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# Synthesis and characterization of $FvW_2(CO)_4L_2(SR)_2$ (L = CO, $PPh_2Me$; R = H, *i*-Pr, $CH_2Ph$, Ph) type (fulvalene)tungsten dihydrosulfides and dithiolates

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Dedicated to: Professor László Markó on the occasion of his 70th birthday.

**Abstract**

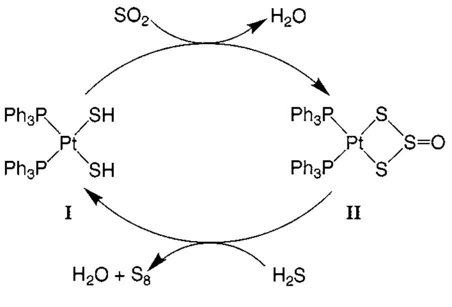
A direct, high-yield synthesis of $(Et_4N)_2[FvW_2(CO)_6]$, where Fv = $\eta^5$:$\eta^5$-$C_{10}H_8$ (fulvalene), from $W(CO)_3(EtCN)_3$, $Li_2[C_{10}H_8]$, and $Et_4NBr$ is reported. It reacted with sulfur-transfer reagents, RSphthalimide (R = *i*-Pr, $CH_2Ph$, Ph), to give the corresponding dithiolato complexes, $FvW_2(CO)_6(SR)_2$. Treating the thiolato complexes, where R = *i*-Pr, $CH_2Ph$, with $CS_2$ gave thioxanthate derivatives $FvW_2(CO)_4(S_2CSR)_2$, via mixed $RSW(CO)_3(\mu\text{-Fv})(CO)_2WS_2CSR$ intermediates. The unstable bishydrosulfido complex $FvW_2(CO)_6(SH)_2$ was obtained from $FvW_2(CO)_6H_2$ and $S_8$ via the mixed hydrido–hydrosulfido intermediate $FvW_2(CO)_6(SH)H$. $FvW_2(CO)_6H_2$ also reacted with $PPh_2Me$ to give the ligand-substituted product $FvW_2(CO)_4(PPh_2Me)_2H_2$, which provided access to the dianion $Li_2[FvW_2(CO)_4(PPh_2Me)_2]$ via methyllithium reduction. Similarly to its parent compound, $[FvW_2(CO)_4(PPh_2Me)_2]^{2-}$ also gave the corresponding dithiolato complexes, $FvW_2(CO)_4(PPh_2Me)_2(SR)_2$ (R = *i*-Pr, $CH_2Ph$, Ph), upon treatment with RSphthalimide. $FvW_2(CO)_4(PPh_2Me)_2(SPh)_2$ was converted into $FvW_2(CO)_4(PPh_2Me)_2(SH)_2$ under an atmosphere of $H_2S$. All $PPh_2Me$-substituted dithiolato complexes as well as the bishydrosulfide derivative exist in solution as an equilibrium mixture of D,L- and *meso-cis,cis*, *cis,trans* and *trans,trans* isomers. However, only the *cis,cis* isomer of the bishydrosulfido complex was present in the crystalline state. © 1999 Elsevier Science S.A. All rights reserved.

*Keywords:* Fulvalene; Tungsten; Thiolate; Hydrosulfide; Carbonyl; Phosphine; Substitution; Thioxanthate; Isomerism

## 1. Introduction

Well-defined, soluble transition metal complexes have been successfully applied in recent years for modeling plausible surface reactions of the heterogenous Claus process [1]. Most notably, it was found that *cis*-$(PPh_3)_2Pt(SH)_2$ (**I**) (Scheme 1), which was selected as a model of preabsorbed $H_2S$ on the catalyst surface, reacted with $SO_2$ to give $(PPh_3)_2PtS_3O$ (**II**) and $H_2O$. Complex **II**, in turn, afforded a mixture of **I**, $H_2O$, and $S_8$ under an atmosphere of $H_2S$, completing a catalytic cycle in which $SO_2$ and $H_2S$ were converted into $H_2O$ and $S_8$ as in the Claus reaction. Complexes **I** and **II** are the first homogeneous catalysts of Claus chemistry [1a].

These observations prompted a search for other bishydrosulfido and dithiolato complexes which might



Scheme 1.

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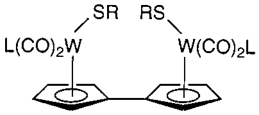
be suitable models for studying the reactions of activated $H_2S$ with $SO_2$ and, ultimately, catalysts of the Claus process in homogeneous phase. Dinuclear (fulvalene)tungsten complexes of the type $FvW_2(CO)_4L_2(SR)_2$ (**III**) (Fv = $\eta^5$:$\eta^5$-$C_{10}H_8$; R = H, alkyl, aryl; L = CO, phosphine) appeared to be particularly interesting.



III

On one hand, fulvalene systems have already been under scrutiny as models for the interactions of organic molecules with metal surfaces [2]. The metal centers anchored to and held in close proximity by the fulvalene ligand such as complex **III** can be considered as two neighboring active sites on a catalyst surface. On the other hand, the chemistry of analogous (cyclopentadienyl)tungsten carbonyl hydrosulfides [3] and thiolates [4], Cp(CO)$_2$(L)WSR (R = H, alkyl, aryl; L = CO, $PPh_3$, CNR′), has been relatively well developed and provide a reliable starting point for the synthesis of the target fulvalene derivatives. In addition, since steric and electronic interactions between the two halves of fulvalene complexes through the bridging π-system often generate reactivity patterns different from those of the corresponding mononuclear cyclopentadienyl analogues, they could easily be used for comparison.

Here we report the synthesis, characterization, and some reactions of the (fulvalene)tungsten complexes $FvW_2(CO)_4L_2(SR)_2$ (L = CO, $PPh_2Me$; R = H, *i*-Pr, $CH_2Ph$, Ph). To our knowledge, only two (fulvalene)metal thiolates, Fv[CpZr(SPh)$_2$]$_2$ and Fv[CpZr(μ-SPh)]$_2$, have been reported to date [5a]. These complexes and the sulfide-bridged complexes Fv[CpTi(μ-S)]$_2$ [5b] and Fv[CpZr(μ-S)]$_2$ [5a] represent the known sulfur chemistry of fulvalene compounds, which therefore remains practically unexplored. Furthermore, dinuclear complexes containing nonbridging hydrosulfide or thiolate groups in general are rare [6], probably owing to the strong Lewis-basicity of sulfur. Thus, it is surprising that the title complexes showed no sign of bridge formation. Note that this work also contributes to the relatively unexplored chemistry of (fulvalene)tungsten carbonyl complexes in general [7], compared to that of molybdenum [8] and chromium derivatives [8i,9].

## 2. Results and discussion

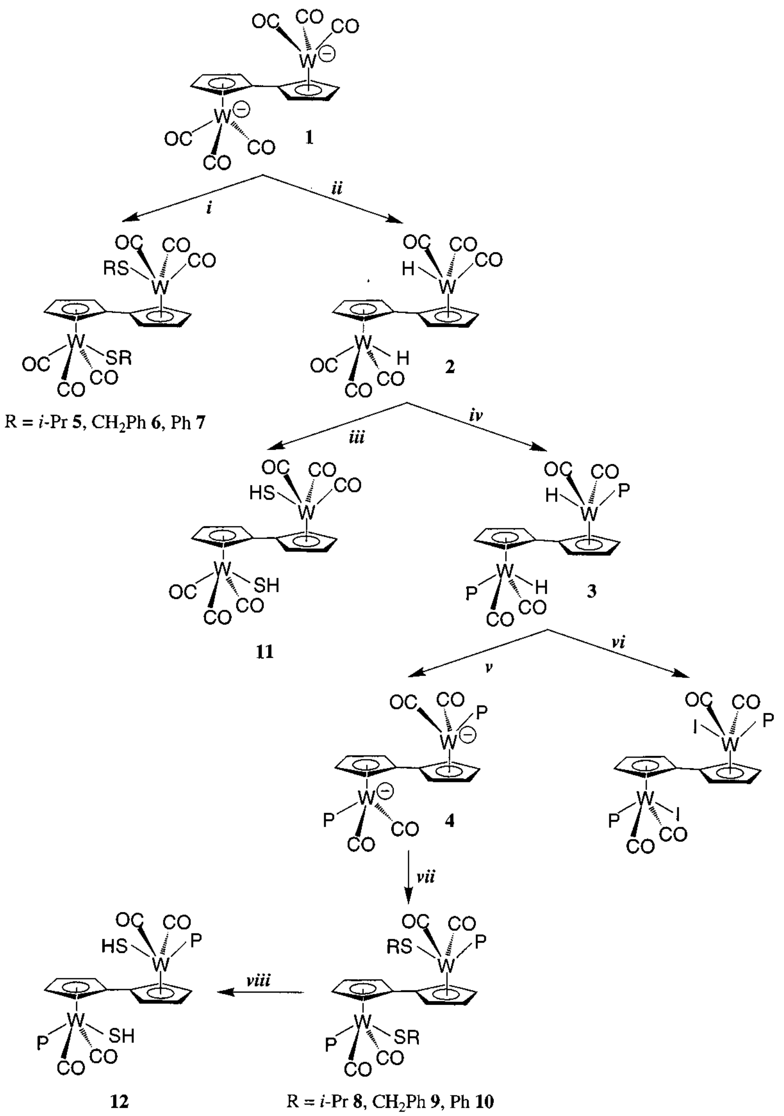
### 2.1. Synthesis and characterization of starting materials and intermediates

The synthetic pathway designed to gain access to the title (fulvalene)tungsten complexes containing hydrosulfide or thiolate functions is outlined in Scheme 2. This required $[FvW_2(CO)_6]^{2-}$ as the starting material in relatively large amounts and thus, a convenient and efficient preparative method was sought. $[FvW_2(CO)_6]^{2-}$ has been prepared recently by the sodium-amalgam reduction of $FvW_2(CO)_6$(*W*–*W*) [7c], but the practical scale synthesis of the latter has a considerable disadvantage in that it requires careful purification of extremely unstable dihydrofulvalene [7e]. Therefore, we established the direct synthesis of $(Et_4N)_2[FvW_2(CO)_6]$ (**1**) by adopting a procedure successfully applied previously for the preparation of its molybdenum [8g] and chromium [9a] congeners. Complex **1** was obtained in practically quantitative yield as a mixture with NaI and LiBr, indifferent side-products of the synthesis of $Li_2[C_{10}H_8]$ and the ion exchange with $Et_4NBr$, respectively, which spontaneously separated in subsequent reactions due to insolubility (Eq. (1)). Complex **1** was identified by its spectroscopic properties [7c].

$$2W(CO)_3(EtCN)_3 + Li_2[C_{10}H_8] + 2Et_4NBr \rightarrow (Et_4N)_2[FvW_2(CO)_6] + 2LiBr + 3EtCN \quad (1)$$

Complex **1** was protonated by glacial acetic acid in toluene to give $FvW_2(CO)_6H_2$ (**2**), which was either isolated by crystallization or utilized in situ. Complex **2** was identified by its spectroscopic properties [7c]. Since we were also interested in phosphine-substituted thiolato and hydrosulfido complexes as dinuclear analogues of $CpW(CO)_2(PPh_3)SR$ (R = H, *i*-Pr, Ph, $CH_2Ph$) [4c,d], complex **2** appeared to be a potential candidate to introduce a relatively large phosphine. Although complex **2** reportedly failed to react with $PPh_3$ [7c], we found that ligand substitution proceeded smoothly with $PPh_2Me$ at elevated temperatures to give the new dihydride $FvW_2(CO)_4(PPh_2Me)_2H_2$ (**3**) in good yield.

The identity of complex **3** was confirmed by IR (Table 1) and NMR spectroscopy, combustion analysis, and indirectly, by converting it into the known diiodide $FvW_2(CO)_4(PPh_2Me)_2I_2$ [7a] by hydrogen–halogen exchange with $CHI_3$. The $^1H$-NMR spectrum of **3**, recorded in acetone-$d_6$ at room temperature (r.t.), exhibited an asymmetric doublet at $\delta$ −7.08 ($J_{P-H} = 55$ Hz) with $^{183}W$ satellites ($J_{W-H} = 48$ Hz) which was assigned to hydridic protons. A well-resolved doublet characteristic of the PMe group appeared at $\delta$ 2.22 ($J_{P-H} = 8.6$ Hz) and additional broad resonances were observed in the downfield region consistent with the presence of fulvalene and phenyl groups. In the $^{13}C\{^1H\}$-NMR spectrum, two fulvalene ($\delta$ 86.3 and 87.6) and three phenyl resonances could be identified, but no quaternary and PMe carbon resonances were detected. The $^{31}P\{^1H\}$-NMR spectrum exhibited a broad signal at $\delta$ 19.3. All these features are fully consistent with the composition of complex **3** and the fact that its four possible isomers: *meso*-*cis*,*cis*, D,L-*cis*,*cis*, *cis*,*trans* and *trans*,*trans* are in a rapid equi-



Scheme 2. (i) RSphth (R = $^{i}$Pr, $CH_2Ph$, Ph), THF, r.t. (ii) excess AcOH, toluene, r.t. (iii) $S_8$, THF, r.t. (iv) $PPh_2Me$, toluene, 110°C ($P = PPh_2Me$). (v) MeLi, THF, −10°C. (vi) $CHI_3$, toluene, r.t. (vii) RSphth (R = $^{i}$Pr, $CH_2Ph$, Ph), THF, r.t. (viii) excess $H_2S$, THF, r.t.

librium on the NMR time scale under ambient conditions (Scheme 3). This behavior has been well documented recently for $FvW_2(CO)_4(PMe_3)_2H_2$ [7c] and the analogous chromium [9a] and molybdenum [8g] dihydrides by variable-temperature measurements.

Complex **3** was reduced by methyllithium to give the dianion $Li_2[FvW_2(CO)_4(PPh_2Me)_2]$ (**4**), which was isolated as a yellow solid. Its IR spectrum exhibited two strong CO bands at 1663 and 1789 $cm^{-1}$, consistent with the high electron density on tungsten. Both the $^1H$- and $^{13}C\{^1H\}$-NMR spectra featured methyl, phenyl, and fulvalene resonances, consistent with the proposed structure. The $^{31}P\{^1H\}$-NMR spectrum exhibited a relatively low-field singlet at $\delta$ 28.8 suggesting a symmetric molecule. Complex **4** readily afforded complex **3** in the presence of a proton source and can be easily oxidized to give the new metal–metal bonded dimer $FvW_2(CO)_4(PPh_2Me)_2$(*W*–*W*). Owing to its high reactivity, complex **4** was usually prepared in situ from complex **3** in THF solutions and used immediately for the synthesis of dithiolato complexes.

### 2.2. Synthesis and characterization of dithiolato complexes $FvW_2(CO)_4L_2(SR)_2$ ($L = CO$, $PPh_2Me$; $R = i\text{-}Pr$, $CH_2Ph$, Ph)

It has been established that reactions of the anions

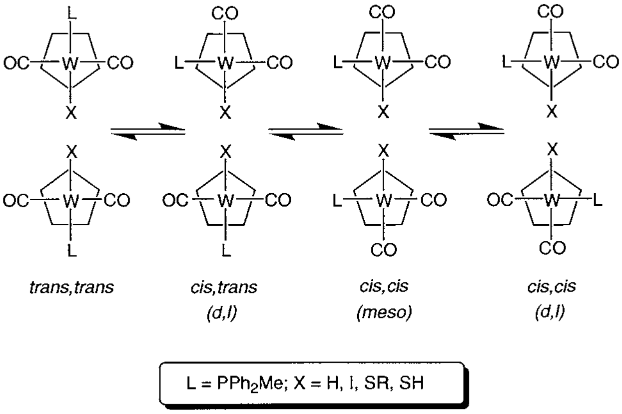
Table 1
Carbonyl stretching frequencies

| Compound | $\nu$(CO) ($cm^{-1}$)[a] |
|---|---|
| $(Et_4N)_2[FvW_2(CO)_6]$ (**1**) | 1892 (s), 1800 (vs),<br>1777 (sh), 1716 (m) |
| $FvW_2(CO)_6H_2$ (**2**) | 2018 (m), 1929 (vs)[b] |
| $FvW_2(CO)_6(S^iPr)_2$ (**5**) | 2017 (s), 1929 (vs) |
| $FvW_2(CO)_4(S_2CS^iPr)_2$ (**5B**) | 1950 (vs), 1874 (m) |
| $FvW_2(CO)_6(SCH_2Ph)_2$ (**6**) | 2018 (s), 1930 (vs) |
| $FvW_2(CO)_6(SPh)_2$ (**7**) | 2024 (s), 1939 (vs) |
| $FvW_2(CO)_6(SH)_2$ (**11**) | 2023 (s), 1937 (vs) |
| $FvW_2(CO)_4(PPh_2Me)_2H_2$ (**3**) | 1928 (vs), 1847 (s) |
| $FvW_2(CO)_4(PPh_2Me)_2I_2$ | 1949 (s), 1870 (vs) |
| $Li_2[FvW_2(CO)_4(PPh_2Me)_2]$ (**4**) | 1789 (s), 1663 (s) |
| $FvW_2(CO)_4(PPh_2Me)_2$(*W–W*) | 1927 (m), 1845 (vs) |
| $FvW_2(CO)_4(PPh_2Me)_2(S^iPr)_2$ (**8**) | 1927 (s), 1846 (vs) |
| $FvW_2(CO)_4(PPh_2Me)_2(SCH_2Ph)_2$ (**9**) | 1930 (s), 1852 (vs) |
| $FvW_2(CO)_4(PPh_2Me)_2(SPh)_2$ (**10**) | 1944 (m), 1862 (vs) |
| $FvW_2(CO)_4(PPh_2Me)_2(SH)_2$ (**12**) | 1937 (vs), 1857 (s) |

[a] Recorded in THF solution unless noted otherwise.

[b] In toluene solution.

$[CpW(CO)_2L]^-$ ($L = CO$, $PPh_3$) with N-alkyl(aryl)thiophthalimides (RSphth) give the corresponding tungsten thiolate complexes, $CpW(CO)_2LSR$ [4c,d]. We found that similar reactions took place with complexes **1** and **4** leading to $FvW_2(CO)_4L_2(SR)_2$ ($L = CO$, $R = i$-Pr (**5**), $CH_2Ph$ (**6**), Ph (**7**); $L = PPh_2Me$, $R = i$-Pr (**8**), $CH_2Ph$ (**9**), Ph (**10**)). Complexes **5**–**10** were isolated as poorly soluble, orange–brown solids in moderate yields. While the phosphine-substituted derivatives **8**–**10** proved to be quite robust in solution even at elevated temperatures, the parent carbonyls **5**–**7** decomposed to unidentified product mixtures under similar conditions. Complexes **5**–**10** were characterized by IR (Table 1) and NMR spectroscopy, the data being fully consistent with the suggested structures.



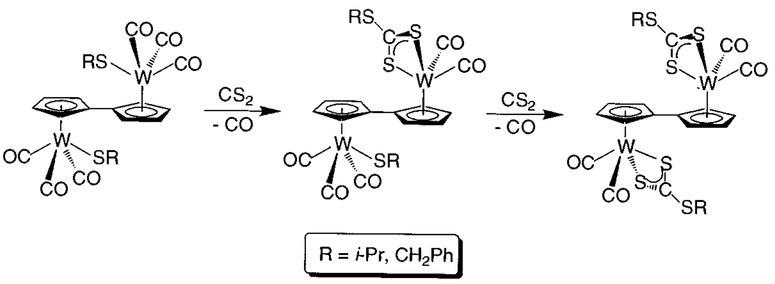
Scheme 3.

The IR spectra of **5**–**7** exhibited two absorbances in the regions 2017–2024 (s) and 1929–1939 (vs) $cm^{-1}$ consistent with the anticipated decrease in the basicity of the thiolate group in the order of $S^iPr > SCH_2Ph > SPh$. Common features of all $^1H$-NMR spectra were two pseudotriplets attributed to $H_\alpha$ and $H_\beta$ protons of the fulvalene ligand. In addition, the resonances for the SR groups indicated two such equivalent groups in each complex. $^{13}C\{^1H\}$-NMR spectroscopic measurements supplemented the above observations. The two low-field resonances of complex **5**, for instance, at $\delta$ 214.1 and 226.5 which are attributed to the *cis* and *trans* CO ligands, respectively, are consistent with the presence of three CO ligands about each metal center and with no exchange on the NMR time scale at r.t. The three fulvalene resonances attributable to $C_\alpha$ and $C_\beta$ and bridgehead carbon atoms ($\delta$ 91.3, 93.2, 108.1) again support the proposed formulations.

The relative thermal instability of **5**–**7** suggested that these complexes might have a versatile chemistry. We have carried out spectroscopic investigations on their reactions with $CS_2$. $CS_2$ readily inserts into the metal–SR bond of $CpW(CO)_2(PPh_3)SR$ and $CpRu(PPh_3)_2SR$ to give the thioxanthate derivatives $CpW(CO)_2S_2CSR$ [4d] and $CpRu(PPh_3)S_2CSR$ [10], respectively. It appeared from these studies that the insertion takes place via precoordination of $CS_2$ to a coordinatively unsaturated intermediate generated by facile dissociation of $PPh_3$. Similar reactions of $CpW(CO)_3SR$ proceeded very slowly to also give $CpW(CO)_2S_2CSR$ [4d,o], consistent with the generally slow CO dissociation from $CpW(CO)_3X$ type complexes.

Monitoring the $^1H$-NMR spectrum of acetone-$d_6$ solutions of **5**–**7** showed that **5** and **6** reacted quantitatively at r.t. with a 10-fold excess of $CS_2$ to give a single final product in which both metal centers were coordinated by a thioxanthate ligand. The reaction of **5** was complete in 3 days, that of **6** in 2 weeks, while complex **7** did not react at all in 2 weeks. This observation points to a marked electronic influence on the reaction rate. IR spectra suggested that one of the three CO ligands per metal center were substituted in the products (for instance, $\nu$(CO): 2017 (s), 1929 (vs) for **5** versus 1950 (vs), 1874 (m) $cm^{-1}$ for the product (**5B**)) and the remaining two occupy mutually *cis* positions, that is, a $W(CO)_2S_2CSR$ system must have been formed. The presence of equivalent CO ligands in **5B**, unlike in **5**, was indicated by a single $^{13}C$-NMR resonance at $\delta$ 243.2.

The formation of similar products in the reactions



Scheme 4.

of analogous cyclopentadienyl and fulvalene tungsten thiolates with CS$_2$ suggests identical reaction mechanisms, e.g. possible involvement of a 16-electron intermediate and precoordination of CS$_2$ [4d]. However, the fulvalene complexes appear to react faster with CS$_2$ than their Cp analogues [4d]. On the other hand, the reactions of **5** and **6** proceed via the formation of monothioxanthate intermediates (**5A**, **6A**) (Scheme 4), identified by the observation of four fulvalene pseudotriplets and two different CHMe$_2$ methyl doublets or CH$_2$Ph methylene singlets of equal intensity in the NMR spectra. These species were the only products in the early stages of reactions and gradually disappeared concomitant with the formation of the bisthioxanthate complexes **5B** and **6B**.

The IR spectra of complexes **8**–**10** exhibited two absorbances in the 1927–1944 (s) and 1846–1862 (vs) cm$^{-1}$ regions. The band positions indicated a decrease in the ligand basicity in the order of S$^i$Pr > SCH$_2$Ph > SPh, while the relative intensities of the bands pointed to an increasing *trans*/*cis* isomeric ratio in the same order. $^1$H- and $^{31}$P{$^1$H}-NMR investigations provided evidence for the presence of all four isomers in equilibrated solutions (Scheme 3), their relative ratio being considerably effected by the solvent used. For example, the ratio of the isomers of complex **9** in CD$_2$Cl$_2$ was 16% *cis,cis* (1:1 mixture of D,L and *meso*), 47% *cis,trans* and 37% *trans,trans* (40:60 total *cis*:*trans* ratio), but in DMSO-$d_6$ it was 39% *cis,cis* (1:1 mixture of D,L and *meso*), 40% *cis,trans* and 21% *trans,trans* (60:40 total *cis*:*trans* ratio). Thus, the *cis,trans* form remains dominant (40–50%) for complex **9**. Similar results were obtained in acetone-$d_6$ solution for complex **10** (33:67 total *cis*:*trans* ratio).

While a single one-dimensional $^1$H-NMR spectrum is usually not enough to characterize isomeric mixtures of fulvalene complexes, that of complex **9** recorded at high-field (500 MHz) in CD$_2$Cl$_2$ solution was extraordinarily informative due to the coexistence of several conditions: (1) significant amounts of all four isomers at equilibrium that do not undergo fast exchange on the NMR time scale; (2) relatively well resolved resonances; and (3) the methylene region exhibited an interesting resonance pattern due to the diastereotopic methylene protons of the SCH$_2$Ph ligand in *cis* isomers, similar to the fulvalene protons. The PMe, methylene, and fulvalene proton resonances of complex **9** are shown in Fig. 1. The methyl doublets exhibit characteristic coupling to phosphorus ($J_{\mathrm{P-H}} = 8.6$ Hz) and were used to determine the exact ratio of individual isomers. The resonances attributable to *cis* isomers often appear upfield from those of *trans* isomers [7c,9a]. The seemingly complex multiplet of methylene protons is mainly due to the *cis,trans* isomer which combines features of both the 'pure' *cis,cis* and *trans,trans* forms. In general, the proton resonances of a methylene group attached to a phosphine-substituted chiral metal center appear as an eight-line ABX system due to coupling of the diastereotopic hydrogens to each other and to phosphorus [11]. The presence of the sulfur ligand prevents coupling to phosphorus in *cis,cis*- and the *cis* half of *cis,trans*-**9** as observed for *cis*-Cp(CO)$_2$(PPh$_3$)-WSCH$_2$Ph [4c,d], and only two doublets ($J = 12$ Hz) can be assigned to each of these environments (the two halves of both the D,L- and *meso*-*cis,cis* isomers are equivalent). *Trans,trans*-**9** is highly symmetric and therefore exhibits only one doublet ($J_{\mathrm{P-H}} = 1.7$ Hz). Finally, the *trans* half of *cis,trans*-**9** is diastereotopic due to its chiral *cis* half and apparently is the only species in this system which exhibits a full ABX resonance pattern. The fulvalene region of the spectrum displays the expected 18 multiplets [8g] relatively well resolved.

### 2.3. Synthesis and characterization of bishydrosulfido complexes FvW$_2$(CO)$_4$L$_2$(SH)$_2$ (L = CO, PPh$_2$Me)

FvW$_2$(CO)$_6$(SH)$_2$ (**11**) was generated in solution by treating **2** with a stoichiometric amount of S$_8$ [3b]. Unlike its cyclopentadienyl analogue, however, **11** proved to be unstable and decomposed to give FvW$_2$(CO)$_6$(*W*–*W*). Complex **11** was characterized in solution by IR (Table 1), $^1$H- and $^{13}$C{$^1$H}-NMR spectroscopy and the data are fully consistent with the proposed structure. The SH proton resonance was detected at $\delta$ −2.28 ($J_{\mathrm{W-H}} = 4.6$ Hz) in C$_6$D$_6$, slightly downfield from that observed for CpW(CO)$_3$SH ($\delta$ −2.51 [3b]).

While the reactions proceeded instantly in polar solvents such as THF or acetone-$d_6$, those carried out in

$C_6D_6$ resulted in a mixture of **2**, **11** and the mixed hydrido–hydrosulfido intermediate $FvW_2(CO)_6(SH)H$. Its $^1H$-NMR spectrum exhibited both hydridic ($\delta$ −6.89, $J_{W-H} = 37$ Hz) and SH ($\delta$ −2.31, $J_{W-H} = 4.6$ Hz) resonances different from those of **2** and **11**, respectively, as well as four fulvalene pseudotriplets at $\delta$ 4.24, 4.50, 4.66, and 4.80 with appropriate integral ratios. These results suggest that the insertion of sulfur into

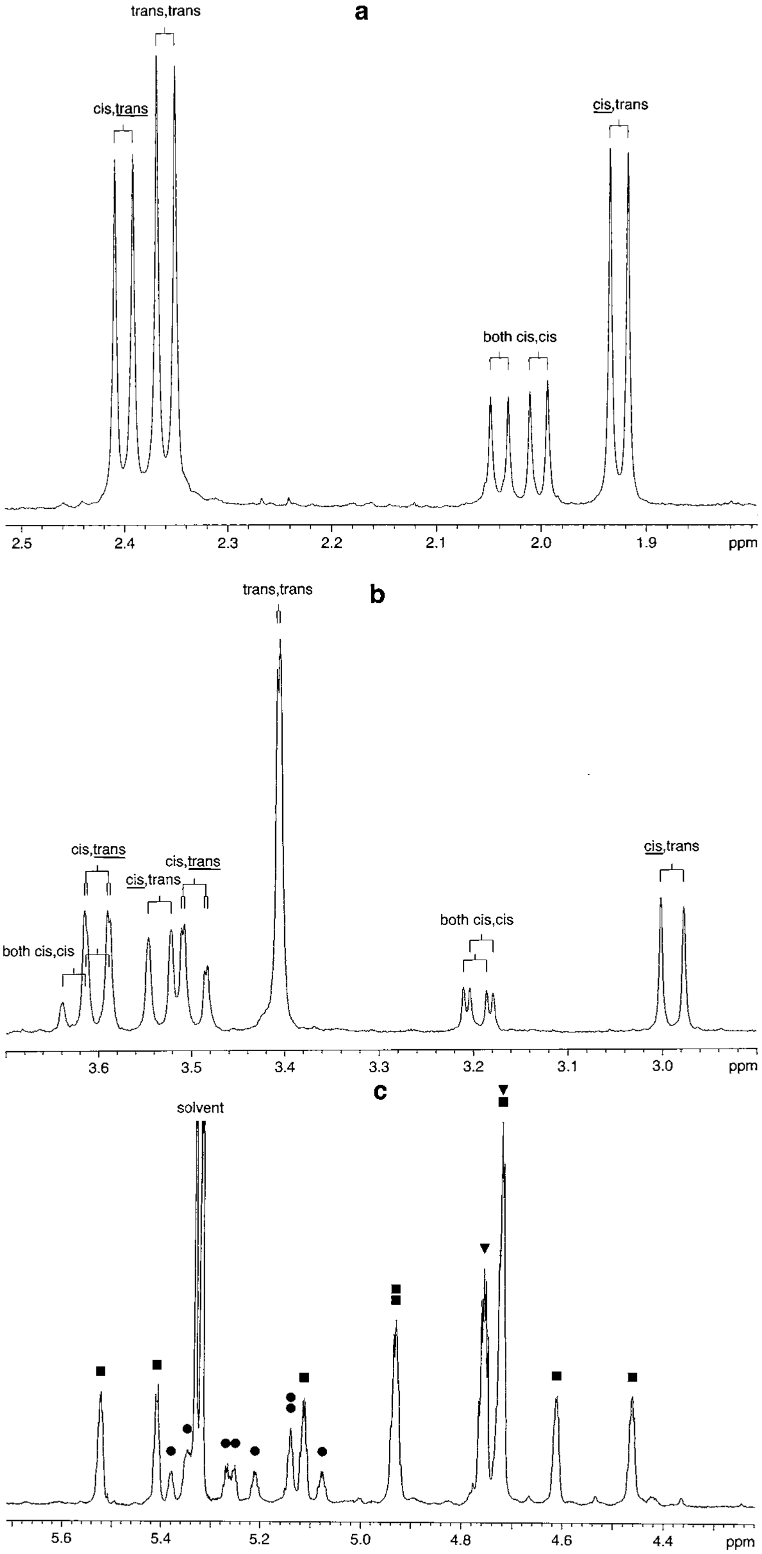


Fig. 1. $^1H$-NMR (500 MHz) spectrum of $FvW_2(CO)_4(PPh_2Me)_2(SCH_2Ph)_2$ in $CD_2Cl_2$. (a) PMe resonances; (b) $SCH_2$– resonances; (c) fulvalene resonances: *cis,cis* isomers, 2H each (●), *cis,trans* isomer, 1H each (■), *trans,trans* isomer, 4H each (▼).

the two W–H bonds of **2** takes place in two distinctive steps. Note that $FvW_2(CO)_6(SH)H$ is formally the product of the oxidative cleavage of the metal–metal bond in $FvW_2(CO)_6(W-W)$ by $H_2S$. Treatment of **11** with $CS_2$ gave only the dimer $FvW_2(CO)_6(W-W)$ as detected by $^1$H-NMR spectroscopy. On the basis of IR band positions (Table 1), the basicity of SH is comparable to that of SPh, while the reactive $S^iPr$ and $SCH_2Ph$ groups are consistently stronger bases.

Similar treatment of **3** with $S_8$ in THF gave only slow degradation, but the reaction of **10** with $H_2S$ gave $FvW_2(CO)_4(PPh_2Me)_2(SH)_2$ (**12**). This is analogous to the treatment of $CpW(CO)_2(PPh_3)SR$ with $H_2S$ to generate $CpW(CO)_2(PPh_3)SH$ [4c]. Complex **12** crystallized with THF in the lattice (NMR) from a $H_2S$ saturated solution of **10** at r.t. Unlike **8**–**10**, these orange crystals were quite soluble in chlorinated hydrocarbons. A $^1$H-NMR spectrum of freshly dissolved **12** in $CDCl_3$ exhibited eight multiplets in the fulvalene region, which is typical for a 1:1 mixture of D,L- and *meso-cis,cis* isomers, as well as two doublets in both the PMe and SH region. A $^{31}P\{^1H\}$-NMR spectrum of this sample exhibited two closely spaced singlet resonances in the upfield region at $\delta$ 4.97 and 5.07, consistent with the $^1$H-NMR observation. In time new resonances appeared in the spectra indicating a relatively fast isomerization process, which was complete in about 3 h at r.t. The equilibrium mixture consisted of 22% D,L-*cis,cis*, 22% *meso-cis,cis*, 45% *cis,trans* and 11% *trans,trans* isomer (total *cis*:*trans* ratio 66:34). In addition to those of the *cis,cis* isomer, three new phosphorus signals were present at $\delta$ 5.20 and 14.8 (*cis,trans*), and 15.0 (*trans,trans*) in the $^{31}P\{^1H\}$-NMR, as well as three new SH and PMe doublets in the $^1$H-NMR spectra, the former exhibiting characteristic couplings to *cis* and *trans* phosphorus atoms while the latter being in positions quite typical for *cis* and *trans* phosphines (the *cis* is upfield from *trans*).

Complexes **11** and **12** were surprisingly unreactive toward $SO_2$. THF and $CH_2Cl_2$ solutions of these complexes were treated with a large excess of $SO_2$ gas at r.t. and the reactions were monitored by IR spectroscopy. Complex **12** remained unchanged for at least 3 days at r.t. Complex **11** slowly decomposed to an insoluble precipitate (ca. 50% conversion in 1 day).

## 3. Experimental

All manipulations were carried out under an inert atmosphere ($N_2$ or Ar), using standard Schlenk techniques and a drybox. Solvents were dried and freshly distilled under nitrogen prior to use. $W(CO)_3(EtCN)_3$ [12], N-phenyl-, benzyl- and (2-propyl)phthalimide [13] were prepared according to literature procedures. $H_2S$ and $SO_2$ were purchased from Matheson (Caution: extreme care must be exercised when working with $H_2S$, which is very toxic and has a bad odor. The reactions must be conducted in a well-ventilated fume hood and every effort must be made to ensure containment of the gas. The recommended procedure for drying and handling $H_2S$ is described in the literature [14]). IR spectra were recorded on a Bruker IFS 48 spectrometer in solutions using a 0.1 mm NaCl cell. $^1$H-, $^{13}C\{^1H\}$-, and $^{31}P\{^1H\}$-NMR measurements were performed on a Jeol CPF 270 spectrometer. FAB(+) mass spectra were obtained on a Kratos MF25RFA instrument using 2-nitrobenzyl alcohol as the matrix. Elemental analyses were carried out by the 'Laboratoire d'Analyse Elementaire' at the University of Montreal.

### 3.1. $(Et_4N)_2[FvW_2(CO)_6]$ (**1**)

A freshly prepared solution of $Li_2[C_{10}H_8]$ (30 mmol) in 264 ml of THF/hexane (9:1) [8g] was transferred by cannula into a three-neck round-bottom flask containing a mixture of $W(CO)_3(EtCN)_3$ (26 g, 60 mmol) and $Et_4NBr$ (12.6 g, 60 mmol). The resulting slurry instantly turned brown in color. It was refluxed with stirring for 1 h to complete the reaction. The solvent was evaporated under reduced pressure, leaving a sticky brown residue which was washed with hexane and dried in vacuum. The crude product was washed with several 50 ml portions of ether until the washings were colorless, leaving a yellow–brown solid. After drying under reduced pressure for several hours, 45 g of an extremely fine, tan powder was collected (65% pure). $^1$H-NMR (acetone-$d_6$): $\delta$ 1.35 (tt, $J = 7.2$, 1.7 Hz, 24H, $CH_3$), 3.43 (q, $J = 7.2$ Hz, 16H, $CH_2N$), 4.78, 5.24 (both 't', $J = 2.3$ Hz, 4H, Fv). $^{13}C\{^1H\}$-NMR (acetone-$d_6$): $\delta$ 82.4, 84.45 (both Fv), 103.2 (Fv C-1), 227.4 (CO).

### 3.2. $FvW_2(CO)_6H_2$ (**2**)

A vigorously stirred slurry of **1** (10 g) containing NaI and LiBr impurities in 50 ml of toluene was treated with 4 ml of glacial acetic acid at r.t. The solids were allowed to settle and the clear, yellow–brown solution was transferred into another flask by cannula. The residues were suspended in 10 ml of toluene for 5 min, allowed to settle and the supernatant transferred. This process was repeated until nearly colorless supernatant solutions formed to give 150 ml combined toluene solution of **2**. $^1$H-NMR (toluene-$d_8$): $\delta$ −6.96 ($J_{W-H} = 37$ Hz, 2H, WH), 4.48, 4.80 (both 't', $J = 2.3$ Hz, 4H, Fv). $^1$H-NMR (acetone-$d_6$): $\delta$ −6.99 ($J_{W-H} = 38$ Hz, 2H, WH), 5.69, 6.23 (both 't', $J = 2.3$ Hz, 4H, Fv). $^{13}C\{^1H\}$-NMR (acetone-$d_6$) $\delta$ 86.8, 87.7 (Fv), 102.8 (Fv C-1), 216.1 (CO).

### 3.3. *FvW$_2$(CO)$_4$(PPh$_2$Me)$_2$H$_2$* (**3**)

To a solution of **2** in 150 ml of toluene (prepared in situ from 10 g of crude **1**), 2.7 ml methyldiphenylphosphine was injected and the mixture was heated at 105–110°C overnight by means of an oil bath. At this point, an IR spectroscopic analysis of the reaction mixture showed complete consumption of **2** and formation of **3** as the sole product. The yellow solution was filtered through Celite and evaporated to dryness. The resulting solid was washed with hexane and recrystallized from toluene at $-30$°C to yield 5.0 g (4.95 mmol, 70% based on W(CO)$_3$(EtCN)$_3$) of yellow **3**. Anal Calc. for $C_{40}H_{36}O_4P_2W_2$: C, 47.55; H, 3.59. Found: 47.65; H, 3.64%. $^1$H-NMR (acetone-*d*$_6$): $\delta$ $-$7.08 (d, $J_{P-H}=55$, $J_{W-H}=48$ Hz, 2H, WH), 2.22 (d, $J_{P-H}=8.6$ Hz, 6H, PCH$_3$), 4.94–5.43 (br m, 8H, Fv), 7.40 (br m, 12H, *m,p*-Ph), 7.51 (m, 8H, *o*-Ph). $^{13}$C{$^1$H}-NMR (acetone-*d*$_6$): $\delta$ 86.3, 87.6 (br, Fv), 128.2 (d, $J_{P-C}=9.4$ Hz, *m*-Ph), 129.7 (*p*-Ph), 131.8 (d, $J_{P-C}=10$ Hz, *o*-Ph). $^{31}$P{$^1$H}-NMR (acetone-*d*$_6$): $\delta$ 17.5 (br).

### 3.4. *FvW$_2$(CO)$_4$(PPh$_2$Me)$_2$I$_2$*

The dihydride **3** (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 r.t. The original yellow color quickly changed to orange and a red microcrystalline solid formed overnight. The mixture was concentrated to about 10 ml under reduced pressure and hexane was added to complete the precipitation. The solid product was filtered, washed with hexane and dried under vacuum. Yield: 1.8 g (1.41 mmol, 95%). For an alternative preparation see Ref. [7a]. The $^1$H-NMR data and assignments reported below revise those reported in [7a].

*Cis,cis* isomers (D,L-/*meso*- = 1:1, 24%); $^1$H-NMR (CDCl$_3$): $\delta$ 2.46 (d, $J_{P-H}=8.2$ Hz, 6H, PMe), 2.48 (d, $J_{P-H}=8.7$ Hz, 6H, PMe), 4.81 (m, 2H, Fv), 4.90 (m, 2H, Fv), 5.10 (m, 2H, Fv), 5.19 (m, 4H, Fv), 5.26 (m, 2H, Fv), 5.67 (m, 2H, Fv), 5.73 (m, 2H, Fv), 7.40–7.67 (m, Ph). $^{31}$P{$^1$H}-NMR (CDCl$_3$): $\delta$ $-4.44$, $-4.31$.

*Cis,trans* isomer (59%); $^1$H-NMR (CDCl$_3$): $\delta$ 2.36 (d, $J_{P-H}=9.0$ Hz, PMe, *trans*), 2.43 (d, $J_{P-H}=8.4$ 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*), 7.40–7.67 (m, Ph). $^{31}$P{$^1$H}-NMR (CDCl$_3$): $\delta$ $-4.26$ (*cis*), 10.26 (*trans*).

*Trans,trans* isomer (17%); $^1$H-NMR (CDCl$_3$): $\delta$ 2.34 (d, $J_{P-H}=9.1$ Hz, 6H, PMe), 4.81, 5.00 (both m, 4H, Fv), 7.40–7.67 (m, Ph). $^{31}$P{$^1$H}-NMR (CDCl$_3$): $\delta$ 10.53.

### 3.5. *Li$_2$[FvW$_2$(CO)$_4$(PPh$_2$Me)$_2$]* (**4**)

A solution of **3** (1.0 g, 0.99 mmol) in 20 ml of THF was stirred and cooled to $-10$°C. Then 1.5 ml of a 1.4 M solution of methyllithium in ether (Aldrich) was added dropwise by means of a syringe. The yellow starting solution instantly became red upon addition of the first drops of methyllithium. After completing the addition, the mixture was allowed to warm to r.t. and stirred for 1 h while a yellow precipitate formed. It was filtered, washed with hexane and dried under reduced pressure. Yield: 1.0 g (0.98 mmol, 98%). $^1$H-NMR (CD$_3$CN): $\delta$ 2.05 (d, $J=8$ Hz, 6H, PMe), 4.50, 4.96 (both m, 4H, Fv), 7.20 (m, 12H, *m,p*-Ph), 7.49 (m, 8H, *o*-Ph). $^{13}$C{$^1$H}-NMR (CD$_3$CN): $\delta$ 23.7 (PMe), 81.2, 83.7 (both Fv), 101.9 (Fv C-1), 127.05 (d, $J_{P-C}=7.3$ Hz, *m*-Ph), 129.1 (*p*-Ph), 131.8 (d, $J_{P-C}=11$ Hz, *o*-Ph). $^{31}$P{$^1$H}-NMR (CD$_3$CN): $\delta$ 28.8.

Yellow–brown solutions of **4** quickly changed color to dark red when briefly exposed to air. The resulting organometallic product was identified as FvW$_2$(CO)$_4$(PPh$_2$Me)$_2$(*W*–*W*) on the basis of spectroscopic data. $^1$H-NMR (CD$_3$CN): $\delta$ 4.32 (m, 4H, Fv), 4.62 (‘t’, 4H, Fv). $^{31}$P{$^1$H}-NMR (CD$_3$CN) $\delta$ 20.5.

### 3.6. *General synthesis of FvW$_2$(CO)$_6$(SR)$_2$ (R = i-Pr* (**5**), *CH$_2$Ph* (**6**), *Ph* (**7**))

To a slurry of **1** (6.0 g, 4.3 mmol) in 100 ml of THF, 8.6 mmol RSphth was added at once at r.t. The reaction mixtures instantly became yellow–orange and were stirred overnight. The resulting mixtures were filtered through Celite and the filtrates were evaporated to dryness. The orange–brown solids were washed with hexane and dried under reduced pressure. Repeated recrystallization from CH$_2$Cl$_2$ did not provide analytically pure samples due to contamination by Et$_4$Nphthalimide. All compounds were identified by spectroscopic techniques.

Data for **5**: FAB(+)-MS: *m*/*z* (%) [M]$^+$ = 814(0.9). $^1$H-NMR (acetone-*d*$_6$): $\delta$ 1.17 (d, $J=6.7$ Hz, 12H, CH$_3$), 2.63 (sept, $J=6.7$ Hz, 2H, CHS), 5.85, 6.25 (both ‘t’, $J=2.3$ Hz, 4H, Fv). $^{13}$C{$^1$H}-NMR (acetone-*d*$_6$): $\delta$ 27.0 (CH$_3$), 36.3 (CHS), 91.3, 93.2 (both Fv), 108.1 (Fv C-1), 214.1 (CO *cis* to S), 226.5 (CO *trans* to S).

Data for **6**: FAB(+)-MS: *m*/*z* (%) [M]$^+$ = 910(0.5). $^1$H-NMR (acetone-*d*$_6$): $\delta$ 3.46 (s, 4H, CH$_2$), 5.71, 6.18 (both ‘t’, $J=2.3$ Hz, 4H, Fv), 7.17–7.42 (m, 10H, Ph). $^{13}$C{$^1$H}-NMR (CD$_2$Cl$_2$): $\delta$ 36.8 (CH$_2$S), 90.6, 91.9 (both Fv), 106.5 (Fv C-1), 123.4, 128.4, 129.0, 134.3 (all Ph).

Data for **7**: $^1$H-NMR (acetone-*d*$_6$): $\delta$ 5.87, 6.41 (both ‘t’, $J=2.3$ Hz, 4H, Fv), 7.16 (m, 10H, Ph).

### 3.7. Reactions of complexes **5**–**7** with $CS_2$

NMR scale experiments were carried out with samples containing 0.05 mmol of complexes **5**–**7** dissolved in 0.7 ml of acetone-$d_6$ and 60 μl of $CS_2$. Reactions proceeded slowly at r.t. with **5** and **6** as indicated by a gradual color change from brown to cherry red. No change in color was observed for **7** in 2 weeks. The transformations were monitored by $^1$H-NMR spectroscopy. In a quantitative reaction, first the monoinsertion product $RS(CO)_3W(\mu\text{-}Fv)W(CO)_2S_2CSR$ (**A**) was formed, followed several hours later by $FvW_2(CO)_4(S_2CSR)_2$ (**B**). Formation of the latter was complete in 3 days for **5** and 2 weeks for **6**. No reaction took place with **7**.

Data for **5A**: $^1$H-NMR (acetone-$d_6$): $\delta$ 1.18, 1.42 (both d, $J = 6.7$ Hz, 6H, $CH_3$), 2.633, 3.99 (both sept, $J = 6.7$ Hz, 1H, CHS), 5.74, 5.79, 6.08, 6.28 (all 't', $J = 2.3$ Hz, 2H, Fv).

Data for **5B**: FAB(+)-MS: $m/z$ (%) $[M]^+ = 910(1.2)$. $^1$H-NMR (acetone-$d_6$): $\delta$ 1.43 (d, $J = 6.7$ Hz, 12H, $CH_3$), 3.99 (sept, $J = 6.7$ Hz, 2H, CHS), 5.70, 6.13 (both 't', $J = 2.3$ Hz, 4H, Fv). $^{13}C\{^1H\}$-NMR (acetone-$d_6$): $\delta$ 22.0 ($CH_3$), 38.0 (CH), 88.7, 90.8 (both Fv), 108.2 (Fv C-1), 243.2 (CO).

Data for **6A**: $^1$H-NMR (acetone-$d_6$): $\delta$ 3.48, 4.46 (both s, 2H, $CH_2$), 5.62, 5.72, 5.92, 6.25 (all 't', $J = 2.3$ Hz, 2H, Fv), 7.17–7.52 (m, 10H, Ph).

Data for **6B**: $^1$H-NMR (acetone-$d_6$): $\delta$ 4.50 (s, 4H, CH), 5.64, 5.96 (both 't', $J = 2.3$ Hz, 4H, Fv), 7.17–7.52 (m, 10H, Ph).

### 3.8. General synthesis of $FvW_2(CO)_4(PPh_2Me)_2(SR)_2$ (R = i-Pr (**8**), $CH_2Ph$ (**9**), Ph (**10**))

Dihydride **3** (2.0 g, 2.0 mmol) was dissolved in 100 ml of THF and treated with 3 ml of a 1.4 M solution of methyllithium in ether (Aldrich) at −10°C, resulting in a color change from yellow to red. The solution was allowed to warm to r.t. and stirred for 2 h to complete the reduction process, which was indicated by the formation of **4** as a yellow precipitate. The mixture was cooled below 0°C and treated with 4.0 mmol of crystalline RSphth. Stirring overnight under ambient conditions led to an orange slurry, which was filtered through Celite and the filtrate was concentrated under reduced pressure. Adding hexane gave a precipitate which was collected and dried under reduced pressure to give orange microcrystalline products. These were poorly soluble in a variety of solvents, including hot THF, toluene, DMSO and $CH_2Cl_2$ and could not be purified. Satisfactory elemental analysis data were obtained only for **9** which was recrystallized from $CH_2Cl_2$ with significant loss. Anal Calc. for $C_{54}H_{48}O_4P_2S_2W_2$: C, 51.69; H, 3.86; S, 5.11. Found: 48.59; H, 3.82; S, 4.94%. All complexes were identified by spectroscopic methods.

Data for **8**: FAB(+)-MS: $m/z$ (%) $[M]^+ = 1159(0.5)$.

Data for **9**: FAB(+)-MS: $m/z$ (%) $[M]^+ = 1254(0.3)$. *Cis,cis* isomer (D,L-/*meso*- = 1:1, 16%); $^1$H-NMR ($CD_2Cl_2$): $\delta$ 2.00 (d, $J_{P-H} = 8.7$ Hz, 6H, $PCH_3$), 2.04 (d, $J_{P-H} = 8.6$ Hz, 6H, $PCH_3$), 3.176 (d, $J = 12$ Hz, 2H, $CH_2$), 3.182 (d, $J = 12$ Hz, 2H, $CH_2$), 3.58 (d, $J = 12$ Hz, 2H, $CH_2$), 3.61 (d, $J = 12$ Hz, 2H, $CH_2$), 5.06 (m, 2H, Fv), 5.12 (m, 4H, Fv), 5.19 (m, 2H, Fv), 5.24 (m, 4H, Fv), 5.33 (m, 2H, Fv), 5.36 (m, 2H, Fv), 6.96–7.51 (m, Ph). $^{31}P\{^1H\}$-NMR ($CD_2Cl_2$): $\delta$ 5.27, 5.34.

*Cis,trans* isomer (47%); $^1$H-NMR ($CD_2Cl_2$): $\delta$ 1.92 (d, $J_{P-H} = 8.5$ Hz, 3H, $PCH_3$, *cis*), 2.40 (d, $J_{P-H} = 8.9$ Hz, 3H, $PCH_3$, *trans*), 2.97 (d, $J = 12$ Hz, 1H, $CH_2$, *cis*), 3.48 (dd, $J_{P-H} = 1.7$ Hz, $J = 12$ Hz, 1H, $CH_2$, *trans*), 3.52 (d, $J = 12$ Hz, 1H, $CH_2$, *cis*), 3.59 (dd, $J_{P-H} = 1.7$ Hz, $J = 12$ Hz, 1H, $CH_2$, *trans*), 4.45, 4.60, 4.71 (all m, 1H, Fv), 4.92 (m, 2H, Fv), 5.10, 5.39, 5.51 (all m, 1H, Fv), 6.96–7.51 (m, Ph). $^{31}P\{^1H\}$-NMR ($CD_2Cl_2$): $\delta$ 6.2 (*cis*), 13.2 (*trans*).

*Trans,trans* isomer (37%); $^1$H-NMR ($CD_2Cl_2$): $\delta$ 2.36 (d, $J_{P-H} = 8.9$ Hz, 6H, $PCH_3$), 3.39 (d, $J_{P-H} = 1.7$ Hz, 4H, $CH_2$), 4.71, 4.75 (both m, 4H, Fv), 6.96–7.51 (m, Ph). $^{31}P\{^1H\}$-NMR ($CD_2Cl_2$): $\delta$ 13.4.

Data for **10**: *cis,cis* isomers (D,L-/*meso*- 1:1, 9%); $^1$H-NMR (acetone-$d_6$): $\delta$ 2.23 (d, $J_{P-H} = 8.6$ Hz, 6H, $PCH_3$), 2.27 (d, $J_{P-H} = 8.4$ Hz, 6H, $PCH_3$). The other proton resonances of this minor component extensively overlapped with those of the major *cis,trans* and *trans,trans* isomers. $^{31}P\{^1H\}$-NMR (acetone-$d_6$): $\delta$ 5.9.

*Cis,trans* isomer (48%); $^1$H-NMR (acetone-$d_6$): $\delta$ 2.17 (d, $J_{P-H} = 8.6$ Hz, 3H, $PCH_3$, *cis*), 2.42 (d, $J_{P-H} = 8.9$ Hz, 3H, $PCH_3$, *trans*), 4.65 (m, 2H, Fv), 4.96, 5.22, 5.32, 5.41, 5.75, 5.90 (all m, 1H, Fv), 6.8–7.5 (m, Ph). $^{31}P\{^1H\}$-NMR (acetone-$d_6$): $\delta$ 5.9 (*cis*), 12.4 (*trans*).

*Trans,trans* isomer (43%); $^1$H-NMR (acetone-$d_6$): $\delta$ 2.38 (d, $J_{P-H} = 8.9$ Hz, 6H, $PCH_3$), 4.85, 5.22 (both m, 4H, Fv), 6.8–7.5 (m, Ph). $^{31}P\{^1H\}$-NMR (acetone-$d_6$): $\delta$ 12.7.

### 3.9. $FvW_2(CO)_6(SH)_2$ (**11**)

To a solution of **2** (40 mg, 0.06 mmol) in 0.7 ml acetone-$d_6$ 4 mg (0.12 mmol) of $S_8$ was added at once at r.t. The reaction mixture instantly changed color from yellow to orange and complete transformation of **2** into **11** was confirmed by NMR spectroscopy. Similar reactions were carried out in THF and $C_6D_6$ solutions. Complex **11** readily converts to $FvW_2(CO)_6(W\text{–}W)$ in these media and could not be purified. $^1$H-NMR ($C_6D_6$): $\delta$ −2.28 ($J_{W-H} = 4.6$ Hz, 2H, WSH), 4.34 ('t', $J = 2.3$ Hz, 4H, Fv), 4.76 ('t', $J = 2.3$ Hz, 4H, Fv). $^1$H-NMR (acetone-$d_6$): $\delta$ −2.34 (s, 2H, SH), 5.81 ('t', $J = 2.3$ Hz, 4H, Fv), 6.27 ('t', $J = 2.3$ Hz, 4H, Fv). $^{13}C\{^1H\}$-NMR (acetone-$d_6$): $\delta$ 90.0, 92.9 (Fv), 110.2 (Fv C-1), 214.4 (CO *cis* to S), 226.8 (CO *trans* to S).

### *3.10.* $FvW_2(CO)_4(PPh_2Me)_2(SH)_2$ (**12**)

A THF solution of **9** was prepared as described above and saturated with $H_2S$ at r.t. An IR analysis of the reaction mixture indicated no reaction at first so it was allowed to stand for 1 week. During this period orange–yellow crystals separated, which were filtered and dried under reduced pressure. They were soluble in chlorinated hydrocarbons. A $^1$H-NMR analysis of the crystalline material suggested that they contained THF of crystallization.

*Cis,cis* isomers (D,L-/*meso*- = 1:1, 44%); $^1$H-NMR ($CDCl_3$): $\delta$ −2.35 (d, $J_{P-H} = 17$ Hz, 2H, SH), −2.32 (d, $J_{P-H} = 17$ Hz, 2H, SH), 2.14 (d, $J_{P-H} = 8.2$ Hz, 6H, $PCH_3$), 2.16 (d, $J_{P-H} = 8.4$ Hz, 6H, $PCH_3$), 5.00 (m, 4H, Fv), 5.16 (m, 2H, Fv), 5.21 (m, 2H, Fv), 5.24 (m, 2H, Fv), 5.27 (m, 2H, Fv), 5.40 (m, 2H, Fv), 5.54 (m, 2H, Fv), 7.38 (m, 40H, Ph). $^{31}P\{^1H\}$-NMR ($CDCl_3$): $\delta$ 4.97, 5.07.

*Cis,trans* isomer (45%); $^1$H-NMR ($CDCl_3$): $\delta$ −2.41 (d, $J_{P-H} = 17$ Hz, 1H, SH, *cis*), −2.29 (d, $J_{P-H} = 1.7$ Hz, 1H, SH, *trans*), 2.13 (d, $J_{P-H} = 8.4$ Hz, 3H, $PCH_3$, *cis*), 2.35 (d, $J_{P-H} = 8.9$ Hz, 3H, $PCH_3$, *trans*), 4.60 (m, 1H, Fv), 4.74 (m, 2H, Fv), 4.85 (m, 1H, Fv), 5.04, 5.20, 5.33, 5.66 (all m, 1H, Fv), 7.37 (m, 10H, Ph, *cis*), 7.45 (m, 10H, Ph, *trans*). $^{31}P\{^1H\}$-NMR ($CDCl_3$): $\delta$ 5.20 (*cis*), 14.79 (*trans*).

*Trans,trans* isomer (11%); $^1$H-NMR ($CDCl_3$): $\delta$ −2.36 (d, $J_{P-H} = 1.7$ Hz, 2H, SH), 2.33 (d, $J_{P-H} = 8.9$ Hz, 6H, $PCH_3$), 4.72, 4.98 (both m, 4H, Fv), 7.45 (m, 20H, Ph). $^{31}P\{^1H\}$-NMR ($CDCl_3$): $\delta$ 15.03.

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