{2+}$ (HMB = hexamethylbenzene), in which the Fe atoms may safely be assumed to be located anti with respect to the Fv ligand, had only one type of Fe atom, as found by Mössbauer spectroscopy even at 4.2 K (time scale of experiment: ca. 10⁻⁹ s!). FvFe₂(HMB)₂ exists as a diradical,^{10b} demonstrating that while there may be electronic communication between the metals,

this does not necessarily lead to spin pairing of electrons. Finally, it was recently shown that the cation radical of $FvMn_2(CO)_4(\mu_2-Ph_2PCH_2PPh_2)$ had a delocalized charge on the ESR time scale (10^{-8} s) but not on the IR spectroscopy time scale $(10^{-12} \text{ s}).^{10c}$

In this contribution we describe the chemistry of complexes $FvW_2(CO)_6$ (1), which has hitherto been relatively unexplored, and of $FvMo_2(CO)_6$ (2), which has already been the focus of a full paper.^{7e} Reactions that



bear relevance both on metal—metal bond energy weakening because of induced strain and on the possible intermetal communication through the Fv ligands will be described.¹¹

Results and Discussion

Synthesis, Structure, and Reactivity of the Dianion $FvW_2(CO)_6^{2-}$ (1²⁻). The metal-metal-bonded complexes $FvM_2(CO)_6$ (M = Cr, Mo, W) undergo twoelectron electrochemical reductive cleavage of the metal-metal bonds to form the corresponding dianions.7h $FvW_2(CO)_6$ (1), reduced at -0.82 V vs NHE, ^{7h} undergoes reduction by LiEt₃BH¹² or Na/Hg to form the Li and Na salts of the non-metal-metal bonded dianion. A color change from purple 1 to yellow 1^{2-} marked the end point of the reduction. The ¹H NMR spectrum (THF- d_8) of $1^{2-}(Na^{+})_{2}$ displayed signals at δ 4.80 and 5.24 in the expected AA'MM' pattern typical of symmetrically substituted dimetallafulvalene complexes of C_{2v} (syn coordination at Fv) or C_{2h} (anti coordination) symmetry. In THF, $1^{2-}(Na^+)_2$ showed three IR ν_{CO} bands at 1745, 1892, and 1889 cm⁻¹, whereas $1^{2-}(Li^+)_2$ displayed a somewhat different spectrum with bands at 1717, 1778 (shoulder), 1803, 1895, and 1897 (shoulder) cm^{-1} . The differences may be attributed to different ion pairing effects with the two counterions.¹³

Treatment of $1^{2-}(Na^+)_2$ with aqueous $Et_4N^+Cl^-$ led to the formation of crystalline $1^{2-}(Et_4N^+)_2$. The IR (acetonitrile) spectrum of this salt displayed only two bands, consistent with the absence of contact ion pairing,¹³ at 1777 and 1888 cm⁻¹. A number of dimetal fulvalene carbonyl compounds without metal--metal

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Figure 1. Side-on SHELXTL view of $[Et_4N^+]_2[FvW_2(CO)_6^{2-}]$ $(1^{2-}(Et_4N^+)_2)$, determined by X-ray crystallography.

Table 1.	Bond	Lengths	and B	ond A	Angles	for
[Et ₄ N	[+]2[Fv	$W_2(\overline{CO})_c$	5 ²⁻] (1 ²	-(Et4	N ⁺) ₂)	

Bond Lengths (Å)				
W(1) - C(1)	1.928(4)	W(1) - C(2)	1.927(5)	
W(1) - C(3)	1.933(5)	W(1) - C(5)	2.362(4)	
W(1) - C(6)	2.354(6)	W(1)-C(7)	2.367(5)	
W(1) - C(8)	2.384(5)	W(1) - C(4)	2.407(4)	
C(1) - O(1)	1.163(6)	C(2)-O(2)	1.187(7)	
C(3)-O(3)	1.170(7)	C(5) - C(6)	1.414(7)	
C(5) - C(4)	1.413(6)	C(6) - C(7)	1.415(8)	
C(7) - C(8)	1.424(7)	C(8)-C(4)	1.427(7)	
C(4) - C(4')	1.466(8)	C(9)-C(10)	1.519(10)	
C(9) - N(1)	1.527(7)	C(11) - C(12)	1.492(8)	
C(11) - N(1)	1.521(6)	C(13) - C(14)	1.519(9)	
C(13) - N(1)	1.526(7)	C(15) - C(16)	1.518(8)	
C(15) - N(1)	1.511(6)			
	Bond An	gles (deg)		
C(1) - W(1) - C(2)	87.3(2)	C(1) = W(1) = C(3)	86.1(2)	
C(2) - W(1) - C(3)	89.0(2)	C(1) - W(1) - C(5)	124.7(2)	
C(2) - W(1) - C(5)	147.6(2)	C(3) - W(1) - C(5)	97.2(2)	
C(1) - W(1) - C(6)	98.2(2)	C(2) - W(1) - C(6)	149.5(2)	
C(3) - W(1) - C(6)	121.1(2)	C(5) - W(1) - C(6)	34.9(2)	
C(1) - W(1) - C(7)	103.3(2)	C(2) - W(1) - C(7)	114.7(2)	
C(3) - W(1) - C(7)	154.6(2)	C(5) - W(1) - C(7)	57.9(2)	
C(6) - W(1) - C(7)	34.9(2)	C(1) - W(1) - C(8)	135.1(2)	
C(2) - W(1) - C(8)	97.5(2)	C(3) - W(1) - C(8)	138.3(2)	
C(5) - W(1) - C(8)	57.5(2)	C(6) - W(1) - C(8)	57.9(2)	
C(7) - W(1) - C(8)	34.9(2)	C(1) - W(1) - C(4)	156.0(2)	
C(2) - W(1) - C(4)	113.3(2)	C(3) - W(1) - C(4)	105.5(2)	
C(5) - W(1) - C(4)	34.5(1)	C(6) - W(1) - C(4)	57.8(2)	
C(7) - W(1) - C(4)	57.9(2)	C(8) - W(1) - C(4)	34.7(2)	
W(1) - C(1) - O(1)	176.8(5)	W(1) - C(2) - O(2)	178.6(5)	
W(1) - C(3) - O(3)	178.1(4)	W(1) - C(5) - C(6)	72.2(3)	
W(1) - C(5) - C(4)	74.5(2)	C(6) - C(5) - C(4)	109.0(4)	
W(1) - C(6) - C(5)	72.9(3)	W(1) - C(6) - C(7)	73.1(3)	
C(5) - C(6) - C(7)	108.0(4)	W(1) - C(7) - C(6)	72.1(3)	
W(1) - C(7) - C(8)	73.2(3)	C(6) - C(7) - C(8)	107.7(5)	
W(1) - C(8) - C(7)	71.9(3)	W(1) - C(8) - C(4)	73.6(3)	
C(7)-C(8)-C(4)	108.3(4)	W(1) - C(4) - C(5)	71.0(2)	
W(1) - C(4) - C(8)	71.8(2)	C(5)-C(4)-C(8)	107.0(4)	
W(1) - C(4) - C(4')	124.9(4)	C(5)-C(4)-C(4')	126.4(5)	
C(8) - C(4) - C(4')	126.5(5)	C(10) - C(9) - N(1)	114.9(5)	
C(12) - C(11) - N(1)	116.2(5)	C(14) - C(13) - N(1)	114.3(5)	
C(16) - C(15) - N(1)	115.1(4)	C(9) - N(1) - C(11)	111.5(4)	
C(9) = N(1) = C(13)	108.9(4)	C(11) - N(1) - C(13)	108.8(4)	
C(9) = N(1) = C(15)	107.9(4)	C(11) - N(1) - C(15)	108.2(4)	
C(13) - N(1) - C(15)	111.6(4)			

bonds or additional bridging ligands have been structurally characterized,¹⁴ and the metal centers are always attached to the Fv ligand in an *anti* manner. No anionic Fv complexes had been previously structurally characterized, so an X-ray structural analysis of $1^{2-}(Et_4N^+)_2$ was undertaken.

Figure 1 shows SHELXTL drawings of the structure of $[Et_4N^+]_2[FvW_2(CO)_6^{2-}]$. Bond lengths and bond angles are listed in Table 1. The dianion consists of two tungsten tricarbonyl units bonded anti to a virtually planar Fv ligand. The two Et_4N^+ cations are well separated from the anionic centers. The average W-CO bond length, 1.929 Å, is significantly shorter than that in $FvW_2(CO)_6$, 1.97 Å,¹⁵ as a consequence of improved W-CO d $\rightarrow \pi^*$ back-bonding in the dianion. The average W-C(ring) distance in 1^{2-} is 2.375 Å, longer than the corresponding distance in 1 (2.32 Å). Similar differences are revealed by comparison of $Cp_2Mo_2(CO)_6^{16a}$ with $[Bu_4N^+][CpMo(CO)_3^-]^{16b}$ and of $Cp_2Cr_2(CO)_6^{16c}$ with $[Me_4N^+][CpCr(CO)_3^-]$.^{16d} The bond that connects the two Cp moieties in the dianion has been lengthened to 1.466 Å from 1.43 Å in 1.15 HMO calculations⁹ show that the LUMO of fulvalene has a node between the two central carbons. Increased π -electron density should lead to a lengthening of this bond due to a reduction in the π -bond order. The difference in bond lengths is in the direction expected, but the change is quite small, and caution must be exerted when attributing the change exclusively to an orbital effect. Other contributing factors may be relief of strain in the fulvalene ligand caused by the cleavage of the metal-metal bond, as well as repulsive Coulomb forces between the two adjacent anionic centers.

The diamion $FvW_2(CO)_6^{2-}$ readily undergoes reactions with electrophiles to give the neutral, disubstituted compounds $FvW_2(CO)_6R_2$ (R = H (3), Me (4), Et, CH₂-CH₂CH₂I (5), CH₂OCH₃ (6), σ -C₃H₅, CH₂Ph) in good to



R = H (3), Me (4), Et, CH₂CH₂CH₂I (5), CH₂OCH₃ (6), σ-C₃H₅, CH₂Ph

excellent yields. Some aspects of the chemistry of compounds 4-6 will be discussed briefly in the following, whereas the dihydride 3 will be the focus of extensive discussions in separate sections of this paper.

Chemistry of Dialkyl Substituted Derivatives of 1. Photolysis of $FvW_2(CO)_6Me_2$ (4) in benzene yielded methane gas (detected by mass spectrometry) and FvW_2 -(CO)₆. This reactivity is reminiscent of the behavior of $FvMo_2(CO)_6Me_2$,^{7e} CpMo(CO)₃Me,^{17a} and CpW(CO)₃Me,^{17b} which also yielded metal-metal-bonded species upon

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photolysis. The photochemical reaction of $FvW_2(CO)_6$ - Me_2 in benzene- d_6 yielded mostly CH_4 (93% of total ion intensity for m/z = 16-20) and CH₃D (7%), demonstrating that the fourth hydrogen in the methane is not derived from the solvent. Photolysis of FvW₂(CO)₆- $(CD_3)_2$ in benzene- d_6 yielded mostly CD_4 (56% of ion intensity) and CD_3H (24%), indicating that the fourth hydrogen (deuterium) largely derives from a second methyl group in 4 or intermediates formed during its degradation to 1. The isotopic selectivity in a puzzling way differs from that of FvMo₂(CO)₆Me₂^{7e} and CpMo- $(CO)_3Me^{17a}$ (the source being mostly the ring systems) and that of $CpW(CO)_3Me$ (extensive solvent involvement^{17b}).

The reaction between 1^{2-} and 1,3-diiodopropane led to the formation of bis(3-iodopropyl) complex 5 as the only isolable product. The corresponding reaction of $FvMo_2(CO)_6^{2-}$ yielded a dinuclear Mo-Mo-bonded 1-ox-acyclopent-2-ylidene Fischer-type carbene complex.^{7e} The lack of formation of Fischer carbene products in the tungsten case points to a considerably less facile CO migratory insertion in tungsten alkyls relative to that in the molybdenum alkyls. This conclusion is in accord with the report that $CpMo(CO)_3^-$, but not $CpW(CO)_3^-$, reacts with 1,3-dibromopropane to yield 1-oxacyclopent-2-ylidene complexes.¹⁸

The dimethyl complex 4 failed to react with Ph₃C⁺BF₄⁻ in an attempt to generate cationic carbene species.¹⁹ However, the bis(methoxymethyl) complex 6 yielded a carbene species in a reaction that qualitatively paralleled the behavior of its Mo analogue^{7e} and other alkoxyalkyl complexes.²⁰ Treatment of $\mathbf{6}$ with HBF₄·Et₂O in dichloromethane- d_2 at -60 °C initially yielded a species which in the ¹H NMR spectrum displayed four Fv signals, a characteristic methylene singlet (δ 13.10, 2 H), and two singlets attributed to a methoxymethyl group at δ 4.73 (3 H) and 3.62 (2 H). We assign the structure $FvW_2(CO)_6(CH_2OCH_3)(=CH_2)^+$ to this compound. Changes in the spectrum occurred upon heating to 0 °C, which led to the gradual appearance of signals arising from a compound that is tentatively assigned the structure $FvW_2(CO)_6(C_2H_4)^{2+}$ (see Experimental Section for spectroscopic data). Presumably, coordinated ethene arises from methylene-methylene coupling in a transient, not detectable bis(methylene) intermediate $FvW_2(CO)_6(=CH_2)_2^{2+}$. Analysis of the volatiles by mass spectrometry after heating the solution to 40 °C confirmed the presence of ethene. We do not know whether the coupling reaction was intramolecular in nature, but the possibility appears likely because of the close proximity of the two methylene groups. Intermolecular methylene coupling reactions

yielding coordinated ethene in mononuclear complexes is a precedented reaction.^{19b,21} Interestingly, the methylene complexes^{19b,21g} CpW(CO)₃(=CH₂)⁺ and CpMo- $(CO)_3 (= CH_2)^+$, the first of which has been observed,^{21g} are considerably less stable than $FvW_2(CO)_6(CH_2OCH_3)$ - $(=CH_2)^+$ and its Mo counterpart. Phosphine substituted analogues are considerably more stable, and a number of such derivatives have been generated at low temperatures.19b



Preparation and Characterization of FvW₂- $(CO)_6H_2$ (3). The dihydride complexes $FvM_2(CO)_6H_2$ (M = Cr, Mo, W) have been implied as plausible, albeit not observed, intermediates en route from metal carbonyl precursors and dihydrofulvalene to the corresponding metal-metal-bonded complexes.^{7b} $FvMo_2(CO)_6H_2$, prepared in situ from the corresponding dianion and trifluoroacetic acid (TFA), underwent quantitative decomposition to the Mo-Mo-bonded dimer and H₂ at 20 °C,^{7e} a temperature at which CpMo(CO)₃H is stable. The study of the thermal H₂ extrusion from the bimetallic dihydride was hampered by its instability. Our attention was therefore turned to the tungsten analogue 3. Considering that M-H bond strengths increase as one moves down in the periodic table,^{4,22} improved thermal stability was anticipated for this complex.

Treatment of a THF solution of $1^{2-}(Na^+)_2$ with TFA caused the color to turn from pale yellow (1^{2-}) to intense yellow after the addition of 1 equiv of TFA. The yellow color is believed to arise from the hydrido anion $FvW_2(CO)_6H^-$ (7; vide infra). After the addition of 2 equiv of TFA, the solution was virtually colorless, and analytically pure dihydride 3 was isolated in 85-95%yield as an air-sensitive, off-white solid (Scheme 1). The ¹H NMR spectrum of **3** unambiguously establishes that the dihydride in solution has two terminally bonded, noninterchanging (on the NMR time scale) hydride

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ligands. The hydride signal is located at δ -6.98 (THF d_8) as a singlet with accompanying ¹⁸³W satellites (J_{WH} = 37.7 Hz). The 1:13:1 intensity ratio of the signals agrees well with the 1:11.7:1 ratio expected for a static structure.²³ The observation of a W-H coupling rules out intermolecular hydride exchange processes on the NMR time scale. A structure involving two bridging hydrides, or two terminally bonded hydrides undergoing rapid intramolecular exchange, is ruled out on the basis of the intensities of the ¹⁸³W satellites relative to the central resonance. These alternatives require a 1:6:1 intensity ratio.²³ The terminal nature of the hydride ligands in 3 is also supported²⁴ by its reactions with CCl₄, CHBr₃, and I₂ to yield the corresponding dihalide complexes $FvW_2(CO)_6X_2$ (X = Cl, Br, I) in excellent yields (Scheme 1).

Thermodynamic Acidity of FvW₂(CO)₆H₂. In an attempt at purifying $FvW_2(CO)_6D_2$ (3-d₂; prepared from 1^{2-} and TFA-d) by passage through a silica gel column, we found that the isolated product was instead FvW₂- $(CO)_6H_2$. Conversely, when 3 was passed through a column of silica gel deactivated with D_2O , 3- d_2 was obtained (Scheme 1) with more than 97% D incorporation, as judged by the absence of the hydride resonance in the ¹H NMR spectrum. The facile H/D exchange suggests that **3** is rather acidic. The factors that influence transition-metal hydride acidity have been thoroughly studied during the last decade.^{22c,25} A comparison of the thermodynamic acidities $(pK_a's)$ of CpW(CO)₃H and FvW₂(CO)₆H₂ should provide information about the electronic properties of the Fv ligand, compared with Cp. The pK_a of $CpW(CO)_3H$ in acetonitrile is 16.1 at 25 °C, as determined by measurement of proton-transfer equilibria between metal hydrides and bases of known pK_{a} .^{25c}

The ambient-temperature ¹H NMR spectrum (acetonitrile- d_3) of near equimolar amounts of $FvW_2(CO)_6H_2$ and $[Et_4N^+][CpW(CO)_3^-]$ displayed extremely broad signals in the Cp/Fv and hydride regions of the spectrum, indicative of rapid intermolecular proton transfer reactions. When the sample was cooled to -45 °C, the signals sharpened and four distinct species were observed in solution. CpW(CO)₃H, CpW(CO)₃⁻, and FvW₂-(CO)₆H₂ were identified by comparison with authentic samples. The last compound displayed four Fv signals and a hydride resonance (see Experimental Section), consistent with a formulation as the hydrido anion FvW₂(CO)₆H⁻(7). The four complexes were present in a 12.8:1.2:1.0:13.0 equilibrium ratio. This information, combined with the known^{25c} pK_a of CpW(CO)₃H in acetonitrile, leads to an estimate of the pK_a of FvW₂-(CO)₆H₂ equal to 14.0, as described in the Experimental Section.



A solution of near equimolar amounts of FvW2(CO)6H2 and $[Et_4N^+]_2[FvW_2(CO)_6^{2-}]$ in acetonitrile- d_3 had an intense yellow color, quite different from the pale colors of either of the two complexes alone. The intense color is attributed to the hydrido anion 7, consistent with the transient yellow color observed during acidification of $1^{2-}(Na^+)_2$ with TFA. The broadened signals in the ambient-temperature ¹H NMR spectrum sharpened upon cooling to -45 °C and allowed the measurement of relative equilibrium concentrations of $FvW_2(CO)_6H_2$, $FvW_2(CO)_6H^-$, and $FvW_2(CO)_6^{2-}$. The equilibrium ratio was 1.3:22.8:1.0, the hydrido anion being by far the most dominant component. As outlined in the Experimental Section, these data lead to an estimate for the second pK_a of $FvW_2(CO)_6H_2$ equal to 16.6. It has been assumed that the pK_a 's of the species involved in the equilibria are the same at -45 °C and at 25 °C. Temperature dependent acidities are conceivable; however, relative

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Table 2. pK_a Values for $(\eta^5-C_5H_4R)W(CO)_3H$ Complexes in Acetonitrile- d_3 at -45 °C

compd	R in $(\eta^5$ -C ₅ H ₄ R)	pK _a
CpW(CO) ₃ H	Н	16.1 ^{24a}
FvW ₂ (CO) ₆ H ₂	$(\eta^{5}-C_{5}H_{4})W(CO)_{3}H$	14.0
FvW ₂ (CO) ₆ H ⁻	$(\eta^{5}-C_{5}H_{4})W(CO)_{3}^{-}$	16.6

 pK_a values of the three species most likely are rather unaffected by temperature changes. In support of this, the broadened hydride resonances allowed the relative amounts of Fv and Cp hydrides to be estimated at ambient temperature. The Fv to Cp ratio was identical, within experimental uncertainties, to that measured at -45 °C.

The pK_a data for CpW(CO)₃H, $FvW_2(CO)_6H_2$, and $FvW_2(CO)_6H^-$ are summarized in Table 2. The neutral dihydride is 2.1 p K_a units more acidic than CpW(CO)₃H, whereas the hydrido anion is 0.5 units less acidic than $CpW(CO)_{3}H$. HMO calculations predict that Fv^{2-} has a higher-lying HOMO than Cp⁻ and hence should be a better donor ligand.⁹ If no other factors were involved, this difference should lead to *less acidic* metal hydrides in Fv complexes relative to the Cp complexes. Our results clearly show that this is not the case. We believe that this originates in strong substituent effects that override the difference in π -electron donating abilities of the ligands. The compounds CpW(CO)₃H, FvW₂- $(CO)_6H_2$, and $FvW_2(CO)_6H^-$ may be viewed as substituted Cp derivatives $(\eta^5 - C_5 H_4 R) W(CO)_3 H$ with R = H, $(\eta^5-C_5H_4)W(CO)_3H$, and $(\eta^5-C_5H_4)W(CO)_3^-$. Compared to $R = H_1 (\eta^5 - C_5 H_4) W(CO)_3 H$ has an electron-withdrawing inductive effect.²⁶ As a consequence, the pK_a of $FvW_2(CO)_6H_2$ is 2.1 units lower than that of CpW- $(CO)_3H$. On the other hand, the electron-rich substituent $(\eta^5 - C_5 H_4) W(CO)_3^-$ acts as an electron donor relative to H. Consequently, $FvW_2(CO)_6H^-$ is less acidic than $CpW(CO)_{3}H$, but only by 0.5 pK_a units. Similar trends in pK_a values are found in organic chemistry. The pK_a of CH₃COOH is 4.76, whereas HOOCCH₂COOH has $pK_{a1} = 2.83$ and $pK_{a2} = 5.69$.^{27a} The 2.5 unit difference between pK_1 and pK_2 of **3** shows that there is extensive electronic communication between the two metal centers. Whether this communication is established through the π or the σ frameworks of the Fv ligand is not clear.

The estimates of the hydride acidities in $FvW_2(CO)_6H_2$ represent the first involving two consecutive acidity constants in a non-metal-metal-bonded transitionmetal polyhydride complex. Weberg and Norton^{25e} have determined the acidity difference (5.5 pK_a units) between the first and second proton removals from the interstitial hydride cluster $H_3Rh_{13}(CO)_{24}^{2-}$. The mononuclear complex $H_2Fe(CO)_4$ is the only other dihydride for which two successive acidity constants have been determined (aqueous pK_a values of 4.4 and 13.4).^{27b}

Thermal H₂ Elimination from $FvW_2(CO)_6H_2$ (3). As mentioned earlier, $FvM_2(CO)_6H_2$ species are obvious candidates for intermediates during the syntheses of FvM₂(CO)₆ complexes from dihydrofulvalene and carbonylmetal precursors. The failure to detect the dihydrides during the reactions raised the question whether these species were inherently kinetically less stable than the Cp analogues. From a thermochemical viewpoint, however, the $FvM_2CO)_6H_2$ dihydrides should be more stable with respect to H₂ elimination than their Cp counterparts, assuming that M-H bond dissociation energies do not change appreciably between the Cp and Fv systems.²⁸ Hydrogenation of the M-M bond in the Fv complexes should release the strain energy caused by the bending of the Fv ligand and render the hydrogenation more favorable than for the Cp dimers. Cp2- $Cr_2(CO)_6^{29a,b}$ and $Cp_2Mo_2(CO)_6$, but not $Cp_2W_2(CO)_6$, 29c undergo hydrogenation to yield the hydrides. We were thus surprised to find that no detectable amounts of $FvM_2(CO)_6H_2$ (M = Cr, Mo, W) were formed during treatment of the metal-metal-bonded species with H₂ under pressure. It is still possible that the Cr and Mo dihydrides form in low concentrations, since $FvCr_2(CO)_6$ and, more slowly, FvMo₂(CO)₆, hydrogenate 1,3-dienes to monoenes under H_2 pressure at 80 °C.⁷¹

Since we could not add H_2 to the M-M bond of 1, our attention was drawn to the reverse process, the elimination of H_2 from 3. When a solution of 3 was heated in diglyme at 160 °C for 2-4 days, 1 was quantitatively



produced. The liberation of H₂ was verified by mass spectrometry. When **3** was heated to 160 °C in dioxane d_8 , the volatiles contained only H₂; HD or D₂ was not detected. Thermolysis of **3**- d_2 in dioxane- d_8 gave 70– 80% D₂, 15–25% HD, and a small amount of H₂. This result pertained even with silylated and flame-dried glassware. We nevertheless suspect that the HD and H₂ originate from H/D exchange with traces of moisture, rather than from Fv ring protons. The latter presumably would lead to some decomposition, whereas the formation of FvW₂(CO)₆ was always quantitative.

In order to clarify whether the H₂ elimination occurred inter- or intramolecularly, a crossover experiment involving a mixture of **3** and **3**- d_2 was desired. However, considering the appreciable acidity of FvW₂-(CO)₆H₂, it was feared that rapid intermolecular H/D exchange would occur under the reaction conditions. This suspicion was verified by the following double labeling experiment. The ring-dimethylated analogue of FvW₂(CO)₆, ($\eta^5:\eta^5$ -(C₅H₃Me)₂)W₂(CO)₆ (Fv'W₂(CO)₆, **8**) was prepared by oxidative coupling of (methylcyclopentadienyl)sodium with I₂, followed by reaction with

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Figure 2. Schematic representation of the six possible isomers, not including enantiomers, of $(\eta^{5:}\eta^{5-}(C_{5}H_{3}Me)_{2})W_{2^{-}}(CO)_{6}$ (8), as viewed from above the Fv ring plane.

 $W(CO)_3(NCEt)_3$. The reaction gave 8 as a mixture of six possible stereoisomers, shown schematically in Figure 2. Eight separate methyl singlets were observed in the 300-MHz ¹H NMR spectrum of the mixture, as expected if all different methyl signals were resolved.

Na/Hg reduction of this mixture, followed by protonation with TFA, gave a mixture of the six isomeric dihydrides $Fv'W_2(CO)_6H_2$ (9). In the ¹H NMR spectrum of 9, the hydride signals from the mixture (δ -6.73 to -6.95) were fully separated from the hydride signal of 3 (δ -6.98).

Equimolar amounts of $3 \cdot d_2$ and 9 were dissolved in THF- d_8 at -75 °C. After 2 h at this temperature, only 5% of the total hydride signal intensity was due to 3 or $3 \cdot d$. H/D scrambling started when the sample was heated. At -40 °C, detectable changes took place within a 10-min period. Scrambling was complete at 0 °C. Clearly, under thermal H₂ elimination conditions at 160 °C, H/D exchange would be too fast to allow the use of a crossover experiment as a measure of the inter- vs intramolecularity of the H₂ extrusion.

The progress of the H_2 elimination from 3 was monitored by the appearance of the $\lambda = 548$ -nm (ϵ 740) absorption of product 1 in the UV-visible spectrum. The reaction rates were rather irreproducible, the time required for complete reaction being ca. 24-48 h. A 1-5-h induction period was needed before the reaction took off at a higher rate. The addition of $FvW_2(CO)_6$ had no effect on the initial reaction rate, ruling out an autocatalytic process. Addition of 20 mol % of the radical chain initiator AIBN or 330 mol % of the spin trap 9,10-dihydroanthracene (DHA) caused the reaction to proceed at a faster rate, primarily by reducing the induction period. Rate enhancements due to spin trap addition have been previously observed³⁰ and may be due to thermal cleavage of the C(10)-H bond in DHA. This would yield a stabilized 9-hydroanthracene radical and a hydrogen atom capable of initiating hydrogen atom abstraction from 3.

Our results point to a radical chain elimination of H_2 , rather than a concerted dinuclear elimination reaction. Theoretical work³¹ suggests that a concerted reaction with a planar, four-center transition state should be symmetry forbidden. Twisting of the M-H bonds relative to each other could remove this restriction, making the process kinetically more favorable. This does, however, not appear to be the case for FvW₂-(CO)₆H₂. One might argue that the presumed *anti* arrangement of the metal centers in **3** could contribute to its stability. However, in view of the facile carbene couplings discussed in a previous section and elsewhere,^{7e} the barrier to rotation around the central C-C bond must be low and should have no appreciable effect on the rate of H_2 elimination.

The above discussion has established that **3** is kinetically inert with respect to H_2 elimination on the time scale and at the temperature that is employed for the synthesis of **1** from dihydrofulvalene and W(CO)₃-(NCEt)₃. Under preparative conditions, however, significant quantities of ill-defined materials that may well initiate the extrusion of H_2 are present. Therefore, we still consider **3** to be a plausible intermediate for the generation of **1**.

Chemistry of Cationic Complexes Derived from FvW₂(CO)₆ and FvW₂(CO)₆H₂. Addition of 10 equiv of HBF4 Et2O to a slurry of FvW2(CO)6 in dry acetonitrile- d_3 gave a deep red solution. The ¹H NMR spectrum showed two Fv resonances at δ 5.65 and 5.91 and an upfield singlet at δ -21.16 (1 H). The singlet was surrounded by ¹⁸³W satellites ($J_{WH} = 36.3$ Hz), the intensity ratios being 1:6:1, as expected for a hydride bonded to two identical tungsten centers²³ (the predicted low-intensity $^{183}W_2$ satellites were not observed). The spectroscopic data unambiguously show that the compound is the bridging cationic hydride $FvW_2(CO)_6(\mu-H)^+$ (10), formed quantitatively by ¹H NMR spectroscopy. The related $[Cp_2W_2(CO)_6(\mu-H)]^+$ cation was formed during protonation of $Cp_2W_2(CO)_6$ in 98% H_2SO_4 and was characterized by means of its δ -24.8 hydride signal.³² We find that treatment of $Cp_2W_2(CO)_6$ with HBF_4 ·Et₂O in dry acetonitrile- d_3 does not produce the bridging hydride. The W-W bond in $FvW_2(CO)_6$ is



therefore significantly more basic than that of Cp_2W_2 -(CO)₆. Presumably, an extra driving force for protonation is provided by release of strain energy contained in 1 due to the bending of the Fv ligand. Treatment of 1 with HBF₄·Et₂O in dichloromethane provided 10(BF₄⁻) in 95% isolated yield. When dissolved in dry acetonitrile- d_3 , 10(BF₄⁻) slowly underwent deprotonation to give 1. When dissolved in dry THF or acetone, 10(BF₄⁻) quantitatively generated 1 within seconds, demonstrating the high acidity of the bridging hydride.

When a solution of $10(BF_4^-)$ and excess $HBF_4 \cdot Et_2O$ (to inhibit deprotonation) was left in acetonitrile- d_3 at ambient temperature for 24 h, ca. 50% conversion to a new compound with four Fv signals at δ 5.71, 5.72, 6.08, and 6.33 (2 H each), and a terminal hydride at δ -6.95

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(1 H) with ¹⁸³W atellites ($J_{WH} = 37.5$ Hz, intensity ratio 1:11:1), occurred. We believe this species to be the cationic monohydride $FvW_2(CO)_6(H)(NCCD_3)^+$ (11) in which the hydride is terminally bonded to a neutral W center and the cationic W center is ligated by a solvent molecule. The amount of 11 increased over the next few days and eventually no 10 was left. Simultaneously, in a much slower reaction, 11 decomposed to give mostly unidentifiable products. The only product that could be identified by comparison with an authentic sample was the dication $FvW_2(CO)_6(NCCD_3)_2^{2+}$ (12-d₆, vide infra). Analysis of the volatiles by mass spectrometry revealed the presence of H_2 . The formation of 11 from 10 is formally a displacement of a W-H bond from a cationic W center by acetonitrile. The time needed for this reaction shows that the W-H bond in a kinetic sense is a relatively good ligand.

Double hydride abstraction from FvW₂(CO)₆H₂ occurred instantaneously when 2 equiv of $Ph_3C^+PF_6^-$ was added to an acetonitrile solution of the dihydride and yielded $[FvW_2(CO)_6(NCMe)_2]^{2+}(PF_6^{-})_2 (12(PF_6^{-})_2)$ quantitatively. This product was also accessible by treatment of bridging hydride 10 with 1 equiv of $Ph_3C^+PF_6^-$, but this reaction needed 10 h to go to completion. The removal of the hydride ligand of **10**, presumably with a significant H⁺ character, as H⁻ must require significant reorganization of the electronic structure when passing through the transition state for the hydride abstraction. It may be that this electronic redistribution at least in part is the source of the kinetic barrier of the reaction. Electrostatic repulsions between substrate and reagent may also contribute to the barrier. Kinetic data are not available, but it is conceivable that the reaction between 10 and $Ph_3C^+PF_6^-$ in part involves slow formation of 11, which has a more reactive terminal hydride ligand at a neutral metal center, as an intermediate from which the hydride is ultimately abstracted.

The selectivity for single vs double hydride abstraction from 3 was probed by treatment of $FvW_2(CO)_6H_2$ with ca. 1 equiv of $Ph_3C^+PF_6^-$ in acetonitrile- d_3 . It was anticipated that the first hydride abstraction would give a cationic monohydride which was somewhat deactivated with respect to a second hydride abstraction because of the positive charge left in the molecule after the first hydride removal. However, 30 min after mixing in acetonitrile- d_3 , the ¹H NMR spectrum showed a mixture of 1 (17%), unreacted 3 (12%), 10 (8%), 11 (43%), and 12 (20%). After 2 h. 10 had been completely converted to 1 by deprotonation. Most likely, all 1 that was present was produced this way, so that the initial yield of 10 should be 25%. From these data, it is apparent that 10 and 11 are generated from 3 at roughly the same rates, presumably via a common intermediate $FvW_2(CO)_6H^+$ (13) possessing a formally coordinatively unsaturated cationic center. Saturation may be achieved by coordinating either the neighboring W-H bond or a solvent molecule (Scheme 2). It has been already mentioned that conversion of **10** to **11** is a slow process (days) and that hydride abstraction from 10 is also slow (hours). Since the dication 12 formed instantaneously and quantitatively from 3 and 2 equiv of $Ph_3C^+PF_6^-$, it cannot be formed from 10 in this reaction. Because 11 is formed at roughly the same rate as 10 when 3 is treated with 1 equiv of $Ph_3C^+PF_6^-$, it appears that the quantitative formation of 12 cannot



be explained with 11 as the only intermediate. There is a need for an intermediate which is capable of reaction with Ph_3C^+ before 10 is produced subsequent to the first hydride abstraction. This suggests that coordinatively unsaturated 13 undergoes direct reaction with Ph_3C^+ prior to achieving saturation by solvent coordination. As a consequence, stabilization of 13 by solvent coordination or intramolecular W-H coordination must be a slower process than the intermolecular reaction of 13 with Ph_3C^+ . It is possible that the $PF_6^$ counterion acts as a weak ligand, providing temporary saturation of 13, thereby blocking the approach of the W-H bond or solvent molecule. PF_6^- and other weakly coordinating anions are capable of bonding to strongly Lewis acidic metal centers.³² Reaction pathways that are in agreement with these observations are summarized in Scheme 2, with relative rates given in a qualitative sense. The production of 10 in this reaction mimics the generation of $[CpW(CO)_3]_2(\mu-H)^+$ from CpW-(CO)₃FBF₃ and CpW(CO)₃H.³⁴

Treatment of $FvW_2(CO)_6H_2$ with 5 equiv of $HBF_4\cdot Et_2O$ in dry acetonitrile- d_3 caused no immediate reaction. However, heating at 65 °C slowly yielded a red solution. By ¹H NMR spectroscopy, **3** slowly disappeared over a period of 10 h. Significant quantities of **11** and **12** were present in the reaction mixture (¹H NMR). In addition, unresolvable multiplets were present at δ 5.6–6.3, in the region expected for cationic Fv species, as well as a sharp singlet at δ –3.56, twice as intense as the hydride signal due to **11** at δ –6.95. No W–H coupling was apparent in the δ –3.56 singlet. This signal may be due to species containing an Fv-bonded W(CO)₃H₂⁺

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Figure 3. Schematic representation of the four different isomers of 14 (not including enantiomers).

moiety (protonation of CpW(CO)₃H in BF₃·H₂O yields CpW(CO)₃H₂⁺,³² the ¹H NMR spectrum of which displayed a broad singlet at δ -1.9). Nonclassical dihydrogen complexes should also be considered as viable sources of the δ -1.9 and -3.56 signals.^{35,36} Hydrogen gas was slowly generated in this reaction.

Phosphine Substitution Reactions of FvW₂-(CO)₆H₂. The M-M-bonded FvM₂(CO)₆ species (M = Mo,^{7e} W (this work)) are less prone to undergo thermal or photochemical substitution reactions by phosphines than are their Cp₂M₂(CO)₆ counterparts.³⁷ Thus, no substitution products were isolated when 1 was treated with PPh₃, Ph₂PCH₂PPh₂, or Ph₂CH₂CH₂PPh₂ under thermal or photochemical conditions. On the other hand, the dihydride **3** undergoes facile substitution of phosphines for CO in analogy with CpM(CO)₃H (M = Mo, W).³⁸

Exposure of an ether solution of **3** to PMe₃ caused rapid precipitation of $FvW_2(CO)_4(PMe_3)_2H_2$ (14) as a yellow solid in quantitative yield. The IR spectrum (THF) showed two bands of equal intensities at 1841 and



 $PR_3 = PMe_3$, PMe_2Ph , $P(OMe)_3$

1922 cm⁻¹, indicative of a near 1:1 mixture of *cis* and *trans* configurations at the metal centers.^{38a} The ambient-temperature ¹H NMR spectrum exhibited broad signals, indicative of fluxional processes. Four different isomers (not including enantiomers) are possible for 14, depicted schematically in Figure 3. A variable-temperature ¹H NMR study was undertaken to have a closer look at the dynamics of the *cis/trans* interconversion.

At -30 °C, the hydride region showed a doublet at δ $-7.28 (J_{\rm PH} = 23.9 \, \text{Hz})$ which must be due to overlapping signals of the trans, trans isomer and the trans half of the cis,trans species, based on the magnitude of the coupling constant.^{38d} Two partially resolved doublets, both with $J_{\rm PH} = 68.9$ Hz, were centered at $\delta -7.73$. These must be due to the two cis, cis complexes and the cis half of the cis,trans isomer. The overall cis:trans ratio was 61:39. In the Fv region of the spectrum, the stereoisomers could be distinguished somewhat better. At δ 5.10 there was a broad signal attributed to the β -hydrogens in the *trans,trans* compound and the *trans* half of the *cis,trans* analogue, while a signal at δ 5.29 was due to the β -hydrogens of the two *cis*, *cis* species and the cis half of the cis, trans complex. (The high-field signals of Fv complexes without metal-metal bonds are believed to be due to the β -protons, based on ¹H-¹³C NOE experiments performed on a number of compounds⁷ⁱ). The *cis:trans* ratio obtained from these signals was 60:40. A multiplet due to the α -protons in the *trans,trans* isomer was located at δ 5.51, and at δ 5.56 there was a multiplet due to the α -hydrogens in the trans half of the cis, trans complex. Again, a 60:40 cis:trans ratio was found. Finally, at δ 5.71 there was a multiplet arising from the α -hydrogens in the *cis* half of the *cis.trans* species, and at δ 5.76 the α -protons in the two cis, cis complexes gave rise to a multiplet. The ³¹P{¹H} NMR spectrum at -30 °C showed two singlets at δ -12.3 (cis; J_{WH} = 253 Hz) and -14.7 (trans; J_{WH} = 277 Hz).

Heating of the sample eventually led to coalescence in both the hydride and Fv regions of the ¹H NMR spectrum. At 85 °C, the hydride signals had sharpened enough to show a doublet $(J_{PH} = 51 \text{ Hz})$. This coupling is a weighted average of the *cis* and *trans* couplings, and a cis:trans ratio of 59:41 may be calculated. The coalescence temperatures T_c and the limiting lowtemperature peak separations $\Delta \nu$ give an approximate estimate of the activation energy for the isomerization, using the well-known relationships³⁹ for a two-site exchange between equally populated sites (the 60:40 ratio actually present is close enough that errors should be small). This way, we calculate $\Delta G^{\dagger} = 14.9 \pm 0.4$ kcal/ mol for the isomerization of 14 (independent calculations were made on the basis of the different $T_{\rm c}$ s that were measured for the hydride and Fv regions of the spectra). The dimolybdenum analogue FvMo₂(CO)₄- $(PMe_3)_2H_2$ (15) was also prepared and the NMR data gave $\Delta G^{\ddagger} = 13.7 \pm 0.3$ kcal/mol. This value is quite similar to those measured for CpMo(CO)₂LH systems,^{38d} ranging from 11.3 to 13.6 kcal/mol.

A number of other phosphine derivatives of 3 have been prepared. Deprotonation of 14 with 2 equiv of *n*-BuLi followed by dialkylation with MeI, PhCH₂Br, and MeOCH₂Cl gave the corresponding dialkyl com-



plexes, and treatment of 14 with I_2 yielded the diiodide.

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Table 3. Equilibrium Cis:Trans Ratios for Selected Fv and
Cp Complexes^a

FvW ₂ (CO) ₄ L ₂ X ₂		CpMo(CO) ₂ LX ^b			
L	X	cis:trans ratio	L	х	cis:trans ratio
PMe ₃	н	60:40	PPh ₃	н	63:37
PMe ₃	Me	10:90	PPh ₃	Me	7:93
PMe ₃	CH_2Ph	<5:95	PPh ₃	CH_2Ph	<2:98
PMe ₃	CH ₂ OCH ₃	<5:95		-	
PMe ₃	I	75:25	PMe ₂ Ph	I	74:26
PMe ₂ Ph	н	50:50	PMe ₂ Ph	Н	48:52
P(OMe) ₃	Н	92:8	$P(OMe)_3$	н	84:16

^a Measured by ¹H NMR spectroscopy at 20 °C. ^b From ref 37d.

While formation of 14 from 3 and PMe₃ was complete in less than 5 min at ambient temperature, reaction of **3** with PMe₂Ph to give $FvW_2(CO)_4(PMe_2Ph)_2H_2$ required 20-30 min. PPh₃ reacted very slowly even at 80 °C, and the product underwent decomposition under the reaction conditions. The reaction of 3 with $P(OMe)_3$ yielded pale yellow $FvW_2(CO)_4(P(OMe)_3)_2H_2$ and required reflux overnight in THF for the reaction to go to completion. Spectroscopic data for these new compounds are included in the Experimental Section. Table 3 lists the cis:trans ratios of these species. For comparison, data for a number of CpMo(CO)₂LH compounds are included. The *cis:trans* interconversion was rapid on the NMR time scale only for the hydrides. Although direct comparisons cannot be made due to differences in metal and ligand system, it is clear that general trends are similar in the Cp and Fv series of complexes.

Reactions of $FvMo_2(CO)_6$ and $FvW_2(CO)_6$ with Strongly Donating Phosphines: Syntheses of Dinuclear Organometallic Zwitterions. Depending on reaction conditions and the electronic and steric properties of PR₃, Cp₂Mo₂(CO)₆ may yield phosphine substituted Mo–Mo-bonded dimers $Cp_2Mo_2(CO)_{6-x}(PR_3)_x$ (x = 1, 2), $^{40a,c-g}$ or disproportionation products [CpMo(CO)₂- $(PR_3)_2^+][CpMo(CO)_3^-].^{40b,41}$ The mechanism of the latter process has been studied in detail by Tyler and coworkers^{37,41} and takes place by a photochemicallyinduced radical chain process involving 17- and 19electron^{37,42} intermediates. Disproportionation is favored over phosphine substituted dimers when electron-rich, sterically undemanding, and/or chelating phosphines are used. Contrasting with this behavior, treatment of 1 or 2^{7e} with PPh₃, Ph₂PCH₂PPh₂, or Ph₂PCH₂CH₂PPh₂ under thermal or photochemical conditions gave no

isolable products. However, interesting reactions occurred when strongly electron-donating phosphines were used.

Treatment of THF solutions of 1 and 2 with PMe₃ or $Me_2PCH_2PMe_2$ (dmpm) caused the precipitation of brown, crystalline, analytically pure products of composition $FvM_2(CO)_5L_2$ (16 M = Mo, L = PMe_3; 17 M =



Mo, $L_2 = dmpm$; **18** M = W, L = PMe₃; **19** M = W, $L_2 = dmpm$) in good yields. The products were poorly (L = PMe₃) or not at all ($L_2 = dmpm$) soluble in THF, were soluble in acetonitrile and DMSO, and decomposed in acetone. NMR and IR spectroscopic data for these compounds are listed in Table 4.

The presence of four Fv resonances in the ¹H NMR spectra showed that the products were less symmetrical than the substrates. Decoupling experiments showed that each signal was coupled to only one other signal, establishing that both phosphines were attached to the same metal. The IR spectra of the materials closely resembled superimposed spectra of $CpM(CO)_3^-$ (1770-1790 and $1880-1915 \text{ cm}^{-1}$) and $\text{CpM}(\text{CO})_2\text{L}_2^+$ (1880-1900 and $1960-1980 \text{ cm}^{-1}$; overlap of the high-energy band of the anion with the low-energy band of the cation was in some cases observed. The close match of the IR $v_{\rm CO}$ bands of 16 with those of $[CpMo(CO)_3^-][CpMo (CO)_2(PMe_3)_2^+$] prepared from $Cp_2Mo_2(CO)_6$ and PMe_3 (1956, 1894, 1874, 1783 cm⁻¹) is noteworthy.⁴³ In fact, the $v_{\rm CO}$ data for the two halves of the molecules indicate very little electronic communication between them, contrasting with the pK_a work described earlier. In the cases where no overlap occurred, the $CpM(CO)_2L_2^+$ half of the molecule displayed two CO absorptions with intensity ratios being consistent with the cis geometry^{38a} when $L_2 = dmpm$ (high-energy band more intense) and with the *trans* geometry when $L = PMe_3$ (low-energy band more intense). The spectroscopic data suggest that products 16-19 have the zwitterionic structures shown.

The novelty of these zwitterionic species warranted an X-ray structural determination. X-ray quality crystals were found in the crude reaction mixture containing **16**. An ORTEP drawing of the structure of **18** is shown in Figure 4. Bond lengths, bond angles, and torsional angles are listed in Table 5. The molecule consists of two Mo centers bonded to an essentially planar Fv ligand in an *anti* manner. Both rings are planar, and the dihedral angle between the two ring planes is 5°. The rings are separated by a distance C(5)-C(6) = 1.455Å, to be compared with a separation of 1.442 Å in FvMo₂- $(CO)_6$.^{7e} The anionic half of the molecule closely resembles $CpMo(CO)_3^-$ (as the Bu₄N⁺ salt^{15b}). Some

⁽³⁹⁾ $k_c = \pi \Delta \nu / \sqrt{2}$ and $\Delta G^{\ddagger} = 2.3RT_c$ (10.32 + log(T_c/k_c)) where k_c is the rate constant for interconversion at T_c : Lambet, J. B.; Shurvell, H. F.; Verbit, L.; Cooks, R. G.; Stout, G. H. Organic Structure Analysis; Macmillan: New York, 1976; p 116.

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IR		¹ H NM		
compd	$\nu_{\rm CO},{\rm cm}^{-1}$	Fv	other	³¹ P{ ¹ H} NMR, δ^a
FvMo(CO) ₅ (PMe ₃) ₂ (16)	1955, 1906, 1871, 1795 ^b	5.06, 5.22, 5.50, 5.53	1.64	19.2
$FvMo(CO)_5(dmpm)$ (17)	1983, 1904, 1788 ^c	5.04, 5.41, 5.49, 5.69	1.68, 1.69, 3.65	-23.4
FvW(CO) ₅ (PMe ₃) ₂ (18)	1953, 1898, 1868, 1785 ^c	5.08, 5.33, 5.48, 5.60	1.76	-16.7
FvW(CO) ₅ (dmpm) (19)	1957, 1889, 1775 ^d	4.96, 5.51, 5.79, 5.90	1.79, 1.89, 4.18, 4.45	-62.6

^a Acetonitrile-d₃ except for 19: DMSO-d₆. ^b THF. ^c Acetonitrile. ^d DMSO.



Figure 4. ORTEP drawing of the structure of FvMo₂(CO)₅-(dmpm) (18), determined by X-ray crystallography.

parameters to be compared are $(CpMo(CO)_3^-)$ data in parentheses) Mo-C(ring) average 2.391 (2.371) Å, Mo-CO average 1.927 (1.909) Å, and C-O average 1.170 (1.176) Å. A comparison of bond lengths in the anionic and cationic halves of 18 reveals that the average Mo(1)(cation)-CO distance is 0.048 Å longer than the Mo(2)(anion)-CO distance, in accord with stabilization of the negative charge by back-bonding into the C-O π^* orbitals. The Mo(2)-Cp separation is greater than that of Mo(1)-Cp by 0.069 Å, indicative of a weakening of the bond between an electrondonating Cp and the negatively charged Mo(2). The ORTEP drawing shows that the dmpm ligand is twisted relative to the plane that bisects the two Fv rings. It is not clear whether the twist is electronic in origin or if it is imposed by crystal packing forces.

Even though conjugated, the molecules prefer the charge-separated structure, as indicated by IR data and reactivity patterns (vide infra), rather than the alternative $M(\eta^{6}$ -fulvene)- $M(\eta^{4}$ -diene) arrangement which is also in accord with the 18-electron rule. Complexes of

Bond Lengths (Å)			
Mo(1) - P(1)	2.466(1)	C(13)-O(3)	1.181(5)
Mo(1) - P(2)	2.474(1)	C(14)-O(4)	1.179(4)
Mo(1) - C(11)	1.974(4)	C(15)-O(5)	1.151(4)
Mo(1)-C(12)	1.975(4)	C(1) - C(2)	1.422(5)
$Mo(1)-Cp(1)^a$	1.999	C(1) - C(5)	1.403(5)
Mo(2) - C(13)	1.923(4)	C(2) - C(3)	1.398(5)
Mo(2) - C(14)	1.924(4)	C(3) - C(4)	1.388(5)
Mo(2) - C(15)	1.935(4)	C(4) - C(5)	1.401(5)
$Mo(2)-Cp(2)^a$	2:068	C(5)-C(6)	1.455(5)
Mo(1) - C(1)	2.307(3)	C(6) - C(7)	1.429(5)
Mo(1) - C(2)	2.300(3)	C(7)-C(8)	1.404(5)
Mo(1) - C(3)	2.325(3)	C(8)-C(9)	1.392(5)
Mo(1)-C(4)	2.343(3)	C(9)-C(10)	1.409(5)
Mo(1) - C(5)	2.365(3)	C(10)-C(6)	1.425(5)
Mo(2) - C(6)	2.391(3)	P(1) - C(16)	1.803(3)
Mo(2)-C(7)	2.397(3)	P(1) - C(17)	1.813(3)
Mo(2) - C(8)	2.386(3)	P(1) - C(18)	1.800(3)
Mo(2) - C(9)	2.395(3)	P(2) - C(16)	1.821(4)
Mo(2) - C(10)	2.388(3)	P(2)-C(19)	1.799(4)
C(11)-O(1)	1.138(4)	P(2)-C(20)	1.802(4)
C(12) - O(2)	1.143(4)		
	Dond Ana	las (dag)	
.	Bollu Alig	ites (deg)	
Cp(1) - Mo(1) - P(1)	120.50	Mo(1) - P(2) - C(16)	97.19(11
Cp(1) - Mo(1) - P(2)	120.12	Mo(1) - P(2) - C(19)	120.65(13
Cp(1) - Mo(1) - C(11)	120.26	Mo(1) - P(2) - C(20)	119.60(14
Cp(1)-Mo(1)-C(12)	118.86	P(1) - C(16) - P(2)	95.25(15
P(1) - Mo(1) - P(2)	65.64(3)	C(16) - P(1) - C(17)	105.58(16
P(1) - Mo(1) - C(11)	79.31(10)	C(16) - P(1) - C(18)	108.73(20
P(1) - Mo(1) - C(12)	120.08(10)	C(17) - P(1) - C(18)	103.16(19
P(2)-Mo(1)-C(11)	119.28(10)	C(16) - P(2) - C(19)	106.24(17
P(2) - Mo(1) - C(12)	78.85(10)	C(16) - P(2) - C(20)	109.55(17
C(11) - Mo(1) - C(12)	78.35(15)	C(19) - P(2) - C(20)	102.59(19
Cp(2)-Mo(2)-C(13)	131.40	C(5) - C(1) - C(2)	109.0(3)
Cp(2)-Mo(2)-C(14)	121.98	C(1) - C(2) - C(3)	106.9(3)
Cp(2)-Mo(2)-C(15)	127.81	C(2) - C(3) - C(4)	108.1(3)
C(13)-Mo(2)-C(14)	87.37(14)	C(3) - C(4) - C(5)	109.9(3)
C(13)-Mo(2)-C(15)	83.94(16)	C(1) - C(5) - C(4)	106.2(3)
C(14)-Mo(2)-C(15)	91.19(16)	C(1) - C(5) - C(6)	127.2(3)
Mo(1) - C(11) - O(1)	178.2(4)	C(4) - C(5) - C(6)	126.6(3)
Mo(1) - C(12) - O(2)	177.1(3)	C(5) - C(6) - C(7)	126.4(3)
Mo(2) - C(13) - O(3)	177.4(3)	C(5) - C(6) - C(10)	126.3(3)
Mo(2) - C(14) - O(4)	175.5(3)	C(7) - C(6) - C(10)	107.2(3)
Mo(2) - C(15) - O(5)	179.1(4)	C(6) - C(7) - C(8)	107.4(3)
Mo(1) - P(1) - C(16)	97.94(11)	C(7) - C(8) - C(9)	109.2(3)

Table 5. Bond Lengths and Bond Angles for FvMo₂(CO)₅(dmpm) (18)

 a Cp(1) and Cp(2) are the centroids of the cyclopentadiene rings of the fulvalene.

C(8) - C(9) - C(10)

C(9) - C(10) - C(6)

108.3(3)

107.9(3)

121.28(12)

118.88(14)

Mo(1)-P(1)-C(17)

Mo(1) - P(1) - C(18)

the type $(\eta^{6}$ -fulvene)M(CO)₃⁴⁴ and $(\eta^{4}$ -diene)M(CO)₂-(PR₃)₂⁴⁵ (M = Cr, Mo, W) have been reported. The chromium fulvene complexes have been discussed in terms of η^{6} - and η^{5} -bonded limiting structures.^{44b} The relative importance of these has been estimated from

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the degree of bending of the exocyclic double bond toward the metal. The bend angle α (varying between



6 and 35° for M = Cr) decreased with the increasing ability of the R group to stabilize a positive charge. If we consider the zwitterions 16–19, the exocyclic (η^4 diene) $M(CO)_2L_2$ substituent on the fulvene unit is clearly capable of stabilizing a positive charge by virtue of the two good phosphine donors. Consequently, in the ground state the molecules assume the zwitterionic coordination mode rather than the fulvene-diene alternative. The alternatives can conceptually be viewed as resonance structures or as rapidly equilibrating species, depending on whether or not atomic positions are fixed. The possible contribution (in resonance terms) or availability (when viewed as rapidly equilibrating structures) of a fulvene-diene structure is of special importance for the discussion of decomplexation reactions to be described later.

Treatment of $FvMo_2(CO)_6$ with slightly more than 2 equiv of PMe₃ in acetonitrile- d_3 at ambient temperature led to the exclusive formation of 16 as soon as the substrate dissolved. No intermediates were detected by ¹H NMR spectroscopy. The reaction proceeded even in the dark. In THF- d_8 , the reaction was slower and less specific; several low-intensity resonances were seen when the reaction was monitored by ${}^{31}P{}^{1}H$ NMR spectroscopy. Significantly, none of these could be attributed to the Mo-Mo-bonded complexes FvMo₂-(CO)₅(PMe₃) and FvMo₂(CO)₄(PMe₃)₂, both of which have been independently prepared (vide infra). Furthermore, neither of these Mo-Mo-bonded species reacted with PMe₃ in THF or acetonitrile, even after 3 days at 50 °C, establishing that they were not intermediates in the formation of 16 from 2. These results contrast with the observation of mono- and disubstituted dimers during phosphine induced disproportionation of $Cp_2Mo_2(CO)_6^{41b}$ and suggest that a different mechanism is operational in the fulvalene systems. It is conceivable that direct nucleophilic attack by the phosphine causes heterolytic cleavage of the Mo-Mo bond to generate a zwitterionic intermediate, as shown in Scheme 3. The relief of strain contained in 1 and 2 because of the bending of the Fv ligand should enhance the reactivity toward nucleophiles. The intermediate may then undergo substitution by the second phosphine. The dependence of the reaction rate on the solvent may reflect improved stabilization by a polar solvent of a partially charge-separated transition state, leading to the dipolar intermediate.



Reactions of Zwitterions with Electrophiles and Nucleophiles. The dipolar structure of zwitterions 16-19 was expected to induce dual reactivity: The anionic half should show nucleophilic behavior, whereas the cationic center ought to react as an electrophile. Such dual reactivity was indeed observed and provided the entry to a number of new and interesting compounds, as will be demonstrated in the following.

In acetonitrile- d_3 , 17 reacted with HBF₄·Et₂O, CF₃-SO₃Me, and I₂ to give [FvMo₂(CO)₅(dmpm)H]⁺, [FvMo₂-(CO)₅(dmpm)Me]⁺, and [FvMo₂(CO)₅(dmpm)I]⁺, respec-



tively, in high yields (¹H NMR). AgPF₆ (2 equiv) caused the formation of $[FvMo_2(CO)_5(dmpm)(NCCD_3)]^{2+}$. These products were not isolated, but characterized by their IR, ¹H, and ³¹P $\{^{1}H\}$ NMR spectra, details of which are given in the Experimental Section. Treatment of 16 with excess MeI in THF gave the salt [FvMo₂(CO)₅- $(PMe_3)_2Me^+]I^-$ (20), which was isolated in a quantitative yield. The IR v_{CO} data for the products demonstrated that the CO stretching frequencies for the unreacted cationic half remained virtually unchanged at ca. 1910 and 1990 cm^{-1} , whereas the formal 2-electron oxidation of the anion from Mo(0) to Mo(II) caused significant changes from 1788 and 1904 cm⁻¹ in 17 to 1932–1965 and 2017-2075 cm⁻¹ in the oxidation products. The ¹H NMR spectra exhibited downfield shifts consistent with an overall oxidation.

Numerous cationic metal carbonyl complexes undergo reduction of coordinated CO upon exposure to metal hydrides in reactions that bear relevance to the heterogeneous or homogeneous Fischer-Tropsch reductive polymerization of CO to hydrocarbons and other products.⁴⁶ Stepwise reduction of coordinated CO to coordinated methyl via formyl and hydroxymethyl species is a well documented process.^{46d,47} FvMo₂(CO)₅(PMe₃)₂ was unreactive toward NaBH₄ (as anticipated due to the reported inertness 47a of $CpMo(CO)_2(PPh_3)_2{}^+$ toward NaBH₄) but underwent a smooth reaction with LiAlH₄ in THF- d_8 at 0 °C to yield the anion $[FvMo_2(CO)_4-$ (PMe₃)₂Me]⁻ in almost quantitative yield (¹H NMR). The ¹H NMR spectrum of the anion showed a methyl triplet at $\delta - 0.76 \ (J = 12.6 \text{ Hz})$, indicative of *trans* geometry at the methyl substituted Mo center. An isolable,

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neutral complex was obtained by CO reduction at the cationic center of **20** (Scheme 4) with LiAlH₄. The product, $FvMo_2(CO)_4(PMe_3)_2Me_2$ (**21**), was isolated as red crystals in 84% yield. The ¹H NMR spectrum (acetone- d_6) showed four Fv signals at δ 4.77, 5.29, 5.37, and 5.62, a PMe₃ doublet at δ 1.32, and resonances from two different metal-bonded methyl groups at δ 0.19 (s) and -0.71 (t, J = 12.5 Hz). The IR spectrum displayed two ν_{CO} bands at 2010 and 1927 cm⁻¹, characteristic of a CpM(CO)₃R group, as well as one at 1778 cm⁻¹ due to the CpMo(CO)L₂Me moiety. Even though no intermediates were detected in these reactions, it is likely that the reduction of CO to methyl proceeds via formyl and hydroxymethyl species.^{47a}

Treatment of zwitterion 16 with excess Na/Hg in THF led to a two-electron reduction and loss of PMe₃ at the cationic half, resulting in the dianion $[FvMo_2(CO)_5-(PMe_3)]^{2-}$ which displayed four Fv signals at δ 4.61, 4.79, 5.02, and 5.22 and a PMe₃ doublet at δ 1.26. The dianion underwent methylation with MeI (Scheme 5) to give dimethyl complex FvMo₂(CO)₅(PMe₃)Me₂ (22) in 78% yield, and protonation of the dianion with TFA generated the dihydride FvMo₂(CO)₅(PMe₃)H₂ (23) which was not isolated, but characterized by its ambienttemperature ¹H NMR spectrum. These compounds, as expected, existed as *cis* and *trans* isomers at the phosphine substituted metal center. Spectroscopic data are given in the Experimental Section.

Synthesis and Characterization of Phosphine Substituted Metal-Metal-Bonded Fulvalene Complexes. In analogy with the behavior of $FvW_2(CO)_6H_2$, irradiation (300 nm) of the dihydrides $FvMo_2(CO)_5$ -(PMe₃)H₂ (23) and $FvMo_2(CO)_4(PMe_3)_2H_2$ (17) led to H₂ elimination and gave the Mo-Mo-bonded complexes $FvMo_2(CO)_5(PMe_3)$ (24) and $FvMo_2(CO)_4(PMe_3)_2$ (25) in



high yields. Both compounds had an intense purple color, diagnostic of the Mo-Mo-bonded structure. The ¹H NMR spectrum of **24** displayed four Fv resonances at δ 4.48, 4.50, 5.14, and 5.33, in addition to a PMe₃ doublet at δ 1.77, establishing C_s symmetry with the PMe₃ group located in the plane bisecting the Fv ligand. The ¹H NMR spectrum of **25** was simpler, with two Fv resonances at δ 4.20 and 4.94, and a PMe₃ doublet at δ 1.67, in accord with C_{2v} symmetry. Compound **24** was also available in good yield by photolysis of dimethyl complex FvMo₂(CO)₄(PMe₃)₂Me₂. Photolysis of zwitterion **16** yielded a 5:95 mixture (¹H NMR) of **24** and **25**, resulting from net loss of PMe₃ and CO, respectively.

With the three Mo–Mo-bonded complexes 2, 24, and 25 in hand, it was of interest to obtain data pertaining to the effect of ligand substitution on the properties of the metal-metal bond. Structural data on the effect of such substitutions in dimers $Cp_2M_2(CO)_6$ (M = Cr, Mo, W) are not very abundant. The symmetrically disubstituted $Cp_2Cr_2(CO)_4(P(OMe)_3)_2$ has a Cr-Cr distance of 3.343 Å,^{29b} 0.062 Å greater than in $Cp_2Cr_2(CO)_6$. The substituted Cr dimer was largely dissociated to $CpCr(CO)_2P(OMe)_3$ radicals in solution, and $CpCr(CO)_2$ -

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Table 6. Electronic Spectral Data for $FvMo_2(CO)_{6-x}(PMe_3)_x$ (x = 0-2) in THF

	$\lambda_{\text{max}}, \text{nm} (\epsilon, M^{-1} \text{ cm}^{-1}) \lambda_{\text{max}}, \text{nm} (\epsilon, M^{-1} \text{ cm}^{-1})$			
compd	$\sigma \rightarrow \sigma^*$	$d\pi \rightarrow \sigma^*$		
FvMo ₂ (CO) ₆ (3)	375 (17 190)	554 (616)		
FvMo ₂ (CO) ₅ (PMe ₃) (24)	366 (15 280)	566 (642)		
FvMo ₂ (CO) ₄ (PMe ₃) ₂ (25)	360 (18 500)	558 (1115)		

(PPh₃) remains monomeric even in the solid state.⁴⁸ Levenson and Gray⁴⁹ suggested that $d\pi - d\pi$ repulsive interactions between the metals would increase with the introduction of donor ligands. Such an electronic effect would lead to a further weakening of the metal-metal bond, enhancing the repulsive steric interactions. Attempts have been made at correlating metal-metal bond strengths in $M_2(CO)_{10}$ derivatives with their UVvisible absorption spectra.⁵⁰ It has been argued that if these near-UV bands are correctly described as the proposed $d\sigma \rightarrow d\sigma^*$ excitations, a red shift should indicate a weaker bond. Whereas such a correlation appears to hold upon successive substitutions with one or two^{51a} PPh₃, or with two or three P(OEt)₃^{51b} ligands in $Mn_2(CO)_{10}$, the trend is reversed in the electronic spectra of corresponding rhenium dimers^{51a} and in several other cases. It was suggested^{52a} that the lack of correlation may be due to the mixing of ligand-tometal charge transfer excitations with the $d\sigma \rightarrow d\sigma^*$ transition. The general validity of the method has been recently questioned.^{52b}

The absorption maxima in the electronic spectra of $FvMo_2(CO)_{6-x}(PMe_3)_x$ (x = 0-2) are listed in Table 6. A blue shift is observed for the $d\sigma \rightarrow d\sigma^*$ transition upon successive substitutions of CO by PMe₃. If the $\lambda_{max}(d\sigma \rightarrow d\sigma^*)$ vs bond strength relationship was to hold, then the data in Table 6 indicate that the introduction of PMe₃ leads to stronger, and presumably shorter, Mo-Mo bonds. This effect was contrary to the expectations. An X-ray structural investigation of **25** was undertaken to clarify the situation.

ORTEP drawings of the structure determined from the diffraction study⁵³ are shown in Figure 5. Intramolecular bond distances, dihedral angles and torsional angles have been previously reported.53 The Mo-Mo bond distance is 3.220 Å. The twist angle between the two rings (around the C(5)-C(6) axis) is 24°, and the dihedral angle between the two ring planes is 27°. Thus, although each ring is planar, the Fv ligand as a whole is severely distorted from planarity by twisting and bending. The C(5)-C(6) bond twist causes the CO ligands on Mo(1) to be in a staggered position relative to those on Mo(2), whereas in $FvMo_2(CO)_6$ they were eclipsed.^{7d} The PMe₃ methyl groups are oriented so as to minimize steric interactions by pointing one methyl group into a staggered position between the two CO ligands at the same metal atom. The most interesting finding in the crystallographic study is that the intro-



Figure 5. ORTEP drawings of the structure of FvM_{0_2} -(CO)₄(PMe₃)₂ (25), determined by X-ray crystallography.⁵³

duction of two sterically demanding PMe₃ ligands causes a shortening of the Mo–Mo bond by as much as 0.15 Å relative to the bond length in $FvMo_2(CO)_6$ -contrary to our expectations. Even in FvMo₂(CO)₆, steric crowding due to nonbonded interactions between CO ligands are severe enough to be a contributing factor to the presence of a long Mo-Mo bond.^{7e} The structure of 25 shows that the molecule has relieved the effects of increased crowding by twisting away from planarity. If the twisting of the Fv ligand is the sole reason for the Mo-Mo bond shortening, such a twist should be possible even in $FvMo_2(CO)_6$. The lack of significant twist in 2 suggests that in these complexes, the introduction of PMe₃ substituents has some other, presumably electronic, stabilizing effect on Mo-Mo bonding, the exact nature and origin of which is presently unknown.

Decomplexation of a Fulvalene-Bonded Molybdenum Center: A Novel "Ring-Slippage" Reaction. While investigating the mechanism of formation of the zwitterion 16, we found that when $FvMo_2(CO)_6$ was treated with excess (6-7 equiv) PMe₃ in acetonitrile d_3 , the product 16, subsequent to its formation, underwent a quantitative reaction which was complete in 2-3 days at ambient temperature. The four Fv resonances in the ¹H NMR spectrum of 16 were replaced by four new signals at δ 4.99, 5.20, 5.63, and 5.90 (2 H each). The PMe₃ resonance at δ 1.64 was replaced by two new signals at δ 1.40 (18 H) and 1.37 (27 H). In the ³¹P-{¹H} NMR spectrum, the δ 19.2 singlet of 16 was replaced by two new singlets at δ +19.4 and -17.8 in a

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2:3 ratio. The δ -17.8 signal had six small but sharp, symmetrically spaced satellites separated by a coupling of 126 Hz. The IR spectrum (THF) showed CO bands at 1936, 1852, and 1838 cm⁻¹. During workup of a preparative-scale reaction, it became apparent that two products were present. A pale yellow, ether-soluble crystalline product was identified as *fac*-Mo(CO)₃-(PMe₃)₃ by comparison with published spectroscopic data.⁵⁴ The satellites in the ³¹P{¹H} NMR spectrum were not previously reported, and are attributed to coupling to ⁹⁵Mo ($I = \frac{5}{2}$, 15.7% natural abundance) or ⁹⁷Mo ($I = \frac{5}{2}$, 9.5%).^{55a} Couplings from Mo to other nuclei are rarely seen because of the quadrupolar line broadening caused by these isotopes.⁵⁵

The other product was the novel mononuclear complex $FvMo(CO)_2(PMe_3)_2$ (26), isolated in 92% yield as red-orange crystals. The ¹H NMR and ³¹P{¹H} NMR spectra have already been described. The IR spectrum



had two bands at 1936 and 1852 cm^{-1} with relative intensities^{38a} indicating a *trans* disposition of the PMe₃ ligands. The ¹³C NMR spectrum showed resonances at δ 78.8 (d), 86.0 (d), and 104.5 (s) attributed to the complexed half of the Fv ligand and at δ 109.1 (d), 110.5 (d), and 133.7 (s) due to the uncomplexed half. The average chemical shift of the uncomplexed ring, 115 ppm, is between the average shifts in fulvalene^{56a} (135) ppm) and the cyclopentadienyl anion^{56b} (103 ppm), suggesting that the structure of 26 should be viewed as intermediate between the dipolar and the fulvene- $(\eta^4$ -diene)-type structures shown above. This conclusion is further substantiated by the IR spectrum. The $\nu_{\rm CO}$ bands of 26 at 1936 and 1852 cm^{-1} are between those found in CpMo(CO)₂(PMe₃)₂+ (1956 and 1874 cm⁻¹)⁴³ and $(\eta^4-C_4H_6)M_0(CO)_2(P(n-Bu)_3)_2$ (1909 and 1820 cm⁻¹).^{45a} An X-ray crystal structure analysis of the analogous complex FvRu(CO)(PMe₃)₂, also prepared in our laboratories,^{7f} confirmed the notion of contributing fulvene-diene and dipolar structures. The importance of the contributing ionic structure of 26 is underscored by the observation that the uncomplexed ring underwent H/D exchange in acetonitrile- d_3 or D_2O (vide infra).

The formation of **26** from **16** constituted the first example of a "ring-slippage" reaction in a fulvalene system.^{7d,g,57} The corresponding slippage of $FvRu_2(CO)_4$ to yield $FvRu(CO)(PMe_3)_2$ required harsher reaction conditions^{7f} to proceed. The diradical $FvFe_2(\eta^6-C_6H_6)_2$ yields the zwitterionic $FvFe(\eta^6-C_6H_6)$, stabilized by ion



+ fac-Mo(CO)3(PMe3)3

pairing with Na⁺ and PF $_6^-,$ when treated with CO in the presence of NaPF $_6.^{58}$

The reaction between 16 and PMe₃ came as a surprise, since the anionic site of 16 would not be expected to react with PMe₃ for electronic reasons and the cationic site should be rendered unreactive for steric reasons. The reaction proceeded cleanly at ambient temperature with no buildup of detectable intermediates. In order to determine whether it was the cationic or the anionic metal center that was displaced from the Fv ligand, the zwitterion $FvMo_2(CO)_5(dmpm)$ (17) was treated with excess PMe₃. The reaction gave the slippage product $FvMo(CO)_2(dmpm)$ (27) and fac-Mo- $(CO)_3(PMe_3)_3$ in excellent yields. The reaction unambiguously establishes that in 17, it is the anionic site that is being displaced by PMe₃. We assume that the same pertains to the reaction between 16 and PMe₃.

Qualitatively, the rate of the reaction between 16 and PMe₃ increased with increasing PMe₃ concentrations. These findings are consistent with a rate determining attack by PMe₃ on 16. Alternatively, 16 could be in equilibrium with $(\eta^4:\eta^4-Fv)Mo_2(CO)_5(PMe_3)_2$ in which the central C-C bond is not coordinated; rate-limiting capture of this species is equally consistent with the qualitative rate observations. Both events would vield $(\eta^4:\eta^4-Fv)Mo_2(CO)_5(PMe_3)_3$ as a crucial intermediate in which the central carbon-carbon double bond is not complexed to the metals (Scheme 6). The availability of this intermediate may be the reason that the anionic metal center in 16 does, but $CpMo(CO)_3^-$ does not, react with PMe₃. In any case, the reaction demonstrates the presence of electronic communication between the two metal centers. Attack of PMe3 at the less hindered metal center in the intermediate then generates the final product through sequential $\eta^4 \rightarrow \eta^2 \rightarrow \eta^0$ slippages of the Fv ligand with consequential loss of the initially anionic Mo center in the substrate. The sequence is complementary to the $\eta^5 \rightarrow \eta^3 \rightarrow \eta^1$ slippage sequence and final loss of Cp⁻ that was observed in the reaction between CpRe(NO)(CO)₂ and PMe₃.^{57b}

Energetics of the Decomplexation Reaction. Contrasting with the facile decomplexation of 16, no

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reaction took place when the Na^+ or Et_4N^+ salts of $CpMo(CO)_3^-$ were heated in the presence of PMe₃ at 95 °C. On the other hand, treatment of $(\eta^6$ -dimethylfulvene) $Mo(CO)_3$ with PMe₃ at 0 °C led to instant and quantitative generation of free dimethylfulvene and fac-Mo(CO)₃(PMe₃)₃.⁵⁹ When the ring-slipped complex 26



was treated with Mo(CO)₃(NCMe)₃, a quantitative reaction ensued to regenerate 16. The use of 26 as a substrate for the designed syntheses of heterobimetallic fulvalene complexes will be described in a forthcoming paper.⁶⁰

Hoff⁴ has compiled enthalpy data for bonding between the $Mo(CO)_3$ fragment and a variety of ligands. The bonding of the fragment to three MeCN groups is worth 84.6 kcal/mol, to three PMe₃ groups 115.2 kcal/mol, and to NaCp 98.3 kcal/mol. On the basis of these data, the hypothetical reaction between $Na^+CpMo(CO)_3^-$ and PMe₃ to give NaCp and Mo(CO)₃(PMe₃)₃ will be exothermic by 16.9 kcal/mol.

The Mo–Cp bond energy in $CpMo(CO)_3H$ is estimated to be 93 kcal/mol.⁴ The observed spontaneous reactions between FvMo(CO)₂(PMe₃)₂ and Mo(CO)₃(NCMe)₃, and between FvMo₂(CO)₅(PMe₃)₂ and PMe₃, suggest that the bond strength between FvMo(CO)₂(PMe₃)₂ and the Mo-(CO)₃ fragment is between 85 and 115 kcal/mol (the values may be subject to change somewhat when entropy effects are taken into account). It appears that the bond between $Mo(CO)_3$ and the Fv ligand in 16 is not particularly weak. Consequently, the reason that the Fv slippage reaction takes place must be that the kinetic barrier is significantly lower than in the unobserved reaction between $CpMo(CO)_3^-$ and PMe_3 . The lowering of the kinetic barrier is probably due to easier access to a reduced hapticity coordination mode for the Fv ligand than for the Cp ligand.

H/D Exchange into the Uncomplexed Ring of FvMo(CO)₂(PMe₃)₂ (26). Slow H/D exchange was seen when 26 was dissolved in acetonitrile- d_3 .⁶¹ Treatment of 26 with 2:1 acetonitrile- d_3/D_2O for 3-4 h gave 26- d_4 with more than 90% D incorporation into the uncomplexed ring. ¹H NMR monitoring of a solution of 26 in 85:15 acetonitrile- d_3/D_2O showed that the two Fv signals of the uncomplexed ring (δ 5.63, 5.90) gradually disappeared. A decoupling experiment demonstrated that the two remaining Fv signals (δ 4.99, 5.20), the former of which displayed coupling to phosphorus, were coupled to each other, and hence were located on the same ring.

The signal at δ 5.90 vanished at about twice the rate of the δ 5.63 signal, indicating different kinetic and/or thermodynamic basicities of the α and β positions of the uncomplexed ring.

In addition to these signals, two Fv peaks of equal intensities, each ca. 30% of the intensity of the Fv peaks from 26-d₄, appeared at δ 5.34 and 5.63, with a corresponding PMe₃ signal at δ 1.65. Finally, two Fv signals, each 9% of the intensities due to $26-d_4$, were found at δ 5.39 and 5.69 with a corresponding PMe₃ signal at δ 1.63. These two extra sets of signals are believed to be due to the two different isomers (27- α and **27**- β) of D⁺ adducts of **26**- d_4 . Such species are likely



intermediates in the H/D exchange process. Rapid rotation around the Cp-Cp bond will render the protons on the complexed ring pairwise equivalent, and only two Fv resonances appear in the ¹H NMR spectra of each of **27-** α and **27-** β . The different concentrations of the two species show that the α and β positions exhibit different thermodynamic basicities. We cannot tell which is the α and which is the β isomer on the basis of the spectra.

The selective incorporation of deuterium into one ring provided a means for the detection of possible "ring walk" processes in which the metal center in $26 - d_4$ shifted from one ring to the other. Such a shift could easily have been detected by ¹H NMR and would be indicated by the reappearance of signals at δ 5.63 and 5.90 in the spectrum, or by the disappearance of the remaining Fv signals in $26-d_4$ if the reaction were studied under conditions of rapid H/D exchange with the solvent. However, no evidence was seen for such a process in 26-d₄ upon prolonged heating at 90 °C in THF- d_8 , acetonitrile- d_3 , or DMSO- d_6 ; nor did the addition of D_2O or PMe_3 induce a ring walk.

Concluding Remarks. It did not come as a surprise that aspects of the chemistry of 1 and 2 resembled the chemistry of the Cp counterparts. Numerous ligand substitution reactions and functional group manipulations that are typical of Cp-bonded metal centers could be faithfully reproduced at the two metal centers that were attached to the Fv ligand. However, the most valuable insight is gained when focus is on the differences in reactivity that were imparted by the two ring systems.

The pK_a equilibrium measurements showed that the metal hydride acidities decreased in the order FvW₂- $(CO)_{6}H_{2}(pK_{a} 14.0) > CpW(CO)_{3}H(16.1) > FvW_{2}(CO)_{6}H^{-1}$ (16.6). The $(\eta^5-C_5H_4)W(CO)_3^-$ moiety serves as an electron donor and $(\eta^5-C_5H_4)W(CO)_3H$ as an acceptor when compared with H. The 2.6 pK_a unit acidity difference between $FvW_2(CO)_6H_2$ and $FvW_2(CO)_6H^$ shows that electronic information is transmitted from one metal center to the other through the Fv ring system.

 $FvW_2(CO)_6$, but not $Cp_2W_2(CO)_6$, undergoes protonation at the metal-metal bond to form a cationic bridging hydride complex in dry acetonitrile. This observation implies a greater basicity of the W-W bond in the Fv

^{(59) (}a) Some reactions between (substituted fulvene) $M(CO)_3$ (M = Cr, Mo) and tertiary phosphines have yielded zwitterionic products Or, have and ter latry phosphiles have yrelete average product of the photon of the stack of phosphile at the exocyclic carbon: Koch, O.; Edelmann, F.; Behrens, U. Chem. Ber. 1982, 115, 1313. (b) Decomplexation of an exocyclic- η^2 -fulvene Pd complex has been previously reported: Werner, H.; Crisp, G. T.; Jolly, P. W.; Kraus, H.-J.;

Krüger, C. Organometallics **1983**, 2, 1369. (60) Huffman, M. A.; Kahn, A. P.; Newman, D. A.; Tilset, M.; Tolman, W. B.; Vollhardt, K. P. C. Manuscript under preparation. (61) H/D exchange of the "naked" Cp⁻ anion of Cp₂Ta(μ -CH₂)₂Pd-(dmpe)⁺Cp⁻ in acetonitrile-d₃ was recently reported: Butts, M. D.; Bergman, R. G. Organometallics 1993, 12, 4269.

complex. We believe that the effect is caused by relief of strain energy upon opening of the W–W bond in $FvW_2(CO)_6$. The higher-lying HOMO (and therefore better donor capacity) of the Fv ligand, relative to Cp, may also contribute to the enhanced W–W bond basicity.

The metal-metal bond cleavage reactions of 1 and 2 that were induced by PMe₃ and dmpm were presumably also energetically favored by the relief of strain. The resulting zwitterionic complexes smoothly underwent decomplexation reactions in the presence of excess PMe₃. These reactions were facilitated by the capacity of the Fv ligand system to undergo a gradual ring slippage to accommodate reduced hapticity bonding modes of the Fv ligand. This reaction mode is not available to an isolated Cp ligand, or to Cp ligands joined by intervening methylene or other saturated linkages. The decomplexation reactions clearly demonstrate the occurrence of electronic communication through the π system of the Fv ligand.

In summary, a comparison of the reactivities of the Cp and Fv ligands reveal diverging behavior in some important aspects. The differences are caused by a combination of strain energy effects and electronic effects. The occurrence of electronic communication between the two rings of the Fv ligand serves to highlight the uniqueness of the Fv system and to emphasize the value of having two metals joined together in close proximity with this ligand.

Experimental Section

General Procedures. All reactions were performed in flame-dried or oven-dried (120 °C) glassware. All reactions involving organometallic reagents were done under an atmosphere of argon, using standard vacuum-line, Schlenk, syringe, and drybox techniques. Ether, THF, THF- d_8 , toluene, and toluene- d_8 were distilled from sodium benzophenone ketyl prior to use. Dichloromethane, dichloromethane- d_2 , acetonitrile, acetonitrile- d_3 , and DMSO- d_6 were distilled from P₂O₅ or CaH₂. Acetone- d_6 was dried over 3-Å molecular sieves. All reagents were used without further purification unless otherwise noted.

¹H NMR spectra were recorded on the UCB 200-, 250-, and 300-MHz instruments equipped with Cryomagnets Inc. magnets and Nicolet Model 1180 and 1280 data collection systems. ¹³C NMR spectra were recorded on the UCB 300 instrument operating at 75 MHz. ¹H and ¹³C NMR spectra are reported downfield from tetramethylsilane using the solvent resonance as the internal standard. The signals due to the AA'MM' spin system in symmetrical Fv ligands are, due to their simple appearance, for simplicity reported as "triplets" with coupling constants equal to half of the separation between the two outer lines. In less symmetrical cases, and when phosphorus couplings are observed, the Fv signals are reported as "multiplets". In diphosphine complexes, the methyl signals are for simplicity reported as "triplets" (dmpm) and "doublets" (PMe₃), respectively. ³¹P{¹H} NMR spectra were recorded on the UCB 300 instrument operating at 121.5 MHz. A solution of 1% trimethyl phosphate in the appropriate solvent, contained in a sealed capillary tube, was used as an external standard after calibration against 85% H₃PO₄. ³¹P{¹H} NMR chemical shifts are reported downfield from 85% H₃PO₄.

Infrared spectra were measured on a Perkin-Elmer 681 infrared spectrometer equipped with a 580B data station. Electronic spectra were obtained on a Hewlett-Packard 8450A diode array spectrophotometer and are reported in nanometers (extinction coefficient ϵ). Low resolution mass spectra were acquired on AEI-MS12 or Finnigan 4000 instruments by the

Mass Spectral Service at the University of California, Berkeley. Mass spectral data are listed as m/z (% intensity of base peak). Only the most intense peak in isotope envelopes are reported. Elemental analyses were performed by the Microanalytical Laboratory of the University of California, Berkeley. Photochemical experiments were carried out with a Rayonet photochemical reactor. Melting points were measured on a Thomas Hoover Unimelt apparatus in capillary tubes sealed under N₂ and are uncorrected.

The compounds $FvW_2(CO)_6$, $FvMo_2(CO)_6$, 7a,b [Et₄N⁺]-[CpMo(CO)₃⁻],³⁴ Mo(CO)₃(NCEt)₃, W(CO)₃(NCEt)₃, 62 and (η^6 -C₆H₄CMe₂)Mo(CO)₃,^{44a} were prepared according to literature procedures.

Na₂FvW₂(CO)₆ (1²⁻(Na⁺)₂). An intense purple solution of FvW₂(CO)₆ (66 mg, 0.10 mmol) in THF (15 mL) was stirred over Na/Hg (ca. 1 g, 1% w/w, 0.43 mmol). After 2 h, the solution had turned pale yellow. A sample was transferred to an IR solution cell: IR (THF) $\nu_{\rm CO}$ 1745, 1792, 1889 cm⁻¹. The solution was filtered (medium frit). Removal of the solvent by vacuum transfer gave $1^{2-}(Na^+)_2$ as a yellow, air-sensitive powder in quantitative yield.

In a separate experiment, $FvW_2(CO)_6$ (6.6 mg, 0.01 mmol) was dissolved in THF- d_8 (0.5 mL) in a 5-mL round-bottom flask. Excess Na/Hg was added, and the solution was stirred for 1 h. The yellow solution was transferred into an NMR tube which was sealed under vacuum. ¹H NMR (300 MHz, THF d_8): δ 4.80 ("t", J = 2.2 Hz, 4 H), 5.24 ("t", J = 2.2 Hz, 4 H). Li₂FvW₂(CO)₆ (1²⁻(Li⁺)₂). A 1 M solution of LiEt₃BH in THF was added dropwise to a solution of 1 (66 mg, 0.10 mmol) in THF (15 mL) at 0 °C until the color turned pale yellow. Gas was evolved during the reaction. An aliquot of the airsensitive solution was transferred to an IR solution cell: IR (THF) ν_{CO} 1717, 1778 (weak shoulder), 1803, 1895, 1897 (weak shoulder) cm⁻¹.

In a separate experiment, 1 (6.6 mg, 0.01 mmol) in THF (1 mL) was reduced with LiEt₃BH in an NMR tube. The volatiles were removed in vacuo, THF- d_8 was added by vacuum transfer, and the tube was sealed under vacuum. ¹H NMR (300 MHz, THF- d_8): δ 4.81 ("t", J = 2.4 Hz, 4 H), 5.25 ("t", J = 2.2 Hz, 4 H).

 $[Et_4N^+]_2[FvW_2(CO)_6^{2-}]$ (1²⁻(Et₄N⁺)₂). Na₂FvW₂(CO)₆ was prepared by Na/Hg reduction of 1 (300 mg, 0.47 mmol) in THF (70 mL). The solution was filtered, and the solvent was removed by vacuum transfer. The yellow residue was dissolved in water (50 mL). Addition of a saturated aqueous solution of Et₄NCl (20 mL) caused $1^{2-}(Et_4N^+)_2$ to precipitate as an off-white powder. The solid was separated by filtration, washed with water $(4 \times 50 \text{ mL})$ and ether $(3 \times 50 \text{ mL})$, and dried in vacuo. The product was dissolved in a minimum amount of acetonitrile, and the solution was filtered and cooled to -20 °C, causing the product to crystallize. Concentration of the mother liquor followed by cooling gave another crop of crystals (combined 384 mg, 92%): yellow prisms; mp 185-186 °C; ¹H NMR (300 MHz, acetonitrile- d_3) δ 1.21 (tt, J = 7.3, 1.9 Hz, 24 H), 3.16 (q, J = 7.3 Hz, 16 H), 4.89 ("t", J = 2.3 Hz, 4 H), 5.27 ("t", J = 2.3 Hz, 4 H); IR (acetonitrile) ν_{CO} 1777, 1888 cm $^{-1}.\,$ Anal. Calcd for $C_{32}H_{48}N_2O_6W_2:\,$ C, 41.58; H, 5.23; N, 3.03. Found: C, 41.81; H, 5.33; N, 2.97.

X-ray Diffraction Analysis of $[Et_4N^+]_2[FvW_2(CO)_6^2^-]$. Suitable crystals were found in the product that was recrystallized from acetonitrile. Crystallographic data are given in Table 7. Bond length and bond angle data are listed in Table 1. Atomic coordinates and displacement coefficients are given in the supplementary material.

 $FvW_2(CO)_6H_2$ (3). Excess Na/Hg (1% w/w) was added to a solution of 1 (200 mg, 0.30 mmol) in THF (50 mL). The mixture was stirred until the solution had turned pale yellow (ca. 2 h). The solution was transferred to a Schlenk flask. The following operations were carried out in the absence of daylight. At 0 °C, trifluoroacetic acid (TFA) was added slowly

⁽⁶²⁾ Kubas, G. J. Inorg. Chem. 1983, 22, 692.

	Table 7. Crystallographic Da	ta
compd	$[Et_4N^+]_2[FvW_2(CO)_6^{2^-}]$	FvMo ₂ (CO) ₅ (dmpm)
formula	$C_{32}H_{48}N_2O_6W_2$	$C_{20}H_{22}Mo_2O_5P_2$
fw	924.44	596.22
cryst syst	monoclinic	orthorhombic
space group	$P2_1/c$	$P2_{1}2_{1}2_{1}$
a. Å	7.687(2)	9.1049(8)
b. Å	13.752(4)	12.2598(4)
c. Å	16.297(5)	20.1606(18)
β , deg	94.80(2)	
V. Å ³	1716.8(8)	2250.4(7)
z	4	4
$d_{\rm calc}$, g cm ⁻³	1.781	1.76
μ_{calc}, cm^{-1}	70.9	12.55
cryst size, mm	$0.43 \times 0.38 \times 0.24$	$0.20 \times 0.23 \times 0.40$
diffractometer	Nicolet R3m/V	Enraf-Nonius CAD4
radiation (λ, \mathbf{A})	Μο Κα (0.710 69)	Μο Κα (0.710 73)
temp, K	298	298
scan mode	Wyckoff	$\theta - 2\theta$
2θ range, deg	3-60	3-45
no. of reflns measd total	5027	1725
no. of obsns	4267 with $F_0 \ge 4\sigma(F)$	1703 with $F^2 \geq 3\sigma(F^2)$
max peak in final diff map, e/Å ³	1.02, 1.05 Å from C2	0.27, near Mo atoms
structure soln	Patterson	Patterson
refinement	block-cascade methods	standard least-squares and Fourier methods
weighting scheme	$w^{-1} = \sigma^2(F_0) + 0.00034F_0^2$	$w = 4F_0^2 / (\sigma_0^2 (F_0^2) + (0.02F^2)^2)$
R	0.0370	0.0164
R _w	0.0352	0.0242

against a stream of argon. The pale yellow solution first turned intense yellow (1 equiv of TFA) and then virtually colorless (2 equiv). The volatiles were removed by vacuum transfer at 0 °C, and the residue was dried *in vacuo* for 1 h at ambient temperature. The solid was extracted with ether (2 × 25 mL), and the pale yellow extract was filtered through a medium frit filter and then through silica gel (1 × 6 cm). Removal of the solvent by vacuum transfer at -20 °C yielded **3** (170–190 mg, 85–95%): pale yellow needles; mp 136–138 °C slow dec; ¹H NMR (300 MHz, toluene-*d*₈) –6.98 (s, *J*_{WH} = 37.7 Hz, 2 H), 4.45 ("t", *J* = 2.2 Hz, 4 H), 4.76 ("t", *J* = 2.2 Hz, 4 H); IR (THF) ν_{CO} 1926, 2016 cm⁻¹; MS *m/z* 664 (M⁺ – 2H, 10.8%), 638 (100). Anal. Calcd for C₁₆H₁₀O₆W₂: C, 28.86; H, 1.51. Found: C, 28.85; H, 1.45.

 $FvW_2(CO)_6D_2$ (3-d₂). The dideuteride was prepared in the same manner as the dihydride 3, except that the silica gel filtration was carried out through gel that was deactivated with D₂O: regular silica was degassed on the vacuum line at ambient temperature for 3 h, then at 70 °C for 3 h, and then at 150 °C overnight. At ambient temperature, the flask was filled with argon, and D₂O (10% w/w) was added. The silica was shaken until no more lumps were seen and left to equilibrate for 10 h. The procedure (degassing, heating, addition of D₂O) was repeated twice. After the last addition of D₂O, equilibration was allowed to proceed for 20 h, and the silica was degassed at 40 °C for 4 h before being taken into the drybox for storage. The dideuteride 3-d₂ (80-90%) obtained by filtration through this silica gel had a hydride content of less than 3% judged by ¹H NMR spectroscopy.

 $FvW_2(CO)_6R_2$ (R = Me, Et, CH₂CH₂CH₂I, CH₂CH=CH₂, CH₂Ph, CH₂OCH₃). The same general procedure was followed in the preparation of all dialkyl complexes. Li2FvW2- $(CO)_6$ was prepared from $FvW_2(CO)_6$ (50-100 mg) as described previously, and 2.5 equiv of the appropriate alkyl halide was added with a syringe at 0 °C. Daylight was avoided from this point and throughout the workup. Reaction times are given below. The yellow or orange solutions were filtered through alumina III $(1 \times 3 \text{ cm})$ and then preadsorbed on ca. 1 g of alumina, and the products were separated by chromatography on alumina III $(1.5 \times 25 \text{ cm})$ with pentane-acetone mixtures. In most cases, a yellow forerun and excess alkyl halide were eluted with pentane. The product FvW2(CO)6R2 was eluted with 10-15% acetone in pentane. Heptane (5 mL) was added to the solution obtained, and the products were crystallized by slow removal of the solvent by rotary evaporation until 2-3 mL was left. The crystalline products were washed with cold pentane and dried *in vacuo*.

FvW₂(CO)₆Me₂ (4): from MeI; 2-h reaction time; 95%; yellow needles; dec without melting 230–235 °C; ¹H NMR (200 MHz, benzene- d_6) δ 0.41 (s, $J_{W-Me} = 1.8$ Hz, 6 H), 4.43 ("t", J = 2.3 Hz, 4 H), 4.51 ("t", J = 2.3 Hz, 4 H); IR (THF) ν_{CO} 1923, 2013 cm⁻¹; MS m/z 694 (M⁺, 8.4%), 509 (100). Anal. Calcd for C₁₈H₁₄O₆W₂: C, 31.15; H, 2.03. Found: C, 31.42; H, 2.04.

FvW₂(CO)₆Et₂: from EtI; 10-h reaction time; 87%; yellow needles; mp 180–181 °C dec; ¹H NMR (200 MHz, benzene- d_6) δ 1.40 (q, J = 7.2 Hz, 4 H), 1.66 (t, J = 7.2 Hz, 6 H), 4.47 ("t", J = 1.9 Hz, 4 H), 4.58 ("t", J = 1.9 Hz, 4 H); IR (THF) ν_{CO} 1917, 2009 cm⁻¹; MS m/z 722 (M⁺, 2.4%), 551 (100). Anal. Calcd for C₂₀H₁₈O₆W₂: C, 33.27; H, 2.51. Found: C, 33.41; H, 2.62.

FvW₂(CO)₆(CH₂CH₂CH₂I)₂ (5): from 1,3-diiodopropane; 10-h reaction time; 71%; orange powder; no clear mp; ¹H NMR (250 MHz, benzene- d_6) δ 1.08 (m, 4 H), 1.91 (m, 4 H), 2.81 (t, J = 7.0 Hz, 4 H), 4.41 ("t", J = 2.3 Hz, 4 H), 4.55 ("t", J = 2.2Hz, 4 H); IR (KBr) ν_{CO} (1912, 1998, 2016 cm⁻¹; CIMS m/z 1003 (M⁺ + 1, 0.3%), 835 (100). Anal. Calcd for C₂₂H₂₀I₂O₆W₂: C, 26.37; H, 2.01; I, 25.33. Found: C, 27.60; H, 2.07; I, 24.76.

FvW₂(CO)₆(CH₂OCH₃)₂ (6): from chloromethyl methyl ether; 1-h reaction time; 87%; yellow needles; mp 124–125 °C dec; ¹H NMR (250 MHz, benzene- d_6) δ 3.14 (s, 6 H), 4.46 (s, 4 H), 4.62 ("t", J = 2.2 Hz, 4 H), 4.99 ("t", J = 2.2 Hz, 4 H); IR (THF) ν_{CO} 1918, 1933, 2018 cm⁻¹; MS m/z 725 (M⁺ – 29, 18.8%), 524 (100). Anal. Calcd for C₂₀H₁₈O₈W₂: C, 31.86; H, 2.41. Found: C, 32.06; H, 2.52.

FvW₂(CO)₆(CH₂CH=CH₂)₂: from 3-bromopropene; 1-h reaction time; 82%; orange powder; mp 155–156 °C dec; ¹H NMR (250 MHz, benzene- d_6) δ 2.23 (dd, J = 8.3, 1.0 Hz, 4 H), 4.44 ("t", J = 2.3 Hz, 4 H), 4.61 ("t", J = 2.3 Hz, 4 H), 4.74 (ddd, J = 9.8, 2.0, 1.0 Hz, 2 H), 4.93 (dd, J = 16.6, 2.0 Hz, 2 H), 6.17 (ddt, J = 16.6, 9.8, 8.3 Hz, 2 H); IR (THF) ν_{CO} 1923, 2013 cm⁻¹; CIMS *m*/z 690 (M⁺ – 2CO, 51.8%), 619 (100). Anal. Calcd for C₂₂H₁₈O₆W₂: C, 35.42; H, 2.43. Found: C, 35.68; H, 2.70.

FvW₂(CO)₆(CH₂Ph)₂: from benzyl bromide; 2-h reaction time; 92%; yellow-orange needles; mp 179–180 °C dec; ¹H NMR (250 MHz, benzene- d_6) δ 2.85 (s, $J_{WCH_2} = 5.5$ Hz, 4 H), 4.43 ("t", J = 2.3 Hz, 4 H), 4.52 ("t", J = 2.3 Hz, 4 H), 7.0–7.1 (m, 2 H), 7.2–7.3 (m, 8 H); IR (THF) ν_{CO} 1915, 2005 cm⁻¹; MS m/z 818 (M⁺ – 2CO, 0.2%), 91 (100). Anal. Calcd for C₃₀H₂₂O₆W₂: C, 42.58; H, 2.62. Found: C, 42.61; H, 2.73.

Photolysis of FvW₂(CO)₆Me₂ (4) and FvW₂(CO)₆(CD₃)₂ (4- d_6). A Pyrex bomb (2 × 10 cm) equipped with a Teflon needle valve was loaded with 4 or $4-d_6$ (21 mg, 0.030 mmol). Degassed benzene or benzene- d_6 (15 mL) was added by vacuum transfer. The needle valve was closed, and the solution was irradiated in a Rayonet photoreactor (300 nm) for 2 h. The color of the solution changed from yellow to purplish brown. The gaseous products, along with ca. 1 mL of the solvent, were vacuum transferred into another bomb which was cooled in liquid N_2 . The contents of this bomb were subjected to an MS analysis. In all cases, methane and some CO, but no ethane or ethene, were detected. Irradiation of 4 in benzene provided CH₄ only; 4 in benzene- d_6 gave CH₄ (93%) and CH₃D (7%); 4-d₆ yielded CH₃D (2%), CH₂D₂ (18), CHD₃ (24%), and CD₄ (56%). The solution remaining in the reaction vessel was concentrated by vacuum transfer. Chromatography of the residue on alumina III with hexane/THF gave $FvW_2(CO)_6$ (13) mg, 65%) as the only isolable product.

Reaction of $FvW_2(CO)_6(CH_2OCH_3)_2$ (6) with HBF_4 : Et₂O. A solution of 6 (8 mg, 0.011 mmol) in dichloromethane- d_2 (0.5 mL) was prepared in an NMR tube equipped with a 14/20 outer joint that was stoppered with a rubber septum. The tube was cooled at -78 °C, and a solution of HBF₄·Et₂O (10 μ L, ca. 0.10 mmol) in dichloromethane- d_2 (0.2 mL) was added by syringe. On mixing, the color of the solution turned from yellow to deep red, and small quantities of a brown precipitate formed. The tube was sealed under vacuum while the solution was kept cold. ¹H NMR spectra (300 MHz) were acquired between -65 $^{\circ}C$ and +25 $^{\circ}C$. Below -25 $^{\circ}C$, the only observable Fv containing species was the methylidene complex FvW₂(CO)₆- $(CH_2OCH_3)(=CH_2)^+$: δ 3.62 (s, 2 H), 4.73 (s, 3 H), 5.45 ("t", J = 2.2 Hz, 2 H), 5.74 ("t", J = 2.2 Hz, 2 H), 6.10 ("t", J = 2.3 Hz, 2 H), 6.26 ("t", J = 2.3 Hz, 2 H), 13.10 (s, 2 H). With further warming, this complex slowly transformed into the ethene complex $FvW_2(CO)_6(C_2H_4)^{2+}\!\!:\ \delta\ 3.56\ (s,\ 4\ H),\ 5.55\ ("t",$ J = 2.3 Hz, 2 H), 5.70 ("t", J = 2.3 Hz, 2 H), 6.36 ("t", J = 2.2Hz, 2 H), 6.48 ("t", J = 2.2 Hz). Prolonged reaction times resulted in extensive decomposition as evidenced by the amount of insoluble material present. MS analysis of the volatiles from a reaction that was carried out in an analogous manner in a bomb revealed the presence of ethene.

FvW₂(CO)₆I₂. I₂ (92 mg, 0.36 mmol) in THF (5 mL) was added to a solution of FvW₂(CO)₆ (200 mg, 0.30 mmol) in THF (50 mL) while stirring. The color immediately turned from purple to red. Heptane (10 mL) was added, and the solution was extracted with aqueous 10% Na₂S₂O₃ (10 mL). The organic layer was washed with water (10 mL), separated, and dried (Na₂SO₄). The solvents were removed by rotary evaporation. Recrystallization of the residue from THF/hexane gave the product¹⁸ (232 mg, 84%): red-orange powder, mp > 320 °C; ¹H NMR (300 MHz, acetone-*d*₆) δ 5.95 ("t", *J* = 2.2 Hz, 4 H), 6.45 ("t", *J* = 2.3 Hz, 4 H); IR (THF) ν_{CO} 1953, 2034 cm⁻¹. Anal. Calcd for C₁₆H₈I₂O₆W₂: C, 20.94; H, 0.88; I, 27.66. Found: C, 21.28; H, 0.76; I, 27.63. Alternatively, the diiodide could be prepared in a quantitative yield from the dihydride **3** and I₂ in ether.

FvW₂(CO)₆Br₂. CHBr₃ (60 μ L, 0.69 mmol) in ether (1 mL) was added to FvW₂(CO)₆H₂ (60 mg, 0.090 mmol) in ether (20 mL). After 2 h, small red cubes of the product had crystallized from the solution. The solvent was decanted and the solid (74 mg, 100%) was washed with ether and dried *in vacuo*: red cubes; dec 250 °C without melting; ¹H NMR (300 MHz, acetone-d₆) δ 5.90 ("t", J = 2.3 Hz, 4 H), 6.44 ("t", J = 2.3 Hz, 4 H); IR (THF) ν_{CO} 1960, 2049 cm⁻¹. Anal. Calcd for C₁₆H₈-Br₂O₆W₂: C, 23.33; H, 0.98; Br, 19.40. Found: C, 23.56; H, 0.95; Br, 19.08.

 $FvW_2(CO)_6Cl_2$. CCl₄ (100 μ L, 159 mg, 1.04 mmol) was added to a solution of $FvW_2(CO)_6H_2$ (60 mg, 0.090 mmol) in ether (20 mL). Dark red cubes of the dichloro complex crystallized slowly from the solution. After 16 h, the solvent was decanted, and the solid was washed with ether and dried *in vacuo* to give the product (66 mg, 100%): dark red cubes; mp >320 °C; ¹H NMR (300 MHz, acetone- d_6) δ 5.86 ("t", J = 2.2 Hz, 4 H), 6.44 ("t", J = 2.1 Hz, 4 H); IR (THF) ν_{CO} 1954, 2048 cm⁻¹. Anal. Calcd for C₁₆H₈Cl₂O₆W₂: C, 26.15; H, 1.10; Cl, 9.65. Found: C, 26.38; H, 1.06; Cl, 9.39.

Determination of the First and Second Acidity Constants of $FvW_2(CO)_6H_2$ (3). In a mixture of $CpW(CO)_3^-$ and $FvW_2(CO)_6H_2$, the following independent proton-transfer equilibria will be established:

$$CpW(CO)_{3}H \stackrel{K_{CpH}}{\rightleftharpoons} CpW(CO)_{3}^{-} + H^{+}$$

$$FvW_{2}(CO)_{6}H_{2} \stackrel{K_{1}}{\rightleftharpoons} FvW_{2}(CO)_{6}H^{-} + H^{+}$$

$$FvW_{2}(CO)_{6}H^{-} \stackrel{K_{2}}{\rightleftharpoons} FvW_{2}(CO)_{6}^{2-} + H^{+}$$

The appropriate expressions for the equilibrium constants may be combined to give the following simple equations for K_1 and K_2 :

$$\begin{split} K_1 &= K_{\rm CpH} \frac{[{\rm FvW}_2({\rm CO})_6{\rm H}^-][{\rm CpW}({\rm CO})_3{\rm H}]}{[{\rm FvW}_2({\rm CO})_6{\rm H}_2][{\rm CpW}({\rm CO})_3^-]} \\ K_2 &= K_1 \frac{[{\rm FvW}_2({\rm CO})_6{\rm H}_2][{\rm FvW}_2({\rm CO})_6^-]}{[{\rm FvW}_2({\rm CO})_6{\rm H}^-]^2} \end{split}$$

Since K_{CpH} is known,^{24a} the two dissociation constants for $FvW_2(CO)_6H_2$, K_1 and K_2 , will be available if relative equilibrium concentrations of the species involved can be measured.

To obtain K_1 , an experiment was carried out in which FvW_2 -(CO)₆H₂ (10 mg, 0.015 mmol) and [Et₄N⁺][CpW(CO)₃⁻] (7 mg, 0.015 mmol) were added to an NMR tube equipped with a 14/20 outer glass joint. Acetonitrile- d_3 (0.5 mL) was added by vacuum transfer, and the tube was sealed under vacuum. The ¹H NMR spectrum (300 MHz) of the yellow solution was acquired at -45 °C. The components that were present in measurable concentrations were CpW(CO)₃H (δ -7.47, 5.61), CpW(CO)₃⁻ (δ 5.09), FvW₂(CO)₆H₂ (δ -7.09, 5.55, 5.98), and FvW₂(CO)₆H⁻ (δ -7.06, 5.02, 5.42, 5.48, 5.83) in relative amounts 12.8:1.2:1.0:13.0.

 K_2 was obtained when an equimolar mixture of FvW₂-(CO)₆H₂ and [Et₄N⁺]₂[FvW₂(CO)₆²⁻] was used. The ¹H NMR spectrum (acetonitrile- d_3 , -45 °C) showed the presence of FvW₂(CO)₆H₂, FvW₂(CO)₆H⁻, and FvW₂(CO)₆²⁻ (δ 4.91, 5.29) in the ratio 1.3:22.8:1.0.

The measured relative concentrations were used to calculate the two dissociation constants by the use of the equations above.

Thermal Decomposition of $FvW_2(CO)_6H_2$ (3) and FvW_2 -($CO)_6D_2$ (3- d_2). A bomb (2 × 10 cm) equipped with a Teflon needle valve was loaded with 3 or 3- d_2 (20 mg, 0.030 mmol) and diglyme or dioxane- d_8 (20 mL, freshly distilled from molten Na and K, respectively). The solution was degassed by four freeze-pump-thaw cycles on the vacuum line, and the needle valve was closed. The solution was heated in a thermostated oil bath at 161 ± 1 °C for 4 days. The volatiles in the bomb were analyzed by mass spectroscopy. Thus, 3 in diglyme yielded only H₂, 3 in dioxane- d_8 also gave only H₂, whereas 3- d_2 provided a mixture containing D₂ (70-80%), HD (15-25%), and H₂ (2-5%). Chromatography of the residue after removal of the solvents gave FvW₂(CO)₆ as the only isolable product (>95%).

Kinetics of the Thermal Decomposition of FvW_2 -(CO)₆H₂ Followed by UV-Visible Spectroscopy. The kinetic runs were carried out in a reaction vessel constructed in the following way: onto three glass tubes (10-mm o.d.) were fused a 14/20 outer joint, a 10-mL pear-shaped flask, and a quartz UV cell, respectively. The ends of the tubes, each ca. 5 cm in length, were fused together in a Y-shaped connection

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at 120° angles. The pear-shaped flask was filled with 5 mL of a $(8-10) \times 10^{-4}$ M solution of 3 in diglyme. AIBN or 9,10dihydroanthracene was added when desired in the reaction. The outer joint was attached to the vacuum line, and the solution contained in the flask was degassed by four freezepump-thaw cycles before the glass tube connecting the joint to the rest of the assembly was sealed off under vacuum. The flask with the solution was immersed in a thermostated oil bath (161 \pm 1 °C), thus avoiding direct contact between the UV cell and the high-temperature bath. The progress of the reaction was monitored by the increase in absorption at 548 nm, corresponding to formation of $FvW_2(CO)_6$. Before each reading on the spectrometer, the reaction assembly was removed from the bath, and the solution was cooled to 22 $^{\circ}\mathrm{C}$ before it was transferred to the UV cell by a 120 °C tilt. After each measurement, the solution was returned to the flask which was immersed in the thermostated bath again. The reaction was monitored until the absorbance was constant for at least 10 h.

Preparation of the Isomer Mixture of $(\eta^5:\eta^5-(Me (C_5H_3)_2W_2(CO)_6$ (8). To a solution of freshly cracked methylcyclopentadiene (800 mg, 10.0 mmol) in THF (100 mL) at 0 °C was added n-BuLi (6.3 mL of a 1.6 M solution in hexanes, 10.1 mmol). The solution was stirred for 1 h and cooled to -78 °C before I₂ (1.30 g, 5.1 mmol) in THF (25 mL) was added. The resulting orange solution was allowed to warm to 0 °C during 30 min. Aqueous $Na_2S_2O_3$ (2%, 100 mL) was added against a flow of argon, followed by heptane (150 mL). The mixture was stirred vigorously for 30 s and poured into a separatory funnel. The aqueous layer was drained, and the organic layer was added to anhydrous Na_2SO_4 (25 g) in a 500mL round-bottom flask. After being swirled for 1 min under N₂, the orange solution was transferred to a 500-mL roundbottom flask which was then capped with a septum and cooled to -78 °C. The resulting solution of dimethyldihydrofulvalene was stored under argon at this temperature until used.

This solution was added to W(CO)₃(EtCN)₃ (prepared from $W(CO)_6$ (3.52 g, 10.0 mmol)) in boiling glyme (500 mL). The addition was done slowly, in 10-mL portions, over a period of 4 h. The reaction mixture was heated at reflux for an additional 10 h. It was then filtered through alumina III (4 \times 30 cm). The filtrate was concentrated to dryness by rotary evaporation. The residue, ca. 1 g, was dissolved in THF, after which alumina III (5 g) was added, and the solvent was slowly removed by rotary evaporation. The solid was added to the top of a column of alumina III $(3 \times 25 \text{ cm})$ which was eluted with hexane-ether mixtures. The product was eluted as an intense bluish purple band with 20-40% ether in hexane. Heptane (25 mL) was added to the solution which subsequently was concentrated by slow rotary evaporation. The product precipitated as a bluish purple powder that was washed with cold hexanes and dried in vacuo to give ${\bf 8}$ as a mixture of six stereoisomers (510 mg, 14.7%): bluish purple powder; ¹H NMR (300 MHz, benzene- d_6) δ 1.12 (s), 1.15 (s), 1.27 (s), 1.30 (s), 1.59 (s), 1.61 (s), 1.64 (s), 1.66 (s) (a total of 6 H), 3.4-4.5 (m, 6 H); IR (THF) v_{CO} 1901, 1921, 1957, 2017 cm^{-1} , MS m/z 692 (M⁺, 14.6%), 260 (100). Anal. Calcd for C₁₈H₁₂O₆W₂: C, 31.24; H, 1.75. Found: C, 31.20; H, 1.72.

Preparation of the Isomer Mixture of $(\eta^5:\eta^5:(Me-C_5H_3))_2W_2(CO)_6H_2$ (9). A solution of 8 (50 mg, 0.072 mmol) in THF (15 mL) was reduced to the corresponding dianion by stirring over excess Na/Hg (1% w/w) for 1 h. The pale yellow solution was filtered (medium frit), and trifluoroacetic acid was added slowly until the intermediate yellow color disappeared. The volatiles were removed *in vacuo*. The sticky, off-white residue was extracted with ether (2 × 10 mL) and filtered through silica (1 × 5 cm). Removal of the solvent from the pale orange filtrate gave the dihydride 9 (44 mg, 88%): pink oily wax; ¹H NMR (300 MHz, toluene- d_8) δ -6.95 to -6.73 (several overlapping singlets and ¹⁸³W satellites, a total of 2 H), 1.48 (s), 1.57 (s), 1.58 (s), 1.60 (s), 1.71 (s), 1.73 (s), 1.78 (s), 1.81 (s) (a total of 6 H), 4.35–5.13 (m, 6 H); IR (THF) ν_{CO} 1922, 2013 cm⁻¹.

H/D Scrambling in a Mixture of $FvW_2(CO)_6D_2$ (3-d₂) and $(\eta^5:\eta^5-(MeC_5H_3))_2W_2(CO)_6H_2$ (9). An NMR tube equipped with a 14/20 outer joint was loaded with $3-d_2$ (5 mg, 0.0075 mmol) and 20 (5 mg, 0.0072 mmol). The tube was cooled at -78 °C, and THF-d₈ (0.4 mL) was added by vacuum transfer before the tube was sealed. The tube was inserted in a precooled (-75 °C) NMR probe, and the ¹H NMR spectra (300 MHz) were initially obtained at this temperature. At first, virtually all the signals in the hydride region were due to 9, less than 2% arising from 3- d_1 or 3. After 2 h at -75 °C, ca. 5% of the hydride intensity was due to the two latter species. The probe was slowly heated. At -40 °C, scrambling occurred at a faster rate (ca. 5% change in 10 min). By the time the temperature reached 0 °C, the scrambling was complete, and 50% of the hydride signal intensity had its origin in $3-d_1$ and 3.

[FvW₂(CO)₆(μ -H)]⁺BF₄⁻ (10(BF₄⁻)). A slurry of FvW₂-(CO)₆ (50 mg, 0.075 mmol) in dichloromethane (20 mL) was treated with HBF₄·Et₂O (60 μ L, ca. 0.6 mmol) overnight with stirring. A red precipitate formed. The solvent was decanted, and the solid was washed with ether (3 × 20 mL) before being dried *in vacuo*, yielding 10(BF₄⁻) (54 mg, 95%): red powder; dec ca. 250 °C without melting; ¹H NMR (300 MHz, acetonitrile-d₃) δ -21.16 (s, J_{WH} = 36.3 Hz, 1 H), 5.65 ("t", J = 2.3 Hz, 4 H), 5.91 ("t", J = 2.3 Hz, 4 H) (traces of ether and FvW₂-(CO)₆ were apparent in the spectrum; the amount of the latter increased with time); IR (acetonitrile) ν_{CO} 1925, 1968, 1993, 2046, 2069 cm⁻¹. Anal. Calcd for C₁₆H₉BF₄O₆W₂: C, 25.56; H, 1.21. Found: C, 28.51; H, 1.84 (the residual ether, apparent in the ¹H NMR spectrum, could not be removed).

 $[FvW_2(CO)_6(NCMe)_2]^{2+}(PF_6^{-})_2 (12(PF_6^{-})_2). A solution of Ph_3C^+PF_6^{-} (120 mg, 0.31 mmol) in acetonitrile (10 mL) was added quickly to FvW_2(CO)_6H_2 (100 mg, 0.150 mmol) in acetonitrile (10 mL). The resulting orange solution was filtered (medium frit) and concentrated to ca. 2 mL by vacuum transfer. Ether (25 mL) was added slowly, causing the precipitation of 12(PF_6^{-})_2 (150 mg, 96\%): yellow needles; mp > 300 °C; ¹H NMR (300 MHz, acetonitrile-d_3) <math>\delta$ 1.94 (s, 6 H), 5.94 ("t", J = 2.2 Hz, 4 H), 6.41 ("t", J = 2.2 Hz, 4 H); IR (acetonitrile) ν_{CO} 1982, 2066 cm⁻¹. Anal. Calcd for C₂₀H₁₄-F₁₂N₂O₆P₂W₂: C, 23.19; H, 1.36; N, 2.70. Found: C, 23.40; H, 1.39; N, 2.70.

Treatment of FvW₂(CO)₆ with HBF₄·Et₂O in Acetonitrile-d₃. FvW₂(CO)₆ (5 mg, 0.0075 mmol) and HBF₄·Et₂O (8 μ L, 0.08 mmol) were added to an NMR tube equipped with a ground-glass joint. Acetonitrile- d_3 (0.5 mL) was added by vacuum transfer, and the tube was sealed under vacuum. The tube was agitated until all substrate had dissolved, providing a deep red solution. The ¹H NMR spectrum (300 MHz) recorded immediately thereafter showed the presence of $FvW_{2}\text{-}$ $(CO)_6(\mu-H)^+$ (10) as the only Fv containing product. During 3 days, 10 was gradually replaced by $FvW_2(CO)_6(H)(NCCD_3)^+$ (11- d_3): δ -6.95 (s, J_{WH} = 37.5 Hz, 1 H), 5.71 ("t", J = 2.3 Hz, 2 H), 5.72 ("t", J = 2.2 Hz, 2 H), 6.08 ("t", J = 2.3 Hz, 2 H), 6.33 ("t", J = 2.2 Hz, 2 H). Prolonged reaction times induced extensive decomposition, as evidenced by the decrease in overall signal intensity in the Fv region (ether internal standard). Minor quantities (ca. 10% based on 1) of FvW_2 - $(CO)_6(NCCD_3)_2^{2+}$ (12-d₆) could be detected in the mixture.

A similar reaction was carried out in a bomb. After 10 days at ambient temperature, the volatiles were subjected to an MS analysis which revealed the presence of H_2 .

Hydride Abstraction from $FvW_2(CO)_6H_2$ with 1 equiv of $Ph_3C^+PF_6^-$. A solution of 3 (8 mg, 0.012 mmol) in acetonitrile- d_3 (0.4 mL) was treated with $Ph_3C^+PF_6^-$ (5 mg, 0.013 mmol) in acetonitrile- d_3 (0.2 mL) under vigorous stirring. The orange solution was transferred to an NMR tube. The ¹H NMR spectrum (300 MHz) was acquired 30 min later and showed the presence of $FvW_2(CO)_6$ (1; 17%), $FvW_2(CO)_6H_2$ (3; 12%), $FvW_2(CO)_6(\mu-H)^+$ (10; 8%), $FvW_2(CO)_6(NCCD_3)_2^{2+}$ (12 d_6 ; 20%), and FvW₂(CO)₆(H)(NCCD₃)⁺ (11- d_3 ; 43%). After 2 h, no FvW₂(CO)₆(μ -H)⁺ was present, whereas the amount of FvW₂(CO)₆ had increased correspondingly.

Hydride Abstraction from $[FvW_2(CO)_6(\mu-H)]^+BF_4^-$ (10(BF₄⁻)). A solution of Ph₃C⁺PF₆⁻ (4 mg, 0.010 mmol) in acetonitrile-d₃ (0.2 mL) was mixed with a solution of $[FvW_2-(CO)_6(\mu-H)]^+BF_4^-$ (7 mg, 0.009 mmol) in acetonitrile-d₃ (0.4 mL) in an NMR tube, and the tube was sealed under vacuum. A ¹H NMR spectrum (300 MHz) recorded 15 min later showed the presence of $FvW_2(CO)_6$ (1; ca. 10%) as well as $FvW_2(CO)_6-(\mu-H)^+$ (10) and $FvW_2(CO)_6(NCCD_3)_2^{2+}$ (12-d₆) in a 2.5:1 ratio. After 3 h, the ratio of 10 to 12-d₆ was 2:3, the amount of 1 being 15%. After 10 h, no 10 was left, as it had all been transformed to 12-d₆ or 1. The final relative yields of the products are not known because 1 crystallized in the tube.

Treatment of FvW2(CO)6H2 (3) with HBF4 Et2O. An NMR tube with a ground-glass joint was loaded with 3 (14 mg, 0.021 mmol). Acetonitrile- d_3 (0.5 mL) was added by vacuum transfer, and HBF₄·Et₂O (20 μ L, ca. 0.18 mmol) was added. The tube was sealed under vacuum. No reaction was detectable by ¹H NMR after 12 h at ambient temperature. The tube was heated in an oil bath at 65 °C. After 3 h, the ¹H NMR spectrum revealed partial conversion (ca. 15%) of 3 to $FvW_2(CO)_6(H)(NCCD_3)^+$ (11-d₃); in addition, several unidentifiable products were apparent in small amounts in the Fv region, and a small singlet without ¹⁸³W satellites was seen at δ -3.56. After 10 h, 3 had reacted completely; 11-d₃ was the major product along with some $12-d_6$ and more of the unidentifiable materials. The signal at δ -3.56 was more intense than the hydride resonance due to 11. Mass spectrometry revealed the presence of H_2 in the volatiles after 15 h at 65 °C.

 $FvW_2(CO)_4(PMe_3)_2H_2$ (14). PMe₃ (ca. 50 μ L, 0.8 mmol) was added by vacuum transfer to a solution of FvW₂(CO)₆H₂ (80 mg, 0.12 mmol) in ether (30 mL) at -78 °C. The solution was heated, and at 0 °C the product started to precipitate as a yellow powder. After 30 min at ambient temperature, the solvent was decanted, and the residue was washed with ether $(2 \times 15 \text{ mL})$. Recrystallization from THF/hexane gave 14 (92 mg, 100%): yellow needles; mp 154-155 °C dec; ¹H NMR (200 MHz, THF- d_8 , -30 °C) (*cis* conformers) δ -7.72 (d, J = 69.6Hz, 2 H), 1.57 (d, J = 9.7 Hz, 18 H), 5.28 (m, 4 H), 5.7–5.8 (m, 4 H); (trans conformers) δ -7.27 (d, J = 24.8 Hz, 2 H), 1.62 (d, J = 9.7 Hz, 18 H), 5.10 (m, 4 H), 5.5–5.6 (m, 4 H); cis: trans ratio 60:40; ³¹P{¹H} NMR (121 MHz, THF- d_8 , -30 °C) δ -12.3 (cis; $J_{WP} = 253$ Hz), -14.7 (trans; $J_{WP} = 277$ Hz); IR (THF) ν_{CO} 1841, 1922 cm⁻¹; MS m/z 760 (M⁺ – 2H, 7.5%), 76 (100). Anal. Calcd for $C_{20}H_{28}O_4P_2W_2$: C, 31.52; H, 3.70. Found: C, 31.60; H, 3.65.

 $FvMo_2(CO)_4(PMe_3)_2H_2$ (15). $FvMo_2(CO)_6H_2$ was prepared from FvMo₂(CO)₆ (100 mg, 0.20 mmol) as previously described,^{7c} and successfully purified by ether extraction and rapid filtration through silica (1 \times 3 cm). PMe₃ (60 μ L, 0.6 mmol) was added by vacuum transfer at -78 °C, causing an instant reaction yielding a light yellow precipitate. The suspension was held at 5 °C for 3 days, causing 15 to form large yellow crystals. After cooling to -45 °C, the solvent was decanted and the residue was washed with cold pentane (-40 °C, 2 \times 10 mL) to give 15 (92 mg, 72%): yellow prisms; ¹H NMR (300 MHz, THF- d_8 , -50 °C) δ -6.31 (d, J = 68.4 Hz) and -6.29 (d, J = 68.3 Hz) (cis), -5.95 (d, J = 23.0 Hz) and -5.93 (d, J =23.0 Hz) (trans) (combined cis + trans, 2 H), 1.41 (d, J = 9.4Hz) (cis), 1.47 (d, J = 9.1 Hz) (trans) (combined PMe₃, 18 H), 5.07 (m), 5.22 (m) (4 H combined), 5.52 (m), 5.57 (m), 5.70 (m), $5.75 (m) (4 \text{ H combined}); cis:trans ratio = 55:45; {}^{31}P{}^{1}H{} NMR$ $(\text{THF-}d_8) \delta 21.8 \text{ (s, } trans), 25.5 \text{ (s, } cis); IR (\text{THF}) \nu_{CO} 1840, 1922$ $\rm cm^{-1};\,MS\;{\it m/z}$ 584 (M^+ - 2H, 8.9%), 61 (100). Anal. Calcd for C₂₀H₂₈Mo₂O₄P₂: C, 40.97; H, 4.81. Found: C, 41.20; H, 4.86.

 $FvW_2(CO)_4(PMe_3)_2Me_2$. To a solution of $FvW_2(CO)_4$ -(PMe_3)_2H₂ (101 mg, 0.133 mmol) in THF (25 mL) at 0 °C was added *n*-BuLi (0.2 mL of a 1.55 M solution in hexanes, 0.31 mmol). There was an instant color change from pale to intense yellow. After stirring at 0 °C for 1 h, MeI (57 mg, 0.4 mmol) was added. The yellow solution was filtered through alumina III (1.5 × 10 cm), heptane (15 mL) was added, and the solution was concentrated to 10 mL by slow rotary evaporation, causing the precipitation of yellow needles. The solid was washed with hexane (2 × 20 mL) and dried *in vacuo* to give the products (87 mg, 83%): yellow needles; mp 220-221 °C dec; ¹H NMR (300 MHz, acetone- d_6) δ -0.13 (d, J = 12.5 Hz, *cis* Me), 0.18 (d, J = 3.2 Hz, *trans* Me) (total 6 H), 1.46 (d, J = 9.1 Hz, *cis* PMe₃), 1.68 (d, J = 9.3 Hz, *trans* PMe₃) (total 18 H), 5.05-5.15 (m, 4 H), 5.15-5.25 (m, 4 H); *cis:trans* ratio = 10:90; ³¹P-{¹H} NMR (acetone- d_6) δ -15.9 (s, J_{WP} = 231 Hz, *trans*), -16.8 (s, *cis*); IR (THF) v_{C0} 1836, 1917 cm⁻¹; MS *m/z* 790 (M⁺, 5.4%), 61 (100). Anal. Calcd for C₂₂H₃₂O₄P₂W₂: C, 33.44; H, 4.08. Found: C, 33.82; H, 4.17.

FvW₂(CO)₄(PMe₃)₂(CH₂Ph)₂. n-BuLi (0.20 mL of a 1.55 M solution in hexanes, 0.31 mmol) was added to a solution of FvW₂(CO)₄(PMe₃)₂H₂ (101 mg, 0.133 mmol) in THF (20 mL) at 0 °C. After stirring for 30 min, PhCH₂Cl (44 mg, 0.35 mmol) was added, and stirring was continued for 1 h. The orange solution was filtered through alumina III $(1 \times 6 \text{ cm})$ and concentrated by rotary evaporation. The oily product was separated by chromatography on alumina III $(1 \times 12 \text{ cm})$ with hexane-acetone mixtures. The product was eluted as an orange band with 10-15% acetone in hexane. Removal of the solvent by rotary evaporation followed by recrystallization from ether/hexane yielded the product (69 mg, 55%): orange powder, mp 184-185 °C dec; ¹H NMR (300 MHz, acetone-d₆) δ 1.64 (d, J = 9.6 Hz, 18 H), 2.72 (d, J = 3.1 Hz, 4 H), 4.98 (m, 4 H), 5.01 (m, 4 H), 6.80 (t, J = 7.4 Hz, 2 H), 7.04 (dd, J = 7.5, 7.5 Hz, 4 H), 7.12 (d, J = 7.4 Hz, 4 H); *cis:trans* ratio < 5:95; ³¹P{¹H} NMR (acetone- d_6) δ -13.4 (s, J_{WP} = 215 Hz); IR (THF) $\nu_{\rm CO}$ 1835, 1917 cm⁻¹; FAB MS m/z 943 (M⁺ + 1, 40.0%), 758 (100). Anal. Calcd for $C_{34}H_{40}O_4P_2W_2$: C, 43.34; H, 4.28. Found: C, 42.87; H, 4.27.

 $FvW_2(CO)_4(PMe_3)_2(CH_2OCH_3)_2$. n-BuLi (0.33 mL of a 1.55 M solution in hexanes, 0.51 mmol) was added to a solution of $FvW_2(CO)_4(PMe_3)_2H_2$ (170 mg, 0.223 mmol) in THF (20 mL) at 0 °C. After stirring for 30 min, CH₃OCH₂Cl (45 mg, 3 mmol) was added. The volatiles were removed in vacuo after 1 h. The residue was dissolved in THF (20 mL), and the yellow solution was filtered through alumina III $(1 \times 15 \text{ cm})$. After rotary evaporation of the solvent, the residue was dissolved in a minimum amount of ether, and the solution was filtered and cooled to -78 °C. The yellow precipitate was washed with cold pentane $(2 \times 20 \text{ mL})$ and dried in vacuo, giving the product (140 mg, 74%): yellow microcrystals; mp 142-143 °C dec; ¹H NMR (300 MHz, acetone- d_6) δ 1.68 (d, J = 9.5 Hz, 18 H), 3.19 (s, 6 H), 4.45 (d, J = 5.0 Hz, 4 H), 5.15 (m, 4 H), 5.35(m, 4 H); cis:trans ratio < 5:95; ${}^{31}P{}^{1}H$ NMR (acetone- d_6) δ -14.7 (s, $J_{WP} = 214$ Hz); IR (THF) ν_{CO} 1834, 1921 cm⁻¹; CIMS m/z 850 (M⁺, 1.5%), 77 (100). Anal. Calcd for C₂₄H₃₆O₆P₂W₂: C, 33.91; H, 4.27. Found: C, 34.18; H, 4.44.

FvW₂(CO)₄(PMe₃)₂I₂. A mixture of FvW₂(CO)₄(PMe₃)₂H₂ (50 mg, 0.066 mmol) and I₂ (45 mg, 0.18 mmol) in THF (20 mL) was stirred for 5 min. The brown solution was poured into aqueous 5% Na₂S₂O₃ (5 mL), and heptane (2 mL) was added. The mixture was stirred, and the organic layer was separated, dried (MgSO₄), filtered, and concentrated by rotary evaporation to give the product (66 mg, 99%): red powder; mp 273-274 °C dec; ¹H NMR (300 MHz, THF-d₈) δ 1.75, 1.81, 1.82, 1.83 (all d, J = 9.6 Hz, 18 H total), 5.1-6.0 (several m, 8 H); *cis:trans* ratio = 75:25 (major isomer determined from relative intensities in IR spectrum); ³¹P{¹H} NMR δ 34.3 (s, $J_{WP} = 250$ Hz), 34.4 (s, $J_{WP} = 249$ Hz); IR (THF) ν_{CO} 1852, 1947 cm⁻¹. Anal. Calcd for C₂₀H₂₈I₂O₄P₂W₂: C, 23.69; H, 2.59; I, 25.03. Found: C, 24.10; H, 2.55; I, 26.97.

 $FvW_2(CO)_4(PMe_2Ph)_2H_2$. PMe_2Ph (50 mg, 0.51 mmol) was added to a solution of $FvW_2(CO)_6H_2$ (70 mg, 0.105 mmol) in ether (30 mL) at 0 °C. A yellow solid started to precipitate within 10 min at ambient temperature. After 30 min, the solvent was decanted, and the residue was washed with ether (3 × 30 mL). Recrystallization from THF/hexane gave the product (51 mg, 77%): yellow needles; mp 142–143 °C dec; ¹H NMR (200 MHz, THF- d_8 , -30 °C) δ -7.42 (d, J = 67.1 Hz, *cis*), -7.07 (d, J = 23.5 Hz, *trans*) (2 H total), 1.8–2.0 (m, 12 H), 4.8–5.6 (m, 8 H), 7.3–7.5 (m, 6 H), 7.6–7.8 (m, 4 H); *cis*: *trans* ratio = 50:50; ³¹P{¹H} NMR (THF- d_8 , -70 °C) δ 0.4 (s, J_{WP} = 283 Hz), 2.3 (s, J_{WP} = 258 Hz); IR (THF) ν_{CO} 1841, 1924 cm⁻¹; MS *m/z* 856 (M⁺ - 30, 0.05%), 138 (100). Anal. Calcd for C₃₀H₃₂O₄P₂W₂: C, 40.66; H, 3.64. Found: C, 40.77; H, 3.68.

FvW₂(CO)₄(P(OMe)₃)₂H₂. P(OMe)₃ (100 mg, 0.81 mmol) was added to a solution of FvW₂(CO)₆H₂ (76 mg, 0.11 mmol) in THF (30 mL). The solution was heated at reflux in the dark for 15 h. Hexane was added to the hot solution until crystallization started. Gradual cooling to 0 °C yielded the product (79 mg, 81%): pale yellow needles; mp 115–116 °C dec; ¹H NMR (300 MHz, acetone-d₆, -65 °C) (*cis*) δ -8.13 (d, J = 72.8 Hz, 2 H), 3.39 (d, J = 12.3 Hz, 18 H), 5.45 (m, 4 H), 6.00 (m, 4 H); (*trans*) δ -7.59 (d, J = 26.4 Hz, 2 H), 3.49 (d, J = 12.4 Hz, 18 H), 5.31 (m, 4 H), 5.85 (m, 4 H); *cis:trans* ratio = 10:1; ³¹P{¹H} NMR (acetone-d₆, -65 °C) δ 163.6 (s, J_{WP} = 429 Hz, *cis*), 167.9 (s, J_{WP} = 574 Hz, *trans*); IR (THF) ν_{CO} 1873, 1945 cm⁻¹; MS *m/z* 856 (M⁺ - 2H, 9.2%), 828 (100). Anal. Calcd for C₂₀H₂₈O₁₀P₂W₂: C, 27.99; H, 3.29. Found: C, 28.24; H, 3.34.

FvMo₂(CO)₆(PMe₃)₂ (16). PMe₃ (150 μ L, ca. 1.6 mmol) was added by vacuum transfer to a solution of FvMo₂(CO)₆ (300 mg, 0.61 mmol) in THF (50 mL) at -75 °C. The solution was heated to 0 °C and held refrigerated, with occasional swirling to dissolve the starting material. A yellow-brown precipitate formed slowly. After 3 days, the solvent was decanted, and the residue was washed with cold THF (2 × 30 mL) and then with ether (5 × 30 mL). Drying *in vacuo* yielded **16** (237 mg, 63%): yellow-brown needles; mp 242-244 °C dec; ¹H NMR (300 MHz, acetonitrile-d₃) δ 1.64 ("d", J = 10.3 Hz, 18 H), 5.06 ("t", J = 2.4 Hz, 2 H), 5.22 (m, 2 H), 5.50 ("t", J = 2.4 Hz, 2 H), 5.53 (m, 2 H); ³¹P{¹H} NMR (acetonitrile-d₃) δ 19.2 (s); IR (THF) ν_{CO} 1795, 1871, 1906, 1955 cm⁻¹; CIMS *m*/z 584 (M⁺ - CO, 28.3%), 77 (100). Anal. Calcd for C₂₁H₂₆Mo₂O₅P₂: C, 41.20; H, 4.28. Found: C, 41.54; H, 4.57.

FvMo₂(CO)₅(dmpm) (17). To a solution of FvMo₂(CO)₆ (90 mg, 0.184 mmol) in THF (30 mL) was added dmpm (50 μ L, 0.46 mmol). The mixture was heated at 50-55 °C. A crystalline material began to precipitate after 2 h. Heating was continued for an additional 14 h. The solvent was decanted, and the brown crystals were washed repeatedly with THF and then with ether. Drying *in vacuo* provided 17 (81 mg, 77%): brown polycrystalline leaves, mp 243-244 °C dec; ¹H NMR (300 MHz, acetonitrile-d₃) δ 1.68 ("t", J = 5.7 Hz, 6 H), 1.69 ("t", J = 5.7 Hz, 6 H), 3.65 (m, 2 H), 5.04 ("t", J = 2.4 Hz, 2 H), 5.41 (m, 2 H), 5.49 ("t", J = 2.4 Hz, 2 H), 5.69 ("t", J = 2.1 Hz, 2 H); ³¹P{¹H} NMR (acetonitrile-d₃) δ -23.4 (s); IR (acetonitrile) ν_{CO} 1788, 1904, 1983 cm⁻¹; MS *m/z* 568 (M⁺ - CO, 3.4%), 61 (100). Anal. Calcd for C₂₀H₂₂Mo₂O₅P₂: C, 40.29; H, 3.72. Found: C, 40.47; H, 3.88.

X-ray Structural Analysis of 17. A single crystal suitable for the purpose was found in the reaction mixture. Crystallographic data are given in Table 7. Bond lengths, bond angles, and torsional angles are listed in Table 5. The positional parameters and temperature factors are given in the supplementary material.

FvW₂(CO)₅(PMe₃)₂ (18). A solution of FvW₂(CO)₆ (100 mg, 0.15 mmol) in THF (50 mL) was treated with PMe₃ (50 μ L, 0.8 mmol) for 12 h at ambient temperature. Orange plates of **18** crystallized slowly. The solvent was decanted, and the brittle crystals were washed with ether (3 × 20 mL) and THF (20 mL). Drying *in vacuo* gave **18** (61 mg, 51%): orange-brown plates; mp > 300 °C; ¹H NMR (300 MHz, acetonitrile- d_3) δ 1.76 ("d", J = 10.4 Hz, 18 H), 5.08 ("t", J = 2.2 Hz, 2 H), 5.33 (m, 2 H), 5.48 ("t", J = 2.2 Hz, 2 H), 5.60 (m, 2 H); ³¹P{¹H} NMR (acetonitrile- d_3) $\delta - 16.7$ (s, $J_{WP} = 196$ Hz); IR (acetonitrile) ν_{C0} 1785, 1868, 1898, 1953 cm⁻¹; MS *m/z* 760 (M⁺ - CO, 13.2%), 77 (100).

 $FvW_2(CO)_5(dmpm)$ (19). To a solution of $FvW_2(CO)_6$ (102) mg, 0.151 mmol) in THF (40 mL) was added dmpm (27 mg, 0.20 mmol). The solution was heated without stirring at 55 °C for 3 days. Slowly, red-brown crystals formed in the solution. After cooling to 0 °C, the brown solution was decanted. The residue was washed with THF $(2 \times 25 \text{ mL})$ and ether $(4 \times 40 \text{ mL})$ and dried in vacuo to give 19 (75 mg, 66%): brown polycrystalline solid; mp 289-290 °C dec; ¹H NMR (300 MHz, DMSO- d_6) δ 1.79 ("t", J = 5.9 Hz, 6 H), 1.89 ("t", J = 5.8 Hz, 6 H), 4.18 (dt, J = 14.8, 13.2 Hz, 1 H), 4.45 (dt, J = 15.0, 11.8 Hz, 1 H), 4.96 ("t", J = 1.7 Hz, 2 H), 5.51("t", J = 1.8 Hz, 2 H), 5.79 (m, 2 H), 5.90 (m, 2 H); ³¹P{¹H} NMR (DMSO- d_6) δ -62.6 (s, J_{WP} = 198 Hz); IR (DMSO) ν_{CO} 1775, 1889, 1957 cm⁻¹; MS m/z 744 (M⁺ – CO, 3.4%), 76 (100). Anal. Calcd for $C_{20}H_{22}O_5P_2W_2$: C, 31.11; H, 2.87. Found: C, 31.77; H, 3.06.

[FvMo₂(CO)₅(dmpm)H]⁺BF₄⁻. HBF₄·Et₂O (3 μL, ca. 0.03 mmol) was added to a slurry of FvMo₂(CO)₅(dmpm) (6 mg, 0.01 mmol) in dichloromethane-d₂ (0.5 mL) in an NMR tube. Thorough agitation caused the starting material to dissolve slowly, providing a yellowish brown solution of the cationic hydride in quantitative yield by NMR. ¹H NMR (300 MHz, dichloromethane-d₂): δ -5.24 (s, 1 H), 1.79 ("t", J = 5.9 Hz, 6 H), 1.83 ("t", J = 5.8 Hz, 6 H), 3.60 (m, 1 H), 4.28 (m, 1 H), 5.41 ("t", J = 2.1 Hz, 2 H). ³¹P{¹H} NMR (dichloromethane-d₂): δ -24.2 (s). IR (dichloromethane): ν_{CO} 1910, 1937, 1984, 2030 cm⁻¹.

[FvMo₂(CO)₅(dmpm)Me]⁺CF₃SO₃⁻. CF₃SO₃Me (2.1 mg, 1.3 mmol) was added to a solution of FvMo₂(CO)₅(dmpm) (6 mg, 0.01 mmol) in acetonitrile- d_3 (0.4 mL) in an NMR tube. A brown solution of the product was obtained in 95% yield by NMR. ¹H NMR (300 MHz, acetonitrile- d_3): δ 0.25 (s, 3 H), 1.73 ("t", J = 5.8 Hz, 6 H), 1.78 ("t", J = 5.8 Hz, 6 H), 3.62 (m, 2 H), 5.37 ("t", J = 2.3 Hz, 2 H), 5.65 ("t", J = 2.3 Hz, 4 H), 5.78 ("t", J = 2.2 Hz, 2 H). ³¹P{¹H} NMR (acetonitrile- d_3): δ -24.7 (s). IR (acetonitrile): ν_{CO} 1908, 1932, 1987, 2017 cm⁻¹.

[FvMo₂(CO)_δ(dmpm)I]⁺I⁻. I₂ (2.6 mg, 0.01 mmol) was added to a solution of FvMo₂(CO)₅(dmpm) (6 mg, 0.01 mmol) in acetonitrile-d₃ (0.4 mL) in an NMR tube. A dark brown solution was obtained after some agitation. The product was quantitatively formed by NMR. ¹H NMR (300 MHz, acetonitrile-d₃): δ 1.74 ("t", J = 5.9 Hz, 6 H), 1.80 ("t", J = 5.8 Hz, 6 H), 3.74 (m, 2 H), 5.54 ("t", J = 2.3 Hz, 2 H), 5.70 (m, 2 H), 5.85 ("t", J = 2.3 Hz, 2 H), 5.95 ("t", J = 2.3 Hz, 2 H). ³¹P{¹H} NMR (acetonitrile-d₃): δ -24.9 (s). IR (acetonitrile): ν_{CO} 1919, 1965, 1988, 2040 cm⁻¹.

[FvMo₂(CO)₅(dmpm)(NCCD₃)]²⁺(PF₆⁻)₂. A solution of FvMo₂(CO)₅(dmpm) (6 mg, 0.010 mmol) in acetonitrile- d_3 (0.5 mL) was treated with AgPF₆ (5.5 mg, 0.022 mmol), providing a dark brown solution containing the product in ca. 90% yield by NMR. ¹H NMR (300 MHz, acetonitrile- d_3): δ 1.73 ("t", J = 5.9 Hz, 6 H), 1.77 ("t", J = 5.9 Hz, 6 H), 3.75 (m, 2 H), 5.33 ("t", J = 2.3 Hz, 2 H), 5.59 (m, 2 H), 5.74 ("t", J = 2.3 Hz, 2 H), 5.77 ("t", J = 2.2 Hz, 2 H). ³¹P{¹H} NMR (acetonitrile- d_3): δ -24.6 (s). IR (acetonitrile): ν_{CO} 1921, 1964, 1993, 2075 cm⁻¹.

[FvMo₂(CO)₅(PMe₃)₂Me]⁺I⁻ (20). A slurry of FvMo₂(CO)₅-(PMe₃)₂ (50 mg, 0.082 mmol) in THF (10 mL) was treated with MeI (28 mg, 0.2 mmol). The mixture was stirred for 2 h, after which a yellow precipitate had formed. The volatiles were removed by vacuum transfer, and the residue was washed with ether (3 × 20 mL) to give 20 (62 mg, 100%): yellow powder; mp 175–180 °C dec; ¹H NMR (300 MHz, acetonitrile-d₃) δ 0.24 (s, 3 H), 1.69 ("d", J = 10.4 Hz, 18 H), 5.39 (m, 2 H), 5.42 ("t", J = 2.3 Hz, 2 H), 5.63 (m, 2 H), 5.68 ("t", J = 2.4 Hz, 2 H); ³¹P{¹H} NMR (acetonitrile-d₃) δ 18.8 (s); IR (acetonitrile) ν_{CO} 1874, 1924, 1958, 2014 cm⁻¹. Anal. Calcd for C₂₂H₂₉-IMo₂O₅P₂: C, 35.04; H, 3.88; I, 16.83. Found: C, 35.25; H, 4.01; I, 16.90.

 $FvMo_2(CO)_4(PMe_3)_2Me^-$. An NMR tube equipped with a ground-glass joint was loaded with 16 (8 mg, 0.013 mmol) and LiAlH₄ (2 mg, 0.051 mmol). THF- d_8 was added by vacuum

transfer at -78 °C, and the tube was sealed under vacuum. The tube was allowed to warm to 0 °C and was held at this temperature with occasional agitation. The substrate slowly dissolved to give a red solution. The ¹H NMR spectrum (300 MHz) revealed that the anion accounted for more than 90% of the products: δ -0.76 (t, J = 12.6 Hz, 3 H), 1.26 ("d", J = 8.0 Hz, 18 H), 4.48 (br "t", J = 2.0 Hz, 2 H), 4.91 ("t", J = 2.4 Hz, 2 H), 4.95 (m, 2 H), 5.27 ("t", J = 2.4 Hz, 2 H); ³¹P{¹H} NMR (THF- d_8) δ 31.8 (s).

FvMo₂(CO)₄(PMe₃)₂Me₂ (21). LiAlH₄ (20 mg, 0.53 mmol) was added to a slurry of 20 (197 mg, 0.26 mmol) in THF (25 mL) at -30 °C. The mixture was stirred for 2 h at -30 °C to -20 °C and then at -10 °C for 30 min. A red solution was obtained. Excess LiAlH₄ was quenched by addition of water (1 mL) at -10 °C. The volatiles were removed by vacuum transfer. The residue was extracted with ether (20 mL) and filtered through alumina III $(1 \times 10 \text{ cm})$. Heptane (5 mL) was added to the orange solution, which was concentrated to 5 mL by vacuum transfer at -20 °C without stirring, giving 21 (135 mg, 84%): red-orange needles; mp 140 °C dec; ¹H NMR (300 MHz, acetone- d_6) δ -0.71 (t, J = 12.5 Hz, 3 H), 0.19 (s, 3 H), 1.32 ("d", J = 8.3 Hz, 18 H), 4.77 (m, 2 H), 5.29 (m, 2 H), 5.37 ("t", J = 2.3 Hz, 2 H), 5.62 ("t", J = 2.3 Hz, 2 H); ³¹P{¹H} NMR (acetone- d_6) δ 31.5 (s); IR (THF) ν_{CO} 1778, 1927, 2010 cm⁻¹; MS m/z 614 (M⁺, 5.3%), 61 (100). Anal. Calcd for C₂₂H₃₂-Mo₂O₄P₂: C, 43.01; H, 5.25. Found: C, 43.25; H, 5.46.

 $[{\bf FvMo_2(CO)_5(PMe_3)}]^{2-}$. A drop of Na/Hg (1% w/w) was added to a slurry of 16 in THF-d_8 (0.5 mL). The solution was stirred at ambient temperature until a yellow solution was obtained. The solution was transferred to an NMR tube which was sealed under vacuum. The ¹H NMR spectrum showed at least 95% conversion to the dianion. ¹H NMR (300 MHz, THF-d_8) δ 1.26 (d, J = 8.2 Hz, 9 H), 4.61 (br "t", J = 2.3 Hz, 2 H), 4.79 ("t", J = 2.3 Hz, 2 H), 5.02 (m, 2 H), 5.22 ("t", J = 2.3 Hz, 2 H) (a doublet due to free PMe₃ was located at δ 0.94 (J = 2.6 Hz); ³¹P{¹H} NMR (THF-d_8) δ 28.9 (s), -61.5 (s, free PMe₃).

FvMo₂(CO)₅(PMe₃)Me₂ (22). A slurry of 16 (100 mg, 0.16 mmol) was stirred over excess Na/Hg (1% w/w) in THF (15 mL) until the substrate had dissolved and the solution was bright yellow. The volatiles were removed by vacuum transfer, the residue was dissolved in THF (15 mL), and the solution was filtered. At 0 °C, MeI (57 mg, 0.40 mmol) was added. The solution was stirred for 30 min at 0 °C. The volatiles were removed by vacuum transfer, and the residue was extracted with ether (40 mL) and filtered through alumina III (1 \times 5 cm). Heptane (5 mL) was added, and the solvent volume was slowly reduced to 5 mL by vacuum transfer. The yellow solid that was obtained was recrystallized from ether-hexane, giving 22 (72 mg, 78%): yellow powder; mp 130-140 °C dec; ¹H NMR (300 MHz, acetone- d_6) (trans) δ 0.08 (d, J = 3.0 Hz, 3 H), 0.19 (s, 3 H), 1.59 (d, J = 9.2 Hz, 9 H), 5.12 (m, 2 H), 5.24 (m, 2 H), 5.42 ("t", J = 2.2 Hz, 2 H), 5.73 ("t", J = 2.3 Hz,2 H); (cis) δ -0.24 (d, J = 11.6 Hz, 3 H), 0.22 (s, 3 H), 1.37 (d, J = 8.8 Hz, 9 H, 5.16 (m, 1 H), 5.45 (m, 1 H), 5.53 (m, 1 H) (cis:trans ratio = 1:2); ${}^{31}P{}^{1}H$ NMR (acetone-d₆) δ 22.9 (s, trans), 20.0 (s, cis); IR (THF) v_{C0} 1851, 1930, 2012 cm⁻¹; MS m/z 566 (M⁺, 10.5%), 188 (100). Anal. Calcd for C₂₀H₂₃-Mo₂O₅P: C, 42.42; H, 4.09. Found: C, 41.31; H, 4.65.

FvMo₂(CO)₅(PMe₃) (24). A slurry of **16** (70 mg, 0.11 mmol) in THF (20 mL) was stirred over excess Na/Hg (1% w/w) until a homogeneous yellow solution was obtained (1-2 h). The solution was filtered (medium frit) and the volatiles were removed *in vacuo*. The residue was dissolved in THF, and trifluoroacetic acid (15 mg, 0.13 mmol) was added at 0 °C. The solvent and excess acid were removed by vacuum transfer, and the residue was extracted with ether (2 × 15 mL). This furnished a yellow solution from which an aliquot was taken for NMR analysis of the dihydride FvMo₂(CO)₅(PMe₃)H₂ (**23**): ¹H NMR (300 MHz, THF-d₈) δ -6.0 (br m, 1 H), -5.34 (s, 1 H), 1.48 (d, J = 9.1 Hz, 9 H), 5.15 (br m, 2 H), 5.46 (m, 2 H), 5.60 (br m, 2 H), 5.91 (m, 2 H). The solvent was removed by vacuum transfer, and the residue was dissolved in THF (60 mL). The pale yellow solution was transferred to a Pyrex bomb that was closed under vacuum. Photolysis for 2 h (Rayonet, 300 nm) resulted in the formation of a deep purple solution. The solution was concentrated, and the residue was separated by chromatography on alumina III $(2 \times 25 \text{ cm})$ with toluene-ether mixtures.

A faint purple band was eluted with toluene. Concentration of the solution and crystallization from THF-heptane gave $FvMo_2(CO)_6$ (4 mg, 9%).

An intense bluish purple band was eluted with 25-50% ether in toluene. Concentration of the solution by vacuum transfer followed by recrystallization of the solid from THF-heptane provided **24** (45 mg, 74%): dark purple prisms; mp 185–190 °C; ¹H NMR (300 MHz, acetone- d_6) δ 1.77 (d, J = 9.5 Hz, 9 H), 4.48 ("t", J = 2.3 Hz, 2 H), 4.50 ("t", J = 2.3 Hz, 2 H), 5.14 (m, 2 H), 5.33 ("t", J = 2.3 Hz, 2 H), 4.50 ("t", J = 2.3 Hz, 2 H), 5.14 (m, 2 H), 5.33 ("t", J = 2.3 Hz, 2 H), 31P{¹H} NMR (acetone- d_6) δ 26.2 (s); IR (THF) ν_{CO} 1837, 1901, 1911, 1984 cm⁻¹; UV (THF) λ_{max} 366 (ϵ 15 280), 566 (642) nm; MS m/z 536 (M⁺, 51%), 376 (100). Anal. Calcd for C₁₈H₁₇Mo₂O₅P: C, 40.32; H, 3.20. Found: C, 41.98; H, 3.62.

 $FvMo_2(CO)_4(PMe_3)_2$ (25). Dihydride 15 was prepared from $FvMo_2(CO)_6$ (100 mg, 0.21 mmol) as described earlier. Crude 15 was dissolved in THF (100 mL), and the solution was transferred to a Pyrex bomb which was closed under vacuum. The solution was irradiated (Rayonet, 300 nm) for 2 h, leading to an intensely colored purple solution. The solvent was removed by vacuum transfer, and the residue was separated by chromatography on alumina III (2 \times 25 cm) with toluene– ether mixtures.

A faint purple band was eluted with 1% ether in toluene. Removal of the solvents followed by recrystallization from THF-heptane gave $FvM_{02}(CO)_5(PMe_3)$ (4 mg, 3%).

An intense purple band was eluted with 5–10% ether in toluene. Removal of the solvents by vacuum transfer, followed by recrystallization from THF-heptane, yielded **25** (96 mg, 80%): dark purple prisms; mp 271–273 °C dec; ¹H NMR (300 MHz, acetone- d_6) δ 1.67 (d, J = 9.0 Hz, 18 H), 4.20 ("t", J = 2.3 Hz, 4 H), 4.94 (m, 4 H); ³¹P{¹H} NMR (acetone- d_6) δ 27.9 (s); IR (THF) ν_{CO} 1805, 1850, 1926 cm⁻¹; UV (THF) λ_{max} 360 (ϵ 18 500), 558 (1115) nm; CIMS m/z 585 (M⁺ + 1, 5.3%), 77 (100). Anal. Calcd for C₂₀H₂₆Mo₂O₄P₂: C, 41.12; H, 4.49. Found: C, 40.86; H, 4.65.

FvMo(CO)₂(**PMe**₃)₂ (26). A 200-mL round-bottom flask equipped with a vacuum adapter was loaded with FvMo₂(CO)₆ (500 mg, 1.02 mmol) and acetonitrile (60 mL). PMe₃ (0.6 mL, 6 mmol) was added by vacuum transfer at -50 °C, and the vessel was closed before the mixture was heated to room temperature. The flask was heated at 35 °C for 3 days, resulting in the formation of a deep red-orange solution. The volatiles were removed by vacuum transfer, and the residue was extracted with ether (90 mL) on a medium frit filter. The filtrate was concentrated to 20 mL and cooled to -20 °C, resulting in the formation of pale yellow crystals of the known⁵³ complex *fac*-Mo(CO)₃(PMe₃)₃ (280 mg, 67%): ¹H NMR (300 MHz, acetonitrile-*d*₃) δ 1.37 ("d", J = 5.3 Hz); ³¹P{¹H} NMR (acetonitrile-*d*₃) δ -17.8 (s, $J_{MoP} = 126$ Hz); IR (acetonitrile) ν_{CO} 1838, 1937 cm⁻¹.

The residue on the filter was dissolved in THF (70-80 mL), filtered (medium frit), and concentrated to 15 mL to yield an intense red solution containing an orange-red solid. Ether (70 mL) was added, causing the precipitation of more material. The mixture was cooled at -20 °C for 2 days, filtered (medium frit), and washed with ether (60 mL). The residue was dried *in vacuo*, yielding **26** (408 mg, 92%): red-orange microcrystals; mp 180 °C dec; ¹H NMR (300 MHz, acetonitrile- d_3) δ 1.40 ("d", J = 10.0 Hz, 18 H), 4.99 (m, 2 H), 5.20 ("t", J = 2.2 Hz, 2 H), 5.63 (br "t", J = 2.2 Hz, 2 H), 5.90 ("t", J = 2.8 Hz, 2 H); ³¹P-{¹H} NMR (acetonitrile- d_3) δ 18.9 (dq, J = 31, 130 Hz), 78.8 (d, J = 175 Hz), 86.0 (d, J = 175 Hz), 104.5 (s), 109.1 (d, J = 158 Hz), 110.5 (d, J = 161 Hz), 133.7 (s), 236.6 (t, J = 28 Hz); IR (THF)

 ν_{CO} 1852, 1936 cm^{-1}; CIMS m/z 432 (M⁺, 1.6%), 77 (100). Anal. Calcd for $C_{18}H_{26}MoO_2P_2:\ C,$ 50.01; H, 6.06. Found: C, 49.88; H, 6.14.

FvMo(CO)₂(dmpm) (27). A 100-mL round-bottom flask equipped with a vacuum adapter was loaded with FvMo₂(CO)₅-(dmpm) (200 mg, 0.34 mmol) and acetonitrile (40 mL). PMe₃ (0.15 mL, 1.5 mmol) was added by vacuum transfer at $-50 \text{ }^{\circ}\text{C}$ before the assembly was closed and warmed to ambient temperature. The mixture was heated at 35 °C for 2 days, yielding a red-orange solution. The volatiles were removed by vacuum transfer, and the solid was extracted with ether (2 \times 15 mL). The residue was dissolved in THF (50 mL), and the resulting red solution was filtered (medium frit) and concentrated to 5 mL. Ether (80 mL) was added, causing the precipitation of an orange-red solid. The mixture was cooled to -20 °C for 2 days, and the suspension was filtered (medium frit) and washed with ether (10 mL), yielding 27 (130 mg, 93%): red microcrystalline powder; mp 195 °C dec; ¹H NMR (300 MHz, acetonitrile- d_3) δ 1.10 ("t", J = 5.4 Hz, 6 H), 1.60 ("t", J = 5.4 Hz, 6 H), 3.33 (m, 2 H), 5.01 ("t", J = 2.1 Hz, 2 H), 5.39 (m, 2 H), 5.64 (m, 2 H), 5.92 ("t", J = 2.5 Hz, 2 H); ³¹P-{¹H} NMR (acetonitrile- d_3) δ -16.2 (s); IR (THF) ν_{CO} 1884, 1959 cm⁻¹; CIMS m/z 416 (M⁺, 1.8%), 55 (100). Anal. Calcd for C₁₇H₂₂MoO₂P₂: C, 49.05; H, 5.33. Found: C, 49.20; H, 5.41.

Reaction between PMe₃ and $(\eta^{6}$ -C₆H₄Me₂)Mo(CO)₃. The dimethylfulvene complex is known to be unstable,^{43a} decomposing to substituted cyclopentadienyl complexes; therefore, the experiment was carried out with crude (pure by ¹H NMR) material freshly prepared from Mo(CO)₃(NCMe)₃ (50 mg, 0.17 mmol) and dimethylfulvene (30 mg, 0.28 mmol) in THF (2 h, ambient temperature). Solvent and excess dimethylfulvene were removed by vacuum transfer. The crude material was dissolved in hexane or THF, and PMe₃ (0.05 mL, 0.5 mmol) was added at -78 °C in the dark. Upon heating to room temperature, an instant reaction took place. The only products detectable by ¹H NMR and IR spectroscopies were *fac*-Mo(CO)₃(PMe₃)₃ and dimethylfulvene.

(Fv-d₄)Mo(CO)₂(PMe₃)₂ (26-d₄). A solution of FvMo(CO)₂-(PMe₃)₂ (50 mg, 0.12 mmol) in acetonitrile-d₃ (2 mL) and D₂O (1 mL) was stirred for 3-4 h at ambient temperature. An aliquot was withdrawn for recording of the ¹H NMR spectrum, which revealed more than 90% D incorporation into the uncomplexed ring (δ 5.63, 5.90). In addition to the signals, due to 26-d₄, two Fv peaks, each with ca. 30% of the intensity of the Fv peaks from 26-d₄, appeared at δ 5.34 and 5.63, with a corresponding PMe₃ signal at δ 1.65. Finally, two Fv signals, each with ca. 9% of the intensity of the 26-d₄ Fv signals, were found at δ 5.39 and 5.69 with a corresponding PMe₃ signal at δ 1.63. These two extra sets of signals are believed to be due to the two different isomers (27- α and 27- β ; see Results) of the D⁺ adducts of 26-d₄. The sample in the NMR tube was combined with the reaction mixture. The solvents were removed in vacuo, the residue was dissolved in THF (10 mL), and the solution was filtered (medium frit). Removal of the solvent provided $26 \cdot d_4$ (90-95% yield) with 90-95% deuterium incorporation in the uncomplexed ring, as judged by ¹H NMR spectroscopy.

Attempted Induction of "Ring Walk" in $(Fv-d_4)Mo$ (CO)₂(PMe₃)₂ (26-d₄). Ferrocene (1-2 mg, 0.005-0.011 mmol, internal standard) and $26-d_4$ (5-10 mg, 0.012-0.023 mmol) were added to an NMR tube equipped with a groundglass joint. The appropriate solvent (0.5 mL) and, when desired, an additional ligand (PMe₃ or D_2O) were added. The tube was sealed under vacuum. The following solvent/liquid combinations were tried: THF- d_8 , acetonitrile- d_3 , DMSO- d_6 , acetonitrile-d₃/15% D₂O, THF/1 equiv of PMe₃, and acetonitrile- $d_3/1$ equiv of PMe₃. The solutions were heated at 80-90°C for 3-4 days or until decomposition became apparent. By ¹H NMR spectroscopy, the intensities of the resonances from both complexed and residual uncomplexed ring protons were measured relative to each other and relative to the ferrocene standard. In no case was any evidence for a "ring walk" process found.

Reaction between FvMo(CO)_2(PMe_3)_2 and Mo(CO)_3 (NCEt)₃. $Mo(CO)_3(NCEt)_3$ (5 mg, 0.015 mmol) was added to a solution of **26** (5 mg, 0.014 mmol) in acetonitrile- d_3 (0.4 mL). A reaction took place instantly, as evidenced by the color change of the solution from orange-red to yellowish brown. By ¹H NMR spectroscopy, the zwitterion **16** had formed in quantitative yield.

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Supplementary Material Available: Tables of positional and thermal parameters for $[Et_4N^+]_2[FvW_2(CO)_6^{-2}]$ and FvM_{02} - $(CO)_5(dmpm)$ (5 pages). Ordering information is given on any current masthead page.

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