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# Synthesis, structure, DFT calculations, and full vibrational analysis of the prototypical thioformaldehyde complex *mer*-[W(CO)$_3$(Me$_2$PC$_2$H$_4$PMe$_2$)($\eta^2$-S=CH$_2$)] †

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Reaction of PPN[W(CO)$_3$(dmpe)(SH)] **2** (PPN = Ph$_3$PNPPh$_3$, dmpe = Me$_2$PC$_2$H$_4$PMe$_2$) with aqueous formaldehyde in the presence of trifluoroacetic acid gives the thioformaldehyde complex *mer*-[W(CO)$_3$(Me$_2$PC$_2$H$_4$PMe$_2$)($\eta^2$-S=CH$_2$)] **3** in almost quantitative yield. The isotopomer *mer*-[W(CO)$_3$(Me$_2$PC$_2$H$_4$PMe$_2$)($\eta^2$-S=CD$_2$)] **3-D$_2$** was obtained analogously. **3** has a slightly distorted pentagonal-bipyramidal structure with one carbonyl group, two P atoms and the C and S atoms of the thioformaldehyde ligand spanning the pentagonal plane. In solution, **3** is in equilibrium with *fac*-[W(CO)$_3$(Me$_2$PC$_2$H$_4$PMe$_2$)($\eta^2$-S=CH$_2$)] **4**. The structures and energies of **3** and **4** and their rotamers **3′** and **4′** were calculated by DFT methods leading to a very good agreement with experimental data. FT-IR and FT-Raman spectra of **3** and **3-D$_2$** were recorded and assigned with the aid of DFT calculations. Calculated vibrational amplitudes emphasize the extensive mixing of modes, particularly in the low-wavenumber region. The HOMO of **3** can approximately be described as a lone-pair at sulfur and is 0.38 eV higher in energy than that of isomer **4**. The LUMOs of both isomers are highly delocalized with that of **4** being 0.45 eV lower in energy. On this basis it is expected that electrophiles will add preferentially at the sulfur atom of **3** while nucleophiles if at all will add to the thiocarbonyl carbon of **4**.

## Introduction

Thioaldehydes,[2] and in particular thioformaldehyde[3] are typical examples of the so-called "double bond rule": the relatively weak π bonding involving 3p orbitals encourages oligo- and poly-merization reactions to such an extent that thioaldehydes RHC=S can not be isolated as monomers unless they are stabilized by bulky substituents R. Transition metal complexes of thioaldehydes are nevertheless well-known,[4] and even the parent thioformaldehyde has been stabilized as a ligand in mononuclear complexes of titanium,[5] zirconium,[6] tantalum,[7] rhenium,[8] ruthenium,[1] osmium,[9] cobalt,[10] and rhodium.[11] The molecular properties of the isolated molecule H$_2$C=S are known from gas-phase[12] and matrix data[13] whereas physical characterization of the complexes of thioformaldehyde remained restricted largely to NMR spectroscopy and X-ray structure determinations.[4]

Vibrational spectroscopy provides direct information on the force field of a molecule or ion and thus on the strength of chemical bonds. However, for larger molecules of low symmetry it is exceedingly difficult to assign the multitude of absorptions (or Raman scattering lines) to the respective normal modes. Selective isotopic substitution is a reliable tool to identify the participation of an individual group in a molecular vibration.[14] Even then, as the result of the extensive mixing of normal modes of like symmetry, it can be very difficult to arrive at an unambiguous assignment of the vibrational spectrum. The use of quantum chemical methods, in particular density functional theory (DFT), has nowadays become almost routine. Indeed, the development of gradient-corrected functionals and the use of small-core relativistic effective core potentials (ECPs)[15,16] have made it possible to predict, often with impressive accuracy, geometries, bond energies, vibrational spectra, NMR chemical shifts, activation energies of chemical reactions and other important properties of transition metal complexes.[16–18]

Here we report the synthesis of a new complex of thioformaldehyde, *mer*-[W(CO)$_3$(dmpe)($\eta^2$-S=CH$_2$)] (dmpe = Me$_2$PC$_2$H$_4$PMe$_2$) and its isotopomer, *mer*-[W(CO)$_3$(dmpe)($\eta^2$-S=CD$_2$)], along with an X-ray structure determination and full vibrational analysis, the latter backed by DFT calculations which also include rotamers and geometrical isomers.

## Results

The reaction of pentacarbonyl-hydrogensulfido-tungstate **1**[19] with 1,2-bis(dimethylphosphino)ethane (dmpe) in THF proceeded with visible gas evolution and formation of the CO-substitution product **2** in essentially quantitative yield (Scheme 1). **2** was obtained as a bright yellow, slightly air-sensitive microcrystalline powder which, according to its ionic nature, is soluble only in polar organic media such as THF, acetone, or acetonitrile. A triplet at −3.78 ppm in the $^1$H NMR spectrum, upfield from the SH signal of **1**,[19] revealed the presence of the SH ligand. A singlet with tungsten satellites in the $^{31}$P NMR spectrum and three intense CO stretching absorptions in the IR spectrum are diagnostic of the facial coordination geometry shown in Scheme 1.

Addition of aqueous formaldehyde and trifluoroacetic acid to a solution of **2** in THF resulted in a spontaneous colour

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† The coordination chemistry of the C=S function, part 16. For part 15 see ref. 1.

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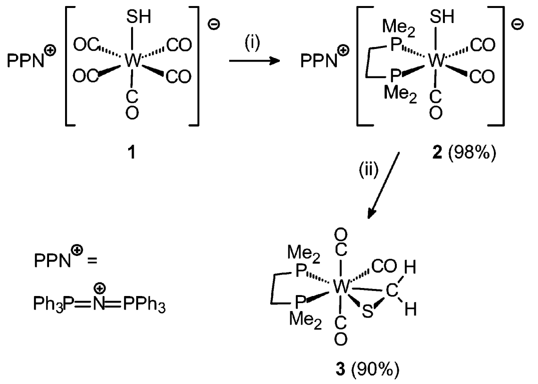
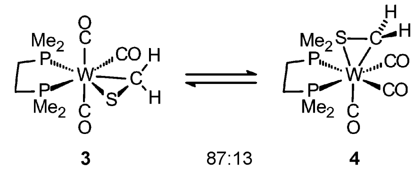


**Scheme 1** Synthesis of the thioaldehyde complex **3**. Reagents and conditions: (i) $Me_2PC_2H_4PMe_2$/THF/60 °C/45 min. (ii) $H_2O/CF_3CO_2H/CH_2O$/THF/20 °C/5 min.

change to deep yellow. After chromatographic work-up the thioformaldehyde complex **3** was isolated in excellent yield as a deep yellow crystalline powder. The isotopomer $[W(CO)_3(dmpe)(\eta^2\text{-}S{=}CD_2)]$ (**3-D$_2$**) was obtained in the same way by using a solution of [D$_2$]formaldehyde in $D_2O$. The IR spectrum of a solid sample of **3** exhibited three CO stretching absorptions in the relative intensity ratio medium–strong–very strong, which is a clear indication of the meridional arrangement of the CO ligands. Spectra taken from THF solutions revealed an additional absorption at 1980 cm$^{-1}$, hinting at the existence of a second isomer of **3**. The $^{31}$P NMR spectra were also in accord with the presence of a mixture of isomers. The main component gave rise to two doublets with tungsten satellites caused by two unequal $J(^{183}W\text{–}^{31}P)$ couplings. The minor isomer was represented by a singlet with tungsten satellites. In the $^1$H NMR spectra the methylene group of the major isomer appeared as a doublet of doublets at $\delta = 3.98$ while the $CH_2$ signal of the minor isomer was visible as a triplet at $\delta = 3.91$. Both signals were absent in the spectra of **3-D$_2$**. The $^{13}$C resonance of the $CH_2$ group appeared at $\delta = 39.7$, in a shift range typical of $\eta^2$-coordinated thioformaldehyde;[8] $\eta^1(S)$-coordinated thioaldehydes have resonances at $\delta = 200$.[20] Thus it was established that in solution, **3** is in equilibrium with the facial isomer **4** (Scheme 2).



**Scheme 2** Equilibrium between **3** and its facial isomer **4**.

The structure of **3** was determined by X-ray crystallography; Fig. 1 shows an ORTEP diagram. The tungsten atom resides in the centre of a distorted pentagonal bipyramid with the thioformaldehyde 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 the range of 80 ± 3° (Table 1). The W–P bonds are slightly different in length. The W–S bond length equals that in the $\eta^1$-thiobenzaldehyde complex $[W(CO)_5(S{=}CHPh)]$,[21] and the W–C(1) distance compares well with the length of metal–carbon bonds in tungsten–alkene complexes.[22] The carbon–sulfur bond is much longer than in free thioformaldehyde[3] and equal in length to that in the rhenium complex $[CpRe(NO)(PPh_3)(\eta^2\text{-}S{=}CH_2)]^+$.[8] Of the two possible orientations of the $H_2C{=}S$ ligand the one with the sulfur atom pointing away from the equatorial carbonyl ligand seems to be preferred. The same geometrical situation was found in a closely analogous complex of thioformaldehyde *S,S*-dioxide, $[W(CO)_3(dppm)(\eta^2\text{-}O_2S{=}CH_2)]$ (dppm = $Ph_2PCH_2PPh_2$).[23]

**Table 1** Selected bond lengths (Å) and angles (°) for *mer*-$[W(CO)_3(dmpe)(\eta^2\text{-}S{=}CH_2)]$ **3**

| | | | |
|---|---|---|---|
| W–S | 2.4937(8) | W–C(13) | 2.031(3) |
| W–P(1) | 2.4716(7) | S–C(1) | 1.745(3) |
| W–P(2) | 2.4992(8) | C(11)–O(1) | 1.161(4) |
| W–C(1) | 2.290(3) | C(12)–O(2) | 1.142(4) |
| W–C(11) | 2.011(3) | C(13)–O(3) | 1.150(4) |
| W–C(12) | 2.021(3) | | |
| S–W–C(1) | 42.52(8) | C(11)–W–C(12) | 89.18(13) |
| P(1)–W–S | 161.94(3) | C(11)–W–C(13) | 178.35(12) |
| P(2)–W–S | 83.25(3) | C(12)–W–C(13) | 91.45(13) |
| P(1)–W–P(2) | 78.82(3) | W–S–C(1) | 62.49(11) |
| C(12)–W–P(1) | 78.39(9) | S–C(1)–W | 74.99(12) |
| C(1)–W–C(12) | 77.18(12) | | |

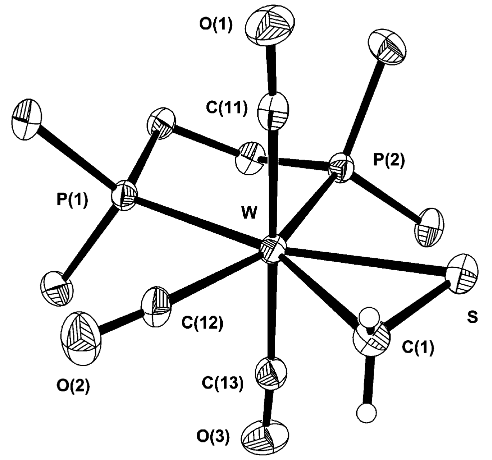


**Fig. 1** ORTEP[44] diagram of *mer*-$[W(CO)_3(dmpe)(\eta^2\text{-}S{=}CH_2)]$ (**3**). Thermal ellipsoids drawn at the 50% level, hydrogen atoms except those at C(1) omitted.

In order to gain a deeper insight into the bonding situation in **3** and **4** we have carried out some DFT calculations on both isomers. Four calculated structures representing local minima are shown in Figs. 2 and 3, calculated bond distances and angles are compiled in Table 2.

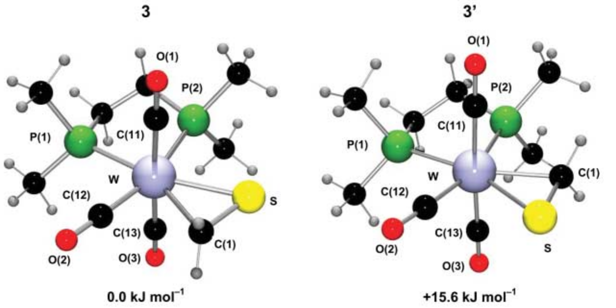


**Fig. 2** Calculated structures and energies of *mer*-$[W(CO)_3(dmpe)(\eta^2\text{-}S{=}CH_2)]$ (**3**, **3′**). Values in kJ mol$^{-1}$ are relative to the preferred form **3**.

The calculations predicted that **4** is slightly lower in energy (by *ca.* 2 kJ mol$^{-1}$) than **3** while experimentally it is actually 5 kJ mol$^{-1}$ higher. Such small differences, however, are well within the uncertainty of the method. The orientation of the thioformaldehyde ligand was correctly predicted, *i.e.* **3′** is *ca.* 15 kJ mol$^{-1}$ higher in energy than **3**. The calculated bond distances and angles of **3** agree very well with experimental values. The largest discrepancy is associated with the W–S bond, the length of which was overestimated by 0.066 Å. Even the trend in W–P bond lengths, $r\{W\text{–}P(2)\} > r\{W\text{–}P(1)\}$, was correctly reproduced. For the facial isomer **4** the rotamer **4′** is again disfavored, in this case by *ca.* 20 kJ mol$^{-1}$.

**Table 2** Calculated bond lengths (Å) and angles (°) for [W(CO)$_3$(dmpe)(η$^2$-S=CH$_2$)]

| | 3 | 3′ | 4 | 4′ |
|---|---|---|---|---|
| W–S | 2.560 | 2.571 | 2.568 | 2.574 |
| W–P(1) | 2.482 | 2.490 | 2.547 | 2.540 |
| W–P(2) | 2.538 | 2.525 | 2.541 | 2.534 |
| W–C(1) | 2.309 | 2.300 | 2.330 | 2.332 |
| W–C(11) | 2.026 | 2.026 | 1.998 | 2.000 |
| W–C(12) | 2.004 | 2.019 | 1.997 | 2.014 |
| W–C(13) | 2.028 | 2.026 | 1.997 | 1.994 |
| S–C(1) | 1.759 | 1.753 | 1.752 | 1.740 |
| C(11)–O(1) | 1.180 | 1.180 | 1.181 | 1.182 |
| C(12)–O(2) | 1.179 | 1.175 | 1.180 | 1.175 |
| C(13)–O(3) | 1.179 | 1.180 | 1.180 | 1.180 |
| S–W–C(1) | 42.0 | 41.8 | 41.6 | 41.2 |
| P(1)–W–S | 161.4 | 160.9 | 85.3 | 89.2 |
| P(2)–W–S | 81.6 | 120.0 | 80.8 | 117.7 |
| P(1)–W–P(2) | 79.9 | 79.0 | 79.1 | 80.0 |
| C(12)–W–P(1) | 83.5 | 83.6 | 87.5 | 92.1 |
| C(1)–W–C(12) | 73.0 | 119.1 | 72.4 | 118.2 |
| C(11)–W–C(12) | 90.6 | 90.8 | 98.4 | 92.6 |
| C(11)–W–C(13) | 177.6 | 177.0 | 84.1 | 88.1 |
| C(12)–W–C(13) | 91.2 | 91.5 | 81.8 | 83.9 |
| W–S–C(1) | 61.3 | 60.8 | 61.9 | 61.9 |
| S–C(1)–W | 76.7 | 77.4 | 76.5 | 76.9 |

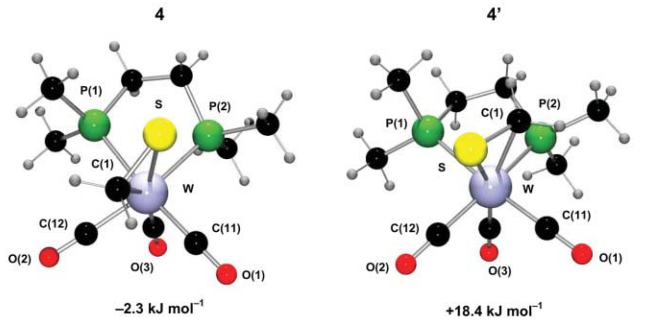


**Fig. 3** Calculated structures and energies of *fac*-[W(CO)$_3$(dmpe)(η$^2$-S=CH$_2$)] (**4**, **4′**). Values in kJ mol$^{-1}$ are relative to the preferred form **3**.

A comparison of the infrared and Raman spectra of **3** and **3-D$_2$** allowed the ready identification of fundamental modes involving the three-membered W–S–C ring. Aside from the $\nu$(CD$_2$) vibrations at 2255 and 2155 cm$^{-1}$, sizeable isotopic shifts were detected for absorptions at 785 and 422 cm$^{-1}$ which were shifted to 755 and 406 cm$^{-1}$ in **3-D$_2$**, respectively. With regard to wavenumber and isotopic shift the higher of the two corresponds very well with the asymmetric $\nu$(C–S) of thiirane (651 cm$^{-1}$, shifted to 618 cm$^{-1}$ in [D$_4$]thiirane[24]). On this basis these two absorptions can confidently be assigned to $\nu$(C–S) and $\nu$(W–C), respectively. The complete vibrational spectra were finally compared with DFT calculations of all fundamental modes of both isotopomers which led to a quite satisfactory agreement between measured and calculated data (Table 3). It should be added here that any assignment which describes a certain vibration of a larger molecule as originating from the motion of but two or three atoms is a gross simplification. Particularly in the low-wavenumber region extensive coupling occurs. To underscore this we have calculated the amplitudes of some of the vibrations of **3**. Figs. 4 and 5 show the results for $\nu$(W–C) (calculated at 401 cm$^{-1}$) and $\nu$(W–S) (calculated at 278 cm$^{-1}$), respectively. $\nu$(W–C) represents a largely unperturbed bond stretching motion, with perhaps some contribution from WCO bending. The $\nu$(W–S) mode, however, is extensively coupled with twisting and deformation motions of the backbone of the dmpe ligand.

In order to further corroborate the assignment of the additional CO stretching absorption observed in solution, some fundamental vibrations of **3′**, **4**, and **4′** were calculated and compared to those of **3** (Table 4). Indeed, the wavenumber of the calculated symmetric CO stretch of isomer **4** exactly matched the observed absorption.

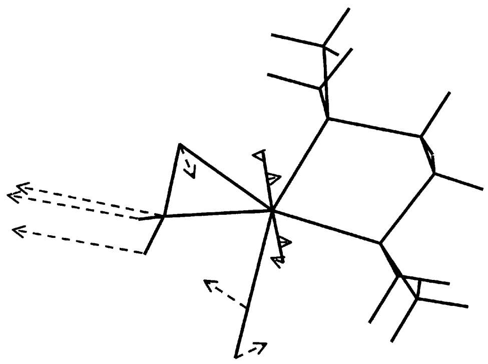


**Fig. 4** Calculated vibrational amplitudes for $\nu$(W–C) of **3**.

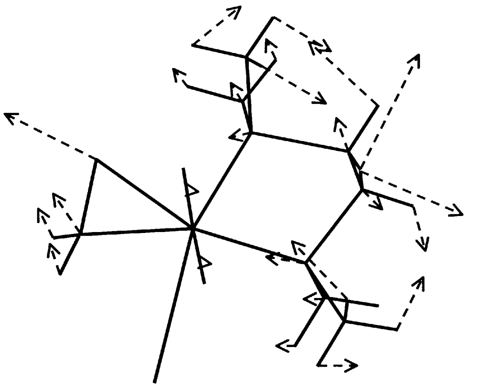


**Fig. 5** Calculated vibrational amplitudes for $\nu$(W–S) of **3**.

## Discussion

The reaction of **1** with aromatic aldehydes in the presence of acid was one of the early syntheses of transition metal complexes of thioaldehydes. It was limited to benzaldehydes bearing electron-releasing substituents in the *para* position and only gave complexes of η$^1$(*S*)-coordinated thioaldehydes.[19] Since the formation of η$^2$(*C*,*S*) complexes should be favored with increasing electron density at the central metal atom — this was *inter alia* observed in a series of related dithioester complexes of the type [W(CO)$_n$(PR$^1_3$)$_{5-n}$(S=C(R$^2$)(SR$^3$))][25] — we looked for appropriate ways to modify reagent **1**. Indeed, the lability of CO ligands on **1** and their facile exchange for tertiary phosphines has been noted on several occasions,[26,27] and accordingly the reaction with the bidentate donor dmpe proceeded in excellent yield. The nucleophilicity of **2** is much higher than that of **1** leading to a clean reaction with aqueous formaldehyde to give **3**. To the best of our knowledge this is the first mononuclear thioformaldehyde complex of a Group 6 metal. A binuclear complex, [Cp$_2$W$_2$(CO)$_3$(μ-S=CH$_2$)], has been obtained from [Cp$_2$W$_2$(CO)$_6$(μ-S)] and diazomethane.[28]

The spectroscopic and structural data of **3** allow some clues with regard to the ligand properties of side-on coordinated thioformaldehyde. The fairly high CO stretching vibrations indicate that H$_2$C=S is a good π acceptor ligand, comparable to maleic acid esters,[29] but not as good as CS$_2$[30] or SO$_2$.[31] As predicted by the Dewar–Chatt–Duncanson model, a high degree of charge transfer into the π* orbital leads to a pronounced lengthening of the C–S bond.[32] From the C–S distance in **3** (1.745 Å, Table 1) one can estimate a C–S bond order of 1.35, taking the C–S bond lengths in thioformaldehyde (1.614 Å)[12] and thiirane (1.815 Å)[33] as standard values for a double and single bond, respectively. A similar interpolation based on the

**Table 3** Selected measured and calculated vibrations (cm$^{-1}$) of *mer*-[W(CO)$_3$(dmpe)($\eta^2$-S=CH$_2$)] **3** and *mer*-[W(CO)$_3$(dmpe)($\eta^2$-S=CD$_2$)] **3-D$_2$** and their assignments

| [W(CO)$_3$(dmpe)($\eta^2$-S=CH$_2$)] (**3**) | | | [W(CO)$_3$(dmpe)($\eta^2$-S=CD$_2$)] (**3-D$_2$**) | | | |
|---|---|---|---|---|---|---|
| R | IR | DFT | R | IR | DFT | Assignment |
| | | | 2257(w) | 2255(w) | 2330 | $\nu$(CD$_2$) |
| | | | 2157(w) | 2155(w) | 2200 | $\nu$(CD$_2$) |
| 1991(s) | 1990(s) | 1986 | 1991(s) | 1990(s) | 1986 | $\nu$(CO) |
| 1905(s) | 1915(s) | 1928 | 1905(s) | 1915(s) | 1928 | $\nu$(CO) |
| | 1850(vs) | 1890 | | 1850(vs) | 1890 | $\nu$(CO) |
| | | 975 | | | | $\omega$(CH$_2$) |
| 786(m) | 785(m) | 800 | 754(m) | 755(m) | 763 | $\nu$(CS) |
| 777(w) | 771(w) | 777 | | | | $\tau$(CH$_2$) |
| | | | | 720(s) | 726 | $\omega$(CD$_2$) |
| | | | | 708(s) | 720 | $\tau$(CD$_2$) |
| | 605(s) | 611 | | 605(s) | 611 | $\delta$(WCO) |
| | 585(s) | 605 | | 585(s) | 605 | |
| | | | | 565(m) | 570 | $\tau$(CD$_2$) |
| | 543(m) | 537 | | 541(m) | 537 | $\delta$(WCO) |
| | 534(w) | 521 | | 534(w) | 519 | |
| | 522(w) | | | 522(w) | | |
| 514(m) | 514(m) | | 511(m) | 509(m) | | |
| 461(s) | 460(m) | 471 | 460(m) | 459(s) | 470 | $\nu$(W–CO) |
| 449(s) | 444(m) | 454 | 444(m) | 449(s) | 454 | |
| 442(s) | | | | 442(w) | | |
| 416(m) | 416(m) | 440 | 416(m) | 416(m) | 439 | $\delta$(WCO) |
| | | 410 | | | 410 | |
| 421(m) | 422(sh) | 401 | 403(m) | 406(m) | 385 | $\nu$(W–C) |
| 347(m) | | 326 | 346(m) | | 326 | $\nu$(W–P) |
| 328(s) | | 309 | 328(s) | | 309 | $\nu$(W–P) |
| 307(s) | | 288 | 306(s) | | 288 | $\delta$(CPC)[a] |
| 262(s) | | 278 | 261(s) | | 278 | $\nu$(W–S)[b] |

[a] Strongly coupled with $\nu$(W–S). [b] Strongly coupled with CH$_2$–CH$_2$ torsion.

**Table 4** Comparison of selected calculated vibrations (cm$^{-1}$) of *mer*-[W(CO)$_3$(dmpe)($\eta^2$-S=CH$_2$)] **3**, **3′** and *fac*-[W(CO)$_3$(dmpe)($\eta^2$-S=CH$_2$)] **4**, **4′** and their assignments

| **3** | **3′** | **4** | **4′** | Assignment |
|---|---|---|---|---|
| 1986 | 1991 | 1981 | 1988 | $\nu$(CO) |
| 1928 | 1940 | 1922 | 1936 | $\nu$(CO) |
| 1890 | 1889 | 1910 | 1907 | $\nu$(CO) |
| 800 | 806 | 810 | 824 | $\nu$(CS) |
| 401 | 402 | 390 | 382 | $\nu$(WC) |
| 326 | 325 | 318 | 326 | $\nu$(WP) |
| 309 | 307 | 302 | 309 | $\nu$(WP) |
| 278 | 286 | 269 | 273 | $\nu$(WS) |

C–S stretching frequencies of thioformaldehyde[12] (1059 cm$^{-1}$), **3**, and thiirane gives a C–S bond order of 1.33. Although the exact match of the two estimates might be somewhat fortuitous, it certainly underscores the correlation between structure, molecular vibrations, and bonding. It might be added here that *ab initio* calculations on the model compound [Fe(CO)$_2$-(PH$_3$)$_2$($\eta^2$-S=CH$_2$)] have indeed shown that the metal–ligand bond energy essentially arises from the back-bonding contribution.[34] The preferred orientation of the thioformaldehyde ligand in **3** and **4** maximizes the overlap of the HOMO of the respective metal complex fragment, *fac*- or *mer*-[W(CO)$_3$-(dmpe)], which is polarized towards the better $\pi$-accepting CO ligands,[35] and the $\pi$* orbital of thioformaldehyde, which has its largest coefficient at carbon.[36] The situation here is thus similar to that found for the rhenium complex [CpRe(NO)(PPh$_3$)-($\eta^2$-S=CH$_2$)]$^+$.[8]

The W–P(1) bond in **3** is marginally shorter than W–P(2). This means that the structural *trans* influence[37] of the side-on coordinated thioformaldehyde ligand is only slightly less than that of the tightly bound CO group. The DFT calculations which were used here tend to overestimate this effect but indicate its presence also in the rotamer **3′** (Table 2). In the facial isomer **4** both W–P bonds are in equivalent positions and therefore equal in length. While the length of the W–S bond does not change on going from **3** to **4**, we observe a notable weakening of the W–C(1) bond. This might indicate that nucleophilic addition and ring opening, if possible at all, should be more feasible for the facial isomer **4**.

In order to gain some deeper insight into the chemical reactivity the frontier orbitals of these thioformaldehyde complexes were calculated (Figs. 6 and 7). For both isomers the LUMO appears highly delocalized and does not give any hint at a preferred site for nucleophilic attack. The HOMO, however, consists mainly of a p orbital at the sulfur atom with a strongly antibonding contribution from one of the occupied d orbitals at tungsten. On this basis one has to expect a facile electrophilic attack at sulfur as the preferred mode of reactivity. At least for uncharged complexes of thioformaldehyde there are many known examples of electrophilic alkylations.[5,6,9–11] The HOMO of **3** is 0.38 eV higher in energy than that of **4** which means that the meridional isomer **3** should be somewhat more reactive in this regard. The LUMO energies follow the opposite trend

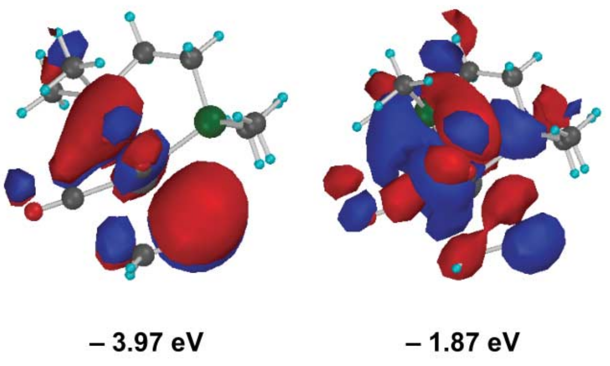


**Fig. 6** Calculated HOMO (left) and LUMO (right) of the preferred conformation of *mer*-[W(CO)$_3$(dmpe)($\eta^2$-S=CH$_2$)] (**3**).

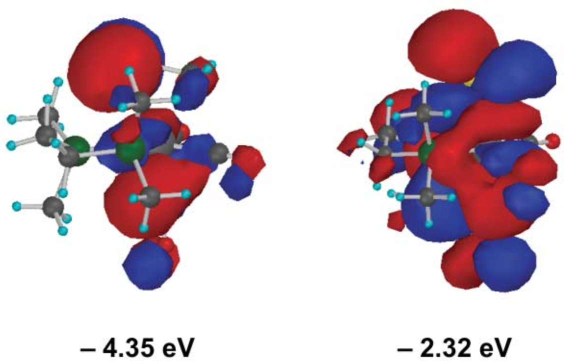


**Fig. 7** Calculated HOMO (left) and LUMO (right) of the preferred conformation of *fac*-[W(CO)$_3$(dmpe)($\eta^2$-S=CH$_2$)] (**4**).

which again marks isomer **4** as the one for which nucleophilic additions, if possible at all, should be preferred.

## Conclusions

Condensation of the highly nucleophilic complex [W(CO)$_3$(dmpe)(SH)]$^-$ **2** with formaldehyde in the presence of acid provides an easy access to the thioformaldehyde complex *mer*-[W(CO)$_3$(Me$_2$PC$_2$H$_4$PMe$_2$)($\eta^2$-S=CH$_2$)] **3** and its isotopomer *mer*-[W(CO)$_3$(Me$_2$PC$_2$H$_4$PMe$_2$)($\eta^2$-S=CD$_2$)] **3-D$_2$**. A complete vibrational analysis — facilitated by the absence of large organic substituents — was undertaken with the aid of DFT calculations. The results confirm the notion that the bonding between metal atom and thioformaldehyde ligand is appropriately described in terms of the Dewar–Chatt–Duncanson model. Due to extensive π-backbonding the C–S bond order is reduced to 1.33 which is also in accord with structural data. Taken together it is demonstrated here that a combination of structural, spectroscopic and modern theoretical methods provides a detailed understanding of bonding and reactivity of transition metal–organic complexes.

## Experimental

PPN[W(CO)$_5$(SH)] was prepared according to literature methods.[19] Other chemicals were obtained commercially and used without further purification.

All experiments were carried out under N$_2$ in dried and deoxygenated solvents. Reactions were routinely monitored by IR and NMR spectroscopy. Chromatographic separations were carried out using silica (Merck, grain size 0.06–0.20 mm) as stationary phase.

IR spectra were recorded on a Bruker IFS-25 spectrometer with the samples prepared either as Nujol mulls between KBr plates or THF solutions in NaCl cells [$\nu$(CO) region]. Raman spectra were recorded on a Bruker IFS-120 spectrometer equipped with a FRA-106 Raman module, a CaF$_2$-beam splitter and a germanium diode detector. Solid samples were placed in a 5 mm NMR tube and irradiated with the 1064 nm emission of a Nd–YAG laser. 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$_3$PO$_4$ with the deuterium signal of the solvent serving as lock and internal reference. X-Ray data were collected on a Bruker Smart-Apex CCD diffractometer using Mo-K$\alpha$ radiation. Analyses were carried out by the Microanalytical Laboratory of the Institut für Anorganische Chemie.

The DFT calculations were performed using Gaussian 98[38] and Becke's 1988 exchange functional[39] in combination with the Perdew–Wang 91 gradient-corrected correlation functional (BPW91).[40] The Los Alamos effective core potential plus double zeta (LANL2DZ)[41] was employed for tungsten, whereas the Dunning–Huzinaga full double zeta basis set with polarization and diffuse function was used [D95 + (d)] for P, C, H, S and O atoms (DFT2).[42]

**Table 5** Crystal data and structure refinement for *mer*-[W(CO)$_3$(dmpe)($\eta^2$-S=CH$_2$)] **3**

| | |
|---|---|
| Empirical formula | C$_{10}$H$_{18}$O$_3$P$_2$SW |
| Formula weight | 464.09 |
| Temperature/K | 130(2) |
| Wavelength/Å | 0.71073 |
| Crystal system, space group | Monoclinic, $P2_1/n$ |
| $a$/Å | 9.1843(5) |
| $b$/Å | 12.4238(7) |
| $c$/Å | 13.6206(7) |
| $\beta$/° | 90.483(1) |
| Volume/Å$^3$ | 1554.11(15) |
| $Z$, Calculated density/Mg m$^{-3}$ | 4, 1.984 |
| Absorption coefficient/mm$^{-1}$ | 7.767 |
| Reflections collected/unique | 25623/3414 |
| Final $R$ indices [$I > 2\sigma(I)$] | $R_1 = 0.019$, $wR_2 = 0.044$ |
| $R$ indices (all data) | $R_1 = 0.021$, $wR_2 = 0.045$ |

### Preparation of PPN[W(CO)$_3$(dmpe)(SH)], 2

A solution of PPN[W(CO)$_5$(SH)] **1** (0.90 g, 1.00 mmol) and dmpe (0.20 mL, 0.18 g, 1.20 mmol) in THF (20 cm$^3$) was kept at 60 °C for 45 min. The solvent was removed under reduced pressure and the residue washed repeatedly with Et$_2$O and hexanes giving **2** as a deep yellow crystalline powder (0.97 g, 98%), mp 34 °C (Found: C, 54.49; H, 4.83; N, 1.43; S, 3.23%. C$_{45}$H$_{47}$NO$_3$P$_4$SW requires C, 54.61; H, 4.79; N, 1.42; S, 3.24%). $\nu_{max}$/cm$^{-1}$ (CO) 1894 (vs), 1799 (s) and 1752 (s) (THF). $\delta_H$ (CD$_3$CN) −3.78 [1 H, t, $J$(HP) 8.7 Hz, WSH], 1.34 [6 H, d, $J$(HP) 7.1 Hz, PCH$_3$], 1.42 [6 H, d, $J$(HP) 6.8 Hz, PCH$_3$], 1.30–1.80 (m, 4 H, PCH$_2$) and 7.43–7.68 (m, 30 H, Ph); $\delta_C$ (CD$_3$CN) 12.4 [d, $J$(CP) 20 Hz, PCH$_3$], 18.4 [d, $J$(CP) 25 Hz, PCH$_3$], 31.2 [vt, $J$(CP) + $J$(CP′) 40 Hz, PCH$_2$], 127.4–134.5 (m, Ph), 215.9 [t, $J$(CP) 6 Hz, CO] and 223.4 [dd, $J$(CP) 7, 38 Hz, CO]; $\delta_P$ (CD$_3$CN) 6.8 [s, $J$(PW) 198 Hz, dmpe] and 20.9 (s, PPN).

### Preparation of *mer*-[W(CO)$_3$(dmpe)($\eta^2$-S=CH$_2$)], 3 and *mer*-[W(CO)$_3$(dmpe)($\eta^2$-S=CD$_2$)], 3-D$_2$

To a solution of PPN[W(CO)$_3$(dmpe)(SH)] **2** (0.50 g, 0.50 mmol) in THF (10 cm$^3$) was added a 40% solution of formaldehyde in water (0.10 cm$^3$, 1.33 mmol) and CF$_3$CO$_2$H (0.04 cm$^3$, 0.06 g, 0.52 mmol). The solvent was removed under reduced pressure, the residue dissolved in dichloromethane and chromatographed over silica using dichloromethane–acetone (40 : 1) as eluent. A broad yellow band was collected, the solvent evaporated, and the remaining yellow oil washed repeatedly with hexanes giving **3** as an orange-colored crystalline solid (0.21 g, 90%), mp 74 °C (dec.) (Found: C, 26.15; H, 3.86; S, 6.45%. C$_{10}$H$_{18}$O$_3$P$_2$SW requires C, 25.88; H, 3.91; S, 6.91%). $\nu_{max}$/cm$^{-1}$ (CO) 1996 (w), 1914 (m) and 1869 (s) (THF). $\delta_H$ (C$_6$D$_6$) 0.90–1.23 (m, 4 H, PCH$_2$) 1.18 [6 H, d, $J$(HP) 8.4 Hz, PCH$_3$], 1.41 [6 H, d, $J$(HP) 8.8 Hz, PCH$_3$] and 3.98 [dd, 2 H, $J$(HP) 2.8, 0.5 Hz, SCH$_2$]; $\delta_C$ (C$_6$D$_6$) 18.2 [d, $J$(CP) 28 Hz, PCH$_3$], 19.6 [d, $J$(CP) 28 Hz, PCH$_3$], 27.9 [dd, $J$(CP) 28, 14 Hz, PCH$_2$], 31.8 [dd, $J$(CP) 30, 17 Hz, PCH$_2$], 39.7 (s, SCH$_2$), 197.7 [dd, $J$(CP) 8, 4 Hz, CO] and 214.0 [dd, $J$(CP) 13, 8 Hz, CO]; $\delta_P$ (C$_6$D$_6$) 12.4 [d, $J$(PP) 15 Hz, $J$(PW) 222 Hz] and 18.7 [d, $J$(PP) 15 Hz, $J$(PW) 205 Hz]. Additional signals are due to the facial isomer **4**: $\nu_{max}$/cm$^{-1}$ (CO) 1980 (w). $\delta_H$ (C$_6$D$_6$) 0.92 [d, $J$(HP) 8.1 Hz, PCH$_3$] and 3.91 [t, $J$(HP) 1.1 Hz, SCH$_2$]; $\delta_P$ (C$_6$D$_6$) 4.9 [s, $J$(PW) 200 Hz].

**3-D$_2$** was obtained by employing CD$_2$O in D$_2$O. Identical spectra were obtained except for the missing signals of the SCH$_2$ group.

### Structure determination of *mer*-[W(CO)$_3$(dmpe)($\eta^2$-S=CH$_2$)] 3

The crystal data for **3** are summarized in Table 5. The structure was solved using the direct methods provided within SHELXS-

97[43] and refined by full-matrix least squares using SHELXL-97.[43]

CCDC reference number 160647.

See http://www.rsc.org/suppdata/dt/b2/b203195g/ for crystallographic data in CIF or other electronic format.

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