Synthesis and Characterization of New **Phosphine-Substituted** (Fulvalene)dimolybdenum **Carbonyl Hydrides and Halides**

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A number of (fulvalene)dimolybdenum carbonyl dihydrides and dihalides of the general formula $FvMo_2(CO)_4L_2X_2$ (X = H, L = CO (1a), PPh₃ (1b), PMe₃ (1c); X = Cl, L = CO (2a), PPh_3 (2b), PCy_3 (Cy = cyclohexyl; 2c), PXy_3 (Xy = 3,5-dimethylphenyl; 2d); X = Br, L = CO (3a), PPh₃ (3b), PCy₃ (3c), PXy₃ (3d), PMe₃ (3e); X = I, L = CO (4a), PPh₃ (4b)) have been synthesized and characterized by IR and ¹H, ¹³C{¹H}, and ³¹P{¹H} NMR spectroscopy and, where possible, by elemental analyses. Spectroscopic data suggest that 2b-d and 3b-e exist solely as *cis,cis* isomers in solution. *cis,cis*-4b was also identified but was found to easily transform into a mixture of cis.cis, cis.trans, and trans.trans isomers. Such an interconversion of 1b is fast on the NMR time scale at room temperature. The radical chain halogenation of **1a**,**b** by activated alkyl halides was found to take place in two distinct steps, involving the intermediate formation of $FvMo_2(CO)_4L_2HX$ (L = CO, X = Cl (5a), Br (6a), I (7a); L = PPh₃, X = Cl (5b), Br (6b), I (7b)). By stepwise addition of different alkyl halides, the hydrido-halo complexes 5a, 6a, and 7a were transformed into the mixed dihalides $FvM_{02}(CO)_6XY$ (X, Y = Cl, Br (8), Cl, I (9), and Br, I (10)). Mixed dihalides were formed alternatively in halide redistribution reactions between pairs of 2a, 3a, and 4a.

Introduction

There is currently considerable interest in the preparation and characterization of 17-electron organotransition-metal compounds (metal-centered radicals).^{1a,b} This class of compounds may be synthesized in a variety of ways¹ and may often be stabilized with respect to dimerization to the 18-electron metal-metal-bonded analogues by substitution of small ligands by more sterically demanding ligands (e.g. CO by tertiary phosphines, η^5 -C₅H₅ by η^5 -C₅Me₅ and η^5 -C₅Ph₅). In general, it has been found that there is a correlation between the proclivity of an 18-electron dimer to undergo thermal homolysis to the corresponding 17-electron species and the length of the metal-metal bond. Thus, the chromium-chromium bond of $[(\eta^5-C_5H_5)Cr(CO)_3]_2$, which dissociates to the extent of a few percent in solution at room temperature,^{1c,d} is much longer (3.281 Å)^{1e} than the metal-metal bond of the analogous, much more homolytically stable molybdenum compound $(3.235 \text{ \AA})^{1f}$ but much shorter than the chromium-chromium bonds of $[(\eta^5 - C_5 H_5)Cr(CO)_2 P(OMe)_3]_2 (3.343 \text{ Å})^{1g}$ and $[(\eta^5 - C_5 - C_5)^{1g}]_2 (3.343 \text{ Å})^{1g}$ Me₅)Cr(CO)₃]₂ (3.311 Å),^{1d} both of which dissociate much more extensively in solution.^{1d,g} Consistent with the apparent role of steric effects on the extent of homolysis, the compounds $(\eta^5-C_5H_5)Cr(CO)_2PPh_3^{1h,i}$ and $(\eta^5-C_5Ph_5)$ - $Cr(CO)_3^{1j}$ are completely monomeric in solution and the solid state.

It was of considerable interest, therefore, to note that the metal-metal bonds of the fulvalene compounds (η^5 : η^5 -C₁₀H₈)M₂(CO)₆ (A; M = Cr, Mo, W)^{2b} are extraordinarily long, *i.e.* 3.471, 3.371, and 3.347 Å,^{2c,f,g,u} respectively, suggesting significant strain. In addition, each compound contains a fulvalene (Fv) ligand bent from planarity as in A, also suggestive of strain in these

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compounds. Interestingly, however, crystal structure data for the substituted derivative FvMo₂(CO)₄(PMe₃)₂ show that substitution by this relatively small phosphine, at least, results in a shorter and presumably stronger Mo-Mo bond than exists in $FvMo_2(CO)_6$ despite severe twisting and bending of the fulvalene ligand from planarity.^{2t,3} Thus, the fulvalene system is much more complex than would be expected on the basis of the above-mentioned putative correlation between the extent of CO substitution and metal-metal bond lengths.

Nevertheless, although no evidence that this class of compounds can exist as isomers not containing metalmetal bonds (biradicals) has been reported,^{2u} it seemed possible either that biradical species might be synthesized by alternative routes or that they might be detectable as reactive intermediates. It therefore seemed important to further probe the structures and chemistry of derivatives containing phosphines of greater steric demand and different electronic parameters, and in view of the relative abundance of available data on fulvalene compounds of the group VI metals,² particularly of molybdenum, we have begun with an investigation of derivatives of $FvMo_2(CO)_6$.

Unfortunately, direct substitutions of the carbonyl ligands of $FvMo_2(CO)_6$ with tertiary phosphines do not generally occur.^{2f,t,u} Furthermore, with very few exceptions (none involving molybdenum), no fulvalene complexes are known with ligands larger than the relatively small PMe₃, suggesting that the preparation and study of compounds of the type $FvMo_2(CO)_4L_2$ (L = bulky ligand) might be difficult.

A potential route to biradicals, not heretofore attempted, could involve abstraction of hydrogen atoms from substituted hydrides of the type FvMo₂(CO)₄L₂H₂, as in eq 1. This approach has been extensively utilized

$$FvMo_2(CO)_4L_2H_2 + 2 CPh_3 \rightarrow FvMo_2(CO)_4L_2 + 2HCPh_3 (1)$$

for the syntheses of simple 17-electron compounds⁴ and has been shown to be of general utility. Furthermore, since the starting dihydride compounds would assume the anti conformation B established for several nonmetal-metal-bonded fulvalene complexes by X-ray crystallography,^{2j,r,s,t} the diradical products would presumably assume the same conformation initially and might well have difficulty coupling if L is a sufficiently bulky ligand.

Of course, utilization of the chemistry of eq 1 requires the availability of the substituted hydrides, FvMo₂- $(CO)_4L_2H_2$; unfortunately, we find that direct substitu-



tion of $FvMo_2(CO)_6H_2$ is not possible with ligands larger than PPh₃. Halo compounds of the type FvMo₂- $(CO)_4L_2X_2$ do undergo such substitutions, however, and these should be reducible, either directly to the desired $FvMo_2(CO)_4L_2$ or indirectly to the dianions $[FvMo_2(CO)_4L_2]^{2-}$, which should undergo protonation to the hydrides. We have therefore synthesized a series of dihydrides and dihalides of the type $FvMo_2(CO)_4L_2X_2$ (C: $L = CO, PPh_3, PCy_3, PXy_3; X^1, X^2 = H, Cl, Br, I$)



(Ph = phenyl, Cy = cyclohexyl, Xy = 3,5-dimethylphenyl), and we describe here the syntheses and properties of these compounds. Some have been reported previously but not fully characterized, but the vast majority are new. In a paper to follow,⁵ we shall describe utilization of these compounds to form metal-metalbonded analogues and our attempts to detect radicallike properties. The compounds discussed here are listed in Table 1.

Experimental Section

General Considerations. All manipulations were carried out under purified nitrogen by using standard Schlenk techniques and a Vacuum Atmospheres glovebox. All solvents were freshly distilled under nitrogen from sodium benzophenone ketyl (hexane, benzene, toluene, ether, and THF) or CaH₂ (CH_2Cl_2) . Deuterated solvents were purchased from Isotec, Inc., and were degassed and stored in the glovebox. Tertiary phosphines (PMe₃ from Aldrich, PPh₃ from Strem, PCy₃ from Organometallics, Inc., PXy₃ from M&T) and other chemicals were used without further purification. Column chromatography was performed with a 1.5×20 cm column packed with silica gel 60 (70-230 mesh, EM Science) using hexane-CH₂-Cl₂ mixtures and ultimately CH₂Cl₂ as eluant. IR spectra were recorded on a Bruker IFS-25 FT-IR spectrometer and NMR spectra on Bruker AC-200 (200.1 MHz, ¹H; 50.32 MHz, ¹³C- $\{^1H\}),\ CXP-200\ (80.98\ MHz,\ ^{31}P\{^1H\}),\ and\ AM-400\ (400.1$ MHz, ¹H; 100.6 MHz, ¹³C{¹H}; 162.0 MHz, ³¹P{¹H}) NMR spectrometers. IR and ¹H, ¹³C{¹H}, and ³¹P{¹H} NMR data are given in Tables 2-6. Elemental analyses were carried out by Canadian Microanalytical Services Ltd. (Delta, BC, Canada).

Preparation of (NEt₄)₂[FvMo₂(CO)₆] and Hexane Solutions of $FvMo_2(CO)_6H_2$ (1a). The following procedure is a modification of that of Smart and Curtis.^{2a} A solution of 5.4 $g\,(30\ mmol)$ of $CpNa(DME)^{2a}$ in 100 mL of THF, cooled to -78°C, was treated dropwise with 20 mL of a THF solution of 3.8 g (30 mmol) I_2 over ${\sim}1.5$ h. At this point, 15 mL of a 2.0 M hexane solution of BuLi (30 mmol) was added dropwise (~20 min) to give a pink reaction mixture, which was warmed to room temperature and then stirred for an additional 1 h. resulting in the formation of a fine, white solid. The mixture was transferred to a flask containing 7.9 g (30 mmol) of Mo-

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Table 1. Compounds of Type C Prepared in ThisPaper

compd	\mathbf{X}^{1}	\mathbf{X}^2	L	compd	X1	\mathbf{X}^2	L
1a	Н	Н	CO	4a	Ι	Ι	CO
1b	н	Η	PPh_3	4b	I	I	PPh_3
1c	н	н	PMe_3	5a	н	Cl	CO
2a	Cl	C1	CO	5b	н	Cl	PPh_3
2b	Cl	Cl	PPh_3	6a	Η	\mathbf{Br}	CO
2 c	Cl	C1	PCy_3	6b	н	Br	PPh_3
2d	Cl	Cl	\mathbf{PXy}_3	7a	Н	I	CO
3a	\mathbf{Br}	\mathbf{Br}	CO	7b	н	Ι	PPh_3
3b	\mathbf{Br}	Br	PPh_3	8	Cl	Br	CO
3c	\mathbf{Br}	\mathbf{Br}	PCy_3	9	Cl	Ι	CO
3d	Br	Br	PXy_3	10	Br	Ι	CO
3e	\mathbf{Br}	\mathbf{Br}	PMe_3				

Table 2. Carbonyl Stretching Frequencies

compd	$\nu_{\rm CO}~({\rm cm}^{-1})^a$
$FvMo_2(CO)_6H_2$ (1a)	2027 (s), 1949 (vs) ^{b,c}
$FvMo_2(CO)_6Cl$ (2a)	$2047 (s), 1976 (vs, br)^d$
$FvMo_2(CO)_6Br_2$ (3a)	2043 (s), 1970 (vs, $br)^d$
$FvMo_2(CO)_6I_2$ (4a)	$2035 (s), 1964 (vs, br)^d$
$FvMo_2(CO)_6HI$ (7a)	2034 (m), 2015 (m),
	1962 (vs), 1930 (s) ^d
$FvMo_{2}(CO)_{4}(PPh_{3})_{2}H_{2}(1b)$	1936 (vs), 1858 (vs)
$FvMo_2(CO)_4(PMe_3)_2H_2$ (1c)	1928 (vs), 1846 (vs) ^e
cis, cis-FvMo ₂ (CO) ₄ (PPh ₃) ₂ Cl ₂ (2b)	1968 (vs), 1883 (m, br)
cis, cis-FvMo ₂ (CO) ₄ (PCy ₃) ₂ Cl ₂ (2c)	1951 (vs), 1871 (m)
cis, cis-FvMo ₂ (CO) ₄ (PXy ₃) ₂ Cl ₂ (2d)	1966 (vs), 1882 (m, br)
cis, cis-FvMo ₂ (CO) ₄ (PPh ₃) ₂ Br ₂ (3b)	1970 (vs), 1890 (m, br)
cis, cis-FvMo ₂ (CO) ₄ (PCy ₃) ₂ Br ₂ (3c)	1955 (vs), 1873 (m)
cis, cis-FvMo ₂ (CO) ₄ (PXy ₃) ₂ Br ₂ (3d)	1965 (vs), 1882 (m)
cis, cis-FvMo ₂ (CO) ₄ (PMe ₃) ₂ Br ₂ (3e)	1965 (vs), 1868 (m, br)
cis, cis-FvMo ₂ (CO) ₄ (PPh ₃) ₂ I ₂ (4b)	1965 (vs), 1887 (s)

 a In CH₂Cl₂, unless denoted otherwise. b In hexane. c Lit.:^{2f} 2020, 1929, 1902 cm⁻¹ in THF. d In THF. e Lit.:^{2t} 1922, 1840 cm⁻¹ in THF.

Table 3. ¹H NMR Data for (Fulvalene)dimolybdenum Hexacarbonyl Complexes

	$\delta~({ m ppm})^a$	
compd	η^{5} : η^{5} -C ₁₀ H ₈	MoH
	4.50 ("t", 4 H), 4.85 ("t", 4 H) 4.24 ("t", 4 H), 4.91 ("t", 4 H) 4.27 ("t", 4 H), 4.86 ("t", 4 H)	-5.298 (s, 2 H)
$ FvMo_2(CO)_6l_2 (\textbf{4a}) \\ FvMo_2(CO)_6HCl (\textbf{5a}) $	$\begin{array}{c} 4.32 \ (``t'', 4 \ H), 4.80 \ (``t'', 4 \ H) \\ 4.24 \ (``t'', 2 \ H), 4.61 \ (``t'', 2 \ H), \\ 4.82 \ (``t'', 2 \ H), 4.93 \ (``t'', 2 \ H) \end{array}$	-5.30 (s, 1 H) ^b
$FvMo_2(CO)_6HBr$ (6a)	4.28 ("t", 2 H), 4.58 ("t", 2 H), 4.73 ("t", 2 H), 4.89 ("t", 2 H)	-5.305 (s, 1 H)
$FvMo_2(CO)_6HI~({\bf 7a})$	4.36 ("t", 2 H), 4.55 ("t", 2 H), 4.69 ("t", 2 H), 4.88 ("t", 2 H)	-5.314 (s, 1 H)
$FvMo_{2}(CO)_{6}ClBr\;(\boldsymbol{8})$	4.23 ("t", 2 H), 4.30 ("t", 2 H), 4.85 ("t", 2 H), 4.91 ("t", 2 H)	
$FvMo_2(CO)_6ClI~(\bm{9})$	4.19 ("t", 2 H), 4.37 ("t", 2 H), 4.81 ("t", 2 H), 4.90 ("t", 2 H)	
$FvMo_2(CO)_6BrI(10)$	$\begin{array}{c} 4.26 \ (``t", 2 \ H), \ 4.36 \ (``t", 2 \ H), \\ 4.82 \ (``t", 2 \ H), \ 4.85 \ (``t", 2 \ H) \end{array}$	

^a In toluene-d₈ (200 MHz). ^b Almost identical with 1a.

 $(CO)_6$ and 6.3 g (30 mmol) of Et₄NBr. The reaction mixture was refluxed for 5 h, after which gas evolution had ceased and IR spectra showed no further changes, although some unreacted Mo(CO)₆ was still present. After the mixture was cooled to room temperature, 100 mL of hexane was added to precipitate a solid mixed with a red oil. The solution was decanted, and the solid material was dried *in vacuo*. The resulting sticky substance was washed thoroughly with several 50 mL portions of ether until colorless washings were obtained. The remaining tan solid was then vacuum-dried again to give 14-19 g of impure, air-sensitive (Et₄N)₂[FvMo₂(CO)₆]. The salt was extracted with THF and reprecipitated with hexane to give a light yellow powder which was characterized on the basis of comparisons with spectroscopic data from the literature. IR (THF): ν_{CO} 1892 (vs), 1795 (vs), 1744 (m, br) cm⁻¹.

Table 4.31P{1H} NMR Data forPhosphine-Substituted (Fulvalene)dimolybdenum
Carbonyl Complexes

compd	$\delta~({ m ppm})^a$
$FvMo_2(CO)_4(PPh_3)_2H_2(1b)$	73.3 (br)
$FvMo_2(CO)_4(PPh_3)_2H_2(1b)^b$	71.90 (sh, <i>trans</i> , <i>trans</i>),
	71.98 (cis,trans),
	73.64 (cis, cis),
	73.69 (sh, cis, trans)
cis, cis-FvMo ₂ (CO) ₄ (PPh ₃) ₂ Cl ₂ (2b)	50.34, 50.49
cis, cis-FvMo ₂ (CO) ₄ (PPh ₃) ₂ Cl ₂ (2b) ^c	49.9
cis, cis-FvMo ₂ (CO) ₄ (PCy ₃) ₂ Cl ₂ (2c) ^c	49.92, 50.02
cis, cis-FvMo ₂ (CO) ₄ (PXy ₃) ₂ Cl ₂ (2d) ^c	47.59, 47.84
cis, cis-FvMo ₂ (CO) ₄ (PPh ₃) ₂ Br ₂ (3b) ^c	47.8
cis, cis-FvMo ₂ (CO) ₄ (PPh ₃) ₂ Br ₂ (3b) ^d	47.90, 48.04
cis, cis-FvMo ₂ (CO) ₄ (PCy ₃) ₂ Br ₂ (3c) ^c	47.89, 48.00
cis, cis-FvMo ₂ (CO) ₄ (PXy ₃) ₂ Br ₂ (3d) ^c	45.68, 45.82
cis, cis-FvMo ₂ (CO) ₄ (PPh ₃) ₂ I ₂ (4b)	45.7, 45.8
cis,trans-4b	46.0 (cis), 67.0 (trans)
trans,trans-4b	67.3
$FvMo_2(CO)_4(PPh_3)_2HCl(5b)$	50.5, 72.9 (br)
$FvMo_2(CO)_4(PPh_3)_2HBr(6b)$	48.6, 72.9
$FvMo_2(CO)_4(PPh_3)_2HI(7b)$	45.9 (cis iodide),
	67.8 (trans iodide),
	73.2 (br, hydride)

 a In toluene-d_8 unless denoted otherwise. Relative to 85% H₃PO₄. b At -70 °C. c In CDCl₃. d At -23 °C.

¹H NMR (acetone- d_6): δ 1.37 (tt, $J_1 = 7.2$ Hz, $J_2 = 1.8$ Hz, 24H, Me), 3.45 (q, J = 7.2 Hz, 16H, CH₂N), 4.73 ("t", 4H, Fv), 5.22 ("t", 4H, Fv). ¹³C{¹H} NMR (acetone- d_6): δ 84.5, 86.6 (Fv), 106.8 (Fv C-1), 237.2 (CO). The IR and ¹H NMR data well agree with those reported for M₂[FvMo₂(CO)₆] (M = Li, Na).^{2f} For the Li salt: IR (THF) ν_{CO} 1900, 1806, 1782, 1716 cm⁻¹; ¹H NMR (THF- d_8) δ 4.76 (m), 5.21 (m). For the Na salt: IR (THF) ν_{CO} 1890, 1790, 1740 cm⁻¹.

To synthesize the hydride, typically 2.0 g of the crude material were suspended in 80 mL of hexane and 0.5 mL of glacial acetic acid was injected at room temperature. After the mixture was stirred for 1 h, a red solid settled and the yellowish solution of **1a** was separated. The unstable hydride was not isolated but was characterized spectroscopically (see Tables 2 and 3 for IR and ¹H NMR data, respectively). ¹³C-{¹H} NMR (benzene-*d*₆): δ 88.2, 89.5 (Fv), 105.3 (Fv C-1), 227.0 (CO). On the basis of amounts of substituted (**1b**,c), halogenated (**2a**, **3a**, **4a**), and decomposition (FvMo₂(CO)₆) products, which were obtained during subsequent reactions of **1a**, **1a** was generally obtained in yields of ~50% based on Mo(CO)₆. Essentially the same result was obtained when trifluoroacetic acid was used for protonation.

FvMo₂(CO)₄(PPh₃)₂H₂ (1b). A solution of **1a** in 80 mL of hexane was added to 1.2 g (4.6 mmol) of PPh₃ dissolved in 10 mL of ether. A precipitate formed within a few minutes, but stirring was continued overnight at room temperature to complete the reaction. Solid **1b** separated, and the hexane solution, which contained no **1a** at this point (IR), was removed by syringe. The product was washed with 3×10 mL of hexane and dried *in vacuo*. Yield: 0.70 g (0.73 mmol, 47% based on Mo(CO)₆). Anal. Calcd for C₅₀H₄₀Mo₂O₄P₂: C, 62.64; H, 4.21. Found: C, 61.81; H, 4.21. ¹H NMR (CD₂Cl₂): δ -5.35 (d, J_{PH} = 48.4 Hz, 2H, MoH), 4.93 ("t", 4H, Fv), 5.18 ("t", 4H, Fv), 7.35 (m, 30H, Ph). ¹³C{¹H} NMR (CD₂Cl₂): δ 133.3 (d, J_{PC} = **11.3** Hz, o-Ph), 130.0 (d, J_{PC} = 2.3 Hz, p-Ph), 128.5 (d, J_{PC} = 9.6 Hz, m-Ph), 89.8 (s, Fv), 88.4 (s, Fv).

Complex 1b is a light yellow, thermally stable powder, which is poorly soluble in aromatic hydrocarbons and CHCl₃ but soluble in THF and CH₂Cl₂. When it is heated to 110 °C in a toluene solution, it completely decomposes within 2 days to an unidentified carbonyl-containing product.

FvMo₂(CO)₄(PMe₃)₂H₂ (1c). Substitution of **1a** with PMe₃ was carried out as described for **1b**, in a modification of a recent published procedure.^{2t} Into a 20 mL hexane solution of **1a** was injected 60 μ L (0.58 mmol) of PMe₃, and the mixture

Table 5.	Selected ¹ H NMR Data for Phosphine-Substituted (Fulvalene)dimolybdenum
	Carbonyl Hydrides and Halides

	$\delta~({ m ppm})^{a}$			
compd	$\eta^5:\eta^5-C_{10}H_8$	MoH		
$FvMo_2(CO)_4(PPh_3)_2H_2(1b)$	4.63 ("t", 4 H), 5.01 ("t", 4 H)	$-5.03 (d, J_{PH} = 52 Hz, 2 H)$		
$FvMo_2(CO)_4(PPh_3)_2H_2$ (1b) ^b	4.24 (m), 4.35 (m), 4.40 (m), 4.45 (m), 4.56 (m), 4.61 (m), 4.68 (m), 4.75 (m), 4.91 (m), 4.98 (m), 5.07 (m), 5.15 (m)	$\begin{array}{l} -4.99(\mathrm{d},J_{\mathrm{PH}}=65\mathrm{Hz}),-5.02(\mathrm{d},J_{\mathrm{PH}}=21\mathrm{Hz}),\\ -5.05(\mathrm{d},J_{\mathrm{PH}}=21\mathrm{Hz}),-5.06(\mathrm{d},J_{\mathrm{PH}}=65\mathrm{Hz}), \end{array}$		
$FvMo_2(CO)_4(PMe_3)_2H_2$ (1c) ^c	4.67 (s, br, 4 H), 5.03 (s, br, 4 H)	-5.66 (s, br, 2 H)		
cis, cis-FvMo ₂ (CO) ₄ (PPh ₃) ₂ Cl ₂ (2b)	4.40 (m, 2 H), 4.65 (m, 1 H), 4.77 (m, 1 H), 4.99 (m, 1 H), 5.14 (m, 1 H), 5.46 (m, 1 H), 5.54 (m, 1 H)			
$cis, cis \text{-} FvMo_2(CO)_4(PPh_3)_2Cl_2\ (\textbf{2b})^d$	$\begin{array}{l} 4.88\ (m,1\ H), 4.96\ (m,1\ H), 5.11\ (m,1\ H), 5.17\ (m,1\ H),\\ 5.28\ (m,1\ H), 5.32\ (m,1\ H), 5.70\ (m,1\ H), 5.75\ (m,1\ H) \end{array}$			
$cis, cis \text{-} FvMo_2(CO)_4(PCy_3)_2Cl_2\ (\textbf{2c})^d$	$\begin{array}{l} 4.85\ (m,1\ H),4.95\ (m,1\ H),5.20\ (m,1\ H),5.28\ (m,1\ H),\\ 5.30\ (m,1\ H),5.34\ (m,1\ H),5.89\ (m,1\ H),5.94\ (m,1\ H) \end{array}$			
$cis, cis \text{-} FvMo_2(CO)_4(PXy_3)_2Cl_2\ (\textbf{2d})^d$	$\begin{array}{c} 4.77 \ (m, 1 \ H), 4.88 \ (m, 1 \ H), 5.03 \ (m, 1 \ H), 5.13 \ (m, 1 \ H), \\ 5.20 \ (m, 2 \ H), 5.63 \ (m, 1 \ H), 5.67 \ (m, 1 \ H) \end{array}$			
$\textit{cis,cis-FvMo}_2(CO)_4(PPh_3)_2Br_2~(\textbf{3b})$	4.36 (m, 2 H), 4.70 (m, 1 H), 4.81 (m, 1H), 4.87 (m, 1H), 5.12 (m, 1 H), 5.51 (m, 1 H), 5.64 (m, 1 H)			
$cis, cis \text{-} FvMo_2(CO)_4(PCy_3)_2Br_2~(\textbf{3c})$	$\begin{array}{c} \textbf{4.41} (\textbf{m, 1 H}), \textbf{4.45} (\textbf{m, 1 H}), \textbf{4.89} (\textbf{m, 2 H}), \textbf{5.05} (\textbf{m, 1 H}), \\ \textbf{5.20} (\textbf{m, 1 H}), \textbf{5.69} (\textbf{m, 1 H}), \textbf{5.85} (\textbf{m, 1 H}) \end{array}$			
$cis, cis \text{-} FvMo_2(CO)_4(PXy_3)_2Br_2\ (\textbf{3d})$	$\begin{array}{c} \textbf{4.49} \ (\textbf{m, 1 H)}, \textbf{4.52} \ (\textbf{m, 1 H)}, \textbf{4.93} \ (\textbf{m, 1 H)}, \textbf{4.98} \ (\textbf{m, 2 H)}, \\ \textbf{5.14} \ (\textbf{m, 1 H)}, \textbf{5.66} \ (\textbf{m, 1 H)}, \textbf{5.77} \ (\textbf{m, 1 H}) \end{array}$			
$\textit{cis,cis-FvMo}_2(CO)_4(PMe_3)_2Br_2~(3e)$	$\begin{array}{c} 4.41 \ (m, 2 \ H), 4.58 \ (m, 1 \ H), 4.83 \ (m, 1 \ H), 4.95 \ (m, 1 \ H), \\ 5.07 \ (m, 1 \ H), 5.18 \ (m, 1 \ H), 5.29 \ (m, 1 \ H) \end{array}$			
$\textit{cis,cis-FvMo}_2(CO)_4(PPh_3)_2I_2~(\textbf{4b})$	$\begin{array}{c} 4.28\ (m,1\ H), 4.33\ (m,1\ H), 4.72\ (m,1\ H), 4.81\ (m,1\ H),\\ 4.85\ (m,1\ H), 5.06\ (m,1\ H), 5.52\ (m,1\ H), 5.79\ (m,1\ H) \end{array}$			
$FvMo_2(CO)_4(PPh_3)_2HCl~({\bf 5b})$	4.40 (m, 2 H), 4.51 (m, 1 H), 4.71 (m, 1 H), 5.07 (m, 1 H), 5.13 (m, 2 H), 5.26 (m, 1 H)	$-4.99 (d, J_{PH} = 52 Hz, 1 H)$		
$FvMo_2(CO)_4(PPh_3)_2HBr~(\textbf{6b})$	4.41 (m, 1 H), 4.60 (m, 1 H), 4.64 (m, 1 H), 4.70 (m, 1 H), 4.94 (m, 1 H), 5.12 (m, 1 H), 5.21 (m, 1 H), 5.32 (m, 1 H)	$-4.98 (d, J_{PH} = 52 Hz, 1 H)$		
$FvMo_2(CO)_4(PPh_3)_2HI~(\textbf{7b})$		$-4.99 (d, J_{PH} = 52 Hz), -5.01 (d, J_{PH} = 52 Hz)$		
a In toluene- d_8 and at 25 °C u	inless noted otherwise. b At -65 °C. c In C ₆ D ₆ . d In CDC	13.		

Table 6.	¹³ C{ ¹ H} NMR Data for (Fulvalene)dimolybdenum Carbonyl Complexes in the
	Fulvalene Carbon Region

compd	δ (ppm)
$(Et_4N)_2[FvMo_2(CO)_6]^a$	106.8 (C-1), 86.6, 84.5
$FvMo_2(CO)_6H_2(1a)^b$	105.3 (C-1), 89.5, 88.2
$FvM_{02}(CO)_{\theta}Cl_2 (2a)^{\alpha}$	115.2 (C-1), 96.1, 91.7
$FvMo_2(CO)_6Br_2 (\mathbf{3a})^a$	113.3 (C-1), 95.7, 92.1
$FvMo_2(CO)_6I_2$ (4a) ^a	110.7 (C-1), 94.8, 92.6
$FvM_{02}(CO)_4(PPh_3)_2H_2(1b)^c$	89.8 (br), 88.4
cis.cis-FvMo ₂ (CO) ₄ (PPh ₃) ₂ Cl ₂ (2b) ^d	111.6 (C-1), 110.6 (C-1), 100.7, 98.6, 95.3, 93.4, 89.1, 87.3, 85.09, 85.06
cis.cis-FvMo ₂ (CO) ₄ (PPh ₃) ₂ Br ₂ (3b) ^d	109.9 (C-1), 108.6 (C-1), 100.4, 98.9, 95.7, 93.8, 88.7, 87.2, 84.50, 84.47
cis.cis-FvMo ₂ (CO) ₄ (PCv ₃) ₂ Cl ₂ (2c) ^d	112.3 (C-1), 111.5 (C-1), 101.7, 100.2, 94.1, 91.6, 86.1 (d, $J \approx 3$ Hz), 85.0 (d, $J \approx 3$ Hz),
,	83.7, 83.5
cis.cis-FvMo ₂ (CO) ₄ (PCv ₃) ₂ Br ₂ (3c) ^d	110.6 (C-1), 109.5 (C-1), 101.3, 100.0, 94.1, 91.8, 86.0 (d, $J \approx 3$ Hz), 84.9 (d, $J \approx 3$ Hz),
	83.1 (d, $J \approx 5$ Hz), 82.9 (d, $J \approx 5$ Hz)
cis, cis-FvMo ₂ (CO) ₄ (PXy ₃) ₂ Br ₂ (3d) ^d	110.7 (C-1), 109.2 (C-1), 99.8, 98.9, 95.5, 93.8, 88.2, 87.0, 84.7, 84.3

^a In acetone-d₆. ^b In C₆D₆. ^c In CD₂Cl₂; no C-1 (bridgehead) carbon resonance was observed. ^d In CDCl₃.

was stirred overnight at room temperature. A fine yellow precipitate settled from the solution, which did not contain unreacted **1a** by this time (IR). The solvent was decanted, and the solid was washed with 3×10 mL of hexane and dried *in vacuo*. Yield: 0.16 g (0.27 mmol, 33% based on Mo(CO)₆). The product was identified by IR and ¹H NMR spectroscopy.^{2t} ¹H NMR (C₆D₆): δ -5.66 (br s, 2H, MoH), 1.00 (d, J_{PH} = 9.0 Hz, 18H, PMe), 4.67 (br s, 4H, Fv), 5.05 (br s, 4H, Fv).

Complex 1c is a light yellow, thermally stable powder which is soluble in many solvents. When heated to 110 °C in toluene, complete decomposition to a carbonyl-containing product occurred in 2 days, similar to the case for 1b.

 $FvMo_2(CO)_6X_2$ (X = Cl (2a), Br (3a), I (4a)). These compounds were obtained by hydrogen-halogen exchange reactions of 1a with activated alkyl halides. In typical syntheses of 2a, 3a, or 4a, a standard solution of 1a (~0.78 mmol) in 80 mL of hexane was treated with 5 mL of CCl₄ (52 mmol), 4 mL of CHBr₃ (46 mmol), or 1 mL of ICH₂CO₂Et (8.5 mmol), respectively, at room temperature. Red, crystalline solids appeared within a few minutes, but stirring was continued overnight in each case. Since the products still contained some hydrido-halide intermediates (see below) at this point, spectroscopically pure samples were obtained by partially dissolving the crude products in 2 mL of CH₂Cl₂ and adding an extra 2 mL of CCl₄ or CHBr₃ or 1 mL of ICH₂CO₂- Et. After 1 day, products were precipitated by the addition of 5 mL of hexane, the solvents were decanted, and the remaining solids were washed with 3 imes 5 mL of hexane and vacuumdried. 2a: yield 0.42 g (0.76 mmol, 49% based on $Mo(CO)_6$); ¹H NMR (acetone- d_6) δ 5.71 ("t", 4H, Fv), 6.29 ("t", 4H, Fv); $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR (acetone-d_6) δ 242.5 (s, CO trans to Cl), 225.9 (s, CO cis to Cl), 115.2 (s, C-1 Fv), 96.1 (s, Fv), 91.7 (s, Fv). 3a: yield 0.40 g (0.62 mmol, 40%); ¹H NMR (acetone- d_6) δ 5.76 ("t" 4H, Fv), 6.29 ("t", 4H, Fv); ${}^{13}C{}^{1}H$ NMR (acetone- d_6) δ 240.2 (s, CO trans to Br), 224.3 (s, CO cis to Br), 113.3 (s, C-1 Fv), 95.7 (s, Fv), 92.1 (s, Fv). 4a: yield 0.54 g (0.72 mmol, 47%); ¹H NMR (acetone- d_6) δ 5.82 ("t", 4H, Fv), 6.31 ("t", 4H, Fv); $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR (acetone- $d_{6})$ δ 237.7 (s, CO trans to I), 222.5 (s, CO cis to I), 110.7 (s, C-1 Fv), 94.8 (s, Fv), 92.6 (s, Fv). IR and further ¹H NMR spectroscopic data of **2a**, **3a**, and **4a** are compiled in Tables 2 and 3, respectively.

Complexes 2a and 4a are brick red, while 3a is deep purple. All are poorly soluble in aromatic and chlorinated hydrocarbons but soluble in THF and acetone; solubilities decrease in the order 2a > 3a > 4a (Cl > Br > I). All are air-sensitive in solution and in the solid state and readily decompose with gas evolution on heating in a toluene solution to 100 °C. None could be obtained analytically pure.

 $FvMo_2(CO)_4L_2HX$ (L = CO, X = Cl (5a), Br (6a), I (7a); L = PPh₃, X = Cl (5b), Br (6b), I (7b)). These hydrido halides were detected and characterized by ¹H NMR spectroscopy (Tables 3 and 5) as intermediates in hydrogen-halogen exchange reactions of **1a**,**b** with CCl₄, CHBr₃, and ICH₂CO₂-Et in toluene- d_8 solutions. Attempts to isolate **5a**, **6a**, and **7a** resulted only in the formation of mixtures of the hydrido halides, the corresponding dihalide, and **1a** (¹H NMR). While the mixtures could not be separated by column chromatography because of hydride and/or halide ligand redistribution reactions, they could be enriched in the hydrido-halide complexes using the following process.

With hexane solutions of 1a and CCl₄, CHBr₃, or ICH₂CO₂-Et as starting materials, as described above for the synthesis of $FvMo_2(CO)_6X_2$, the initially formed red precipitates were separated after ~30 min by removing the supernatant liquid (which contained no 1a). The solids were washed with 3×5 mL portions of hexane and dried *in vacuo*. When the crude products were dissolved in CDCl₃ or toluene-d₈ for NMR studies, it was found that most of the dihalo species were of low solubility and samples containing up to 80% pure 5a, 6a, or 7a were obtained.

FvMo₂(**CO**)₆**XY** (**X**, **Y** = **Cl**, **Br** (8), **Cl**, **I** (9), **Br**, **I** (10)). **Method A.** To the enriched toluene- d_8 solutions of **6a** and **7a**, prepared as described above, was added 10 μ L of CCl₄ or CHBr₃ at room temperature. The reactions were monitored by ¹H NMR spectroscopy, and the consumption of the hydride halides as well as the formation of the corresponding mixed dihalides were unambiguously established after several hours. For spectroscopic data, see Table 3.

Method B. All three mixed dihalides were also identified by ¹H NMR spectroscopy as products of halide ligand redistribution reactions between pairs of the homodihalides; *e.g.*, complex 8 formed from 2a and 3a and 9 from 2a and 4a, as well as 10 from 3a and 4a. The reactions were carried out on NMR-scale samples in toluene- d_8 or acetone- d_6 at room temperature, and mixtures of the products and starting dihalides were obtained in 1 day.

 $FvMo_2(CO)_4(PPh_3)_2X_2$ (X = Cl (2b), Br (3b), I (4b)). Method A. A slurry of 2a (0.14 g, 0.25 mmol) and PPh₃ (0.13 g, 0.50 mmol) in 10 mL of toluene was heated in an oil bath at \sim 110 °C, resulting in dissolution of the solid, vigorous gas evolution, and a color change to deep red. Gas evolution stopped after ~ 10 min, and the solution was cooled to room temperature to give a red precipitate, which was a mixture of 2b and FvMo₂(CO)₆ (IR, ¹H NMR). These two compounds exhibit considerably different solubilities in toluene, and analytically pure 2b was obtained as the cis, cis isomer by extracting the $FvMo_2(CO)_6$ with 5 \times 5 mL of toluene and subsequent vacuum drying. Yield: 0.13 g (0.13 mmol, 52%). Anal. Calcd for C₅₀H₃₈Cl₂Mo₂O₄P₂: C, 58.44; H, 3.73. Found: C, 58.18; H, 3.74. ¹H NMR (CDCl₃): δ 4.88 (m, 1H, Fv), 4.96 (m, 1H, Fv), 5.11 (m, 1H, Fv), 5.17 (m, 1H, Fv), 5.28 (m, 1H, Fv), 5.32 (m, 1H, Fv), 5.70 (m, 1H, Fv), 5.75 (m, 1H, Fv), 7.37 (m, 30H, Ph). ${}^{13}C{}^{1}H$ NMR (CDCl₃): δ 255.9 (d, $J_{\rm PC} = 28.7$ Hz, CO trans to Cl), 255.8 (d, $J_{\rm PC} = 28.5$ Hz, CO trans to Cl), 242.6 (d, $J_{PC} = 5.1$ Hz, CO cis to Cl), 242.5 (d, J_{PC} = 5.3 Hz, CO cis to Cl), 133.8 (d, J_{PC} = 10.4 Hz, o-Ph), 133.7 (d, $J_{PC} \approx 44$ Hz, *ipso-Ph*), 130.3 (d, $J_{PC} \approx 2$ Hz, *p-Ph*), 128.4 $(d, J_{PC} = 9.8 \text{ Hz}, m$ -Ph). The fulvalene carbon chemical shifts are given in Table 6.

The bromide *cis,cis*-**3b** was prepared similarly from **3a** (0.15 g, 0.23 mmol) and PPh₃ (0.12 g, 0.46 mmol) and was purified by column chromatography. Yield: 0.17 g (0.15 mmol, 66%). Anal. Calcd for C₅₀H₃₈Br₂Mo₂O₄P₂: C, 53.79; H, 3.43. Found: C, 52.94; H, 3.38. ¹H NMR (CDCl₃): δ 4.86 (m, 1H, Fv), 4.90 (m, 1H, Fv), 5.10 (m, 1H, Fv), 5.19 (m, 1H, Fv), 5.21 (m, 1H, Fv), 5.31 (m, 1H, Fv), 5.74 (m, 2H, Fv), 7.37 (m, 30H, Ph). ¹³C{¹H} NMR (CDCl₃): δ 253.7 (d, J_{PC} = 28.1 Hz, CO trans to Br), 253.6 (d, J_{PC} = 28.6 Hz, CO trans to Br), 240.2 (d, J_{PC} = 5.1 Hz, CO cis to Br), 240.1 (d, J_{PC} = 4.9 Hz, CO cis to Br), 134.0 (d, J_{PC} = 43.1 Hz, *ipso*-Ph), 133.9 (d, J_{PC} = 10.3 Hz, o-Ph), 130.4 (d, $J_{PC} = 2.5$ Hz, p-Ph), 128.4 (d, $J_{PC} = 9.9$ Hz, m-Ph). The fulvalene carbon chemical shifts are given in Table 6.

The iodo complex 4b was also obtained from 0.15 g of 4a (0.20 mmol) and PPh₃ (0.11 g, 0.40 mmol) as described above. Yield: 0.13 g (0.11 mmol, 54%). Although no analytically pure material could be isolated by column chromatography, the product was thoroughly characterized by spectroscopic methods and appears to be a mixture of *cis,cis, cis,trans*, and trans,trans isomers. IR (toluene): ν_{CO} 1964 (vs), 1891 (vs) cm⁻¹. ¹H NMR (toluene- d_8): δ 4.28 (m), 4.30 (m), 4.33 (m), 4.36 (m), 4.72 (m), 4.81 (m), 4.82 (m), 4.85 (m), 4.97 (m), 5.06 (m), 5.07 (m), 5.21 (m), 5.24 (m), 5.52 (m), 5.76 (m), 5.79 (m) (all Fv resonances; see Table 5 for assignments for the major *cis,cis* isomer). ¹³C{¹H} NMR (CDCl₃): δ 134 (d, br, $J_{PC} = 10.4$ Hz, o-Ph), 130.85 (d, $J_{PC} = 3.1$ Hz, p-Ph), 130.79 (d, $J_{PC} = 3.1$ Hz, p-Ph), 130.38 (d, $J_{PC} = 2.9$ Hz, p-Ph), 130.31 (d, $J_{PC} = 3.1$ Hz, p-Ph), 128.72 (d, $J_{PC} = 9.8$ Hz, m-Ph), 128.69 (d, $J_{PC} =$ 10.6 Hz, *m*-Ph), 128.27 (d, J_{PC} = 9.8 Hz, *m*-Ph), 128.22 (d, J_{PC} = 10.5 Hz, m-Ph), 108.4-83.5 (Fv). The CO and *ipso-Ph* resonances were not identified.

cis,cis-2b is a purple powder, insoluble in toluene and acetone but soluble in chlorinated hydrocarbons and THF, giving orange solutions. It is air-sensitive but thermally stable both in solution and in the solid state under an inert atmosphere. cis,cis-3b is a purple solid of higher solubility with properties otherwise similar to those of 2b; the isomeric mixture of 4b is a brick red solid of higher solubility.

Method B. Into 0.6 mL of a toluene- d_8 solution of **1b** (ca. 5 mg, 5.2×10^{-3} mmol), $10 \ \mu$ L of CCl₄ (0.10 mmol), benzyl bromide (0.08 mmol), or ICH₂CO₂Et (0.08 mmol) was injected. After about 1 h, the ¹H and ³¹P{¹H} NMR spectra of the reaction mixtures showed complete transformation of **1b** into *cis,cis*-**3b**, and an isomeric mixture of **4b**, respectively.

Method C. Pure cis,cis-4b was obtained by titrating an NMR sample of 1b in toluene- d_8 with iodine dissolved in a minimum amount of the same solvent. The reaction was instantaneous, complete consumption of 1b being indicated by both ¹H and ³¹P{¹H} NMR spectroscopy. cis,cis-4b transformed into the mixture of isomers obtained by method A on standing at room temperature overnight.

 $FvMo_2(CO)_4(PCy_3)_2X_2$ (X = Cl (2c), Br (3c)). Compound **2c** (*cis,cis* isomer) was synthesized essentially as the PPh₃substituted derivative from 0.20 g (0.36 mmol) of 2a and 0.20 g (0.71 mmol) of PCy_3 in 15 mL of toluene. It was obtained reasonably pure by column chromatography, although several attempts to obtain an analytically pure sample failed. Yield: 0.24 g (0.22 mmol, 61%). ¹H NMR (CDCl₃): δ 1.23-1.45 (m, 30H, Cy), 1.69-1.82 (m, 30H, Cy), 2.28 (m, 6H, Cy), 4.85 (m, 1H, Fv), 4.95 (m, 1H, Fv), 5.20 (m, 1H, Fv), 5.28 (m, 1H, Fv), 5.30 (m, 1H, Fv), 5.34 (m, 1H, Fv), 5.89 (m, 1H, Fv), 5.94 (m, 1H, Fv). ¹³C{¹H} NMR (CDCl₃): δ 258.4 (d, J_{PC} = 26.1 Hz, CO trans to Cl), 258.0 (d, $J_{PC} = 25.8$ Hz, CO trans to Cl), \sim 245.5 (two br s, CO cis to Cl), 35.5 (d, $J_{\rm PC}$ = 17.0 Hz, C-1 Cy), 30.5 (d, $J_{PC} = 1.3$ Hz, C-3 Cy), 29.6 (s, C-3, Cy), 28.0 (d, $J_{\rm PC} = 8.9$ Hz, C-2 Cy), 27.8 (d, $J_{\rm PC} = 10.7$ Hz, C-2 Cy), 26.5 (s, C-4 Cy). The fulvalene carbon chemical shifts are given in Table 6.

The dibromide *cis*,*cis*-**3c** was obtained similarly from 0.09 g (0.14 mmol) of **3a** and 0.08 g (0.28 mmol) of PCy₃ and purified by column chromatography. Yield: 0.13 g (0.11 mmol, 80%). Anal. Calcd for C₅₀H₇₄Br₂Mo₂O₄P₂: C, 52.10; H, 6.47. Found: C, 51.79; H, 6.46. ¹H NMR (CDCl₃): δ 1.24–1.40 (m, 30H, Cy), 1.70–1.79 (m, 30H, Cy), 2.30 (m, 6H, Cy), 4.86 (m, 1H, Fv), 4.97 (m, 1H, Fv), 5.09 (m, 1H, Fv), 5.25 (m, 1H, Fv), 5.34 (m, 1H, Fv), 5.38 (m, 1H, Fv), 5.86 (m, 1H, Fv), 5.90 (m, 1H, Fv). ¹³C{¹H} NMR (CDCl₃): δ 256.2 (d, $J_{PC} = 25.7$ Hz, CO trans to Br), 255.8 (d, $J_{PC} = 26.6$ Hz, CO trans to Br), ~243.4 (two d, $J_{PC} \approx 3$ Hz, CO cis to Br), 36.6 (d, $J_{PC} = 17.6$ Hz, C-1 Cy), 30.8 (d, $J_{PC} = 4.6$ Hz, C-3 Cy), 29.9 (s, C-3 Cy), 27.9 (d, $J_{PC} = 9.0$ Hz, C-2 Cy), 27.7 (d, $J_{PC} = 11.1$ Hz, C-2 Cy),

Phosphine-Substituted Mo₂ Fulvalene Complexes

26.4 (s, C-4 Cy). The fulvalene carbon chemical shifts are given in Table 6. For IR and ${}^{31}P{}^{1}H{}$ NMR data for both *cis,cis-2c* and *cis,cis-3c*, see Tables 2 and 4, respectively.

The complex cis,cis-2c is a violet crystalline solid which is completely insoluble in hexane, toluene, and acetone but which gives cherry red solutions in chlorinated solvents and THF. The dibromide cis,cis-3c is a pink-red solid which exhibits solubility similar to that of 2c. Both compounds are thermally stable in solution as well as in the solid state.

 $FvMo_2(CO)_4(PXy_3)_2X_2$ (X = Cl (2d), Br (3d)). Compound 2d was obtained as the *cis,cis* isomer from 0.22 g (0.39 mmol) of 2a and 0.27 g (0.79 mmol) of PXy₃ in 20 mL of refluxing toluene in ~10 min. The deep red product was isolated in 75% yield (0.35 g, 0.29 mmol) and was identified by spectroscopic methods (Tables 2 and 4–6) by analogy with 3d and analogues containing PPh₃ and PCy₃.

Similarly, cis,cis-3d was obtained by reacting 0.05 g (0.08 mmol) of 3a with 0.06 g (0.16 mmol) of PXy₃ in 10 mL of toluene. In this particular case, however, ~ 2 h of refluxing was necessary to achieve complete transformation of 3a, as monitored by IR spectroscopy. The product was isolated by column chromatography in 54% yield (0.06 g, 0.04 mmol) as a purple solid. Anal. Calcd for C₆₂H₆₂Br₂Mo₂O₄P₂: C, 57.96; H, 4.86. Found: C, 56.37; H, 4.11. ¹H NMR (CDCl₃): δ 2.245 (s, 18H, Me), 2.251 (s, 18H, Me), 4.75 (m, 1H, Fv), 4.83 (m, 1H, Fv), 5.02 (m, 1H, Fv), 5.12 (m, 1H, Fv), 5.14 (m, 1H, Fv), 5.17 (m, 1H, Fv), 5.65 (m, 2H, Fv), 6.97 (s, 6H, p-Xy), 7.00 (s, 12H, o-Xy). ¹³C{¹H} NMR (CDCl₃): δ 254.5 (d, J_{PC} = 30.1 Hz, CO trans to Br), 241.4 (d, $J_{\rm PC} \approx 6$ Hz, CO cis to Br), 137.5 (d, $J_{\rm PC}$ = 10.3 Hz, C-3 Xy), 133.9 (d, $J_{\rm PC}$ = 42 Hz, C-1 Xy), 133.8 (d, $J_{\rm PC} = 42$ Hz, C-1 Xy), 132.0 (s, C-4 Xy), 131.6 (d, $J_{\rm PC} = 10.2$ Hz, C-2 Xy), 21.6 (s, Me). The fulvalene carbon chemical shifts are given in Table 6. IR and ${}^{31}P{}^{1}H}$ NMR data are listed in Tables 2 and 4, respectively.

FvMo₂(CO)₄(PMe₃)₂Br₂ (3e). This compound was observed *in situ* by IR and ¹H NMR spectroscopy as a red product of the reaction of **1c** (~10 mg, 1.7×10^{-2} mmol) with 10 μ L of CHBr₃ in 0.6 mL of toluene-*d*₈. It was identified as the *cis,cis* isomer by analogy with the well-characterized derivatives containing other phosphines and halo groups (Tables 2 and 5). In addition to the fulvalene resonances, the ¹H NMR spectrum also exhibited two doublets of equal intensity at δ 1.13 (*J*_{PH} = 9.5 Hz, 9H) and 1.14 (*J*_{PH} = 9.5 Hz, 9H), attributed to two different PMe₃ ligands in the *meso* and *dl* forms.

CpMo(CO)₂(PPh₃)I. This compound was synthesized by a modification of the literature method.⁶ A mixture of 0.20 g (0.54 mmol) of CpMo(CO)₃I and 0.145 g (0.54 mmol) of PPh₃ was dissolved in 15 mL of toluene and refluxed for 1.5 h. Slow gas evolution was observed, and IR spectroscopic monitoring indicated nearly complete transformation into the substituted product. The solvent was removed under reduced pressure, and the resulting solid was washed with 3×5 mL of hexane to remove unreacted starting materials. After the solid was dried under vacuum, 0.21 g (0.35 mmol, 64% yield) of CpMo-(CO)₂(PPh₃)I was collected as spectroscopically pure orange crystals. IR (toluene): ν_{CO} 1968 (vs), 1891 (vs) cm⁻¹. ¹H NMR (toluene- d_8): δ 4.68 (d, $J_{PH} = 1.9$ Hz, Cp, trans) and 4.82 (s, Cp, cis), 5H altogether, 6.99 (m, 9H, m,p-Ph), 7.51 (m, 6H, o-Ph). ³¹P{¹H} NMR (toluene- d_8): δ 45.4 (s, *cis*), 67.2 (s, *trans*). Both NMR spectra revealed a cis:trans = 60:40 ratio, in agreement with the literature.6

Results and Discussion

Preparation of Hexane Solutions of FvMo₂-(CO)₆H₂ (1a). Much of our research has involved utilization of the known dihydride^{2f} 1a as starting material, and we required a facile procedure for its synthesis in good yields. The salt, $(NEt_4)_2[FvMo_2(CO)_6]$, was prepared by a modification of the procedure of Smart and Curtis for the synthesis of the corresponding Li salt.^{2a} We routinely generate **1a** by protonation of $(NEt_4)_2[FvMo_2(CO)_6]$ with an excess of glacial acetic acid, in this way forming hexane solutions of ~0.01 M concentration. This method proved to be quite straightforward and reproducible.^{2f} Furthermore, since the solid dianion can be synthesized free of hexane-soluble impurities, **1a** can be readily obtained pure by IR and ¹H NMR spectroscopy. The use of hexane as solvent is also an advantage since all products formed in subsequent reactions of **1a** are insoluble in hexane and can therefore be easily isolated.

Reaction of 1a with PPh₃: Synthesis and Characterization of FvMo₂(CO)₄(PPh₃)₂H₂ (1b). We find that 1a reacts smoothly with PPh3 at ambient temperature to give the light yellow product in quantitative yield. Its solution IR spectrum exhibits two strong bands at 1936 and 1858 cm⁻¹, while the ³¹P{¹H} NMR spectrum exhibits a single, sharp resonance at δ 73.3, all data being comparable with those of the analogous Cp compound, CpMo(CO)₂(PPh₃)H.⁷ The ¹H NMR spectrum of 1b was not simple, however, exhibiting an unsymmetrical doublet at δ -5.03 ($J_{\rm PH}$ = 52 Hz), indicating nonequivalent hydride ligands (see below). and two poorly resolved fulvalene multiplets at δ 4.63 and 5.01. The ${}^{13}C{}^{1}H$ NMR spectrum revealed little additional information, one strong, sharp and one weak, broad resonance appearing at δ 88.4 and 89.8, respectively, attributable to fulvalene carbons, and three phenyl doublets, attributable to PPh₃; no quaternary carbon or carbonyl resonances could be observed.

The reactivity of 1a toward phosphines has been recently reported.^{2t} as has the isolation and spectroscopic characterization of the symmetrically substituted (fulvalene)dimolybdenum carbonyl dihydride, FvMo2- $(CO)_4(PMe_3)_2H_2$ (1c).⁸ Interestingly, similar reactions with other phosphorus ligands have not been reported.9 The smooth reaction of 1a with PPh₃, in contrast to the behavior of both FvCr₂(CO)₆H₂¹⁰ and FvW₂(CO)₆H₂,^{2t} indicates much greater substitutional lability of (fulvalene)molybdenum complexes compared with the chromium and tungsten counterparts. As well, this reaction seems to represent the reactivity limit of 1a with sterically demanding phosphines, since the relatively rapid thermal decomposition^{2f} of **1a** prevented substitution with both PCy3 and PXy3. For comparison, CpMo-(CO)₃H reacts with these ligands in refluxing benzene to give CpMo(CO)₂LH.^{7b} Nevertheless, 1b is the first hydrido-fulvalene complex containing a phosphorus ligand as bulky as PPh_3 .

Compounds of the type $FvMo_2(CO)_4L_2H_2$ may exist as four different geometrical isomers, *trans*, *trans*, *cis*,*trans* (*dl*), *cis*,*cis* (*meso*), and *cis*,*cis* (*dl*) (Figure 1),^{2t}

⁽⁶⁾ Manning, A. R. J. Chem. Soc. A 1967, 1984.

⁽⁷⁾ Data for CpMo(CO)₂(PPh₃)H are as follows. (a) IR (C₆H₆): ν_{CO} 1940 vs, 1865 s cm⁻¹. ¹H NMR (C₆D₆): δ -5.12 (d, J_{PH} = 48 Hz, MoH).^{4d} (b) ³¹P{¹H} NMR (C₆D₆/C₆H₆): δ 74.5 (s). Drake, P. R.; Baird, M. C. Queen's University at Kingston, unpublished results.

⁽⁸⁾ $FvMo_2(CO)_5(PMe_3)H_2$ has also been reported^{2t} but was obtained from the zwitterionic compound $FvMo_2(CO)_5(PMe_3)_2$ by reduction and protonation. It was not investigated whether this monosubstituted derivative was an intermediate in the reaction of 1a with PMe₃.

⁽⁹⁾ An unsuccessful attempt was made to substitute 1a with dmpm: Tilset, M. Ph.D. Dissertation, University of California, Berkeley, 1986; *Diss. Abstr. Int. B* 1987, 47, 2924 (University Microfilms, Inc., Order No. AAC 8624962).

⁽¹⁰⁾ $FvCr_2(CO)_6H_2$ shows reactivity in substitution reactions with phosphines similar to that of $FvW_2(CO)_6H_2$; that is, PMe₂Ph is the bulkiest ligand with which smooth reaction takes place at room temperature. Kovács, I.; Baird, M. C. To be submitted for publication.



Figure 1. Stereoisomers possible for compounds of the type $FvMo_2(CO)_4L_2H_2$.

giving rise potentially to nine α - and nine β -hydrogen sites. Since several substituted cyclopentadienylmolybdenum carbonyl hydrides¹¹ and $1c^{2t}$ are fluxional, facile interconversion of the various *cis* and *trans* isomers of **1b** was also anticipated. It is noteworthy that, for **1c**, four doublets from both the hydridic and PMe₃ protons but only six multiplets from the ring protons were observed at -50 °C, consistent with a 55: 45 cis:trans isomer ratio. In accord with more detailed studies on its tungsten counterpart,^{2t} these resonances were assigned to *cis*,*cis* (both *meso* and *dl*), *cis*,*trans*, and *trans*,*trans* isomers. The ³¹P{¹H} NMR spectrum of **1c** exhibited singlets at δ 21.8 (*trans*) and 25.5 (*cis*), also indicative of a mixture of *cis* and *trans* isomers.^{2t}

When a toluene- d_8 solution of **1b** was cooled to -65 °C, we observed four hydride doublet resonances centered at δ -4.99 ($J_{\rm PH} = 65$ Hz), -5.02 ($J_{\rm PH} = 21$ Hz), -5.05 ($J_{\rm PH} = 21$ Hz), and -5.06 ($J_{\rm PH} = 65$ Hz) in the ¹H NMR spectrum. The P-H coupling constants may be utilized to infer stereochemistry of such compounds,^{2t,11} the 65 and 21 Hz couplings respectively indicating that *cis* and *trans* isomers are present in a ratio of 65:35, reminiscent of the isomeric ratio (63:37) found for CpMo-(CO)₂(PPh₃)H.¹¹ The ratio of *cis,cis, cis,trans,* and *trans,trans* isomers was found to be 4:2.5:1 on the basis of integrals.

In contrast to the case for 1c, however, 12 individual fulvalene multiplet resonances were observed in the ¹H spectrum of 1b, in addition to weaker, completely obscured resonances revealed by careful integrations. Although the spectrum of 1b was too complex and poorly resolved for unambiguous assignments to be possible, detailed analyses of the similarly complicated spectra of the analogous substituted dihalo complexes were possible and are discussed below.

The ³¹P{¹H} NMR spectrum of **1b** at room temperature exhibits only a broad singlet at δ 73.3, but the spectrum at -70 °C (Table 4) was consistent with the ¹H NMR spectrum. Four partially overlapped resonances were observed at δ 73.64 (*cis,cis*) and 71.90 (*trans,trans*), as well as at 73.69 and 71.98 (*cis* and *trans* halves, respectively, of the *cis,trans* isomer). Integrals of the upfield *trans* and downfield *cis* resonances suggested a *cis:trans* ratio of ~60:40.

Reactions of 1a with Activated Alkyl Halides: Synthesis and Characterization of the Complexes $FvMo_2(CO)_6X_2$ (X = Cl (2a), Br (3a), I (4a)) and $FvMo_2(CO)_6XY$ (X = Cl, Br, I; Y = H, Cl, Br, I) (5a, 6a, 7a, 8–10). Since our attempts to substitute 1a with phosphines bulkier than PPh₃ failed, we turned our attention to the dihalides, $FvMo_2(CO)_6X_2$, to possibly provide access to (fulvalene)molybdenum(I) dimers or diradicals substituted with PCy₃ and PXy₃. If the more electrophilic dihalides would undergo ligand substitution with all three phosphines at elevated temperatures, the substituted $FvMo_2(CO)_4L_2X_2$ derivatives might be reduced either directly to $FvMo_2(CO)_4L_2$ or to dianions, $[FvMo_2(CO)_4L_2]^{2-}$, which could be either protonated to dihydrides or oxidized directly to radicals/dimers.

Surprisingly, of this series of compounds, only **4a** had previously been reported;^{2g} it was prepared by the reaction of iodine with $FvMo_2(CO)_6$, no practical details or spectroscopic data being given. On attempting to employ this method for the synthesis of **3a** in CH₂Cl₂, we observed rapid CO evolution and precipitation of a brown solid, containing no carbonyl ligands; **3a** was formed only in minor amounts. However, the reaction of benzyl bromide or bromoform with **1a** gave **3a** in excellent yields.

Indeed, reaction of **1a** with the appropriate alkyl halides provided general access to all of the three dihalides, 2a, 3a, and 4a, although all were sufficiently labile that none could be obtained analytically pure. Typically, 1a was stirred with a large excess of CCl₄, CHBr₃, or ICH_2CO_2Et in hexane at ambient temperature; 2a, 3a, and 4a, respectively, precipitated as red solids and were characterized by IR and ¹H and ¹³C- ${^{1}H}$ NMR spectroscopy (Tables 2, 3, and 6). Each IR spectrum exhibits two strong carbonyl stretching bands. which are shifted to lower frequencies in the order 4a > 3a > 2a, consistent with the relative electronegativities of the halogens and similar to behavior of the analogous Cp and indenyl complexes.¹² In addition, the ¹H NMR spectra each exhibited two well-resolved virtual "triplets" of equal intensity, characteristic of H_{α} and H_{β} fulvalene protons (AA'MM' spin systems).^{2h} The $^{13}C{^{1}H}$ NMR spectra were also fully consistent with the formulations, exhibiting resonances attributable to the three types of fulvalene sites as well as the CO ligands. Indeed, separate CO resonances were observed for CO ligands cis and trans to X, as has been observed previously for the corresponding Cp compounds.¹³

During the syntheses of these compounds, additional weak bands were occasionally observed in both the IR and ¹H NMR spectra of the products. In an attempt to identify the minor species, we monitored an in situ reaction of **1a** with benzyl bromide in toluene- d_8 by ¹H NMR spectroscopy. Interestingly, during the first 20 min of the reaction, only four fulvalene "triplet" resonances at δ 4.28, 4.58, 4.73, and 4.89, all of equal intensity and corresponding to the above-mentioned weak resonances, could be observed. After this time, the two "triplet" resonances of 3a slowly began to emerge at δ 4.27 and 4.86 and gradually became the dominant resonances, as those of 1a (δ 4.52, 4.87) and, later, of the intermediate species diminished (~ 2 h). While both 1a and the intermediate were present in the reaction mixture, two hydridic resonances, separated only by 0.007 ppm, also appeared at $\delta \sim -5.30$. This observation suggested the formation of the mixed hydrido bromide **6a**, and subsequently the corresponding hydrido-chloride and -iodide analogues were also

⁽¹²⁾ Hart-Davis, A. J.; White, C.; Mawby, R. J. Inorg. Chim. Acta 1970, 4, 431.

⁽¹¹⁾ Faller, J. W.; Anderson, A. S. J. Am. Chem. Soc. 1970, 92, 5852.

⁽¹³⁾ Todd, L. J.; Wilkinson, J. R.; Hickey, J. P. J. Organomet. Chem. 1978, 154, 151.

identified in the reactions of 1a with CCl₄ and ICH₂-CO₂Et, respectively. ¹H NMR data for these complexes are listed in Table 3.

The kinetic stabilities of the initially formed **5a**, **6a**, and **7a** in the presence of excess alkyl halides must be attributed to deactivation by the halo ligand on the metal center adjacent to that bearing the hydride ligand. Fortunately, our method of preparation of the dihalides provided a basis to obtain the hydrido halides in the solid state as mixtures with the corresponding dihalides, although the resulting mixtures could not be separated. As shown in eq 2 for **7a**, hydrido halides readily undergo

$$2FvMo_{2}(CO)_{6}HI \rightleftharpoons FvMo_{2}(CO)_{6}H_{2} + FvMo_{2}(CO)_{6}I_{2} \rightarrow FvMo_{2}(CO)_{6}I_{2} + FvMo_{2}(CO)_{6} + H_{2}$$
(2)

redistribution reactions which prevent separation by chromatography. As a result of decomposition of 1a, the final organometallic products from the hydrido halides are the corresponding dihalides and FvMo₂-(CO)₆. On the other hand, since the three hydrido halides all react further with alkyl halides to form the corresponding dihalides, it seemed likely that treatment of these isolated compounds with a second alkyl halide would result in formation of the mixed dihalides. Indeed, we succeeded in the *in situ* preparation of mixed dihalides **8**, **9**, and **10**, which were characterized by ¹H NMR spectroscopy (Table 3).

Complexes 8-10 were also obtained by a second method, avoiding the use of alkyl halides. The facile nature of the redistribution reaction of the hydrido halides (eq 2) suggested that pairs of dihalides might also exchange halide ligands reversibly. Indeed, when the dihalides 2a, 3a, and 4a were dissolved in pairs in toluene- d_8 or acetone- d_6 , slow equilibration reactions leading to the formation of the corresponding mixed dihalides were observed by ¹H NMR spectroscopy (eq 3; X, Y = Cl, Br, I). Because of these ligand exchange

$$FvMo_2(CO)_6X_2 + FvMo_2(CO)_6Y_2 \rightleftharpoons$$

 $2FvMo_2(CO)_6XY$ (3)

processes, the mixed-halogen compounds could not be obtained pure.

Synthesis and Characterization of the Complexes $FvMo_2(CO)_4L_2X_2$ (L = PPh₃, PCy₃, PXy₃; X = Cl, Br, I (2b-d, 3b-d, 4b) and FvMo₂- $(CO)_4(PPh_3)_2HX$ (X = Cl (5b), Br (6b), I (7b)). Phosphine-substituted (fulvalene)dimolybdenum carbonyl dihalo compounds containing PPh₃, PCy₃, and PXy₃ were readily prepared by direct substitution of a CO ligand at each Mo center of the parent dihalides 2a, 3a, and 4a. These reactions were surprisingly facile, substitution with PPh₃ being complete in less than 1 day at room temperature (similarly to 1a) and the bulkier ligands reacting with vigorous gas evolution in ${\sim}10$ min to 2 h on heating to 110 °C. Interestingly, while a considerable amount (<40%) of the starting materials decomposed to $FvMo_2(CO)_6$ during these reactions, it was found that the thermal decomposition of 2a in toluene at ~ 100 °C in the absence of added phosphine proceeds with gas evolution to yield an unidentified, insoluble precipitate and only traces of $FvMo_2(CO)_6$. In contrast, analogous Cp complexes require refluxing in benzene for at least several hours to produce CpMo $(CO)_2LX (L = PPh_3, PCy_3, PXy_3)$, and do not decompose to $[CpMo(CO)_3]_2$.^{7b}

Complexes 2b-d, 3b-d, and 4b were isolated as brick red, purple, or violet solids in good yields. The PPh₃-substituted products were identical with 2b, 3b, and 4b, formed by the hydrogen-halogen exchange of 1b with CCl₄, PhCH₂Br, and ICH₂CO₂Et, respectively. In addition, 4b was obtained in solution by reacting 1bwith iodine. IR and multinuclear NMR techniques were used to characterize the products (Tables 2 and 4-6), all of which are new.

For all of the substituted dichlorides and dibromides, as well as for **4b** freshly prepared from **1b** and iodine, the IR spectra exhibited two carbonyl stretching bands (Table 2). However, while the ${}^{31}P{}^{1}H$ NMR spectra of **2b** and **3b** in CDCl₃ exhibited sharp singlets at δ 49.9 and 47.8, respectively, the ${}^{31}P{}^{1}H$ NMR spectra in toluene- d_8 each exhibited two resonances of equal intensity (Table 4). In addition, the ${}^{13}C{}^{1}H$ NMR spectra of both 2b and 3b (CDCl₃) exhibited two sets of five resonances in the fulvalene region (Table 6), while only a single set of PPh₃ phenyl ${}^{13}C{}^{1}H$ resonances was observed. In addition, four doublets appeared in the low-field region of coordinated CO ligands, arranged in two pairs (each pair having the same P-C coupling constants) due to the difference between ligands being in positions cis or trans to halogen (or phosphine).¹³

In contrast, the ${}^{31}P{}^{1}H$ NMR spectra of 2c,d and 3c,d all exhibited two singlets of equal intensity even in CDCl₃, the chemical shift difference between these resonances increasing with the bulk of phosphines, i.e. $PPh_3 < PCy_3 < PXy_3$.¹⁴ Furthermore, the ¹³C{¹H} NMR spectra of 2c and 3c,d exhibited five pairs of singlets in the fulvalene carbon region, similar to the PPh3substituted derivatives. Interestingly, the high-field resonances of 2c and 3c, which probably belong to the C_{α} carbons, 2h appear as doublets, suggesting unusual coupling to phosphorus. The cyclohexyl carbon region of 2c and 3c also provided new information, there being two pairs of doublets, attributed to C-2 and C-3, and a doublet and a singlet, attributed to C-1 and C-4, respectively. For 3d, only single resonances were found in the methyl and aromatic carbon region, except that the weak and broad C-1 Xy resonance appeared as two doublets. In contrast to the PPh₃- and PCy₃-substituted derivatives, only one pair of doublet CO carbon resonances was observed in the ¹³C{¹H} NMR spectrum of 3d.

The ¹H NMR spectra of all four compounds exhibited eight fulvalene multiplets of equal intensity, consistent with the ${}^{13}C{}^{1}H$ NMR spectra, although some spectra were complicated by an overlap of resonances (Table 5). Utilization of ¹H-¹H decoupling experiments made possible assignments of the resonances as belonging to identical or different rings. As an example, the ¹H NMR spectrum of 2b, recorded in CDCl₃, exhibited a readily recognizable pattern of eight well-separated multiplets arranged into four pairs at δ 4.88 and 4.96, 5.11 and 5.17, 5.28 and 5.32, and 5.70 and 5.75 (Figure 2). These resonances were assigned as belonging to the two different ring systems as follows: H_{β} , $H_{\beta'}$, $H_{\alpha'}$, and H_{α} resonate at δ 4.88, 5.11, 5.32 and 5.75, respectively, in one ring, and at δ 4.96, 5.17, 5.28, and 5.70, respectively, in the other. As we show below, the two rings probably

⁽¹⁴⁾ Tolman, C. A. Chem. Rev. 1977, 77, 313.





Figure 2. ¹H NMR spectrum (400 MHz) of cis,cis- $FvMo_2(CO)_4(PPh_3)_2Cl_2$ (2b) in the fulvalene proton region.

do not represent the two halves of a single fulvalene system but, rather, two different fulvalene systems in which the halves are spectroscopically identical.

The ¹H NMR spectrum of **2b** also exhibited a remarkable temperature dependence of the chemical shifts, gradual cooling of the solution to -70 °C resulting in a shifting of the eight resonances to δ 4.86, 5.04, 5.11, 5.24, 5.19, 5.38, 5.81, and 5.86, respectively. Furthermore, while heating a toluene- d_8 solution of **2b** resulted in pairs of resonances coalescing at 110 °C to give a four-resonance spectrum, the resulting $H_{\alpha}-H_{\alpha'}$ and $H_{\beta}-H_{\beta'}$ pairs of resonances did not coalesce to give a two-resonance spectrum similar to that of **1b** at room temperature.

The ¹H NMR spectrum of a CDCl₃ solution of **2c** also exhibited eight separate multiplets in the fulvalene region (Table 5), and these were also readily differentiated into two groups of four on the basis of ¹H-¹H decoupling experiments as follows: H_{β} , $H_{\beta'}$, $H_{\alpha'}$, and H_{α} resonate at δ 4.85, 5.20, 5.30, and 5.94, respectively, in one ring and at δ 4.95, 5.28, 5.34, and 5.89, respectively, in the other. Surprisingly, when **2c** was freshly dissolved in CD₂Cl₂ and the spectrum recorded without delay, the first set of resonances were of approximately twice the intensity of the other. Within about 2 h, however, all of the resonances had became equal, indicating that a relatively slow equilibration process had taken place between two different species.

These results are consistent with structures containing the CO ligands in mutually *cis* arrangements and the pairs of α and β fulvalene protons and carbons being diastereotopic because of the chiral Mo centers. By analogy, while the compounds cis-CpMo(CO)₂LX are chiral,^{11,15} the chirality has only been confirmed by ¹H NMR investigations on derivatives where X = CH_2R or $L = PMe_2Ph$, in which the chiral center rendered the methylene or methyl protons diastereotopic. While examples with diastereotopic cyclopentadienyl nuclei are rare, we note that the chirality of the identyl complex $(\eta^5 - C_9 H_7) M_0(CO)_2(PPh_3)$ results in nonequivalence of H_{α} and $H_{\alpha'}$ protons.¹⁵ In the case of the fluorenylisopropyl-substituted complex (η^5 -C₅H₄- $CMe_2C_{13}H_9)Mo(CO)_2(PMe_3)H$, nonequivalence of the cyclopentadienyl carbons was reported.¹⁶

As mentioned above, fulvalene compounds of the type cis,cis-FvMo₂(CO)₄L₂X₂ contain two chiral centers and can form *meso* and *dl* stereoisomers.^{2t} The *meso* isomer has a plane of symmetry between the two rings, and thus only four Fv protons, five Fv carbons, and one phosphorus environment are expected. On the other hand, while the *dl* isomers contain no plane of symmetry, there is a C_2 axis perpendicular to the Fv plane (Figure 1), and again only four Fv protons, five Fv carbons, and one phosphorus environment are expected. On this basis, the spectral changes described above seem best interpreted in terms of *meso-dl* interconversion, presumably *via* intramolecular CO-phosphine exchange.

In view of the differences in the NMR spectra of 1b,c, arising from substitution of the small PMe₃ with the larger bulky PPh₃, we decided to investigate the consequences of changing the halide ligands as well. First, **3e** was generated *in situ* by reacting **1c** with PhCH₂Br and was found to exhibit the same IR and ¹H NMR characteristics as do most of the complexes of bulkier phosphines. That is, **3e** exists in solution as the *cis,cis* isomer, which gives rise to eight fulvalene proton resonances (two of them completely overlapping at δ 4.41) in the ¹H NMR spectrum. Thus, substitution of a small hydride ligand by a bulkier halide ligand results in the same effect on the appearance of the spectra as replacing a small phosphine with a sterically more demanding one.

Unlike the dichlorides and dibromides, *cis,cis*-4b, obtained in situ by reacting 1b with iodine, was not stable in solution. While the IR spectrum of a sample which had remained in solution at room temperature for 1 day did not exhibit any new carbonyl stretching bands, the medium-intensity band of cis,cis-4b at 1887 cm⁻¹ gained in relative intensity and became as strong and sharp as the band at 1965 cm^{-1} , suggesting the formation of one or more trans isomers.¹¹ In accordance with this, the ${}^{31}P{}^{1}H$ NMR spectrum exhibited three additional resonances at δ 45.9, 67.0, and 67.3, downfield from those of *cis*, *cis*-**4b** at δ 45.7 and 45.8. Those at δ 67.0 and 45.9 were of equal intensity and are tentatively assigned to the nonequivalent sites of the cis, trans isomer; by default, then, the resonance at δ 67.3 is tentatively assigned to the trans, trans isomer. The ¹³C{¹H} NMR spectrum of the reaction mixture supported the ³¹P{¹H} NMR spectroscopic interpretation. Altogether, four doublet resonances were observed for both the C-3 and C-4 carbon atoms of the coordinated PPh₃, suggesting four different phosphine environments. The doublets characteristic of both types of carbons were clearly arranged in two distinct pairs, suggesting that each pair contained resonances of two similar ligands, *i.e.* two *cis* and two *trans*, as in the ³¹P-{¹H} NMR spectrum.

The ¹H NMR spectrum of the mixture exhibited eight fulvalene multiplets at δ 4.30, 4.36, 4.82, 4.97, 5.07, 5.21, 5.24, and 5.76, in addition to those of *cis,cis*-4b. A mixture of *cis,trans* and *trans,trans* isomers of 4b should exhibit 10 new resonances, but there is considerable overlap and a possibility of coincidence of some resonances of the *cis,trans* isomer. Thus, the spectrum is taken as being reasonably consistent with conversion to a mixture of *cis,trans* and *trans,trans* isomers of 4b, established above on the basis of IR and ³¹P NMR data.

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Phosphine-Substituted Mo₂ Fulvalene Complexes

When **4b** was prepared by direct substitution of **4a** with PPh₃, the same ¹H NMR spectrum was obtained. In fact, pure *cis,cis*-**4b** could not be prepared in this way, possibly because equilibration of the three isomers took place quickly at 110 °C or over 1 day at room temperature. Hydrogen-halogen exchange reactions of **1b** with ICH₂CO₂Et, ICH₂CN, or *t*-BuI gave varying ratios of the three isomers of **4b**.

Consistent with the above spectroscopic results, we note that while *cis*-CpMo(CO)₂(PPh₃)I also readily isomerizes, the corresponding chloro and bromo compounds remain exclusively as the *cis* isomer.^{11,17} The ³¹P{¹H} NMR spectral data for *cis*- and *trans*-CpMo(CO)₂(PPh₃)I have not been reported, but we find that the ³¹P{¹H} NMR spectrum of an equilibrium mixture of the *cis* and *trans* isomers exhibits singlets at δ 45.4 and 67.2, respectively, supporting the above assignments.

The intermediate formation of hydrido-halide complexes in the reaction of **1a** with activated alkyl halides suggested that similar reactions of 1b might proceed in the same way. Indeed, ¹H and ³¹P{¹H} NMR monitoring of the reactions of 1b with CCl₄, PhCH₂Br, and ICH₂CO₂Et or ICH₂CN unambiguously established the sole formation of **5b**, **6b**, and **7b**, respectively, early in the reactions. The hydridic doublet and fulvalene multiplet resonances of 5b and 6b could be readily assigned (Table 5), but overlapping of the various isomers of the iodo system rendered assignments of the fulvalene proton resonances of 7b ambiguous. Nevertheless, two new hydridic doublets were observed at δ -4.99 and -5.01, attributed to hydrido-iodide compounds having both *cis* and *trans* iodide "halves", respectively. Consistent with this, new cis and trans ${}^{31}P{}^{1}H$ NMR resonances were also observed (Table 4).

The mechanism of hydrogen-halogen exchange in both substituted and unsubstituted dihydrides also merits comment. According to a recent review,¹⁸ several mechanistic studies suggest that the reactions between alkyl halides and metal carbonyl hydrides may involve radical chain processes, as in eqs 4-6.

$$\operatorname{In}^{\bullet} + \operatorname{HM}(\operatorname{CO})_n \mathcal{L} \to \operatorname{In}\mathcal{H} + {}^{\bullet}\mathcal{M}(\operatorname{CO})_n \mathcal{L}$$
 (4)

$$^{\bullet}\mathrm{M}(\mathrm{CO})_{n}\mathrm{L} + \mathrm{RX} \rightarrow \mathrm{XM}(\mathrm{CO})_{n}\mathrm{L} + \mathrm{R}^{\bullet}$$
(5)

$$\mathbf{R}^{\bullet} + \mathbf{H}\mathbf{M}(\mathbf{CO})_{n}\mathbf{L} \rightarrow \mathbf{R}\mathbf{H} + {}^{\bullet}\mathbf{M}(\mathbf{CO})_{n}\mathbf{L}$$
(6)

$In^{\bullet} = unidentified radical initiator$

The particular structure of fulvalene complexes, coupled with our experimental results and the known behavior of the analogous chromium-centered radical $CpCr(CO)_3$,¹⁹ permit speculation on the involvement of



novel bimetallic radical intermediates. As shown in Scheme 1 for a fulvalene system of the type FvMo₂- $(CO)_4L_2H_2$, hydrogen atom abstraction should result in two types of chain-propagating, metal-centered radicals: an initially formed radical hydride species and a subsequently formed halo radical species. In addition, the hydrogen or halogen atoms in the radical intermediates may also undergo rapid exchange processes involving the two metals, as occurs between $CpCr(CO)_3$ and the compounds $CpCr(CO)_3X$ (X = H, Br, I).^{1h,19} The forced proximity of the metals in fulvalene complexes would increase the possibility of intramolecular atom exchange, but it is also reasonable to suppose that the radical intermediates may undergo intermolecular exchange processes of hydride and/or halide ligands, consistent with the reactions outlined in eqs 2 and 3. Note that the possible radical chain hydride and halide ligand redistributions in our fulvalene systems provide a novel mechanistic alternative. Such ligand redistributions have received considerable attention recently but were studied exclusively on coordinatively unsaturated complexes, and no other mechanisms were considered.²⁰

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