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Hydrogen–halogen exchange reactions of $(\eta^5:\eta^5\text{-}C_{10}H_8)W_2(CO)_4(PPh_2Me)_2H_2$ with CCl_4 and CHI_3; characterization of $(\eta^5:\eta^5\text{-}C_{10}H_8)W_2(CO)_4(PPh_2Me)_2X_2$ (X = Cl, I) and crystal structure determination of the iodide

Istvan Kovacs *, Celine Pearson, Alan Shaver

Department of Chemistry, McGill University, 801 Sherbrooke St. W., Montreal, Quebec, H3A 2K6, Canada

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Abstract

Hydrogen–halogen exchange reactions of $FvW_2(CO)_4(PPh_2Me)_2H_2$ (**1**) with CCl_4 and CHI_3 gave $FvW_2(CO)_4(PPh_2Me)_2Cl_2$ (**2**) and $FvW_2(CO)_4(PPh_2Me)_2I_2$ (**3**), respectively, in nearly quantitative isolated yield (Fv = $\eta^5:\eta^5\text{-}C_{10}H_8$, fulvalene). Both reactions were shown by ^1H- and $^{31}P\{^1H\}$-NMR spectroscopy to proceed via $FvW_2(CO)_4(PPh_2Me)_2HX$ (X = Cl, I) intermediates. Two isomers of the hydrido–halide complexes, containing a *cis* or *trans* halide half, were identified in the reaction mixtures. When the reactions were complete, **3** was found to maintain an equilibrium mixture of *cis*,*cis* (D,L-/*meso*- = 1:1), *cis*,*trans* and *trans*,*trans* isomers in solution. The equilibrium was strongly solvent dependent. While minor amounts of the *cis*,*trans* (but no *trans*,*trans*) isomer were also detected during the formation of **2**, this compound was found to exist solely as a 1:1 mixture of D,L- and *meso*-*cis*,*cis* isomers in equilibrated solutions. Crystallization of **3** gave the *meso*-*cis*,*cis* isomer, which was characterized by X-ray diffraction. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Metal hydrides; Metal halides; Hydrogen–halogen exchange; Fulvalene complexes; Tungsten complexes; Carbonyl complexes; Phosphine substitution; Isomerization; NMR spectroscopy; Crystal structure

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1. Introduction

The hydrogen–halogen exchange reaction of metal carbonyl hydrides ($HM(CO)_nL_m$; L = phosphine) with sufficiently activated alkyl halides (RX; X = Cl, Br, I) is a mild and straightforward method to produce the corresponding metal halide derivatives in practically quantitative yield [1]. One of the most recent applications of this reaction has been the synthesis of $FvM_2(CO)_4L_2X_2$ (Fv = $\eta^5:\eta^5\text{-}C_{10}H_8$ (fulvalene); M = Cr, Mo, W; L = CO, phosphine; X = Cl, Br, I) type dihalides from the corresponding dihydrides [2]. In a number of cases, this method was not only more convenient and economic than the alternative syntheses utilizing the elemental halogen and/or phosphine substitution but is the only way to obtain the target compounds. Such dihalides are versatile intermediates in the synthesis of other fulvalene derivatives and also are interesting in their own right [2,3]. The chemistry of dinuclear (fulvalene)metal carbonyl and related complexes has attracted considerable interest in recent years due to their unique reactivity, different from that of analogous cyclopentadienyl complexes, which is a result of the close proximity and electronic communication of neighbouring metal centres anchored to the fulvalene ligand [4]. As for the hydrogen–halogen exchange reaction, it has been reported that (fulvalene)chromium and molybdenum dihydrides react in two distinctive steps, via hydrido–halide intermediates of the type

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* Corresponding author.

E-mail address: ezc4@musica.mcgill.ca (I. Kovacs)

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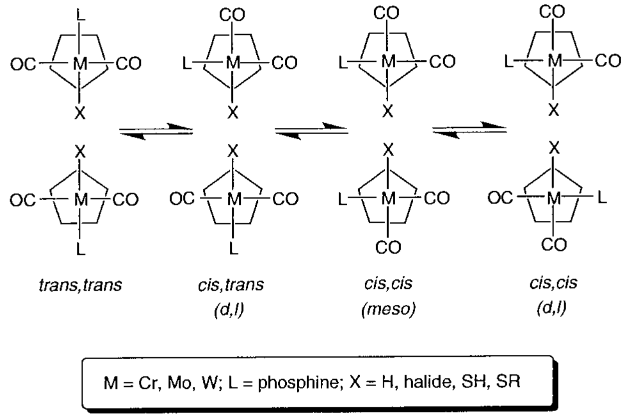
$FvM_2(CO)_4L_2HX$, to give the corresponding dihalides [2b,c]. Although the complexes $FvW_2(CO)_6X_2$ (X = Cl, Br) were also prepared by this method, no comment was made about the course of the reaction [2a]. $FvW_2(CO)_6I_2$ was obtained by treatment of the corresponding dihydrides with iodine [2a]. Its ligand-substituted derivatives were obtained by Me_3NO assisted ligand substitution of the parent hexacarbonyl [3e].

One of the most interesting features of ligand-substituted fulvalene complexes of the general formula $FvM_2(CO)_4L_2X_2$ (M = Cr, Mo, W; L = phosphine, phosphite; X = H, halide, SH, SR) type complexes is their isomerization behaviour. Four isomers (not including enantiomers) are possible: *cis,cis* (D,L- and *meso*-), *cis,trans* and *trans,trans* (Scheme 1). Each isomer can easily be identified by its complex NMR pattern reflecting its symmetry [2,3e]. In particular, the dihalide isomers, unlike the dihydrides, undergo slow exchange on the NMR time scale at room temperature and thus exhibit well resolved spectra. NMR studies indicate that sometimes the equilibrium lies completely in favour of the *cis,cis* isomers. Although this cannot be predicted on the basis of present knowledge of the combined steric and electronic effects of the metal, ligand and halide, it suggests that $FvM_2(CO)_4L_2X_2$ dihalides might have a general tendency to assume the *cis,cis* arrangement under appropriate conditions. This is supported by our most recent observation that $FvW_2(CO)_4(PPh_2Me)_2(SH)_2$, which shows an isomerization behaviour similar to $FvW_2(CO)_4(PPh_2Me)_2I_2$ in solution (four isomers), crystallized solely as the *cis,cis* isomer(s) [2d]. Upon dissolution, a 1:1 mixture of D,L- and *meso-cis,cis* isomers slowly transformed into the equilibrium mixture of four isomers. The reverse process, however, has been demonstrated previously for *cis,cis*-$FvMo_2(CO)_4(PPh_3)_2I_2$ [2b].

Furthermore, the *cis,cis* isomers are always present in solution as a 1:1 mixture of D,L and *meso* forms. In only one instance has this equilibrium, which is generally much faster than the *cis*↔*trans* equilibrium, been shifted upon crystallization. The ^1H-NMR spectrum of freshly dissolved *cis,cis*-$FvMo_2(CO)_4(PCy_3)_2Cl_2$ in CD_2Cl_2 exhibited a ca. 2:1 ratio of D,L and *meso* forms and the final 1:1 ratio was achieved quite slowly [2b]. In order to determine which one of the two *cis,cis* forms of a particular complex is present in the crystalline state, an X-ray diffractional analysis has to be carried out. However, no crystallographic data at all are available in the literature for substituted fulvalene complexes of the general formula $FvM_2(CO)_4L_2X_2$ (M = Cr, Mo, W; L = phosphine, phosphite; X = H, halide, SH, SR, alkyl, acyl, etc.).

Here we report a multinuclear NMR study of the hydrogen–halogen exchange reaction of $FvW_2(CO)_4(PPh_2Me)_2H_2$ (**1**) with CCl_4 and CHI_3, characterization of the corresponding dihalide products $FvW_2(CO)_4(PPh_2Me)_2X_2$ (X = Cl (**2**), I (**3**)), as well as the crystal structure of *meso-cis,cis*-**3**. A remarkable solvent and phase dependency of the isomeric composition of **3** was observed.



Scheme 1.

2. Experimental

2.1. General procedures

All manipulations were carried out under an inert atmosphere (N_2 or Ar) at room temperature, using standard Schlenk technique and a drybox. Solvents were dried and freshly distilled under nitrogen prior to use. $FvW_2(CO)_4(PPh_2Me)_2H_2$ (**1**) was prepared as reported [2d]. IR spectra were recorded on a Bruker IFS 48 spectrometer in THF solutions using a 0.1 mm NaCl cell. ^1H-, $^{13}C\{^1H\}$-, and $^{31}P\{^1H\}$-NMR measurements were performed on Jeol CPF 270 and Varian Unity 500 spectrometers at operating frequencies 270.167 (499.843), 67.940 and 109.376 MHz, respectively. COSY experiments were performed on the 500 MHz instrument. Elemental analyses were carried out by the 'Laboratoire d'Analyse Elementaire' at the University of Montreal.

2.2. $FvW_2(CO)_4(PPh_2Me)_2Cl_2$ (2)

To a 50 ml CH_2Cl_2 solution of **1** (1.0 g, 0.99 mmol) 5 ml of CCl_4 was injected at room temperature. The originally yellow solution rapidly changed colour to red and after stirring for 1 day a red precipitate had formed. The volume of the solution was reduced to about 10 ml under vacuum and hexane was added to complete the precipitation of **2**. The solid product was filtered, washed with hexane and dried under reduced pressure. Yield: 1.08 g (1.00 mmol, 99%). Complex **2** is very poorly soluble in most commonly used solvents. Crystalline samples were obtained by performing the reaction in a filtered and concentrated acetone-d_6 solution of **1** without agitation. Combustion analysis suggested that two solvent molecules per complex were retained in the lattice upon crystal formation, similar to **3** (see below). Anal. Calc. for $C_{46}H_{34}D_{12}Cl_2O_6P_2W_2$: C, 45.76; H(D), 3.84. Found: C, 45.56; H(D), 3.84. IR (THF): ν(CO) 1949 (vs), 1856 (m) cm^{-1}.

2.2.1. NMR data in acetone-d_6 solution (270 MHz)

cis,cis isomers (D,L-/*meso*- = 1:1, 100%); ^{1}H-NMR: δ 2.28, 2.29 (both d, J(P–H) = 9 Hz, 6H, PMe), 5.17 (m, 6H, Fv), 5.31, 5.64, 5.76, 5.83, 6.10 (all m, 2H, Fv), 7.45 (m, 24H, *m,p*-Ph), 7.52, 7.63 (both m, 8H, *o*-Ph). $^{13}C\{^1H\}$-NMR: δ 84.5, 84.6, 86.1, 87.0, 90.2, 92.2, 96.9, 97.3 (all Fv), 128.3, 128.4 (both d, J(P–C) = 8 Hz, *m*-Ph), 130.1, 130.4 (both *p*-Ph), 132.3, 132.4 (both d, J(P–C) = 9 Hz, *o*-Ph). The weak PMe, C-1 fulvalene and *ipso*-Ph resonances could not be distinguished unequivocally due to low concentration of the samples. $^{31}P\{^1H\}$-NMR: δ 7.9, 8.1 (both s, J(W–P) = 260 Hz, 2P).

2.3. $FvW_2(CO)_4(PPh_2Me)_2I_2$ (**3**)

Complex **1** (1.5 g, 1.48 mmol) was dissolved in 50 ml of toluene and solid iodoform (1.2 g, 3.05 mmol) was added to the stirred solution at room temperature. The starting yellow colour quickly changed to orange and a red–orange solid precipitated overnight. Following a workup similar to that of **2**, complex **3** was obtained as an orange powder. Yield: 1.8 g (1.41 mmol, 95%). For an alternative preparation see reference [3e]. Again, a crystalline sample was obtained by performing the reaction in a concentrated acetone-d_6 solution of **1**. Combustion analysis suggested that the crystals consisted of **3** and solvent in the lattice in a 2:1 molar ratio. This was verified by an X-ray crystal structure. Anal. Calc. for $C_{46}H_{34}D_{12}I_2O_6P_2W_2$: C, 39.74; H(D), 3.33. Found: C, 39.39; H(D), 3.13. IR (THF): ν(CO) 1949 (s), 1870 (vs) cm^{-1}.

2.3.1. NMR data in acetone-d_6 solution (270 MHz)

cis,cis isomers (D,L-/*meso*- = 1:1, 28%); ^{1}H-NMR: δ 2.63 (d, J(P–H) = 8 Hz, 12H, PMe), 5.16, 5.20, 5.26, 5.45, 5.56, 5.71 (all m, 2H, Fv), 6.14 (m, 4H, Fv), ≈7.4–7.7 (m, 40H, PPh). $^{31}P\{^1H\}$-NMR: δ −3.5, −3.2 (both s, J(W–P) = 240 Hz, 2P).

cis,trans isomer (48%); ^{1}H-NMR: δ 2.43 (d, J(P–H) = 9 Hz, 3H, PMe, *trans*), 2.57 (d, J(P–H) = 9 Hz, 3H, PMe, *cis*), 4.96 (m, 1H, Fv), 5.16 (m, 2H, Fv), 5.20, 5.27, 5.42, 5.56, 6.03 (all m, 1H, Fv), ≈7.4–7.7 (m, 20H, PPh). $^{31}P\{^1H\}$-NMR: δ −3.5 (s, J(W–P) = 240 Hz, 1P, *cis*), 9.4 (s, J(W–P) = 240 Hz, 1P, *trans*).

trans,trans isomer (24%); ^{1}H-NMR: δ 2.40 (d, J(P–H) = 9 Hz, 6H, PMe), 5.13 (m, 8H, Fv), ≈7.4–7.7 (m, 20H, PPh). $^{31}P\{^1H\}$-NMR: δ 9.7 (s, J(W–P) = 240 Hz, 2P).

2.3.2. NMR data in DMSO-d_6 solution (500 MHz)

cis,cis isomers (D,L-/*meso*- = 1:1, 14%); ^{1}H-NMR: δ 2.57 (d, J(P–H) = 9 Hz, 12H, PMe), 5.07, 5.23, 5.28, 5.70, 5.94 (all m, 2H, Fv), 6.35 (m, 4H, Fv), ≈7.3–7.5 (m, 40H, PPh). $^{31}P\{^1H\}$-NMR: δ −1.9, −1.3 (both s, J(W–P) = 240 Hz, 2P).

cis,trans isomer (53%); ^{1}H-NMR: δ 2.35 (d, J(P–H) = 9 Hz, 3H, PMe, *trans*), 2.52 (d, J(P–H) = 9 Hz, 3H, PMe, *cis*), 5.00, 5.20, 5.28, 5.33, 5.38, 5.43, 5.70, 6.17 (all m, 1H, Fv), ≈7.3–7.5 (m, 20H, PPh). $^{31}P\{^1H\}$-NMR: δ −1.9 (s, J(W–P) = 240 Hz, 1P, *cis*), 9.1 (s, J(W–P) = 240 Hz, 1P, *trans*).

trans,trans isomer (33%); ^{1}H-NMR: δ 2.33 (d, J(P–H) = 9 Hz, 6H, PMe), 5.20 (m, 8H, Fv), ≈7.3–7.5 (m, 20H, PPh). $^{31}P\{^1H\}$-NMR: δ 9.3 (s, J(W–P) = 240 Hz, 2P).

2.3.3. NMR data in $CDCl_3$ solution (270 MHz)

cis,cis isomers (D,L-/*meso*- = 1:1, 24%); ^{1}H-NMR: δ 2.46, 2.48 (both d, J(P–H) = 8 Hz, 6H, PMe), 4.81, 4.90, 5.10, 5.26, 5.67, 5.73 (all m, 2H, Fv), 5.19 (m, 4H, Fv), ≈7.4–7.7 (m, 40H, PPh). $^{31}P\{^1H\}$-NMR: δ −4.4, −4.3 (both s, 2P).

cis,trans isomer (59%); ^{1}H-NMR: δ 2.36 (d, J(P–H) = 9 Hz, PMe, *trans*), 2.43 (d, J(P–H) = 8 Hz, PMe, *cis*), 4.66 (m, 1H, Fv, *trans*), 4.75 (m, 1H, Fv, *trans*), 4.90 (m, 1H, Fv, *cis*), 4.95 (m, 1H, Fv, *trans*), 5.00 (m, 1H, Fv, *trans*), 5.14 (m, 1H, Fv, *cis*), 5.19 (m, 1H, Fv, *cis*), 5.79 (m, 1H, Fv, *cis*), Å7.4-7.7 (m, 20H, PPh). $^{31}P\{^1H\}$-NMR: δ −4.3 (s, 1P, *cis*), 10.3 (s, 1P, *trans*).

trans,trans isomer (17%); ^{1}H-NMR: δ 2.34 (d, J(P–H) = 9 Hz, 6H, PMe), 4.81, 5.00 (both m, 4H, Fv), ≈7.4–7.7 (m, 20H, PPh). $^{31}P\{^1H\}$-NMR: δ 10.5 (s, 2P).

2.4. Characterization of the hydrido–halide intermediates

Reactions of **1** (30 mg, 0.03 mmol) with CCl_4 (40 µl, 0.41 mmol) or CHI_3 (24 mg, 0.06 mmol) in 0.7 ml acetone-d_6 solutions were monitored by ^{1}H- (270 MHz) and $^{31}P\{^1H\}$-NMR spectroscopy at room temperature. The following data were collected:

cis-$FvW_2(CO)_4(PPh_2Me)_2HCl$; ^{1}H-NMR: δ −7.07 (br d, J(P–H) = 55 Hz, J(W–H) = 48 Hz, 1H, WH), 2.24 (d, J(P–H) = 9 Hz, 3H, PMe of hydride), 2.27 (d, J(P–H) = 9 Hz, 3H, PMe of chloride), 5.04, 5.09, 5.21, 5.70, 5.92 (all m, 1H, Fv). The missing fulvalene resonances were hidden under those of **1** and **2**, probably in the range of δ 5.13–5.20. Phenyl resonances could not be distinguished from those of **1** and **2**. $^{31}P\{^1H\}$-NMR: δ 8.2 (s, 1P, chloride), 18.9 (br s, 1P, hydride).

trans-$FvW_2(CO)_4(PPh_2Me)_2HCl$; ^{1}H-NMR: δ −7.06 (br d, J(P–H) = 55 Hz, J(W–H) = 48 Hz, 1H, WH). No other resonances of this minor intermediate could be positively identified due to extensive overlap with

Table 1
Crystallographic data and structure refinement for $FvW_2(CO)_4(PPh_2Me)_2I_2 \cdot 2(CD_3)_2CO$

Empirical formula	$C_{46}H_{34}D_{12}I_2O_6P_2W_2$
Formula weight	1390.29
T (K)	299 (2)
Radiation, λ (Å)	Mo–K_α, 0.70930
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	13.2577 (2)
b (Å)	9.6743 (2)
c (Å)	20.2480 (2)
α (°)	90
β (°)	112.103 (1)
γ (°)	90
V (Å^3)	2406.13 (7)
Z	2
D_{Calc} (Mg m^{-3})	1.919
μ (mm^{-1})	0.626
Transmission range	0.67 to 0.91
F(000)	1308
Crystal size (mm)	0.24 × 0.20 × 0.02
Limiting indices	$-17 \leq h \leq 16$ $-12 \leq k \leq 10$ $-11 \leq l \leq 25$
Reflections collected	16 789
Independent reflections (R_{int})	5408 (0.055)
Observed reflections (criterion)	3769 ($I > 2\sigma(I)$)
Goodness-of-fit on F^2	1.058
Final R indices ($I = 2\sigma(I)$)	$R_1 = 0.0496$, $wR_2 = 0.1032$[a]
R indices (all data)	$R_1 = 0.0857$, $wR_2 = 0.1123$[a]

[a] $R_1 = \Sigma(F_o - F_c)/\Sigma F_o$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

those of major species. $^{31}P\{^1H\}$-NMR: δ 14.5 (s, 1P, chloride), 19.5 (br s, 1P, hydride).

cis,trans-**2**; ^1H-NMR: δ 2.25 (d, J(P–H) = 9 Hz, 3H, PMe, *cis*), 2.42 (d, J(P–H) = 9 Hz, 3H, PMe, *trans*), 4.81, 4.89 (both m, 1H, Fv), 5.10, ≈ 5.21 (both m, 2H, Fv), 5.85, 6.03 (both m, 1H, Fv), ≈ 7.4–7.5 (m, 20H, PPh). $^{31}P\{^1H\}$-NMR: δ 7.8 (s, J(W–P) = 260 Hz, 1P, *cis*), 13.8 (s, J(W–P) = 220 Hz, 1P, *trans*).

Table 2
Selected bond lengths (Å) and angles (°) for *meso-cis,cis*-**3**

Bond lengths (Å)			
W–C(2)	2.0000(9)	C(2)–O(2)	1.1603(9)
W–C(3)	1.9997(8)	C(3)–O(3)	1.1599(9)
W–C(4)	2.426(8)	C(4)–C(5)	1.450(11)
W–C(5)	2.333(9)	C(5)–C(6)	1.431(13)
W–C(6)	2.285(9)	C(6)–C(7)	1.407(14)
W–C(7)	2.306(9)	C(7)–C(8)	1.443(13)
W–C(8)	2.387(8)	C(4)–C(8)	1.394(12)
W–(P)	2.508(2)	C(4)–C(4′)	1.45(2)
W–I(1)	2.8122(9)		
Bond angles (°)			
C(2)–W–P	121.3(2)	C(6)–C(5)–C(4)	108.5(8)
C(2)–W–I(1)	78.6(3)	C(7)–C(6)–C(5)	107.4(8)
C(3)–W–P	79.8(2)	C(8)–C(7)–C(6)	108.2(8)
C(3)–W–I(1)	125.2(2)	C(4)–C(8)–C(7)	109.0(9)
P–W–I(1)	78.79(6)	C(8)–C(4)–C(5)	106.9(7)
O(2)–C(2)–W	176.8(8)	C(4′)–C(4)–C(5)	125.3(10)
O(3)–C(3)–W	178.1(11)	C(8)–C(4)–C(4′)	127.7(10)

cis-$FvW_2(CO)_4(PPh_2Me)_2HI$; ^1H-NMR: δ −7.03 (br d, J(P–H) = 55 Hz, J(W–H) = 48 Hz, 1H, WH), 2.27 (d, J(P–H) = 9 Hz, 3H, PMe of hydride), 2.58 (d, J(P–H) = 9 Hz, 3H, PMe of iodide). The fulvalene and phenyl resonances could not be assigned due to overlap with those of **1** and **3**. $^{31}P\{^1H\}$-NMR: δ −3.2 (s, 1P, iodide), 19.0 (br s, 1P, hydride).

trans-$FvW_2(CO)_4(PPh_2Me)_2HI$; ^1H-NMR: δ −7.06 (br d, J(P–H) = 55 Hz, J(W–H) = 48 Hz, 1H, WH), 2.23 (d, J(P–H) = 9 Hz, 3H, PMe of hydride), 2.39 (d, J(P–H) = 9 Hz, 3H, PMe of iodide). The fulvalene and phenyl resonances could not be assigned due to overlap with those of **1** and **3**. $^{31}P\{^1H\}$-NMR: δ 9.9 (s, J(W–P) = 240 Hz, 1P, iodide), 19.0 (br s, 1P, hydride).

*2.5. X-ray structure determination for **3***

Orange crystals of **3** were obtained from a reaction of **1** with iodoform carried out overnight in a filtered and saturated acetone-d_6 solution at room temperature. A well-shaped crystal was selected by optical microscopy. Intensity data were collected on a Siemens P4 diffractometer equipped with a SMART 1K CCD area detector. Data collection and structure solution parameters are listed in Table 1. The initial unit cell parameters were determined by a least-squares fit of the angular setting of 7231 strong reflections, collected by a 4.5° scan in 15 frames over three different parts of reciprocal space (45 frames total). One complete hemisphere of data was collected to better than 0.8 Å resolution. Upon completion of data collection, the first 50 frames were recollected to improve decay correction analysis. A decay correction and an empirical absorption correction based on redundant reflections were performed by the program SADABS. The program SAINT was applied for Lorentz and polarization corrections.

The structure was solved by the Patterson method using SHELXS-96. All non-hydrogen atoms were refined anisotropically, the hydrogen (deuterium) atoms were introduced in calculated positions. Selected bond distances and angles are listed in Table 2. The crystal structure of **3** is shown in Fig. 2. A full listing of bond distances and angles, atomic coordinates, isotropic and anisotropic displacement parameters are available as Supplementary Material.

3. Results and discussion

*3.1. Synthesis and characterization of $FvW_2(CO)_4(PPh_2Me)_2X_2$ (X = Cl (**2**), I (**3**))*

Reactions of $FvW_2(CO)_4(PPh_2Me)_2H_2$ (**1**) with carbon tetrachloride and iodoform readily gave red

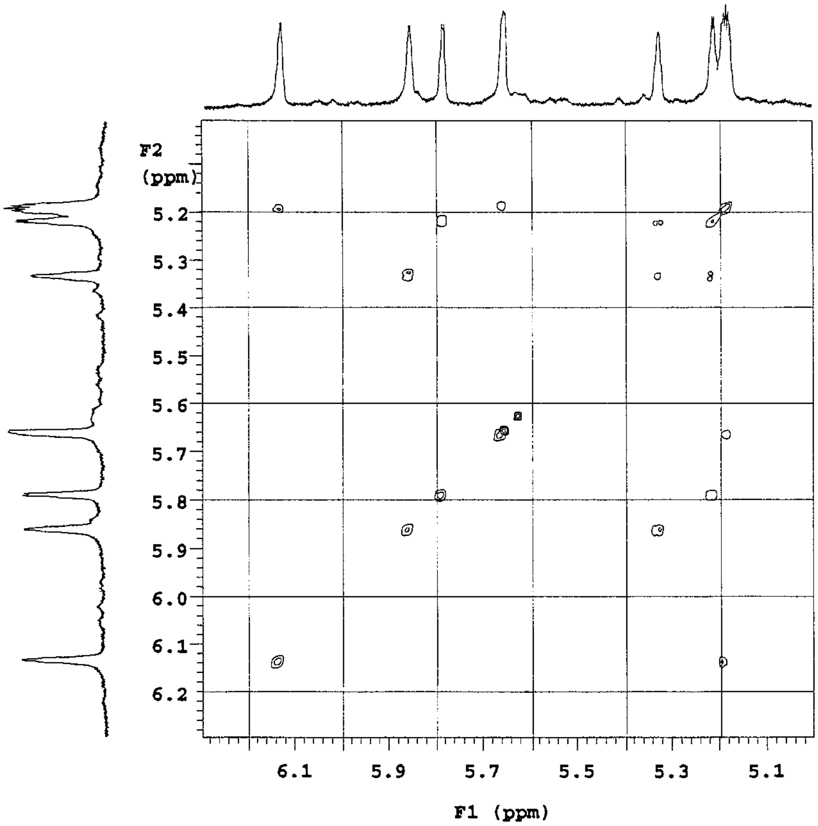


Fig. 1. COSY (500 MHz) spectrum of complex **2** in acetone-d_6 solution.

$FvW_2(CO)_4(PPh_2Me)_2Cl_2$ (**2**) and orange $FvW_2(CO)_4(PPh_2Me)_2I_2$ (**3**), respectively, in excellent isolated yields. The use of iodoform as hydrogen–iodine exchange reagent is more advantageous than ethyl iodoacetate, iodoacetonitrile, *t*-butyl iodide, etc. [2b,c], because it is an inexpensive, stable and easy-to-handle solid with high reactivity toward tungsten hydrides. In addition, the hydrogenated side-products (CH_2I_2 or MeI) are volatile and exhibit very simple proton spectra, which do not obscure those of the fulvalene complexes. In general, hydrogen–iodine exchange reactions give metal iodides of higher purity than those utilizing I_2. Both **2** and **3** were isolated as poorly soluble crystalline materials and characterized by combustion analysis, IR, ^1H- and $^{31}P\{^1H\}$-NMR spectroscopy. The crystal structure of **3** was also determined. While this work was in progress, an alternative synthesis of **3** via triethylamine oxide assisted substitution of $FvW_2(CO)_6I_2$ with PPh_2Me was reported [3e].

Complex **2** had two absorbances in the IR spectrum at 1949 (vs), 1856 (m) cm^{-1}, suggesting that both hydridic sites had been chlorinated and the chloride and phosphine ligands occupy mutually cis positions about each metal centre. The 270 MHz ^1H-NMR spectrum in acetone-d_6 solution exhibited two doublets of equal intensity at δ 2.28 and 2.29 attributable to PMe protons, six different fulvalene multiplets at 5.17 (3 ×), 5.31, 5.64, 5.76, 5.83, 6.10, and phenyl resonances consistent with two different PPh environments. The observed resonance pattern is characteristic of a 1:1 equilibrium mixture of D,L- and *meso*-*cis*,*cis* isomers. It is also supported by the $^{31}P\{^1H\}$-NMR spectrum which featured two closely spaced signals of equal intensity at δ 7.9 and 8.1. Evidence for four different C_α and C_β fulvalene carbon atoms and two different PPh environments was obtained in the $^{13}C\{^1H\}$-NMR spectrum. The spectroscopic results also suggested that the *cis*,*cis* isomers of **2** did not transform into the *trans* isomers to any significant extent and their interconversion was slow on the NMR time scale. The same isomeric composition has been established recently for $FvMo_2(CO)_4(PR_3)_2X_2$ (X = Cl, Br) [2b], $FvCr_2(CO)_4(PPh_2Me)_2X_2$ (X = Br, I) [2c] and $FvW_2(CO)_4(PCy_3)_2I_2$ [3e].

Additional information about **2** was obtained by a 500 MHz COSY experiment. Fig. 1 demonstrates that the resonances at δ 5.19 (2 ×) are coupled to those at 5.66 and 6.13 and probably to each other, while those at δ 5.22 and 5.33 are coupled to those at 5.86 and 5.79, respectively, as well as to each other. Each group of four signals therefore belong to different *cis*,*cis* forms. The coupling pattern also suggests that all four upfield signals represent H_β protons and all four downfield signals belong to H_α protons. This is in complete agreement with previous heteronuclear NOE difference measurements [5].

Complex **3** shows markedly different isomerization behaviour than **2**. Both the ^{1}H- and $^{31}P\{^1H\}$-NMR spectra indicated that this compound maintains a permanent equilibrium of all four isomers (Scheme 1), the *cis,trans* being in the highest concentration. In acetone-d_6 solution, the $^{31}P\{^1H\}$-NMR spectrum exhibited two distant sets of signals, those at high-field (δ −3.5 and −3.2) being characteristic to cis and those at low-field (δ 9.4 and 9.7) to *trans* P–W–I arrangements. Peak integrals suggested that the resonance of one of the *cis,cis* forms was hidden under that of the *cis* half of the *cis,trans* isomer at δ −3.5. Accordingly, there were four sharp doublets (δ 2.40, 2.43, 2.57, 2.63) in the high-field region of the 270 MHz ^{1}H-NMR spectrum attributable to PMe protons, the one at δ 2.63 being considerably broader than the others. It was therefore assigned to both *cis,cis* isomers, which were quite unusually not separated, and appeared at lower field than those of *trans* isomers. The doublet at δ 2.40 was assigned to the *trans,trans* isomer and the others to the *cis,trans* isomer by default. This spectrum also exhibited at least 11 multiplets in the fulvalene ‘fingerprint’ region (δ 4.96–6.14) due to multiple overlaps. Full assignment of this spectrum to the individual isomers was aided by a 500 MHz NMR spectrum. The total *cis/trans* ratio was found to be 52:48 (48% *cis,trans*, 24% *trans,trans* and 28% *cis,cis* (D,L-/*meso*- = 1:1)).

When the ^{1}H-NMR spectrum of **3** was recorded in DMSO-d_6 solution, a considerable solvent effect on both the chemical shift values and the isomeric ratio was evident. Four PMe doublets were observed at high field, the two most shielded at δ 2.33 (*trans,trans*) and 2.35 (*cis,trans*) being attributable to *trans* isomers and the well separated other two doublets at δ 2.52 (*cis,trans*) and 2.57 (both D,L- and *meso*-*cis,cis*) to *cis* isomers. In the fulvalene region of the 270 MHz spectrum (δ 5.00–6.35), at least 11 individual multiplets were exhibited due to various overlaps. Full assignment was made on the basis of a 500 MHz NMR spectrum. The total *cis/trans* ratio was found to be 40:60 (53% *cis,trans*, 33% *trans,trans* and 14% *cis,cis*).

NMR spectroscopic data recorded in $CDCl_3$ solutions for **3**, including a COSY experiment, have been reported recently [3e]. We repeated both the ^{1}H- and $^{31}P\{^1H\}$-NMR spectroscopic measurements in $CDCl_3$ and found several discrepancies with the published ^{1}H-NMR results. Firstly, the literature describes an unfortunate situation where the equilibrium consisted of a 1:4:4 ratio of *trans,trans*, *cis,trans* and *cis,cis* (D,L-/*meso*- = 1:1) isomers, respectively, and therefore all fulvalene resonances are of equal intensity. Consequently, no assignments were made on the basis of the relative concentration of different isomers, which is otherwise easily determined by integrating both the phosphorus and methyl proton signals. As a COSY experiment only determines the proton resonances attributable to individual η^5-ring environments, correct identification of the three types of cis environments (D,L- and *meso*-*cis,cis* as well as the *cis* half of *cis,trans*, each having four proton resonances of equal intensity) was not at all obvious. Since we were able to shift the equilibrium by crystallization (see below), we recorded ^{1}H-NMR spectra exhibiting an intensity ratio of fulvalene signals attributable to *cis,cis*- and *cis,trans*-**3** different from that found in the literature. After the major *cis,trans* (59%) and minor *cis,cis* (2 × 12%) isomers had been identified on the basis of their phosphorus and methyl signals, it became evident that the fulvalene resonances at δ 5.79, 5.19, 5.14 and 4.90 belong to the *cis* half of *cis,trans*-**3**, instead of one of the *cis,cis* isomers as reported [3e]. Secondly, six PMe resonances were reported for this mixture, four of them singlets [3e]. However, it is obvious that only five η^5-rings out of ten (Scheme 1) are magnetically non-equivalent and each must be represented by a PMe doublet due to pronounced ^2J(P–H) coupling. A complete set of revised ^{1}H-NMR data is listed in Section 2.3.3.

3.2. Crystal and molecular structure of 3

Analysis of the structural data for **3** revealed that this complex assumes the *meso*-*cis,cis* form in the crystalline

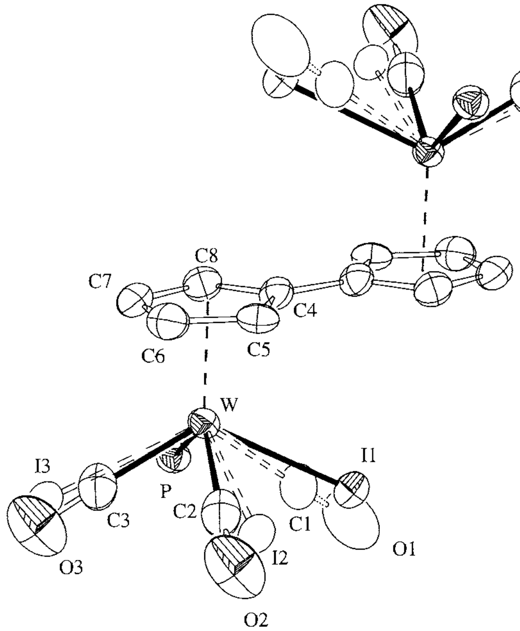


Fig. 2. An ORTEP plot of complex **3** demonstrating the probability of different isomers. P, I(1), C(2), C(3): 71%; P, C(1), I(2), C(3): 20%; P, C(1), C(2), I(3): 9%. Thermal ellipsoids are drawn at the 40% probability level. Hydrogen and PPh_2Me carbon atoms are omitted for clarity.

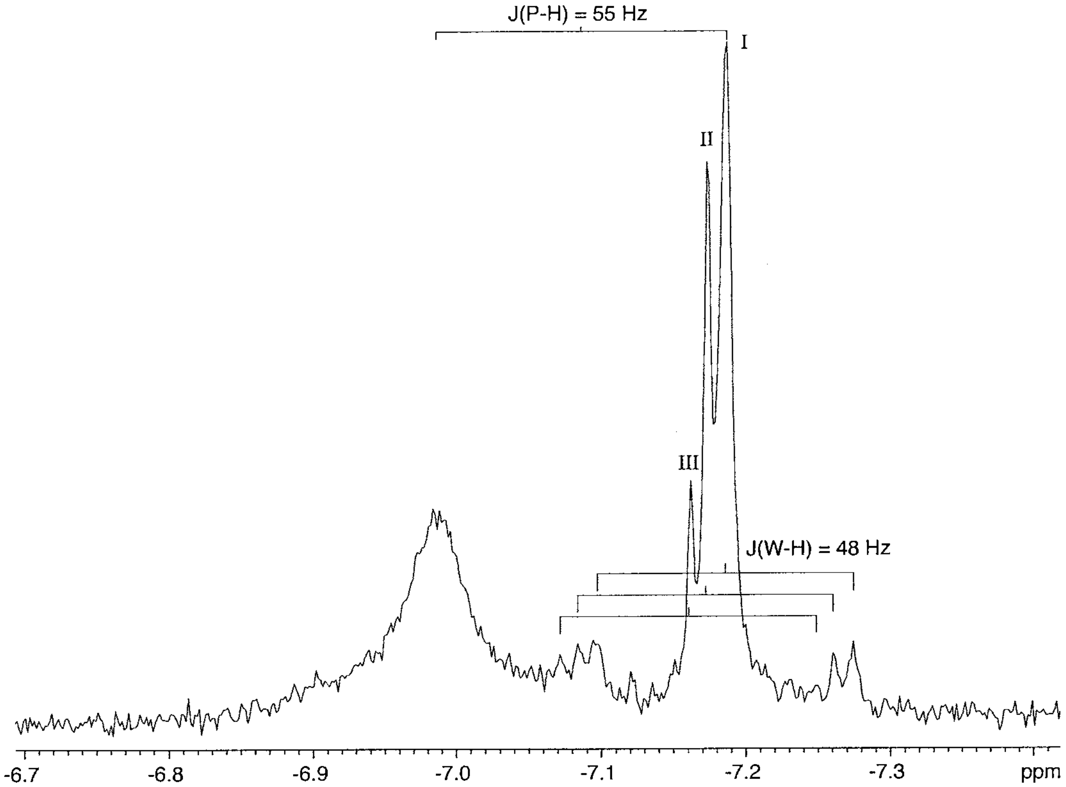


Fig. 3. Hydridic proton region of the ^{1}H-NMR (270 MHz) spectrum of a reaction mixture of **1** with CCl_4 in acetone-d_6. (**I**) Complex **1**; (**II**) *cis*-$FvW_2(CO)_4(PPh_2Me)_2HCl$; (**III**) *trans*-$FvW_2(CO)_4(PPh_2Me)_2HCl$.

state (Fig. 2). The two $W(CO)_2(PPh_2Me)I$ units are situated in the sterically least congested anti position with respect to the perfectly planar fulvalene ligand, which is typical for non-metal–metal bonded fulvalene complexes in the solid state [2a,3e], and there is a crystallographically imposed centre of inversion in the molecule. The ligands about each tungsten centre define a square pyramidal structure. The bridgehead C(4)–C(4′) (1.45(2) Å) and the W–I (2.81(9) Å) distances are shorter, while the C≡O (1.16 Å) and the average W–C_{ring} (2.35 Å) distances are longer than in the parent hexacarbonyl, $FvW_2(CO)_6I_2$ [3e], indicating an increased electron density at the tungsten centre due to the phosphine being a better donor than CO. Interestingly, there is a 0.14 Å ring slippage from the centre of each C_5H_4-ring. The structural analysis also determined the position of the two solvent molecules in the lattice, one acetone-d_6 per tungsten centre.

Initial data processing suggested severe distortion of one of the C≡O ligands and that it might have been replaced by a heavy iodine atom. Full refinement revealed that the iodine atom occupied position I(1) with 71%, position I(2) with 20% and I(3) with 9% probability (Fig. 2). Nevertheless, considering that the *meso-cis,cis* form constituted only 7% of the equilibrium mixture in the starting solution, a ca. tenfold increase in its concentration was achieved upon crystal formation. These results support our initial hypothesis that the *cis* conformation is preferred by phosphine-substituted $FvM_2(CO)_4L_2X_2$ dihalides and the D,L↔*meso* equilibrium can be shifted in the solid state, apparently in favour of the *meso* form. Moreover, due to a similarity between the isomerization behaviour of **3** and that of recently characterized $FvW_2(CO)_4(PPh_2Me)_2(SR)_2$ (R = H, alkyl) hydrosulfide and thiolate complexes [2d], it seems reasonable to assume that the latter probably crystallize in the same way.

3.3. Mechanism of the formation of 2 and 3

By carefully monitoring the hydrogen–halogen exchange of **1** with CCl_4 and CHI_3 in acetone-d_6 by ^{1}H- and $^{31}P\{^1H\}$-NMR spectroscopy, the formation of the corresponding hydrido–halide intermediates, $FvW_2(CO)_4(PPh_2Me)_2HX$ (X = Cl, I), was unambiguously established. These intermediates were detectable in significant concentration throughout the reactions and slowly transformed into **2** and **3**, indicating that the hydrogen-for-halogen exchange took place in two distinctive steps. Similar stepwise hydrogen–halogen exchanges, which probably proceed by a radical-chain mechanism [1], have recently been demonstrated for analogous (fulvalene)chromium [2c] and molybdenum dihydrides [2b]. The formation and persistence of such intermediates suggest lower reactivity of the hydride function of hydrido-halides than that of the starting dihydrides. Decreased reactivity could be due to an electronic effect of the distant halogen atom on the hydride moiety, which would suggest efficient electronic communication between the two halves via the fulvalene π-system, consistent with electrochemical studies [3d,6].

Each $FvW_2(CO)_4(PPh_2Me)_2HX$ intermediate was present in the reaction mixtures in two isomeric forms, containing a *cis* and *trans* halide half, while the hydride halves remained stereochemically nonrigid on the NMR time scale. Both forms were most conveniently identified in the high-field hydridic and PMe proton regions of the ^1H-NMR spectra, as well as by their $^{31}P\{^1H\}$-NMR spectra. Figs. 3 and 4 show the WH and PMe regions of ^1H-NMR spectra recorded during the formation of **2** and **3**, respectively. In Fig. 3, there are two new, asymmetric doublets in addition to that of **1**, demonstrating the extent of deshielding on the hydridic proton brought about by the electron-withdrawing chlorine atom occupying *cis* and *trans* positions relative to the phosphine ligand in the halide half of the molecule. Both species were also detected by their phosphorus resonances being different from those of **2** (δ 8.2 (*cis* chloride), 14.5 (*trans* chloride)). However, only fragmented information could be obtained from the PMe and fulvalene proton regions due to excessive overlaps with the resonances attributable to **1** and **2**. The available data indicate that *trans*-$FvW_2(CO)_4(PPh_2Me)_2HCl$ is only a minor intermediate in this reaction.

Fig. 4 shows nine methyl doublets clearly distributed into three groups; the PMe protons in three different hydridic environments being the most shielded, while those in three different *cis* iodide environments being the most deshielded (D,L- and *meso*-*cis*,*cis*-**3** completely overlap). In addition to this, the presence of *cis*- and *trans*-$FvW_2(CO)_4(PPh_2Me)_2HI$ isomers was confirmed by two new hydridic doublets in the WH proton region, a number of new multiplets in the fulvalene region and phosphorus resonances at δ −3.2 (*cis* iodide) and 10.0 (*trans* iodide). The two isomers were detected in nearly equal concentrations.

When the exchange was complete, all four isomers of **3** were present in substantial amounts and no other species could be detected in the reaction mixture. The isomeric composition did not change subse-

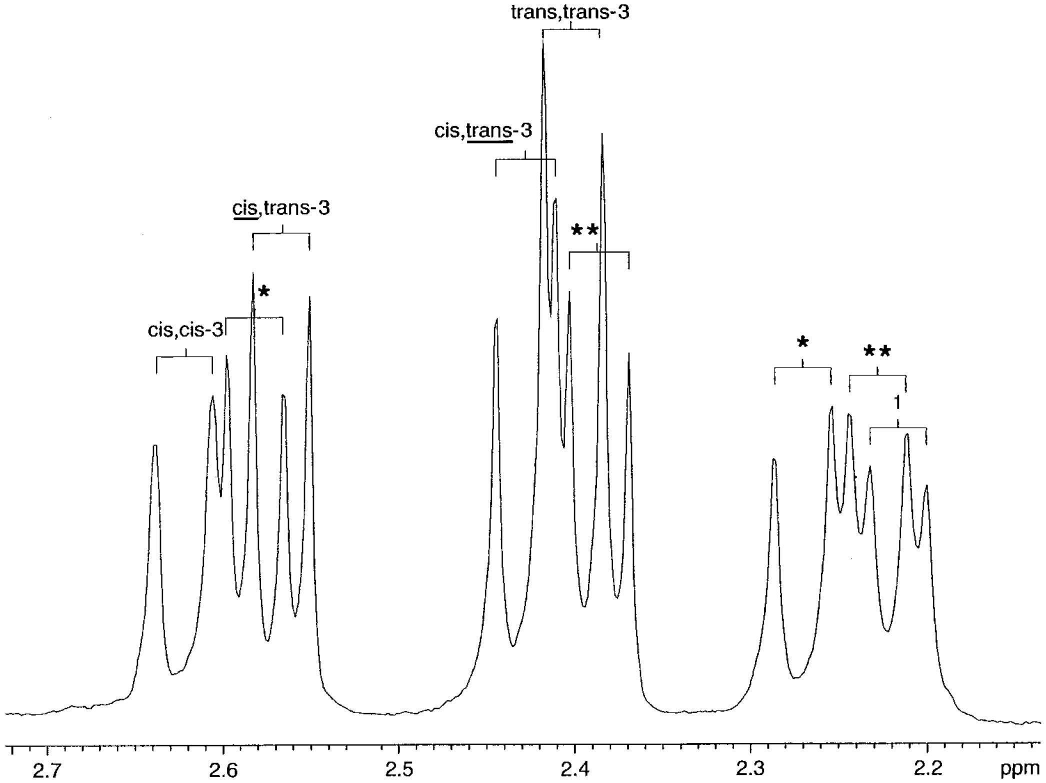


Fig. 4. Methyl proton region of the ^1H-NMR (270 MHz) spectrum of a reaction mixture of **1** with CHI_3 in acetone-d_6. * *cis*-$FvW_2(CO)_4(PPh_2Me)_2HI$; ** *trans*-$FvW_2(CO)_4(PPh_2Me)_2HI$.

quently, as long as the homogeneity of the solution was maintained. However, when the formation of **2** was complete, only small amounts of its *cis*,*tran*s and no *trans*,*trans* isomers were present along with the major *cis*,*cis* isomers. After several hours, when the final equilibrium was achieved, only the *cis*,*cis* isomers could be detected. Thus, *cis*,*trans*-**2** can also be considered as an intermediate in the formation of the end-product *cis*,*cis*-**2**. Interestingly, neither the *cis*,*trans* isomer nor the *trans*-$FvM_2(CO)_4L_2HX$ intermediate was previously reported in reaction mixtures giving $FvM_2(CO)_4L_2X_2$ (M = Cr, Mo) which exist exclusively as the *cis*,*cis* isomer [2b,c]. We believe that in the particular reaction of **1** with CCl_4 the hydrogen–chlorine exchange must be successfully competing with the isomerization of **1**, probably because the latter is slow. It also implies that the *cis* hydride isomer is more reactive than the *trans* isomer, that is, the W–H bond is weaker in the *cis* form. Since no *trans*,*trans*-**2** was detected and the hydride function has lower reactivity in the mixed intermediates, *cis*,*trans*-**2** was probably generated from *trans*-$ClW(CO)_2(PPh_2Me)(\mu$-Fv)*cis*-$HW(CO)_2(PPh_2Me)$.

4. Supplementary material

Crystallographic data for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC 115338. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

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