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Tungsten complexes of aromatic and aliphatic thioaldehydes ☆

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Dedicated to Professor Helmut Werner on the occasion of his 70th birthday, in grateful recognition of his outstanding contributions to organometallic chemistry

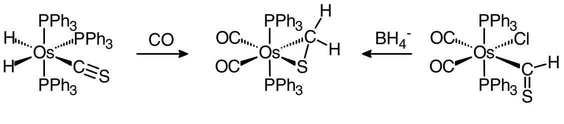
Abstract

Reaction of PPN[W(CO)$_3$(R$_2$PC$_2$H$_4$PR$_2$)(SH)] (PPN = Ph$_3$PNPPh$_3$; R = Me, **1**; R = Ph, **2**) with aromatic aldehydes in the presence of trifluoroacetic acid gave tungsten complexes of thiobenzaldehydes *mer*-[W(CO)$_3$(R$_2$PC$_2$H$_4$PR$_2$)(η^2-S=CHR′)] (R = Me, **3a**–**3f**; R = Ph, **4a**–**4e**) in high yields. Analogous complexes of aliphatic thioaldehydes *mer*-[W(CO)$_3$(Me$_2$PC$_2$H$_4$PMe$_2$)(η^2-S=CHR′)] (**3g**–**3l**) could only be obtained from the highly electron-rich thiolate complex **1**. The structure of **3i** (R′ = *i*-Bu) was determined by X-ray crystallography. In solution the complexes **3** and **4** are in equilibrium with small quantities of their isomers *fac*-[W(CO)$_3$(R$_2$PC$_2$H$_4$PR$_2$)(η^2-S=CHR′)]. Reaction of complexes **3** with dimethylsulfate followed by salt metathesis with NH$_4$PF$_6$ gave the alkylation products *mer*-[W(CO)$_3$(Me$_2$PC$_2$H$_4$PMe$_2$)(η^2-MeS=CHR′)]PF$_6$ (**5a**–**5l**) as mixtures of *E* and *Z* isomers. The methylated thioformaldehyde complex *mer*-[W(CO)$_3$(Me$_2$PC$_2$H$_4$PMe$_2$)(η^2-MeS=CH$_2$)]PF$_6$ (**5m**) was prepared similarly. Nucleophilic addition of hydride (from LiAlH$_4$) to **5** initially gave thioether complexes *mer*-[W(CO)$_3$(Me$_2$PC$_2$H$_4$PMe$_2$)(MeSCH$_2$R′)] (*mer*-**6**) which rapidly isomerized to *fac*-[W(CO)$_3$(Me$_2$PC$_2$H$_4$PMe$_2$)(MeSCH$_2$R′)] (*fac*-**6**).

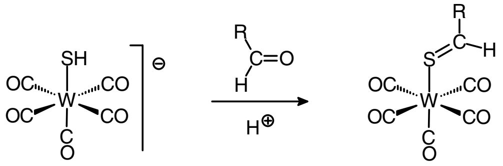
Keywords: Thioaldehyde; Tungsten; Structure; Electrophilic addition

1. Introduction

Shortly after the first synthesis of a thioformaldehyde complex of osmium by hydride transfer Eq. (1) [1], Gingerich and Angelici published a seemingly straightforward route to thiobenzaldehyde complexes of tungsten Eq. (2). Surprisingly, this reaction was limited to a few benzaldehydes carrying electron-releasing substituents in the para position [2]. Lateron, a somewhat wider range of W(CO)$_5$ complexes of aromatic thioaldehydes was obtained by using imines instead of aldehydes [3]



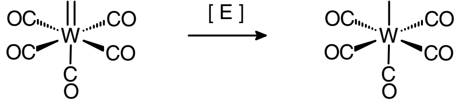
(1)



(2)

R = 4-C$_6$H$_4$Me, 4-C$_6$H$_4$OMe, 4-C$_6$H$_4$NMe$_2$

Fischer et al. [4] developed a general access to tungsten complexes of thiobenzaldehydes as well as the corresponding seleno and telluro analogs, namely, the insertion of sulfur (selenium, tellurium) into the tungsten–carbon double bond of the corresponding phenylcarbene complexes Eq. (3) [4]



(3)

E = S, Se, Te

☆ The coordination chemistry of the C=S function, part 18. For part 17 see [11a].

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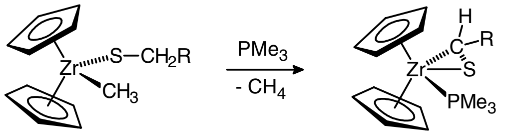
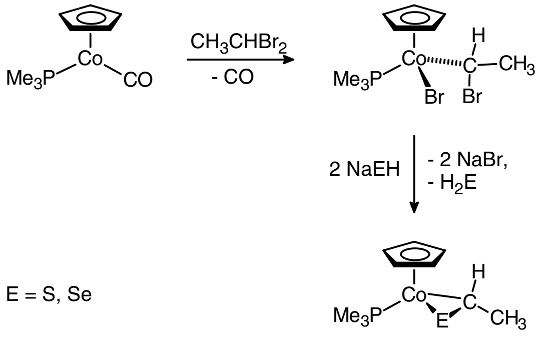
In fact, most of our knowledge about structure, dynamics and reactivity of thioaldehyde complexes originates from a systematic investigation of these prototypical compounds [5]. While complexes of the parent thioformaldehyde are now known for most of the transition metals [5] and even uranium [6], there are still surprisingly few complexes of aliphatic thioaldehydes. Some titanium and zirconium complexes originated from an intramolecular deprotonation of thiolate ligands such as described by Eq. (4) [7]

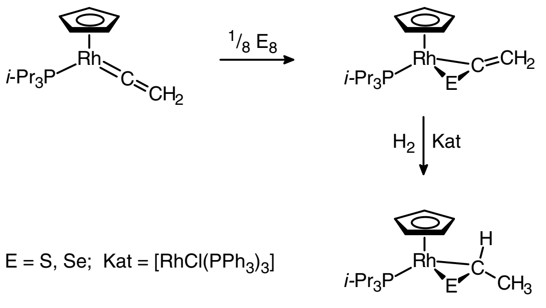


(4)

Thio- and selenoacetaldehyde complexes of cobalt and rhodium were synthesized by Werner et al. [8] in two rather unique ways: the half-sandwich cobalt complexes resulted from a double nucleophilic substitution (Eq. (5)), while the analogous rhodium complexes were obtained from the corresponding vinylidene complex by chalcogen addition followed by catalytic hydrogenation as shown in Eq. (6)

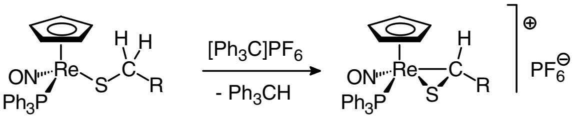


(5)

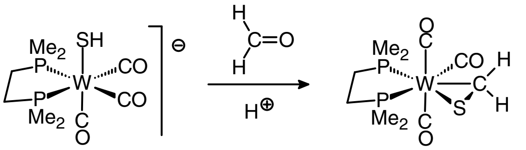


(6)

A series of rhenium complexes including some carrying functional groups on the side chain were generated by hydride abstraction (Eq. (7)) [9]. Recently we found that Angelici's condensation reaction [2] can be extended to the synthesis of a thioformaldehyde complex of tungsten by replacing two of the carbon monoxide ligands of the starting SH complex by the strongly electron donating chelate ligand $Me_2PC_2H_4PMe_2$ (dmpe) (Eq. (8)) [10]



(7)

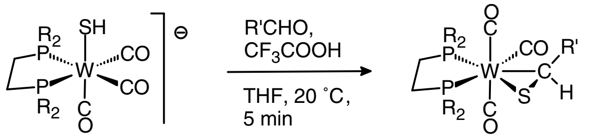


(8)

Here, we report an extension of this methodology to the synthesis of tungsten complexes of aromatic as well as aliphatic thioaldehydes. Furthermore, the reactivity of these electron-rich complexes will be compared with that of the cationic ruthenium complexes $[CpRu(PR_3)_2(S{=}CHR')]^+$ [11].

2. Results and discussion

Addition of a slight excess of trifluoroacetic acid to a THF solution containing **1** [10] or **2** [12] and the respective benzaldehyde leads to an instantaneous colour change to brown. Workup by column chromatography provides the corresponding thiobenzaldehyde complexes in high yields as orange-colored crystalline materials Eq. (9)



1, 2

R = Me: **1**, **3**; R = Ph: **2**, **4**

3a: 90%, **4a**: 80%,
3b: 89%, **4b**: 82%,
3c: 95%, **4c**: 75%,
3d: 99%, **4d**: 84%,
3e: 76%, **4e**: 59%,
3f: 85%

R'	C_6H_5	$3\text{-}C_6H_4F$	$4\text{-}C_6H_4F$	$4\text{-}C_6H_4Cl$	$4\text{-}C_6H_4OMe$	$4\text{-}C_6H_4NMe_2$
	a	**b**	**c**	**d**	**e**	**f**

(9)

The new compounds are soluble in most of the common organic solvents except aliphatic hydrocarbons. In solution, the dppe derivatives **4** decompose slowly while solutions of the dmpe complexes **3** are perfectly stable at ambient temperature. The meridional coordination geometry around the central tungsten atom as well as the side-on coordination of the thioaldehyde ligand are readily inferred from the wavenumbers and intensity pattern of the $\nu(CO)$ vibrations in the IR spectra (Table 1). Further support comes from the observation of a signal with ^{183}W satellites at $\delta = 50$–60 in the ^{13}CNMR spectra and the resonances of two nonequivalent phosphorus nuclei in the ^{31}P NMR spectra.

Table 1
Characteristic IR, ^{1}H and ^{13}CNMR spectroscopic data of the thioaldehyde complexes *mer*-$[W(CO)_3(R_2PC_2H_4PR_2)(\eta^2\text{-}S{=}CHR')]$[a]

No.	R	R′	IR (THF)			^{1}H NMR (C_6D_6)		^{13}C NMR (C_6D_6)		
			ν(CO) (cm^{-1})			δ(C–H)	$^3J(P_A\text{–}H)$	δ(C=S)	$^2J(P_A\text{–}C)$	$^2J(P_B\text{–}C)$
3a	Me	Ph	1994 (w)	1918 (s)	1867 (vs)	5.83 (d)	3.1	52.7 (dd)[b]	1.0	1.9
3b	Me	3-C_6H_4F	1996 (w)	1920 (s)	1868 (vs)	5.65 (d)	2.7	51.4 (d)		2.8
3c	Me	4-C_6H_4F	1994 (w)	1917 (s)	1868 (vs)	5.69 (d)	2.7	51.7 (dd)	1.9	1.9
3d	Me	4-C_6H_4Cl	1995 (w)	1919 (s)	1869 (vs)	5.61 (d)	2.8	51.7 (s)		
3e	Me	4-C_6H_4OMe	1992 (w)	1916 (s)	1866 (vs)	5.86 (d)	2.8	51.7 (d)		2.3
3f	Me	4-$C_6H_4NMe_2$	1990 (w)	1913 (s)	1864 (vs)	6.02 (d)	2.9	54.4 (dd)	2.0	2.1
3g	Me	Et	1991 (w)	1909 (s)	1864 (vs)	4.70 (ddd)[c]	2.9	58.7 (s)		
3h	Me	Pr	1991 (w)	1909 (s)	1864 (vs)	4.92 (ddd)[d]	3.4	56.8 (dd)[e]	1.9	2.9
3i	Me	*i*-Bu	1990 (w)	1909 (s)	1863 (vs)	4.90 (ddd)[f]	2.7	54.9 (d)[g]		5.1
3k	Me	*t*-Bu	1988 (w)	1905 (s)	1861 (vs)	5.21 (d)	2.2	72.0 (dd)[h]	3.1	3.1
3l	Me	$CHCHC_6H_4NMe_2$	1992 (w)	1918 (s)	1865 (vs)	5.61 (dd)[i]	2.6	55.5 (s)		
4a	Ph	Ph	2002 (w)	1927 (s)	1886 (vs)	5.88 (d)	2.8	53.8 (s)		
4b	Ph	3-C_6H_4F	2004 (w)	1929 (s)	1888 (vs)	5.73 (d)	2.4	52.1 (s)		
4c	Ph	4-C_6H_4F	2002 (w)	1926 (s)	1886 (vs)	5.79 (d)	2.7	52.2 (s)		
4d	Ph	4-C_6H_4Cl	2003 (w)	1927 (s)	1887 (vs)	5.74 (d)	2.2	52.3 (s)		
4e	Ph	4-C_6H_4OMe	2002 (w)	1923 (s)	1884 (vs)	5.72 (d)	2.7	54.4 (s)		

[a] See Section 4 for data of the corresponding *fac* isomers.
[b] ^1J(W–C) = 16.2 Hz.
[c] ^3J(H–H) = 2.9, 9.9 Hz.
[d] ^3J(H–H) = 3.4, 9.4 Hz.
[e] ^1J(W–C) = 16.2 Hz.
[f] ^3J(H–H) = 2.7, 10.5 Hz.
[g] ^1J(W–C) = 17.3 Hz.
[h] ^1J(W–C) = 24.8 Hz.
[i] ^3J(H–H) = 9.3 Hz.

Two fairly different couplings ^{183}W–^{31}P reflect the unique positions of the phosphorus atoms *trans* to CO and thioaldehyde, respectively (Table 2).

The thioformaldehyde complex *mer*-$[W(CO)_3(Me_2PC_2H_4PMe_2)(\eta^2\text{-}S{=}CH_2)]$ was found to be in a 87:13 equilibrium in solution with its facial isomer [10]. Minor additional signals in the IR and ^{31}P NMR spectra of complexes **3** and **4** (see Section 4) suggest a similar situation here although the fraction of the facial isomer is significantly smaller.

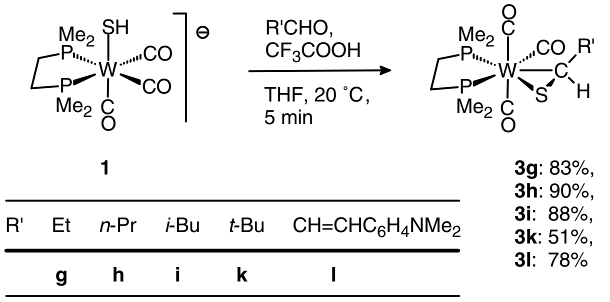
Treatment of **2** with aqueous formaldehyde or aliphatic aldehydes and acid did not lead to any isolable products. However, reactions of **1** with a series of aliphatic aldehydes in the presence of trifluoroacetic acid gave, after chromatographic workup, the expected thioaldehyde complexes **3g**–**3k** as well as the

Table 2
^{31}P NMR spectroscopic data of the thioaldehyde complexes *mer*-$[W(CO)_3(R_2PC_2H_4PR_2)(\eta^2\text{-}S{=}CHR')]$[a]

No.	R	R′	^{31}P NMR (C_6D_6)				
			$\delta(P_A)$	$^1J(W\text{–}P_A)$	$\delta(P_B)$	$^1J(W\text{–}P_B)$	$^2J(P_A\text{–}P_B)$
3a	Me	Ph	12.9	215	18.7	196	15
3b	Me	3-C_6H_4F	12.7	215	18.9	196	15
3c	Me	4-C_6H_4F	12.8	215	18.5	194	15
3d	Me	4-C_6H_4Cl	12.8	214	18.7	194	15
3e	Me	4-C_6H_4OMe	13.0	219	18.1	194	14
3f	Me	4-$C_6H_4NMe_2$	13.2	221	17.7	194	13
3g	Me	Et	12.6	219	17.5	197	13
3h	Me	Pr	12.6	222	17.5	197	13
3i	Me	*i*-Bu	12.6	220	17.5	197	13
3k	Me	*t*-Bu	13.5	204	18.9	190	15
3l	Me	$CHCHC_6H_4NMe_2$	13.2	221	17.7	194	13
4a	Ph	Ph	44.1	233	42.0	203	12
4b	Ph	3-C_6H_4F	44.1	232	42.0	202	12
4c	Ph	4-C_6H_4F	44.3	233	42.0	203	12
4d	Ph	4-C_6H_4Cl	44.2	232	42.2	203	12
4e	Ph	4-C_6H_4OMe	44.5	236	41.7	199	12

[a] See Section 4 for data of the corresponding *fac* isomers.

thiocinnamaldehyde complex **3l** (Eq. (10)). Their properties are very similar to those of the thiobenzaldehyde complexes **3a**–**3f**, including the presence in small quantities of the corresponding facial isomers



(10)

An X-ray structure determination was carried out on **3i**, Fig. 1 shows a view of the molecule. As in the corresponding thioformaldehyde complex [10], the coordination geometry around the central tungsten atom can be described as distorted pentagonal-bipyramidal with the thioaldehyde ligand occupying two adjacent sites. The largest angle deviation within the pentagonal base is associated with the three-membered W–S–C ring, all other angles between neighboring bonds in this plane are in a range of 79 ± 5° (Table 3). As expected, all the bond lengths are almost equal to those of the thioformaldehyde complex [10] with exception of the C–S bond which is slightly elongated (by 3 pm). Of the two possible orientations of the *i*-BuHC=S ligand the one with the sulfur atom pointing towards one of the phosphorus atoms is obviously preferred.

DFT calculations carried out on the parent thioformaldehyde complex *mer*-[W(CO)$_3$ (Me$_2$PC$_2$H$_4$PMe$_2$)(η^2-S=CH$_2$)] have identified an energetically high HOMO at −3.97 eV with the largest contribution arising from a p orbital at sulfur [10]. In accord with this, the dmpe complexes **3a**–**3l** as well as the thioformaldehyde complex reacted smoothly with dimethylsulfate in benzene (Eq. (11)). After salt metathesis with NH$_4$PF$_6$ in methanol, the corresponding *S*-methylated complexes **5a**–**5m** were isolated in high yields

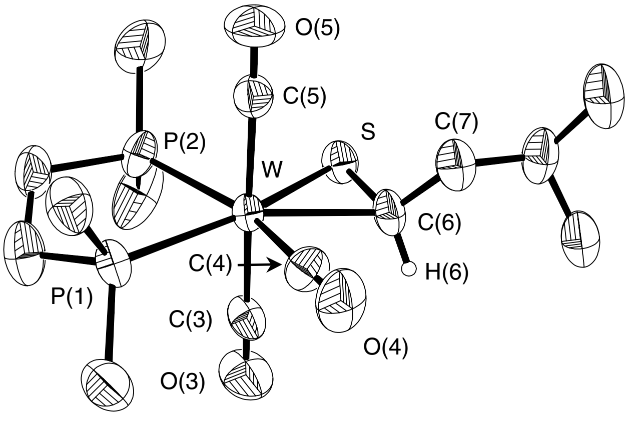
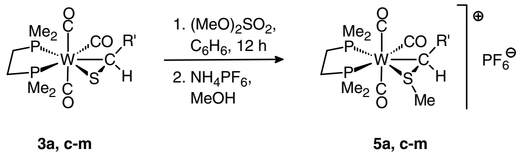


Fig. 1. ORTEP diagram of *mer*-[W(CO)$_3$(Me$_2$PC$_2$H$_4$PMe$_2$)(η^2-S=CH-*i*-Bu)] (**3i**). Hydrogen atoms except H(6) omitted.

Table 3
Selected bond lengths (Å) and angles (°) for *mer*-[W(CO)$_3$(Me$_2$PC$_2$H$_4$-PMe$_2$)(η^2-S=CH-*i*-Bu)] (**3i**)

W–S	2.501(2)	W–C(6)	2.286(8)
W–P(1)	2.457(2)	S–C(6)	1.772(9)
W–P(2)	2.489(2)	C(6)–C(7)	1.480(13)
W–C(3)	2.007(10)	C(3)–O(3)	1.151(10)
W–C(4)	2.021(9)	C(4)–O(4)	1.133(9)
W–C(5)	2.006(10)	C(5)–O(5)	1.147(10)
S–W–C(6)	43.2(2)	C(3)–W–C(5)	177.0(4)
P(1)–W–S	162.60(7)	C(3)–W–C(6)	85.7(4)
P(2)–W–S	84.46(8)	C(4)–W–C(5)	87.7(4)
P(1)–W–P(2)	79.14(8)	C(4)–W–C(6)	73.5(3)
P(1)–W–C(4)	80.4(3)	C(5)–W–C(6)	92.4(4)
C(3)–W–C(4)	93.8(4)	W–S–C(6)	61.9(3)



No.	R'	Yield	No.	R'	Yield
5a	C_6H_5	85%	5g	Et	93%
5c	4-C_6H_4F	97%	5h	*n*-Pr	90%
5d	4-C_6H_4Cl	95%	5i	*i*-Bu	88%
5e	4-C_6H_4OMe	89%	5k	*t*-Bu	85%
5f	4-$C_6H_4NMe_2$	95%	5l	$CHCHC_6H_4NMe_2$	89%
			5m	H	81%

(11)

These are stable yellow crystalline compounds which, as a consequence of their ionic composition, are soluble only in polar organic media such as THF, dichloromethane or acetone. Their IR spectra in the ν(CO) region are similar in appearance to those of **3a**–**3k** but shifted to higher wavenumbers as a result of the positive charge introduced by methylation. Both the ^{1}H and ^{13}C signals of the thioformyl group are shifted upfield, and the newly introduced methyl group gives resonances at $\delta = 2.9$ (^{1}H) and $\delta = 31$ (^{13}C), respectively (Table 4).

The methylated thiobenzaldehyde derivatives **5a**–**5f** were obtained as single isomers. NOE experiments showed that the methyl group and the aryl substituent occupy *trans* positions at the three-membered W–C–S ring: Saturation of the aldehyde proton at $\delta = 5.2$ enhanced both the methyl and aryl signals while irradiation of the methyl signal at $\delta = 2.8$ led to a gain of only the aldehyde resonance, and saturation of the aryl resonances at $\delta = 7.5$ enhanced only the thioaldehyde signal. **5g**–**5k**, on the other hand, were obtained as

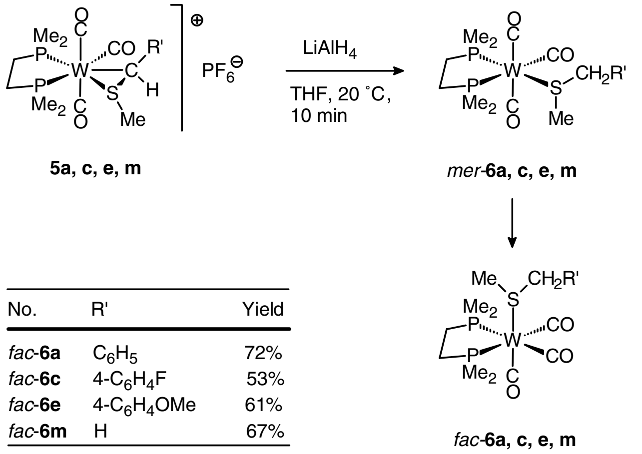
Table 4
Characteristic IR, ^{1}H and ^{13}CNMR spectroscopic data of the methylated thioaldehyde complexes *mer*-[W(CO)$_3$(R$_2$PC$_2$H$_4$PR$_2$)(η^2-*E*-MeS=CHR′)]PF$_6$[a]

No.	IR (THF)			^{1}H NMR ([D$_6$]-acetone)			^{13}C NMR ([D$_6$]-acetone)			
	ν(CO) (cm^{-1})			δ(SCH$_3$)	δ(C–H)	^3J(P$_A$–H)	δ(SCH$_3$)	δ(C=S)	^2J(P$_B$–C)	^1J(W–C)
5a	2027(w)	1961(s)	1902(vs)	2.87(s)	5.18(d)	1.5	31.2(s)	45.8(d)	5.0	18.3
5c	2027(w)	1961(s)	1902(vs)	2.91(s)	5.25(d)	1.7	31.3(s)	44.8(d)	4.8	23.8
5d	2027(w)	1961(s)	1903(vs)	2.87(s)	5.21(d)	1.8	31.1(s)	44.5(d)	5.1	20.3
5e	2025(w)	1959(s)	1900(vs)	2.89(s)	5.21(d)	2.2	31.3(d)[b]	45.8(d)	4.8	19.1
5f	2023(w)	1958(s)	1899(vs)	2.90(s)	5.19(d)	2.0	31.2(d)[b]	46.7(d)	4.8	17.2
5g	2024(w)	1956(s)	1899(vs)	2.69(s)	3.98(ddd)[c]	2.5	30.8(s)	50.6(d)	6.1	22.4
5h	2023(w)	1956(s)	1899(vs)	2.68(s)	4.00(ddd)[d]	2.0	30.6(d)[b]	47.9(d)	4.8	21.9
5I	2023(w)	1955(s)	1899(vs)	2.74(s)	4.05(ddd)[e]	2.0	31.0(d)[b]	45.7(d)	5.7	21.0
5k	2023(w)	1955(s)	1897(vs)	2.69(s)	4.27(d)	1.5	30.9(d)[b]	61.0(d)	5.7	24.8
5l	2024(w)	1960(s)	1900(vs)	2.78(s)	4.88(dd)[f]	2.0	30.6(s)	48.0(d)	4.8	18.1
5m	2029(w)	1962(s)	1901(vs)	2.64(s)	3.18(d)[g] 3.37(d)[g]	[h] [h]	30.9(s)	22.9(s)[i]		

[a] See Section 4 for data of the corresponding *Z* isomers.
[b] ^3J(P$_A$–C) = 1.9 Hz.
[c] ^3J(H–H) = 10.6, 2.5 Hz.
[d] ^3J(H–H) = 11.2, 2.0 Hz.
[e] ^3J(H–H) = 11.4, 2.0 Hz.
[f] ^3J(H–H) = 10.2 Hz.
[g] ^2J(H–H) = 5.0 Hz.
[h] j(P–H) not resolved.
[i] J(P–C) not resolved.

mixtures containing up to 10% of the respective *Z* isomers. In this regard the thioaldehyde complexes **3** are similar to the isostructural complexes of methyl and benzyl dithioformate *mer*-[W(CO)$_3$(dmpe)η^2-S=C(H)(SR)] which upon alkylation also gave mixtures of *E* and *Z* configured products [13]. The ^{31}P NMR spectra of complexes **5** (Table 5) show line broadening at 20°C. Sharp spectra are obtained at −20°C and at +70°C. This is obviously a result of a rapid rotation of the olefin-like ligand [14].

A selection of the methylated thioaldehyde complexes was treated with LiAlH$_4$ in THF. After chromatographic workup, the thioether complexes *fac*-**6a**, **c**, **e**, **m** were isolated in moderate to good yields (Eq. (12))



5a, c, e, m

mer-**6a, c, e, m**

fac-**6a, c, e, m**

No.	R′	Yield
fac-**6a**	C$_6$H$_5$	72%
fac-**6c**	4-C$_6$H$_4$F	53%
fac-**6e**	4-C$_6$H$_4$OMe	61%
fac-**6m**	H	67%

(12)

Table 5
^{31}P NMR spectroscopic data of the methylated thioaldehyde complexes *mer*-[W(CO)$_3$(R$_2$PC$_2$H$_4$PR$_2$)(η^2-*E*-MeS=CHR′)]PF$_6$[a]

No.	δ(P$_A$)	^1J(W–P$_A$)	δ(P$_B$)	^1J(W–P$_B$)	^2J(P$_A$–P$_B$)
5a	15.8	194	12.8	185	15
5c	15.8	196	12.8	185	16
5d	15.8	198	12.8	185	16
5e	15.4	198	12.8	187	15
5f	16.5	194	12.8	189	14
5g	14.6	198	12.6	189	15
5h	14.5	198	12.6	189	15
5I	14.4	198	12.8	190	15
5k	16.0	192	13.4	170	15
5l	14.4	198	12.8	193	14
5m[b]	15.7	205	12.6	192	16

[a] Recorded in [D$_6$]-acetone; PF$_6^-$ signal of all compounds: $\delta = -144.1$(sept), ^1J(P–F) = 708 Hz; see Section 4 for data of the corresponding *Z* isomers.
[b] Recorded in CD$_2$Cl$_2$ at −70 °C.

6a–**6m** are light yellow crystalline materials which are soluble without decomposition in most of the common organic solvents. The *fac* coordination geometry is evident from the observation of three intense ν(CO) absorptions in their IR spectra and a singlet phosphorus NMR resonance (Table 6).

However, as the immediate result of a nucleophilic hydride transfer to the meridional complexes **5**, the corresponding meridional thioether complexes should be obtained. These could indeed be observed by recording NMR spectra of the crude reaction mixtures.

Table 6
Characteristic IR and ^{31}P NMR spectroscopic data of the thioether complexes *fac*-[$W(CO)_3(R_2PC_2H_4PR_2)(MeSCH_2R')$][a]

No.	IR (THF)			^{31}P NMR (CD_2Cl_2)	
	ν(CO)(cm^{-1})			δ	^1J(W–P)
6a	1924(s)	1834(s)	1815(s)	11.6	219
6c	1924(s)	1832(s)	1816(s)	11.5	218
6e	1924(s)	1832(s)	1814(s)	11.5	218
6m	1925(s)	1833(s)	1815(s)	11.7	219

[a] See Section 4 for data of the corresponding *mer* isomers.

The *mer* isomers show resonances for two nonequivalent P nuclei with the expected P–P coupling. The downfield resonance exhibits an unusually large ^{183}W–^{31}P coupling of ca. 300 Hz indicating that the phosphorus atom from which it arises is situated *trans* to a weakly bonded ligand with a low structural *trans* influence [15]. The *mer* to *fac* isomerization can easily be followed by NMR, in solution at room temperature it is complete in less than 1 h.

3. Conclusions

The synthesis of thioaldehyde complexes by condensation of aldehydes with transition metal–SH complexes can be extended to the less electrophilic aliphatic aldehydes, provided that highly electron-rich anionic hydrogen sulfido complexes are employed. The products contain the newly formed thioaldehyde as a *hapto-2* ligand which readily undergoes electrophilic addition. This contrasts with the cationic ruthenium complexes [$CpRu(PR_3)_2(\eta^1\text{-}S{=}CHR')]^+$ which can be obtained similarly but react preferably with nucleophiles [11]. In both cases further transformations are available to give metal-coordinated thioethers.

4. Experimental

The complexes PPN[$W(CO)_3(R_2PC_2H_4PR_2)(SH)$] (**1** [10], **2** [12], PPN = $Ph_3P{=}N{=}PPh_3$) were prepared according to published methods. Other chemicals were obtained commercially and used without further purification. All experiments were carried out under an atmosphere of N_2 in dried and deoxygenated solvents. Reactions were routinely monitored by IR and NMR spectroscopy. Chromatographic separations were carried out using a 25 cm column of 2.5 cm diameter filled with silica (Merck, grain size 0.06–0.20 mm) as stationary phase.

IR spectra of the ν(CO) region were recorded on a Bruker IFS-25 spectrometer with the samples prepared as THF solutions in 0.1 mm NaCl cells. NMR spectra were recorded on a Jeol JNM-LA 300 instrument. ^{1}H (300.4 MHz) and ^{13}C (75.45 MHz) chemical shifts are reported relative to internal TMS; ^{31}P (121.5 MHz) chemical shifts are relative to external 85% H_3PO_4 with the deuterium signal of the solvent serving as lock and internal reference. ^{1}H and ^{13}C NMR signals of the phosphine ligands are uncharacteristic and have therefore been omitted from the lists of spectroscopic data. Also not listed here are data given already in the tables. Analyses were carried out by the Microanalytical Laboratory of the Institut für Anorganische Chemie.

4.1. Preparation of thioaldehyde complexes mer-[$W(CO)_3(Me_2PC_2H_4PMe_2)(\eta^2\text{-}S{=}CHR')$] (3a–3l)

To a solution of the hydrogensulfido complex **1** (200 mg, 0.20 mmol) in THF (10 ml) was added the respective aldehyde (0.25 mmol) and CF_3COOH (15 µl, 0.20 mmol). An immediate color change to brownish-orange was observed (the synthesis of **3l** requires a reaction time of 30 min). All volatiles were removed under vacuum, and the sticky residue dissolved in hexanes and chromatographed using dichloromethane/acetone 40:1 as eluent. The yellow fraction was collected and evaporated to dryness. The residue was twice washed with 2-ml portions of pentane and dried under vacuum giving a yellow or orange crystalline powder.

mer-[$W(CO)_3$(dmpe){$S{=}C(H)C_6H_5$}](*mer*-**3a**): Yield: 97 mg (90%), m.p. 70 °C (dec.). Calc. for $C_{16}H_{22}O_3P_2SW$ (MW 540.2): C, 35.57; H, 4.10; S, 5.94. Found: C, 35.41; H, 3.91; S, 5.72%. ^{1}H NMR (C_6D_6): $\delta = 6.91–7.76$ (m, 5H, C_6H_5); $^{13}C\{^1H\}$ NMR (C_6D_6): $\delta = 125.8, 127.3, 129.1, 145.4$ (s, C_6H_5), 197.3 (dd, ^2J(P–C) = 7.5, 3.8 Hz, CO), 198.8 (dd, ^2J(P–C) = 6.5, 3.8 Hz, CO), 211.5 (dd, ^2J(P–C) = 13.3, 9.6 Hz, CO).

fac-**3a**: IR, (ν(CO), THF, cm^{-1}): 1976.

mer-[$W(CO)_3$(dmpe){$S{=}C(H)(3\text{-}C_6H_4F)$}] (*mer*-**3b**): Yield: 99 mg (89%), m.p. 66 °C. Calc. for $C_{16}H_{21}FO_3P_2SW$ (MW 558.2): C, 34.43; H, 3.79; S, 5.74. Found: C, 34.25; H, 3.87; S, 5.65%. ^{1}H NMR (C_6D_6): $\delta = 6.87–7.55$ (m, 4H, C_6H_4F); $^{13}C\{^1H\}$NMR (C_6D_6): $\delta = 114.5–162.5$ (m, C_6H_4F), 197.0 (dd, ^2J(P–C) = 7.5, 3.8 Hz, CO), 198.7 (dd, ^2J(P–C) = 6.5, 3.8 Hz, CO), 214.2 (dd, ^2J(P–C) = 13.4, 9.7 Hz, CO).

fac-**3b**: IR, (ν(CO), THF, cm^{-1}): 1977.

mer-[$W(CO)_3$(dmpe){$S{=}C(H)(4\text{-}C_6H_4F)$}] (*mer*-**3c**): Yield: 106 mg (95%), m.p. 76 °C (dec.). Calc. for $C_{16}H_{21}FO_3P_2$ SW (MW 558.2): C, 34.43; H, 3.79; S, 5.74. Found: C, 34.21; H, 3.51; S, 5.49%. ^{1}H NMR (C_6D_6): $\delta = 6.87–7.55$ (m, 4H, C_6H_4F); $^{13}C\{^1H\}$NMR (C_6D_6): $\delta = 114.5–162.5$ (m, C_6H_4F), 197.1 (dd, ^2J(P–C) = 7.5, 3.8 Hz, CO), 198.8 (dd, ^2J(P–C) = 6.5, 3.5 Hz, CO), 211.5 (dd, ^2J(P–C) = 13.4, 9.7 Hz, CO).

fac-**3c**: IR, (ν(CO), THF, cm^{-1}): 1977.

mer-$[W(CO)_3(dmpe)\{S{=}C(H)(4\text{-}C_6H_4Cl)\}]$ (*mer*-**3d**): Yield: 113 mg (98%), m.p. 76 °C. Calc. for $C_{16}H_{21}ClO_3P_2SW$ (MW 574.7): C, 33.44; H, 3.69; S, 5.58. Found: C, 33.39; H, 3.72; S, 5.51%. ^1H NMR (C_6D_6): $\delta = 7.20$ (d, 2H, $^3J(H–H) = 8.4$ Hz, C_6H_4Cl), 7.49 (d, 2H, $^3J(H–H) = 8.4$ Hz, C_6H_4Cl); $^{13}C\{^1H\}$NMR (C_6D_6): $\delta = 130.1$, 149.7 (s, C_6H_4Cl), 197.0 (dd, $^2J(P–C) = 7.2$, 3.8 Hz, CO), 198.8 (dd, $^2J(P–C) = 6.5$, 3.5 Hz, CO), 214.3 (dd, $^2J(P–C) = 13.4$, 9.7 Hz, CO).

fac-**3d**: IR, (ν(CO), THF, cm^{-1}): 1976.

mer-$[W(CO)_3(dmpe)\{S{=}C(H)(4\text{-}C_6H_4OMe)\}]$ (*mer*-**3e**): Yield: 87 mg (76%), m.p. 69 °C (dec.). Calc. for $C_{17}H_{24}O_4P_2SW$ (MW 570.2): C, 35.81; H, 4.24; S, 5.62. Found: C, 35.32; H, 4.09; S, 5.18%. ^1H NMR (C_6D_6): $\delta = 3.25$ (s, 3H, OCH_3), 6.88 (d, 2H, $^3J(H–H) = 8.4$ Hz, C_6H_4), 7.75 (d, 2H, $^3J(H–H) = 8.4$ Hz, C_6H_4); $^{13}C\{^1H\}$NMR (C_6D_6): $\delta = 54.7$ (s, OCH_3), 113.6, 127.1, 143.0, 157.9 (s, C_6H_4), 197.4 (dd, $^2J(P–C) = 7.5$, 3.8 Hz, CO), 199.0 (dd, $^2J(P–C) = 6.5$, 3.4 Hz, CO), 214.3 (dd, $^2J(P–C) = 12.8$, 10.0 Hz, CO).

fac-**3e**: IR, (ν(CO), THF, cm^{-1}): 1972.

mer-$[W(CO)_3(dmpe)\{S{=}C(H)(4\text{-}C_6H_4NMe_2)\}]$ (*mer*-**3f**): Yield: 99 mg (85%), m.p. 74 °C (dec.). Calc. for $C_{18}H_{27}NO_3P_2SW$ (MW 583.3): C, 37.07; H, 4.67; N, 2.40; S, 5.50. Found: C, 36.66; H, 4.78; N, 2.36; S, 5.24%. ^1H NMR (C_6D_6): $\delta = 2.26$ (s, 6H, $N(CH_3)_2$), 6.70 (d, 2H, $^3J(H–H) = 8.8$ Hz, C_6H_4), 7.74 (d, 2H, $^3J(H–H) = 8.4$ Hz, C_6H_4); $^{13}C\{^1H\}$NMR (C_6D_6): $\delta = 40.6$ (s, $N(CH_3)_2$), 113.0, 127.0, 139.2, 149.0 (s, C_6H_4), 197.9 (dd, $^2J(P–C) = 7.2$, 3.8 Hz, CO), 199.0 (dd, $^2J(P–C) = 7.2$, 3.8 Hz, CO), 215.1 (dd, $^2J(P–C) = 12.8$, 10.7 Hz, CO).

fac-**3f**: IR, (ν(CO), THF, cm^{-1}): 1968.

mer-$[W(CO)_3(dmpe)\{S{=}C(H)CH_2CH_3\}]$ (*mer*-**3g**): Yield: 82 mg (83%), m.p. 72 °C (dec.). Calc. for $C_{12}H_{22}O_3P_2SW$ (MW 492.2): C, 29.29; H, 4.51; S, 6.52. Found: C, 29.17; H, 4.61; S, 6.44%. ^1H NMR (C_6D_6): $\delta = 1.47$ (t, br, 3H, $^3J(H–H) = 8.7$ Hz, CH_3), 1.89–2.03 (m, 1H, CH_2), 3.10–3.23 (m, 1H, CH_2); $^{13}C\{^1H\}$NMR (C_6D_6): $\delta = 23.3$ (s, CH_3), 40.5 (s, CH_2), 197.2 (dd, $^2J(P–C) = 7.9$, 3.8 Hz, CO), 199.5 (dd, $^2J(P–C) = 6.9$, 3.5 Hz, CO), 215.4 (dd, $^2J(P–C) = 13.1$, 9.3 Hz, CO).

fac-**3g**: IR, (ν(CO), THF, cm^{-1}): 1973; ^1H NMR (C_6D_6): $\delta = 2.24–2.38$ (m, 1H, CH_2), 3.01–3.10 (m, 1H, CH_2), 4.40 (ddd, 1H, $^3J(H–H) = 9.0$ Hz, $^3J(H–H) = 3.0$ Hz, $^3J(P–H) = 3.0$ Hz, S=CH); $^{13}C\{^1H\}$NMR (C_6D_6): $\delta = 21.9$ (s, CH_3), 39.9 (s, CH_2), 69.0 (d, $^2J(P–C) = 2.5$ Hz, S=CH); $^{31}P\{^1H\}$NMR (C_6D_6): $\delta = 2.3$ (s, $^1J(W–P) = 202$ Hz), 6.6 (s, $^1J(W–P) = 190$ Hz).

mer-$[W(CO)_3(dmpe)\{S{=}C(H)CH_2CH_2CH_3\}]$ (*mer*-**3h**): Yield: 91 mg (90%), m.p. 70 °C (dec.). Calc. for $C_{13}H_{24}O_3P_2SW$ (MW 506.2): C, 30.85; H, 4.78; S, 6.33. Found: C, 30.79; H, 4.81; S, 6.38%. ^1H NMR (C_6D_6): $\delta = 1.05$ (t, 3H, $^3J(H–H) = 7.1$ Hz, CH_3), 1.90-1.95 (m, 1H, CH_2), 2.01-2.10 (m, 2H, CH_2), 3.24-3.32 (m, 1H, CH_2); $^{13}C\{^1H\}$NMR (C_6D_6): $\delta = 14.3$ (s, CH_3), 32.1 (s, CH_2), 49.9 (s, CH_2), 197.2 (dd, $^2J(P–C) = 7.6$, 3.8 Hz, CO), 199.4 (dd, $^2J(P–C) = 7.6$, 3.8 Hz, CO), 215.4 (dd, $^2J(P–C) = 12.4$, 9.5 Hz, CO).

fac-**3h**: IR, (ν(CO), THF, cm^{-1}): 1973; ^1H NMR (C_6D_6): $\delta = 2.31–2.38$ (m, 1H, CH_2), 3.15–3.22 (m, 1H, CH_2), 4.52 (ddd, 1H, $^3J(H–H) = 9.1$ Hz, $^3J(H–H) = 3.2$ Hz, $^3J(P–H) = 3.2$ Hz, S=CH); $^{13}C\{^1H\}$NMR (C_6D_6): $\delta = 14.2$ (s, CH_3), 32.1 (s, CH_2), 49.1 (s, CH_2), 67.5 (d, $^2J(P–C) = 3.8$ Hz, $^1J(W–C) = 14.3$ Hz, S=CH); $^{31}P\{^1H\}$NMR (C_6D_6): $\delta = 2.2$ (s, $^1J(W–P) = 205$ Hz), 6.6 (s, $^1J(W–P) = 190$ Hz).

mer-$[W(CO)_3(dmpe)\{S{=}C(H)CH_2CH(CH_3)_2\}]$ (*mer*-**3i**): Yield: 92 mg (88%), m.p. 60 °C (dec.). Calc. for $C_{14}H_{26}O_3P_2SW$ (MW 520.2): C, 32.32; H, 5.04; S, 6.16. Found: C, 32.17; H, 5.09; S, 6.06%. ^1H NMR (C_6D_6): $\delta = 1.12$ (d, 3H, $^3J(H–H) = 6.6$ Hz, CH_3), 1.17 (d, 3H, $^3J(H–H) = 6.6$ Hz, CH_3), 1.92–2.02 (m, 1H, CH_2), 2.09-2.22 (m, 1H, CH), 3.07–3.19 (m, 1H, CH_2); $^{13}C\{^1H\}$NMR (C_6D_6): $\delta = 22.0$ (s, CH_3), 23.6 (s, CH_3), 36.3 (s, CH_2), 57.0 (s, CH), 197.2 (dd, $^2J(P–C) = 7.1$, 3.0 Hz, CO), 199.3 (dd, $^2J(P–C) = 7.1$, 3.0 Hz, CO), 215.4 (dd, $^2J(P–C) = 13.2$, 10.2 Hz, CO).

fac-**3i**: IR, (ν(CO), THF, cm^{-1}): 1973; ^1H NMR (C_6D_6): $\delta = 4.52$ (ddd, 1H, $^3J(H–H) = 9.9$ Hz, $^3J(H–H) = 2.7$ Hz, $^3J(P–H) = 2.7$ Hz, S=CH); $^{13}C\{^1H\}$NMR (C_6D_6): $\delta = 22.1$ (s, CH_3), 22.3 (s, CH_3), 35.5 (s, CH_2), 55.9 (s, CH); $^{31}P\{^1H\}$NMR (C_6D_6): $\delta = 2.0$ (s, $^1J(W–P) = 202$ Hz), 6.4 (s, $^1J(W–P) = 191$ Hz).

mer-$[W(CO)_3(dmpe)\{S{=}C(H)C(CH_3)_3\}]$ (*mer*-**3k**): Yield: 53 mg (51%), m.p. 50 °C (dec.). Calc. for $C_{14}H_{26}O_3P_2SW$ (MW 520.2): C, 32.32; H, 5.04; S, 6.16. Found: C, 32.64; H, 5.14; S, 6.02%. ^1H NMR (C_6D_6): $\delta = 1.59$ (s, 9H, CH_3); $^{13}C\{^1H\}$NMR (C_6D_6): $\delta = 33.5$ (s, CH_3), 39.9 (s, CMe_3), 197.1 (dd, $^2J(P–C) = 7.5$, 3.8 Hz, CO), 200.1 (dd, $^2J(P–C) = 6.5$, 3.8 Hz, CO), 214.1 (dd, $^2J(P–C) = 14.12$, 8.3 Hz, CO).

fac-**3k**: IR, (ν(CO), THF, cm^{-1}): 1970; $^{31}P\{^1H\}$NMR (C_6D_6): $\delta = 17.5$ (d, $^2J(P–P) = 13.4$ Hz), 12.6 (d, $^2J(P–P) = 13.4$ Hz).

mer-$[W(CO)_3(dmpe)\{S{=}C(H)CH{=}CH(4\text{-}C_6H_4NMe_2)\}]$ (*mer*-**3l**): Yield: 95 mg (78%), m.p. 79 °C (dec.). Calc. for $C_{20}H_{29}NO_3P_2SW$ (MW 609.3): C, 39.42; H, 4.80; N, 2.30; S, 5.26. Found: C, 39.28; H, 4.71; N, 2.33; S, 5.26%. ^1H NMR (C_6D_6): $\delta = 2.43$ (s, 6H, $N(CH_3)_2$), 6.47 (m, 2H, C_6H_4), 6.72 (dd, 1H, $^3J(H–H) = 15.4$, 9.3 Hz, CH), 6.86 (d, 1H, $^3J(H–H) = 15.4$ Hz, CH), 7.42 (m, 2H, C_6H_4); $^{13}C\{^1H\}$NMR (C_6D_6): $\delta = 40.3$ (s, $N(CH_3)_2$), 112.8 (s, CH), 124.3 (s, CH), 113.0, 127.3, 140.9, 149.5 (s, C_6H_4), 197.0 (dd, $^2J(P–C) = 7.5$, 3.8 Hz, CO), 199.1 (dd, $^2J(P–C) = 6.9$, 3.5 Hz, CO), 213.4 (dd, $^2J(P–C) = 12.8$, 10.7 Hz, CO).

fac-**3l**: IR, (ν(CO), THF, cm^{-1}): 1970; ^1H NMR (C_6D_6): $\delta = 2.48$ (s, 6H, $N(CH_3)_2$), 5.47 (dd, 1H, $^3J(H–H) = 9.0$, 4.4 Hz, S=CH); $^{31}P\{^1H\}$NMR (C_6D_6): $\delta = 22.2$ (d, $^2J(P–P) = 9.7$ Hz), 15.7 (d, $^2J(P–P) = 9.7$ Hz).

4.2. Preparation of thioaldehyde complexes *mer*-$[W(CO)_3(Ph_2PC_2H_4PPh_2)(\eta^2\text{-}S{=}CHR')]$ (**4a–4e**)

To a solution of the hydrogensulfido complex **2** (500 mg, 0.40 mmol) in THF (20 ml) was added the respective aldehyde (0.50 mmol) and CF_3COOH (30 μl, 0.40 mmol). An immediate color change to brownish-orange was observed. All volatiles were removed under vacuum, and the sticky residue dissolved in hexanes and chromatographed using dichloromethane/acetone 40:1 as eluent. The yellow fraction was collected and evaporated to dryness. The oily residue was triturated with pentane, and the resulting solid was twice washed with 5-ml portions of pentane and dried under vacuum giving an orange crystalline powder.

mer-$[W(CO)_3(dppe)\{S{=}C(H)C_6H_5\}]$ (*mer*-**4a**): Yield: 250 mg (80%), m.p. 70 °C (dec.). Calc. for $C_{36}H_{30}O_3P_2SW$ (MW 788.5): C, 54.84; H, 3.84; S, 4.07. Found: C, 54.63; H, 4.00; S, 3.88%. $^{13}C\{^1H\}$NMR (C_6D_6): $\delta = 125.7$–149.0 (m, C_6H_5), 198.2 (dd, ^2J(P–C) = 6.5, 3.5 Hz, CO), 200.2 (dd, ^2J(P–C) = 6.5, 3.5 Hz, CO), 213.6 (dd, ^2J(P–C) = 15.2, 12.1 Hz, CO).

fac-**4a**: IR, (ν(CO), THF, cm^{-1}): 1976.

mer-$[W(CO)_3(dppe)\{S{=}C(H)(3\text{-}C_6H_4F)\}]$ (*mer*-**4b**): Yield: 265 mg (82%), m.p. 78 °C. Calc. for $C_{36}H_{29}FO_3P_2SW$ (MW 806.5): C, 53.61; H, 3.62; S, 3.98. Found: C, 53.97; H, 3.86; S, 3.76%. $^{13}C\{^1H\}$NMR (C_6D_6): $\delta = 122.2$–159.0 (m, C_6H_4F), 198.1 (dd, ^2J(P–C) = 5.7, 3.8 Hz, CO), 200.2 (dd, ^2J(P–C) = 5.7, 3.8 Hz, CO), 213.6 (dd, ^2J(P–C) = 14.9, 12.0 Hz, CO).

fac-**4b**: IR, (ν(CO), THF, cm^{-1}): 1979.

mer-$[W(CO)_3(dppe)\{S{=}C(H)(4\text{-}C_6H_4F)\}]$ (*mer*-**4c**): Yield: 240 mg (75%), m.p. 59 °C. Calc. for $C_{36}H_{29}FO_3P_2SW$ (MW 806.5): C, 53.61; H, 3.62; S, 3.98. Found: C, 53.39; H, 3.64; S, 3.66%. $^{13}C\{^1H\}$NMR (C_6D_6): $\delta = 128.7$–164.7 (m, C_6H_4F), 198.2 (dd, ^2J(P–C) = 5.7, 3.8 Hz, CO), 200.2 (dd, ^2J(P–C) = 5.7, 3.8 Hz, CO), 213.7 (dd, ^2J(P–C) = 13.4, 12.4 Hz, CO).

fac-**4c**: IR, (ν(CO), THF, cm^{-1}): 1977.

mer-$[W(CO)_3(dppe)\{S{=}C(H)(4\text{-}C_6H_4Cl)\}]$ (*mer*-**4d**): Yield: 275 mg (84%), m.p. 57 °C. Calc. for $C_{36}H_{29}ClO_3P_2SW$ (MW 822.9): C, 52.54; H, 3.55; S, 3.90. Found: C, 52.67; H, 3.71; S, 3.55%. $^{13}C\{^1H\}$NMR (C_6D_6): $\delta = 114.6$–162.8 (m, C_6H_4Cl), 198.1 (dd, ^2J(P–C) = 6.8, 3.6 Hz, CO), 200.2 (dd, ^2J(P–C) = 6.8, 3.6 Hz, CO), 213.6 (dd, ^2J(P–C) = 15.1, 12.3 Hz, CO).

fac-**4d**: IR, (ν(CO), THF, cm^{-1}): 1979.

mer-$[W(CO)_3(dppe)\{S{=}C(H)(4\text{-}C_6H_4OMe)\}]$ (*mer*-**4e**): Yield: 190 mg (59%), m.p. 52 °C (dec.). This compound, although spectroscopically pure, did not analyse satisfactorily. Calc. for $C_{17}H_{24}O_4P_2SW$ (MW 570.2): C, 35.81; H, 4.24; S, 5.62%. ^1H NMR (C_6D_6): $\delta = 2.88$ (s, 3H, OCH_3); $^{13}C\{^1H\}$NMR (C_6D_6): $\delta = 54.5$ (s, OCH_3), 128.7–147.7 (m, C_6H_4), 198.3 (dd, ^2J(P–C) = 6.6, 3.8 Hz, CO), 200.2 (dd, ^2J(P–C) = 6.6, 3.8 Hz, CO), 214.0 (dd, ^2J(P–C) = 13.4, 12.4 Hz, CO).

fac-**4e**: IR, (ν(CO), THF, cm^{-1}): 1973.

4.3. Preparation of methylated thioaldehyde complexes *mer*-$[W(CO)_3(Me_2PC_2H_4PMe_2)(\eta^2\text{-}MeS{=}CHR')]PF_6$ (**5a–5m**)

To a solution of the respective thioaldehyde complex (0.20 mmol) in benzene (20 ml) was added dimethylsulfate (21 μl, 0.22 mmol). After 12 h at 20 °C the mixture was evaporated to dryness and the remaining oil dissolved in methanol (10 ml). After addition of NH_4PF_6 (160 mg, 1.00 mmol) the mixture was stirred for 15 min and again evacuated to dryness. The residue was extracted with dichloromethane (10 ml) and filtered over celite. The filtrate was taken to dryness and the residue washed twice with pentane (5 ml). The product remained as a yellow microcrystalline powder.

mer-$[W(CO)_3(dmpe)\{MeS{=}C(H)C_6H_5\}]PF_6$ (**5a**): Yield: 120 mg (85%), m.p. 143 °C (dec.). Calc. for $C_{17}H_{25}F_6O_3P_3SW$ (MW 700.2): C, 29.16; H, 3.60; S, 4.58. Found: C, 29.18; H, 3.68; S, 4.65%. ^1H NMR ($[D_6]$-acetone): $\delta = 7.10$–7.32 (m, 5H, C_6H_5); $^{13}C\{^1H\}$NMR ($[D_6]$-acetone): $\delta = 125.8$–145.4 (m, C_6H_5), 197.8 (dd, ^2J(P–C) = 7.1, 5.1 Hz, CO), 198.8 (dd, ^2J(P–C) = 7.1, 4.1 Hz, CO), 211.5 (dd, ^2J(P–C) = 16.3, 9.2 Hz, CO).

mer-$[W(CO)_3(dmpe)\{MeS{=}C(H)(4\text{-}C_6H_4F)\}]PF_6$ (**5c**): Yield: 140 mg (97%), m.p. 148 °C (dec.). Calc. for $C_{17}H_{24}F_7O_3P_3SW$ (MW 718.2): C, 28.43; H, 3.37; S, 4.46. Found: C, 28.43; H, 3.46; S, 4.61%. ^1H NMR ($[D_6]$-acetone): $\delta = 7.08$–7.24 (m, 4H, C_6H_4F);$^{13}C\{^1H\}$ NMR ($[D_6]$-acetone): $\delta = 115.8$–163.4 (m, C_6H_4F), 197.7 (dd, ^2J(P–C) = 6.7, 4.8 Hz, CO), 198.7 (dd, ^2J(P–C) = 7.2, 4.8 Hz, CO), 211.5 (dd, ^2J(P–C) = 16.2, 8.6 Hz, CO).

mer-$[W(CO)_3(dmpe)\{MeS{=}C(H)(4\text{-}C_6H_4Cl)\}]PF_6$ (**5d**): Yield: 140 mg (95%), m.p. 140 °C (dec.). Calc. for $C_{17}H_{24}ClF_6O_3P_3SW$ (MW 734.7): C, 27.79; H, 3.29; S, 4.36. Found: C, 27.56; H, 3.28; S, 4.65%. ^1H NMR ($[D_6]$-acetone): $\delta = 7.05$–7.20 (m, 4H, C_6H_4Cl);$^{13}C\{^1H\}$ NMR ($[D_6]$-acetone): $\delta = 125.4$–142.1 (m, C_6H_4Cl), 197.7 (dd, ^2J(P–C) = 7.1, 5.1 Hz, CO), 198.5 (dd, ^2J(P–C) = 7.1, 4.1 Hz, CO), 211.4 (dd, ^2J(P–C) = 16.3, 8.1 Hz, CO).

mer-$[W(CO)_3(dmpe)\{MeS{=}C(H)(4\text{-}C_6H_4OMe)\}]PF_6$ (**5e**): Yield: 130 mg (89%), m.p. 144 °C (dec.). Calc. for $C_{18}H_{27}F_6O_4P_3SW$ (MW 730.2): C, 29.61; H, 3.73; S, 4.39. Found: C, 29.77; H, 3.84; S, 4.49%. ^1H NMR ($[D_6]$-acetone): $\delta = 3.78$ (s, 3H, OCH_3), 6.88-7.13 (m, 4H, C_6H_4); $^{13}C\{^1H\}$NMR ($[D_6]$-acetone): $\delta = 55.7$ (s, OCH_3), 114.6, 127.1, 137.0, 149.4 (s, C_6H_4), 197.8 (dd, ^2J(P–C) = 6.7, 4.8 Hz, CO), 198.9 (dd, ^2J(P–C) = 6.7, 4.8 Hz, CO), 211.6 (dd, ^2J(P–C) = 16.2, 8.6 Hz, CO).

mer-$[W(CO)_3(dmpe)\{MeS{=}C(H)(4\text{-}C_6H_4NMe_2)\}]$ PF_6 (**5f**): Yield: 140 mg (95%), m.p. 149 °C (dec.). Calc. for $C_{19}H_{30}F_6NO_3P_3SW$ (MW 743.3): C, 30.70; H, 4.07; N, 1.88; S, 4.31. Found: C, 30.63; H, 4.00; N, 2.03; S, 4.43%. ^1H NMR ($[D_6]$-acetone): $\delta = 2.93$ (s, 6H,

$N(CH_3)_2$), 6.68–7.05 (m, 4H, C_6H_4); $^{13}C\{^1H\}$NMR ([D$_6$]-acetone): $\delta = 40.4$ (s, $N(CH_3)_2$), 112.8, 127.2, 132.2, 150.2 (s, C_6H_4), 197.8 (dd, ^2J(P–C) = 7.2, 3.8 Hz, CO), 199.0 (dd, ^2J(P–C) = 6.7, 3.4 Hz, CO), 211.7 (dd, ^2J(P–C) = 15.3, 8.6 Hz, CO).

mer-$[W(CO)_3(dmpe)\{MeS{=}C(H)CH_2CH_3\}]PF_6$ (*E*-**5g**): Yield: 120 mg (93%), m.p. 164 °C (dec.). Calc. for $C_{13}H_{25}F_6O_3P_3SW$ (MW 652.2): C, 23.94; H, 3.86; S, 4.92. Found: C, 23.95; H, 3.79; S, 4.96%. ^1H NMR ([D$_6$]-acetone): $\delta = 1.42$ (dd, 3H, ^3J(H–H) = 7.1, 6.5 Hz, CH_3), 1.49–1.64 (m, 2H, CH_2); $^{13}C\{^1H\}$NMR ([D$_6$]-acetone): $\delta = 21.5$ (s, CH_3), 36.4 (s, CH_2), 197.6 (dd, ^2J(P–C) = 7.1, 5.1 Hz, CO), 198.9 (dd, ^2J(P–C) = 6.6, 5.1 Hz, CO), 211.8 (dd, ^2J(P–C) = 16.3, 8.1 Hz, CO).

Z-**5g**: ^1H NMR ([D$_6$]-acetone): $\delta = 1.35$ (dd, 3H, ^3J(H–H) = 7.1, 7.1 Hz, CH_3), 2.61 (s, 3H, SCH_3); $^{13}C\{^1H\}$NMR ([D$_6$]-acetone): $\delta = 22.7$ (s, CH_3), 30.9 (s, CH_2), 42.2 (d, ^2J(P–C) = 6.1 Hz, S=CH), 195.1 (dd, ^2J(P–C) = 7.1, 5.1 Hz, CO), 200.3 (dd, ^2J(P–C) = 6.1, 5.1 Hz, CO), 212.0 (dd, ^2J(P–C) = 16.3, 8.1 Hz, CO); $^{31}P\{^1H\}$NMR ([D$_6$]-acetone): $\delta = 12.9$ (d, ^2J(P–P) = 15.1 Hz, ^1J(W–P) = 177 Hz), 14.0 (d, ^2J(P–P) = 15.1 Hz, ^1J(W–P) = 199 Hz).

mer-$[W(CO)_3(dmpe)\{MeS{=}C(H)CH_2CH_2CH_3\}]PF_6$ (*E*-**5h**): Yield: 120 mg (90%), m.p. 128 °C (dec.). Calc. for $C_{14}H_{27}F_6O_3P_3SW$ (MW 666.2): C, 25.24; H, 4.09; S, 4.81. Found: C, 25.20; H, 4.15; S, 4.95%. ^1H NMR ([D$_6$]-acetone): $\delta = 1.03$ (dd, 3H, ^3J(H–H) = 7.4, 7.1 Hz, CH_3), 1.50–1.54, 1.73–1.89 (m, 4H, CH_2); $^{13}C\{^1H\}$NMR ([D$_6$]-acetone): $\delta = 13.9$ (s, CH_3), 45.3 (d, ^2J(P–C) = 2.0 Hz, CH_2), 197.5 (dd, ^2J(P–C) = 7.1, 4.7 Hz, CO), 198.9 (dd, ^2J(P–C) = 6.7, 3.8 Hz, CO), 211.8 (dd, ^2J(P–C) = 16.2, 7.6 Hz, CO).

Z-**5h**: ^1H NMR ([D$_6$]-acetone): $\delta = 2.61$ (s, 3H, SCH_3); $^{13}C\{^1H\}$NMR ([D$_6$]-acetone): $\delta = 14.0$ (s, CH_3), 39.5 (s, CH_2), 39.8 (d, ^2J(P–C) = 5.7 Hz, ^1J(W–C) = 22 Hz, S=CH), 195.5 (dd, ^2J(P–C) = 7.1, 4.7 Hz, CO), 200.3 (dd, ^2J(P–C) = 6.7, 3.8 Hz, CO), 212.0 (dd, ^2J(P–C) = 16.2, 8.6 Hz, CO); $^{31}P\{^1H\}$NMR ([D$_6$]-acetone): $\delta = 12.9$ (d, ^2J(P–P) = 15.1 Hz), 14.0 (d, ^2J(P–P) = 15.1 Hz).

mer-$[W(CO)_3(dmpe)\{MeS{=}C(H)CH_2CH(CH_3)_2\}]$ PF_6 (*E*-**5i**): Yield: 120 mg (88%), m.p. 138 °C (dec.). Calc. for $C_{15}H_{29}F_6O_3P_3SW$ (MW 680.2): C, 26.49; H, 4.30; S, 4.71. Found: C, 26.44; H, 4.16; S, 4.97%. ^1H NMR ([D$_6$]-acetone): $\delta = 1.06$ (d, 3H, ^3J(H–H) = 6,8 Hz, CH_3), 1.12 (d, 3H, ^3J(H–H) = 6,8 Hz, CH_3), 1.41–1.51 (m, 2H, CH_2); $^{13}C\{^1H\}$ NMR ([D$_6$]-acetone): $\delta = 21.9$ (s, CH_3), 23.0 (s, CH_3), 35.2 (s, CH), 52.3 (s, CH_2), 197.4 (dd, ^2J(P–C) = 7.2, 4.8 Hz, CO), 198.9 (dd, ^2J(P–C) = 6.7, 3.8 Hz, CO), 212.0 (dd, ^2J(P–C) = 16.2, 8.6 Hz, CO).

Z-**5i**: ^1H NMR ([D$_6$]-acetone): $\delta = 1.07$ (d, 3H, ^3J(H–H) = 6.4 Hz, CH_3), 1.17 (d, 3H, ^3J(H–H) = 6.4 Hz, CH_3), 2.63 (s, 3H, SCH_3), 4.12 (ddd, 1H, ^3J(H–H) = 10.3, 2.8, 2.8 Hz, S=CH); $^{13}C\{^1H\}$NMR ([D$_6$]-acetone): $\delta = 21.6$ (s, CH_3), 23.3 (s, CH_3), 33.6 (s, CH), 37.9 (d, ^2J(P–C) = 5.7 Hz, ^1J(W–C) = 21 Hz, S=CH), 46.1 (s, CH_2); $^{31}P\{^1H\}$NMR ([D$_6$]-acetone): $\delta = 12.9$ (d, ^2J(P–P) = 14.9 Hz), 13.9 (d, ^2J(P–P) = 14.9 Hz).

mer-$[W(CO)_3(dmpe)\{MeS{=}C(H)CH_2C(CH_3)_3\}]PF_6$ (*E*-**5k**): Yield: 115 mg (85%), m.p. 69 °C (dec.). Calc. for $C_{15}H_{29}F_6O_3P_3SW$ (MW 680.2): C, 26.49; H, 4.30; S, 4.71. Found: C, 26.37; H, 4.24; S, 4.61%. ^1H NMR ([D$_6$]-acetone): $\delta = 1.30$ (s, 9H, CH_3); $^{13}C\{^1H\}$NMR ([D$_6$]-acetone): $\delta = 32.4$ (s, CH_3), 39.8 (s, CMe_3), 52.3 (s, CH_2), 198.5 (dd, ^2J(P–C) = 6.7, 4.8 Hz, ^1J(W–C) = 130 Hz, CO), 200.1 (dd, ^2J(P–C) = 7.6, 5.7 Hz, ^1J(W–C) = 134 Hz, CO), 214.1 (dd, ^2J(P–C) = 18.1, 6.6 Hz, ^1J(W–C) = 125 Hz, CO).

Z-**5k**: $^{31}P\{^1H\}$NMR ([D$_6$]-acetone): $\delta = 12.6$ (d, ^2J(P–P) = 15.3 Hz), 14.5 (d, ^2J(P–P) = 15.3 Hz).

mer-$[W(CO)_3(dmpe)\{MeS{=}C(H)CH{=}CH(4\text{-}C_6H_4NMe_2)\}]PF_6$ (*E*-**5l**): Yield: 140 mg (89%), m.p. 70 °C (dec.). Calc. for $C_{21}H_{32}F_6NO_3P_3SW$ (MW 769.3): C, 32.79; H, 4.19; N, 1.82; S, 4.17. Found: C, 33.05; H, 4.30; N, 2.03; S, 3.86%. ^1H NMR ([D$_6$]-acetone): $\delta = 2.92$ (s, 6H, $N(CH_3)_2$), 5.93 (dd, 1H, ^3J(H–H) = 15.5, 10.2 Hz, CH), 6.65–6.71 (m, 2H, C_6H_4), 6.84 (d, 1H, ^3J(H–H) = 15.5 Hz, CH), 7.21–7.24 (m, 2H, C_6H_4); $^{13}C\{^1H\}$NMR ([D$_6$]-acetone): $\delta = 40.4$ (s, $N(CH_3)_2$), 112.6 (s, CH), 125.3 (s, CH), 113.1, 128.0, 139.5, 151.2 (s, C_6H_4), 197.1 (dd, ^2J(P–C) = 6.7, 4.8 Hz, CO), 198.8 (dd, ^2J(P–C) = 6.7, 4.8 Hz, CO), 210.6 (dd, ^2J(P–C) = 15.3, 8.6 Hz, CO).

Z-**5l**: ^1H NMR ([D$_6$]-acetone): $\delta = 2.81$ (s, 3H, SCH_3), 2.94 (s, 6H, $N(CH_3)_2$), 4.92 (dd, 1H, ^3J(H–H) = 10.1, ^3J(P–H) = 2.2 Hz, S=CH), 6.05 (dd, 1H, ^3J(H–H) = 15.2, 10.1 Hz, CH), 6.71–6.73 (m, 2H, C_6H_4), 6.91 (d, 1H, ^3J(H–H) = 15.2 Hz, CH), 7.31–7.34 (m, 2H, C_6H_4); $^{13}C\{^1H\}$NMR ([D$_6$]-acetone): $\delta = 40.3$ (s, $N(CH_3)_2$), 48.0 (d, ^2J(P–C) = 3.8 Hz, ^1J(W–C) = 18 Hz, S=CH), 112.6 (s, CH), 125.3 (s, CH), 113.0, 128.3, 139.5, 151.5 (s, C_6H_4), 196.9 (dd, ^2J(P–C) = 7.6, 5.7 Hz, CO), 198.3 (dd, ^2J(P–C) = 7.6, 4.8 Hz, CO), 210.4 (dd, ^2J(P–C) = 15.3, 8.6 Hz, CO); $^{31}P\{^1H\}$NMR ([D$_6$]-acetone): $\delta = 12.9$ (d, ^2J(P–P) = 14.9 Hz), 15.3 (d, ^2J(P–P) = 14.9 Hz).

mer-$[W(CO)_3(dmpe)\{MeS{=}CH_2\}]PF_6$ (**5m**): Yield: 100 mg (81%), m.p. 109 °C. Calc. for $C_{11}H_{21}F_6O_3P_3SW$ (MW 624.1): C, 21.17; H, 3.39; S, 5.14. Found: C, 21.45; H, 3.26; S, 5.11%. $^{13}C\{^1H\}$NMR (CD_2Cl_2, −80 °C): $\delta = 193.2$ (dd, ^2J(P–C) = 6.7, 4.8 Hz, CO), 198.4 (dd, ^2J(P–C) = 6.7, 4.8 Hz, CO), 207.6 (dd, ^2J(P–C) = 16.2, 6.7 Hz, CO).

4.4. Preparation of thioether complexes *fac*-$[W(CO)_3(Me_2PC_2H_4PMe_2)(MeSCH_2R')]$ (6a, c, e, m)

To a solution of the methylated thioaldehyde complex (0.20 mmol) in THF (10 ml) was added $LiAlH_4$ (40 mg, 1.0 mmol) and the mixture stirred for 10 min at 20

°C. Excess hydride reagent was quenched by careful addition of water. The mixture was evaporated to dryness and the residue extracted with dichloromethane (10 ml). Rapidly recorded NMR spectra showed the presence of 30–40% *mer* isomer at this stage. The filtered extract was chromatographed using dichloromethane as eluent, and the yellow band collected and taken to dryness. The residue was washed twice with pentane (2 ml) and dried under vacuum.

fac-[W(CO)$_3$(dmpe){MeSCH$_2$C$_6$H$_5$}] (**6a**): Yield: 80 mg (72%), m.p. 76 °C (dec.). Calc. for $C_{17}H_{26}O_3P_2SW$ (MW 556.3): C, 36.71; H, 4.71; S, 5.76. Found: C, 36.04; H, 4.37; S, 5.52%. ^{1}H NMR (CD$_2$Cl$_2$): $\delta = 2.32$ (s, 3H, SCH$_3$), 3.91 (s, 2H, SCH$_2$), 7.23–7.31 (m, 5H, C$_6$H$_5$); ^{13}C{^{1}H}NMR (CD$_2$Cl$_2$): $\delta = 26.9$ (t, ^3J(P–C) = 4.8 Hz, SCH$_3$), 52.0 (t, ^3J(P–C) = 4.8 Hz, SCH$_2$), 128.7, 129.0, 129.4, 137.3 (s, C$_6$H$_5$), 212.5 (t, ^2J(P–C) = 5.7 Hz, CO), 217.2 (dd, ^2J(P–C) = 30.5, 5.7 Hz, CO).

mer-**6a**: ^{1}H NMR (CD$_2$Cl$_2$): $\delta = 2.44$ (d, 3H, ^4J(P–H) = 1.1 Hz, SCH$_3$), 3.93 (s, 2H, SCH$_2$); ^{31}P{^{1}H}NMR (CD$_2$Cl$_2$): $\delta = 5.3$ (d, ^2J(P–P) = 10.9 Hz, ^1J(W–P) = 218 Hz), 19.1 (d, ^2J(P–P) = 10.9 Hz, ^1J(W–P) = 302 Hz).

fac-[W(CO)$_3$(dmpe){MeSCH$_2$(4-C$_6$H$_4$F)}] (**6c**): Yield: 60 mg (53%), m.p. 96 °C (dec.). Calc. for $C_{17}H_{25}FO_3P_2SW$ (MW 574.2): C, 35.56; H, 4.39; S, 5.58. Found: C, 35.74; H, 4.46; S, 5.48%. ^{1}H NMR (CD$_2$Cl$_2$): $\delta = 2.32$ (s, 3H, SCH$_3$), 3.90 (s, 2H, SCH$_2$), 7.00–7.33 (m, 4H, C$_6$H$_4$F); ^{13}C{^{1}H}NMR (CD$_2$Cl$_2$): $\delta = 26.9$ (t, ^3J(P–C) = 4.8 Hz, SCH$_3$), 51.2 (t, ^3J(P–C) = 4.8 Hz, SCH$_2$), 115.8 (d, ^2J(F–C) = 20 Hz, CH), 130.8 (d, ^3J(F–C) = 9 Hz, CH), 133.2 (s, CH), 162.6 (d, ^1J(F–C) = 245 Hz, CF), 212.5 (t, ^2J(P–C) = 5.7 Hz, CO), 217.2 (dd, ^2J(P–C) = 30.5, 5.7 Hz, CO).

mer-**6c**: ^{1}H NMR (CD$_2$Cl$_2$): $\delta = 2.45$ (d, 3H, ^4J(P–H) = 1.3 Hz, SCH$_3$), 3.94 (s, 2H, SCH$_2$); ^{31}P{^{1}H}NMR (CD$_2$Cl$_2$): $\delta = 5.3$ (d, ^2J(P–P) = 10.9 Hz, ^1J(W–P) = 218 Hz), 19.0 (d, ^2J(P–P) = 10.9 Hz, ^1J(W–P) = 302 Hz).

fac-[W(CO)$_3$(dmpe){MeSCH$_2$(4-C$_6$H$_4$OMe)}] (**6e**): Yield: 70 mg (61%), m.p. 38 °C (dec.). Calc. for $C_{18}H_{28}O_4P_2SW$ (MW 586.3): C, 36.88; H, 4.81; S, 5.47. Found: C, 36.63; H, 4.67; S, 5.27%. ^{1}H NMR (CD$_2$Cl$_2$): $\delta = 2.31$ (s, 3H, SCH$_3$), 3.67 (s, 3H, OCH$_3$), 3.86 (s, 2H, SCH$_2$), 6.81–7.25 (m, 4H, C$_6$H$_4$); ^{13}C{^{1}H}NMR (CD$_2$Cl$_2$): $\delta = 26.7$ (t, ^3J(P–C) = 4.8 Hz, SCH$_3$), 51.5 (t, ^3J(P–C) = 4.8 Hz, SCH$_2$), 55.6 (s, OCH$_3$), 114.3, 129.3, 130.6, 159.6 (s, C$_6$H$_4$), 212.6 (t, ^2J(P–C) = 5.7 Hz, CO), 217.3 (dd, ^2J(P–C) = 30.0, 5.7 Hz, CO).

mer-**6e**: ^{1}H NMR (CD$_2$Cl$_2$): $\delta = 2.44$ (d, 3H, ^4J(P–H) = 1.1 Hz, SCH$_3$), 3.77 (s, 3H, OCH$_3$), 3.88 (s, 2H, SCH$_2$); ^{31}P{^{1}H}NMR (CD$_2$Cl$_2$): $\delta = 5.2$ (d, ^2J(P–P) = 10.9 Hz, ^1J(W–P) = 218 Hz), 19.1 (d, ^2J(P–P) = 10.9 Hz, ^1J(W–P) = 303 Hz).

fac-[W(CO)$_3$(dmpe){SMe$_2$}] (**6m**): Yield: 65 mg (67%), m.p. 53 °C (dec.). Calc. for $C_{11}H_{22}O_3P_2SW$ (MW 480.2): C, 27.52; H, 4.62; S, 6.68. Found: C, 27.10; H, 4.49; S, 6.14%. ^{1}H NMR (CD$_2$Cl$_2$): $\delta = 2.51$ (s, 6H, SCH$_3$); ^{13}C{^{1}H}NMR (CD$_2$Cl$_2$): $\delta = 30.7$ (t, ^3J(P–C) = 5.1 Hz, SCH$_3$), 212.7 (t, ^2J(P–C) = 6.1 Hz, CO), 217.4 (dd, ^2J(P–C) = 30.0, 6.1 Hz, CO).

Table 7
Crystal data and structure refinement for *mer*-[W(CO)$_3$(Me$_2$PC$_2$H$_4$PMe$_2$)(η^2-S=CH-*i*-Bu)] (**3i**)

Empirical formula	$C_{14}H_{26}O_3P_2SW \cdot \frac{1}{2}C_6H_{14}$
Formula weight	556.23
Temperature (K)	143(2)
Wavelength (Å)	0.71073
Crystal size (mm)	$0.2 \times 0.1 \times 0.1$
Crystal system, space group	monoclinic, $P2_1/c$
a (Å)	9.7636(3)
b (Å)	13.5384(4)
c (Å)	16.9630(5)
β (°)	92.634(1)
Volume (Å^3)	2239.9(2)
Z, calculated density (Mg m^{-3})	4, 1.649
Absorption coefficient (mm^{-1})	5.398
Reflections collected/unique	21,806/3209
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.038$, $wR_2 = 0.083$
R indices (all data)	$R_1 = 0.038$, $wR_2 = 0.083$
Largest differential peak and hole (e Å^{-3})	0.807 and −0.798

4.5. Structure determination of mer-[W(CO)$_3$(Me$_2$PC$_2$H$_4$PMe$_2$)(η^2-S=CH-i-Bu)] (3i)

Yellow crystals of **3i** suitable for structure determination were obtained by diffusion of hexane into a toluene solution at 0 °C. X-ray data were collected on a Bruker Smart-Apex CCD diffractometer using Mo Kα radiation. The crystal data are summarized in Table 7. The structure was solved using the direct methods provided within SHELXS 97 [16] and refined by full-matrix least squares methods using SHELXL 97 [16]. Half a disordered molecule of hexane per formula unit was found but could not be fully refined.

5. Supplementary material

Further details of the structure determination are available from the Cambridge Crystallographic Data Centre, CCDC reference number 223075.

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