

# The photochemical generation of heterobimetallic complexes containing carbon disulfide

Peter V. Broadhurst, Nicholas E. Leadbeater,\* Jack Lewis and Paul R. Raithby

Department of Chemistry, Lensfield Road, Cambridge, UK CB2 1EW

Photochemistry has been used to generate a number of heterobimetallic complexes containing  $\pi + \sigma$  CS<sub>2</sub> bridging groups. Broad-band UV photolysis of tetrahydrofuran (thf) solutions of [M(CO)<sub>6</sub>] (M = Cr, Mo or W) with [Fe(CO)<sub>2</sub>(PR<sub>3</sub>)<sub>2</sub>( $\eta^2$ -CS<sub>2</sub>)] (R = Et or Ph) leads to the formation of the bimetallic complexes [(PR<sub>3</sub>)<sub>2</sub>(CO)<sub>2</sub>Fe( $\mu$ - $\eta^2$ : $\eta^1$ -CS<sub>2</sub>)M(CO)<sub>5</sub>]. Photolysis of acetonitrile solutions of [Os<sub>3</sub>(CO)<sub>12</sub>] with [Fe(CO)<sub>2</sub>(PR<sub>3</sub>)<sub>2</sub>( $\eta^2$ -CS<sub>2</sub>)] leads to [(PR<sub>3</sub>)<sub>2</sub>(CO)<sub>2</sub>Fe( $\mu$ - $\eta^2$ : $\eta^1$ -CS<sub>2</sub>)Os<sub>3</sub>(CO)<sub>11</sub>]. Photolysis of a thf solution of (PEt<sub>3</sub>)<sub>2</sub>(CO)<sub>2</sub>Fe( $\mu$ - $\eta^2$ : $\eta^1$ -CS<sub>2</sub>)M(CO)<sub>5</sub>] with PEt<sub>3</sub> results in the formation of the phosphine-substituted complex [(PPh<sub>3</sub>)<sub>2</sub>(CO)<sub>2</sub>Fe( $\mu$ - $\eta^2$ : $\eta^1$ -CS<sub>2</sub>)M(CO)<sub>4</sub>-(PEt<sub>3</sub>)]. Single-crystal X-ray diffraction has been used to determine the molecular structures of [(PPh<sub>3</sub>)<sub>2</sub>(CO)<sub>2</sub>Fe( $\mu$ - $\eta^2$ : $\eta^1$ -CS<sub>2</sub>)W(CO)<sub>5</sub>], [(PEt<sub>3</sub>)<sub>2</sub>(CO)<sub>2</sub>Fe( $\mu$ - $\eta^2$ : $\eta^1$ -CS<sub>2</sub>)Os<sub>3</sub>(CO)<sub>11</sub>] and [(PPh<sub>3</sub>)<sub>2</sub>(CO)<sub>2</sub>Fe( $\mu$ - $\eta^2$ : $\eta^1$ -CS<sub>2</sub>)Cr(CO)<sub>4</sub>(PEt<sub>3</sub>)].

The interaction of heteroallene molecules such as carbonyl sulfide (COS), carbon disulfide (CS<sub>2</sub>) and carbon dioxide (CO<sub>2</sub>) with transition metals has become an area of increased research interest.<sup>1,2</sup> Firstly, petrochemical feedstocks have sulfur-containing compounds as impurities which poison many hetero- or homo-geneous catalysts used in processing.<sup>3</sup> If the behaviour of these impurities with transition-metal centres is established, an insight into the mechanism for poisoning could be gained and attempts made to prevent it. In addition, heteroallenes show interesting chemistry undergoing a number of transformations such as insertion, dimerisation and disproportionation.<sup>1a</sup>

Work in our research group has focused on the photochemical generation of carbon disulfide-containing complexes of the Group 8 transition metals and their subsequent reaction chemistry. To date, many of the Group 8 transition-metal-CS<sub>2</sub> complexes reported have been prepared by thermolysis or pyrolysis routes. Although illustrating interesting chemistry, in many cases the CS<sub>2</sub> moiety does not remain intact, often forming, for example, carbide, sulfide, CS, C<sub>2</sub>S<sub>2</sub>, CS<sub>3</sub> and C<sub>2</sub>S<sub>4</sub> groups in various co-ordination modes.<sup>4</sup> Photochemistry offers a simple, and often highly selective, route to organometallic compounds, overcoming large enthalpy barriers.<sup>5,6</sup> As a consequence, it is often possible to prepare complexes that are otherwise inaccessible by conventional thermochemical routes. We have studied the photochemical behaviour of [Fe(CO)<sub>5</sub>] **1** and [Fe(CO)<sub>3</sub>(PR<sub>3</sub>)<sub>2</sub>] (R = Et **2a** or Ph **2b**) with CS<sub>2</sub> and the reaction chemistry of the photolysis products has been investigated.

## Results and Discussion

### Photolysis of [Fe(CO)<sub>5</sub>] **1** and [Fe(CO)<sub>3</sub>(PR<sub>3</sub>)<sub>2</sub>] (R = Et **2a** or Ph **2b**) with CS<sub>2</sub>

Broad-band UV photolysis of a hexane solution of [Fe(CO)<sub>5</sub>] **1** containing CS<sub>2</sub> leads rapidly to the formation of a brown precipitate, which is insoluble in organic solvents. Due to this insolubility, characterisation of the reaction product has not been possible. The aim of this experiment was to prepare the  $\eta^2$ -CS<sub>2</sub> co-ordinated complex [Fe(CO)<sub>4</sub>( $\eta^2$ -CS<sub>2</sub>)], analogous to the olefin complex [Fe(CO)<sub>4</sub>( $\eta^2$ -C<sub>2</sub>H<sub>4</sub>)]. Since carbon disulfide is not as good a  $\pi$ -acceptor ligand as ethene, the formation of the  $\eta^2$ -CS<sub>2</sub> complex is not possible using the present experimental methods due to the inherent instability of the complex.

Attention was turned to phosphine-substituted mononuclear iron carbonyl complexes since, by replacing carbonyl groups by

phosphines,  $\eta^2$ -co-ordinating ligands can be stabilised. This is as a result of a strong increase in binding energy which is consistent with increased  $\pi$ -back donation in the phosphine-substituted complex. Indeed, *ab initio* calculations<sup>7</sup> have shown that replacement of carbonyl groups by phosphines in iron(0) carbon disulfide complexes results in an increased overlap between the interacting orbitals on Fe and CS<sub>2</sub>, this being concomitant with deformation of the CS<sub>2</sub> geometry which itself enhances the effect.

Irradiation of a tetrahydrofuran (thf) solution of [Fe(CO)<sub>3</sub>(PR<sub>3</sub>)<sub>2</sub>] (R = Et **2a** or Ph **2b**) with CS<sub>2</sub> leads to the  $\eta^2$ -CS<sub>2</sub> co-ordinated complex [Fe(CO)<sub>2</sub>(PR<sub>3</sub>)<sub>2</sub>( $\eta^2$ -CS<sub>2</sub>)] (R = Et **3a** or Ph **3b**) [equation (1)] as characterised by comparison of the



spectral data with those reported previously for **3b**.<sup>8</sup> The *trans* stereochemistry of **3a** and **3b** was evident from the <sup>1</sup>H NMR parameters (see below). The disulfide products are formed in high yields, this being a marked improvement on the conventional synthetic routes of either refluxing [Fe<sub>2</sub>(CO)<sub>9</sub>] and tertiary phosphine in CS<sub>2</sub> as the solvent<sup>8,9</sup> or ligand exchange reactions.<sup>10</sup> The bonding of the CS<sub>2</sub> group is considered to be analogous to the Dewar-Chatto model proposed for alkenes. The net structural effect of  $\sigma$  donation from the  $\pi$  molecular orbitals (MO) on CS<sub>2</sub> to the iron and back donation from iron to a  $\pi^*$  MO on the disulfide is a distortion of the CS<sub>2</sub> moiety towards the geometry observed in the first excited state.<sup>10</sup> Concomitant with this is a lengthening of the CS bonds as shown by the decrease in CS stretching frequency from 1535 cm<sup>-1</sup> in free carbon disulfide ( $\nu_2$ )<sup>11</sup> to 1116 in **3a**. From comparison of this value with those for analogous  $\eta^2$ -CS<sub>2</sub> complexes reported in the literature,<sup>8-10</sup> a correlation between  $\nu_{\text{CS}}$  and the electronic properties of the phosphorus ligand is found, phosphite ligands having higher  $\nu_{\text{CS}}$  values than analogous phosphines. Although informative, data for the C-S stretching frequency must be considered carefully since coupling with other ligand modes is often severe in the  $\nu_{\text{CS}}$  region of the infrared spectrum<sup>12</sup> with the result that significance cannot be placed on absolute values of frequencies reported here or in other CS<sub>2</sub>-containing molecules.<sup>10</sup> The analogous complex [Fe(CO)<sub>2</sub>(PMe<sub>3</sub>)(PPh<sub>3</sub>)( $\eta^2$ -CS<sub>2</sub>)] **3c** has been characterised crystallographically and shows definitively both the lengthening of the CS bonds and also significant deformation of the CS<sub>2</sub> moiety, the S-C-S angle being 139°.<sup>10</sup>

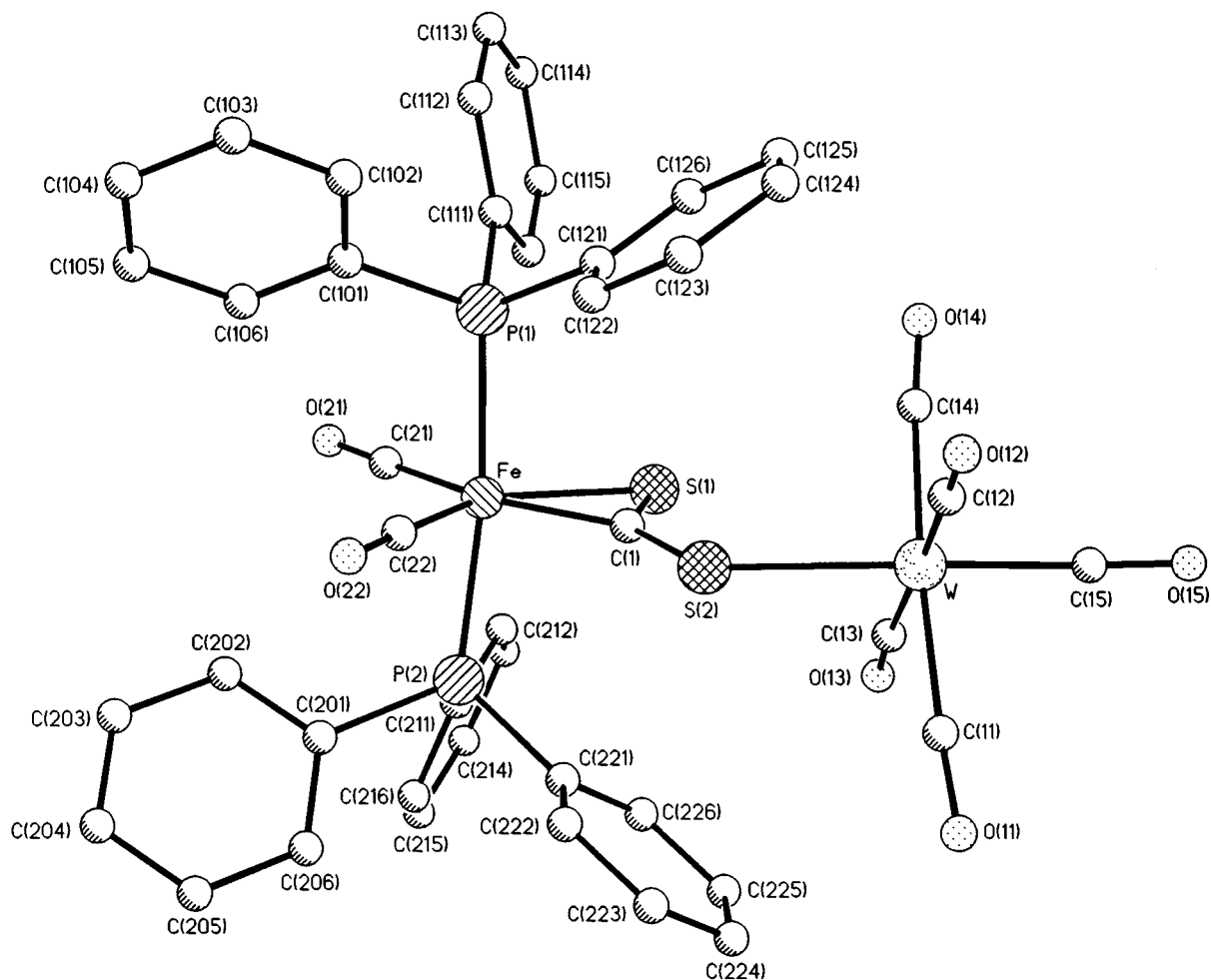


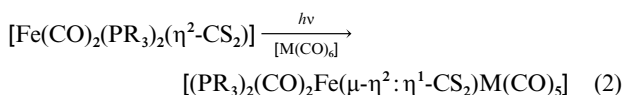
Fig. 1 The molecular structure of  $[(\text{PPh}_3)_2(\text{CO})_2\text{Fe}(\mu\text{-}\eta^2\text{:}\eta^1\text{-CS}_2)\text{W}(\text{CO})_5]$  **7b**

The  $\eta^2\text{-CS}_2$  co-ordinated complexes **3a** and **3b** are stable in solution for extended periods. In addition, the complexes are stable to displacement of  $\text{CS}_2$  by phosphines, this being in contrast to that of  $[\text{Fe}(\text{CO})_4(\eta^2\text{-C}_2\text{H}_4)]^5$  in which the alkene moiety is substituted readily. If a solution of **3a** or **3b** is heated under an atmosphere of carbon monoxide, the  $\text{CS}_2$  group is replaced by CO to yield **2a** or **2b**.

#### The reaction chemistry of $[\text{Fe}(\text{CO})_2(\text{PEt}_3)_2(\eta^2\text{-CS}_2)]$ and $[\text{Fe}(\text{CO})_2(\text{PPh}_3)_2(\eta^2\text{-CS}_2)]$ with mononuclear and cluster carbonyl fragments

The reaction chemistry of  $[\text{Fe}(\text{CO})_2(\text{PEt}_3)_2(\eta^2\text{-CS}_2)]$  **3a** and  $[\text{Fe}(\text{CO})_2(\text{PPh}_3)_2(\eta^2\text{-CS}_2)]$  **3b** with  $[\text{M}(\text{CO})_6]$  ( $\text{M} = \text{Cr}, \text{Mo}$  or  $\text{W}$ ) and  $[\text{Os}_3(\text{CO})_{12}]$  has been investigated. The unco-ordinated sulfur in transition-metal  $\eta^2$ -co-ordinated  $\text{CS}_2$  complexes is highly nucleophilic and is therefore susceptible to attack by electrophiles.<sup>13</sup> This is demonstrated clearly by reaction with methyl iodide yielding, in the case of **3a**,  $[\text{Fe}(\text{CO})_2(\text{PEt}_3)_2(\eta^2\text{-CS}_2\text{Me})]^+$  **4a**.

Broad-band UV photolysis of a thf solution of complex **3a** with  $[\text{M}(\text{CO})_6]$  ( $\text{M} = \text{Cr}, \text{Mo}$  or  $\text{W}$ ) leads to the formation of the  $\text{CS}_2$ -bridged complex  $[(\text{PEt}_3)_2(\text{CO})_2\text{Fe}(\mu\text{-}\eta^2\text{:}\eta^1\text{-CS}_2)\text{M}(\text{CO})_5]$  ( $\text{M} = \text{Cr}$  **5a**,  $\text{Mo}$  **6a** or  $\text{W}$  **7a**) [equation (2)] as characterised



initially by IR and  $^1\text{H}$  NMR spectroscopy. Analogous complexes **5b**, **6b** or **7b** are formed with **3b**.

The complexes are formed presumably by attack of **3a** on  $[\text{M}(\text{CO})_5(\text{thf})]$ , the latter intermediate being formed photo-

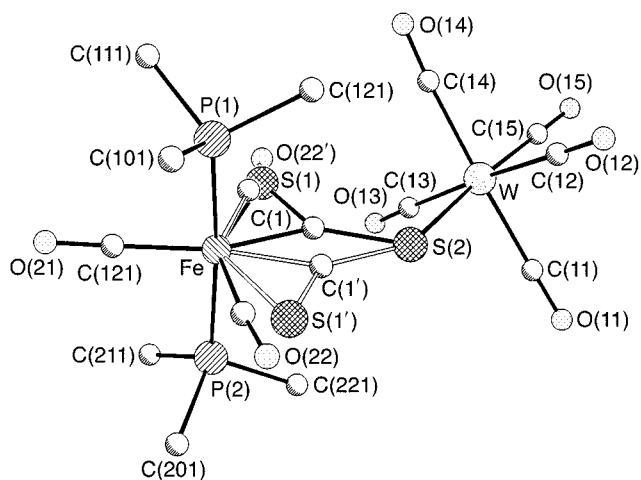


Fig. 2 The molecular structure of  $[(\text{PPh}_3)_2(\text{CO})_2\text{Fe}(\mu\text{-}\eta^2\text{:}\eta^1\text{-CS}_2)\text{W}(\text{CO})_5]$  **7b** showing the crystallographic disorder of the  $\text{CS}_2$  and one CO ligand (phenyl rings removed for clarity)

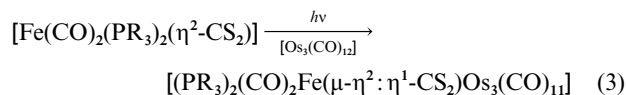
chemically. The IR spectrum of the products shows five bands in the CO stretching region this being in agreement with local  $\text{C}_{4v}$  symmetry at the M centre (three  $\nu_{\text{CO}}$  bands) and retention of the local  $\text{C}_{2v}$  symmetry of the  $[\text{Fe}(\text{CO})_2(\text{PR}_3)_2(\eta^2\text{-CS}_2)]$  fragment. Slight splitting of one of the bands due to the M centre is observed, this being attributed to the slight deviation from a regular octahedral geometry. This assignment has been confirmed by the determination of the molecular structure of  $[(\text{PPh}_3)_2(\text{CO})_2\text{Fe}(\mu\text{-}\eta^2\text{:}\eta^1\text{-CS}_2)\text{W}(\text{CO})_5]$  **7b** by a single-crystal X-ray diffraction study (Figs. 1 and 2). Selected bond lengths and angles are shown in Table 1. The molecular structure shows disorder in the  $\text{CS}_2$  group and one of the carbonyl groups at

**Table 1** Selected bond lengths and angles for complex **7b**

W–S(2)	2.531(4)	W–C(11)	2.02(2)
W–C(12)	2.017(17)	W–C(13)	2.044(18)
W–C(14)	2.039(16)	W–C(15)	1.977(16)
Fe–P(1)	2.293(4)	Fe–P(2)	2.289(4)
Fe–S(1)	2.299(1)	Fe–S(1')	2.300(1)
Fe–C(1)	1.850(1)	Fe–C(1')	1.850(1)
Fe–C(21)	1.790(15)	Fe–C(22)	1.79(2)
Fe–C(22')	1.800(1)	S(1)–C(1)	1.669(9)
C(1)–S(2)	1.760(1)	C(1')–S(1')	1.576(12)
C(1')–S(2)	1.760(1)	C(11)–O(11)	1.15(2)
C(12)–O(12)	1.134(16)	C(13)–O(13)	1.15(2)
C(14)–O(14)	1.138(16)	C(15)–O(15)	1.161(16)
C(21)–O(21)	1.151(16)	C(22)–O(22)	1.17(3)
C(22')–O(22')	1.150(1)		
C(11)–W–S(2)	89.7(4)	C(12)–W–S(2)	83.5(4)
C(13)–W–S(2)	93.8(4)	C(14)–W–S(2)	95.6(4)
C(15)–W–S(2)	174.6(4)	W–C(11)–O(11)	175.2(15)
W–C(12)–O(12)	179.0(15)	W–C(13)–O(13)	176.1(14)
W–C(14)–O(14)	175.4(13)	W–C(15)–O(15)	177.9(13)
W–S(2)–C(1)	109.0(2)	W–S(2)–C(1')	151.0(4)
S(2)–C(1)–S(1)	138.7(3)	S(2)–C(1')–S(1')	136.2(4)
S(2)–C(1)–Fe	139.8(4)	S(2)–C(1')–Fe	139.8(4)
C(1)–S(1)–Fe	52.7(1)	C(1)–Fe–S(1)	45.9(3)
C(1)–Fe–P(1)	94.1(6)	C(1)–Fe–P(2)	94.0(6)
C(1)–Fe–C(21)	153.7(5)	C(1)–Fe–C(22)	99.1(7)
C(1')–S(1')–Fe	53.1(1)	C(1')–Fe–P(1)	90.3(12)
C(1')–Fe–P(2)	92.2(12)	C(1')–Fe–C(21)	167.2(5)
C(1')–Fe–C(22')	87.5(16)		

iron which precludes an assessment of the bond parameters in **7b**. It is, however, clear from the structure that the CS<sub>2</sub> group interacts in a  $\pi$  manner with the iron centre and in a  $\sigma$  manner with the tungsten; this bridging bonding mode being denoted as  $\pi + \sigma$ . Of all the bridging modes of CS<sub>2</sub> structurally characterised, the  $\pi + \sigma$  motif is relatively uncommon.<sup>14</sup> The reasons why **7b** adopts this configuration are not clear but the stability of the  $\pi$  bond between iron and CS<sub>2</sub> and the mild reaction conditions used in the coupling reaction with [W(CO)<sub>6</sub>] may be significant factors. Although not statistically different at the 3 $\sigma$  level, the W–C(15) bond, at 1.977(16) Å, is apparently shorter than the other W–C (O) bonds, average 2.02(4) Å. This is indicative of the increased back donation as a result of the replacement of a *trans* carbonyl by a *trans*  $\sigma$  bonding sulfur which is not competing for the electron density available for back donation. This effect has been reported previously for sulfur-substituted Group 6 carbonyls.<sup>15,16</sup> The other bond lengths and the angles in the W(CO)<sub>5</sub>S moiety are unexceptional, a very slight distortion from a regular octahedral geometry being observed.

Broad-band UV photolysis of an acetonitrile solution of complex **3a** with [Os<sub>3</sub>(CO)<sub>12</sub>] leads to the formation of the mononuclear-cluster linked compound [(PET<sub>3</sub>)<sub>2</sub>(CO)<sub>2</sub>Fe( $\mu$ - $\eta^2$ : $\eta^1$ -CS<sub>2</sub>)Os<sub>3</sub>(CO)<sub>11</sub>] **8a** [equation (3)] as characterised

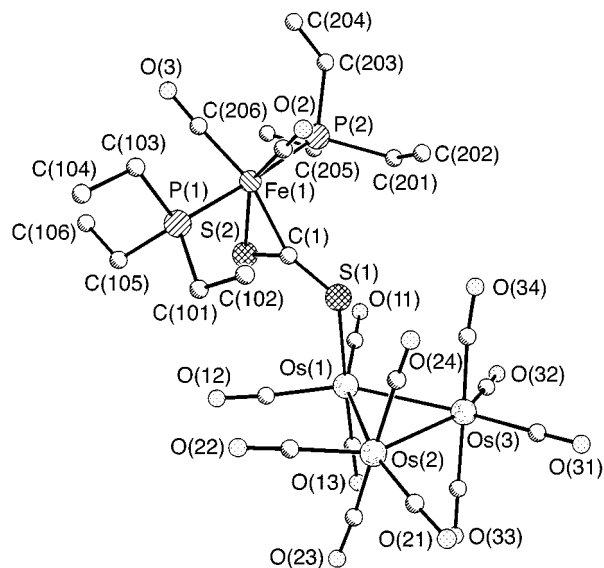


initially by IR and <sup>1</sup>H NMR spectroscopy. An analogous compound **8b** is formed with **3b**. Again, the *trans* stereochemistry of the iron centre is unchanged in the reaction and the bonding of the CS<sub>2</sub> is  $\pi$  to the iron centre and  $\sigma$  to one of the osmium atoms of the trinuclear cluster. It is presumed that the reaction occurs by way of an attack of **3a** or **3b** on [Os<sub>3</sub>(CO)<sub>11</sub>(MeCN)], the latter formed by photosubstitution of a carbonyl group for acetonitrile.<sup>17</sup>

The molecular structure of **8a** has been determined by single-crystal X-ray diffraction (Fig. 3) and selected bond lengths and angles are presented in Table 2. The  $\pi + \sigma$  co-ordination of CS<sub>2</sub>

**Table 2** Selected bond lengths and angles for complex **8a**

Os(1)–Os(2)	2.886(2)	Os(1)–Os(3)	2.883(1)
Os(2)–Os(3)	2.877(2)	Os(1)–C(11)	1.861(3)
Os(1)–C(12)	1.91(3)	Os(1)–C(13)	1.85(3)
Os(1)–S(1)	2.461(6)	Os(2)–C(21)	1.86(3)
Os(2)–C(22)	1.92(3)	Os(2)–C(23)	1.83(3)
Os(2)–C(24)	1.93(3)	Os(3)–C(31)	1.92(2)
Os(3)–C(32)	1.86(4)	Os(3)–C(33)	1.93(3)
Os(3)–C(34)	1.83(4)	C(11)–O(11)	1.17(4)
C(12)–O(12)	1.16(3)	C(13)–O(13)	1.15(3)
C(1)–S(1)	1.64(2)	C(1)–S(2)	1.65(2)
Fe–C(1)	1.95(2)	Fe–S(2)	2.341(7)
Fe–C(2)	1.81(1)	Fe–C(3)	1.803(19)
Fe–P(1)	2.270(9)	Fe–P(2)	2.284(10)
C(2)–O(2)	1.091(1)	C(3)–O(3)	1.13(3)
Os(2)–Os(1)–Os(3)	59.8(1)	Os(1)–Os(2)–Os(3)	60.0(1)
Os(1)–Os(3)–Os(2)	60.1(1)	Os(2)–Os(1)–C(11)	160.1(7)
Os(3)–Os(1)–C(11)	101.3(6)	Os(2)–Os(1)–C(12)	95.8(9)
Os(3)–Os(1)–C(12)	154.5(10)	Os(2)–Os(1)–C(13)	96.1(9)
Os(3)–Os(1)–C(13)	84.3(6)	C(11)–Os(1)–C(13)	87.3(12)
C(11)–Os(1)–C(12)	103.7(11)	C(12)–Os(1)–C(13)	91.6(11)
Os(2)–Os(1)–S(1)	87.4(2)	Os(3)–Os(1)–S(1)	95.9(1)
C(11)–Os(1)–S(1)	88.7(8)	C(12)–Os(1)–S(1)	89.9(9)
C(13)–Os(1)–S(1)	176.0(1)	Os(1)–Os(2)–C(21)	163.4(8)
Os(3)–Os(2)–C(21)	103.9(8)	Os(1)–Os(2)–C(22)	90.2(11)
Os(3)–Os(2)–C(22)	149.4(11)	C(21)–Os(2)–C(22)	106.2(14)
Os(1)–Os(2)–C(23)	84.9(11)	Os(3)–Os(2)–C(23)	95.1(11)
Os(1)–C(11)–O(11)	177.4(19)	Os(1)–C(12)–O(12)	176(3)
Os(1)–C(13)–O(13)	178(3)	Os(1)–S(1)–C(1)	110.5(9)
S(1)–C(1)–S(2)	140.5(16)	S(1)–C(1)–Fe	138.8(14)
S(2)–C(1)–Fe	80.7(9)	C(1)–S(2)–Fe	55.3(8)
S(2)–Fe–C(1)	43.9(7)	S(2)–Fe–C(2)	149.7(7)
S(2)–Fe–C(3)	108.9(7)	S(2)–Fe–P(1)	91.5(3)
S(2)–Fe–P(2)	91.5(3)	C(2)–Fe–C(3)	101.3(10)
C(2)–Fe–P(1)	88.9(9)	C(2)–Fe–P(2)	89.4(9)
C(3)–Fe–P(1)	88.5(8)	C(3)–Fe–P(2)	89.4(9)
P(1)–Fe–P(2)	176.8(3)		

**Fig. 3** The molecular structure of [(PET<sub>3</sub>)<sub>2</sub>(CO)<sub>2</sub>Fe( $\mu$ - $\eta^2$ : $\eta^1$ -CS<sub>2</sub>)Os<sub>3</sub>(CO)<sub>11</sub>] **8a**

is confirmed, the bonding to the iron centre being unchanged and the second S atom of the disulfide bonding to an osmium atom in an axial position. The site preference of ligands depends on a balance of steric and electronic factors.<sup>18,19</sup> Simple calculations on [Os<sub>3</sub>(CO)<sub>12</sub>–*n*L<sub>*n*</sub>] systems show that the equatorial sites in approximately anticuboctahedral structures are less sterically hindered than axial sites.<sup>20</sup> It is therefore interesting that in **8a**, co-ordination occurs through an axial site on the osmium atom of the cluster especially since in the only other structurally characterised example of a triosmium cluster

containing a  $\sigma$ -co-ordinated sulfur moiety,  $[\text{Os}_3(\text{CO})_{11}\text{-}\{\text{S}(\text{CH}_2)_3\}]$ ,<sup>21</sup> the ligand occupies the expected equatorial position. If the S was co-ordinated equatorially in **8b** there would be considerable steric repulsions between the carbonyl groups on the osmium cluster with those on the iron centre. Electronic arguments must also be taken into account. Both  $[\text{Os}_3(\text{CO})_{11}\text{-(MeCN)}]$  and  $[\text{Os}_3(\text{CO})_{10}\text{-(MeCN)}_2]$  exhibit axial co-ordination of the  $\sigma$ -donor ligands, this being due to the  $\sigma$ -donor characteristics of these ligands. Good  $\sigma$ -donor ligands, such as acetonitrile, prefer to lie *trans* to a carbonyl group rather than, in the case of good  $\pi$ -acceptor ligands, *trans* to the metal–metal bonds.<sup>22</sup>

The Os–Os bonds are not significantly different to those in  $[\text{Os}_3(\text{CO})_{12}]$ <sup>23</sup> in contrast to the case of  $[\text{Os}_3(\text{CO})_{11}\text{-}\{\text{S}(\text{CH}_2)_3\}]$ <sup>21</sup> where the equatorially situated thietane group exerts a significant *trans* influence lengthening one of the metal–metal bonds. Unlike the case of **7b**, in **8a** the  $\sigma$ -co-ordinated sulfur atom does not seem to have any significant effect on the *trans* situated carbonyl group on Os(1). This may be explained by a delocalisation of the electron density across all the carbonyl bonds in the cluster rather than the localised effect seen in **7b**.

The photochemical reaction of  $[\text{Fe}(\text{CO})_2(\text{PR}_3)_2(\eta^2\text{-CS}_2)]$  with  $[\text{Os}_3(\text{CO})_{12}]$  is significantly lower for R = Ph (**3a**) than for R = Et (**3b**). In the case of the former, reaction is significantly slower and a significant quantity of  $[\text{Os}_3(\text{CO})_{11}(\text{PPh}_3)]$  is formed as a by-product. Since a facile phosphine exchange has been observed for  $[\text{Fe}(\text{CO})_2(\text{PR}_3)_2(\eta^2\text{-CS}_2)]$ <sup>9,10</sup> complexes and **3b** is particularly unstable in solution,<sup>8</sup> dissociation of triphenylphosphine is not unexpected. The slower reaction of **3a** as compared to **3b** may be due to both the increased steric bulk<sup>24</sup> and decreased basicity<sup>25</sup> of  $\text{PPh}_3$  as compared to  $\text{PEt}_3$  which both restricts access of **3b** to the available co-ordination site on the osmium cluster and results in a less nucleophilic donor sulfur atom in the  $\text{PPh}_3$ -substituted compound.

#### The reaction chemistry of $[(\text{PEt}_3)_2(\text{CO})_2\text{Fe}(\mu\text{-}\eta^2\text{:}\eta^1\text{-CS}_2)\text{-M}(\text{CO})_5]$ (M = Cr, Mo or W)

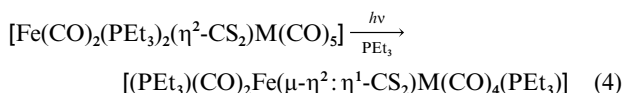
There are few  $\text{CS}_2$ -containing compounds for which reactivity studies have been reported. These include  $[\{\text{Pt}(\text{Ph}_2\text{PCH}_2\text{-PPh}_2)\text{Cl}\}_2(\mu\text{-CS}_2)]$ <sup>26</sup> and  $[\text{Pt}_2(\text{PBu}_2\text{Ph})_2(\mu\text{-CS}_2)]$ <sup>27,28</sup> which contain a dithiocarboxylate-type disulfide unit. In an attempt to compare the chemistry of the dithiocarboxylate and  $\sigma + \pi$  bonding modes of carbon disulfide, some reaction chemistry of  $[(\text{PEt}_3)_2(\text{CO})_2\text{Fe}(\mu\text{-}\eta^2\text{:}\eta^1\text{-CS}_2)\text{M}(\text{CO})_5]$  (M = Cr **5a**, Mo **6a** or W **7a**) has been investigated. Since one approach to building organometallic clusters involves the interaction of a metal fragment with the  $\text{CS}_2$  moiety of a co-ordinated disulfide complex inducing fragmentation of  $\text{CS}_2$  to yield S and CS ligands, attempts at cluster synthesis have been made here. There are only a few examples of clusters reported in the literature as a result of this type of fragmentation of  $\text{CS}_2$ ; these include  $[(\text{CoCp})_3(\mu_3\text{-CS})(\mu\text{-S})]$  (Cp =  $\eta^5\text{-C}_5\text{H}_5$ )<sup>29</sup> and  $[\text{Fe}_4(\text{CO})_{12}(\mu_3\text{-CS})(\mu\text{-S})]$ .<sup>30</sup>

No reaction was observed between  $[(\text{PEt}_3)_2(\text{CO})_2\text{Fe}(\mu\text{-}\eta^2\text{:}\eta^1\text{-CS}_2)\text{M}(\text{CO})_5]$  (**5a–7a**) and  $[\text{N}(\text{PPh}_3)_2][\text{BF}_4]$  or  $\text{NEt}_3$  using either 1 equivalent or a significant excess of the reagents. There was also no observed reaction between **5a**, **6a** or **7a** and ammonia at either room temperature or at elevated temperatures. This suggests that these complexes are not susceptible to nucleophilic attack either at the  $\text{CS}_2$  moiety or at the Group 6 metal centre. This parallels the reaction chemistry of  $[\text{Pt}_2(\text{PBu}_2\text{Ph})_2(\mu\text{-CS}_2)]$ .<sup>30</sup> This is in agreement with the proposal<sup>14</sup> that the  $\text{CS}_2$  ligand must bridge a metal–metal bond before fragmentation can occur.

Broad-band UV photolysis of a thf solution of **5a**, **6a** or **7a** with  $\text{PEt}_3$  leads to substitution of the Group 6 metal centre yielding  $[(\text{PEt}_3)_2(\text{CO})_2\text{Fe}(\mu\text{-}\eta^2\text{:}\eta^1\text{-CS}_2)\text{M}(\text{CO})_4(\text{PEt}_3)]$  (M = Cr **9a**, Mo **10a**, W **11a**) [equation (4)] as characterised initially by

**Table 3** Selected bond lengths and angles for complex **9a**

Fe–S(1)	2.342(1)	Fe–C(1)	1.934(3)
Fe–P(1)	2.276(1)	Fe–P(2)	2.273(1)
Fe–C(14)	1.796(4)	Fe–C(15)	1.755(4)
S(1)–C(1)	1.674(3)	C(1)–S(2)	1.639(3)
S(2)–Cr	2.431(1)	P(1)–C(2)	1.805(5)
P(1)–C(4)	1.840(6)	P(1)–C(6)	1.801(4)
C(2)–C(3)	1.514(8)	C(4)–C(5)	1.496(7)
C(6)–C(7)	1.536(8)	P(2)–C(8)	1.839(5)
P(2)–C(10)	1.837(3)	P(2)–C(12)	1.829(4)
C(14)–O(1)	1.138(5)	C(15)–O(2)	1.142(5)
Cr–P(3)	2.398(1)	Cr–C(22)	1.823(4)
Cr–C(23)	1.850(4)	Cr–C(24)	1.884(3)
Cr–C(25)	1.885(4)	P(3)–C(16)	1.850(4)
P(3)–C(18)	1.852(3)	P(3)–C(20)	1.829(5)
C(16)–C(17)	1.519(5)	C(18)–C(19)	1.521(5)
C(20)–C(21)	1.539(7)	C(20)–O(3)	1.160(5)
C(23)–O(4)	1.158(5)	C(24)–O(5)	1.149(4)
C(25)–O(6)	1.139(5)		
S(1)–Fe–C(1)	44.8(1)	S(1)–Fe–P(1)	93.0(1)
S(1)–Fe–P(2)	89.0(1)	S(1)–Fe–C(14)	115.1(1)
S(1)–Fe–C(15)	141.9(1)	C(1)–Fe–P(1)	93.2(1)
C(1)–Fe–P(2)	91.7(1)	C(1)–Fe–C(14)	160.0(2)
C(1)–Fe–C(15)	96.2(2)	P(1)–Fe–P(2)	174.7(1)
P(1)–Fe–C(14)	86.9(1)	P(1)–Fe–C(15)	90.2(1)
P(2)–Fe–C(14)	87.9(1)	P(2)–Fe–C(15)	91.4(1)
C(14)–Fe–C(15)	103.8(2)	Fe–S(1)–C(1)	54.6(1)
Fe–C(1)–S(1)	80.6(1)	Fe–C(1)–S(2)	139.7(2)
S(1)–C(1)–S(2)	139.7(2)	C(1)–S(2)–Cr	120.3(1)
Fe–C(14)–O(1)	177.2(3)	Fe–C(15)–O(2)	175.9(4)
S(2)–Cr–P(3)	92.9(1)	S(2)–Cr–C(22)	172.2(2)
S(2)–Cr–C(23)	88.5(1)	S(2)–Cr–C(24)	96.2(1)
S(2)–Cr–C(25)	87.5(1)	P(3)–Cr–C(22)	93.5(1)
P(3)–Cr–C(23)	179.1(1)	P(3)–Cr–C(24)	90.0(1)
P(3)–Cr–C(25)	89.7(1)	C(22)–Cr–C(23)	85.9(2)
C(22)–Cr–C(24)	89.0(2)	C(22)–Cr–C(25)	87.3(2)
C(23)–Cr–C(24)	89.3(2)	C(23)–Cr–C(25)	90.9(2)
C(24)–Cr–C(25)	176.3(2)	Cr–C(22)–O(3)	176.3(4)
Cr–C(23)–O(4)	176.3(3)	Cr–C(24)–O(5)	174.8(3)
Cr–C(25)–O(6)	175.0(3)		



IR and <sup>1</sup>H NMR spectroscopy. Vibrational analysis of the IR spectra points towards a *cis* disposition of the phosphine and  $\text{CS}_2$  ligands at the Group 6 metal centre. It is presumed that the reaction occurs by way of a simple attack of  $\text{PEt}_3$  on  $[(\text{PEt}_3)_2(\text{CO})_2\text{Fe}(\mu\text{-}\eta^2\text{:}\eta^1\text{-CS}_2)\text{M}(\text{CO})_4(\text{thf})]$ , the latter formed by photosubstitution of a carbonyl group by thf. Definitive characterisation of  $[(\text{PEt}_3)_2(\text{CO})_2\text{Fe}(\mu\text{-}\eta^2\text{:}\eta^1\text{-CS}_2)\text{Cr}(\text{CO})_4(\text{PEt}_3)]$  **9a** was made by a single-crystal X-ray diffraction study (Fig. 4). Selected bond lengths and angles are given in Table 3.

The bonding around the iron centre in **9a** is unaffected by the phosphine substitution at chromium. As in **7b** and **8a**, the disulfide unit forms a  $\pi$  bond to iron and a  $\sigma$  bond to the Group 6 metal. The C(1)–S(1) and C(1)–S(2) bond lengths are not significantly different at the  $3\sigma$  level. By extending the currently accepted theory for bonding of  $\text{CS}_2$  to transition metals,<sup>8</sup> a possible explanation for the similarity in C(1)–S(1) and C(1)–S(2) bond lengths may be forwarded. The good  $\pi$ -accepting properties of the  $\pi$ -co-ordinating  $\text{CS}_2$  ligand are explained in terms of three modes of interaction. Initially the  $\pi^*$  orbitals on the  $\pi$ -co-ordinated C–S bond accept electron density from the metal centre. This is augmented by  $\pi$  acceptance by the d orbitals of the co-ordinated sulfur from the metal in a  $d_\pi\text{-}d_\pi$  interaction and by  $\pi^*$  orbitals of the unco-ordinated C–S bond which lies perpendicular to the *xy* plane and is able to accept electron density from the filled  $d_{xz}$  and  $d_{yz}$  orbitals on the metal. These three interactions result in lengthening of both the C–S co-ordinated and C–S unco-ordinated bonds as is seen in

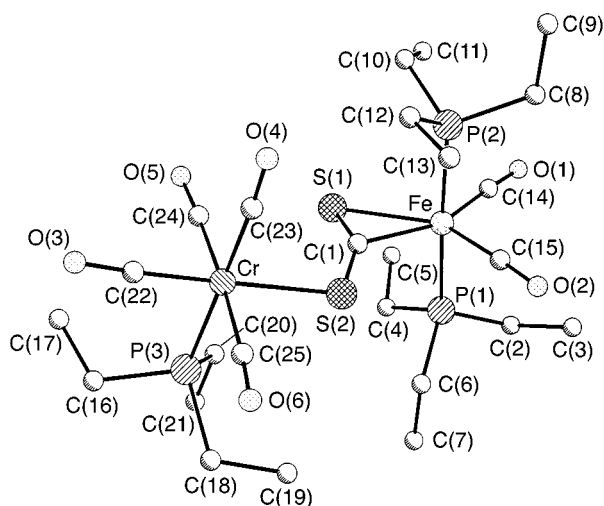


Fig. 4 The molecular structure of  $[(\text{PEt}_3)_2(\text{CO})_2\text{Fe}(\mu\text{-}\eta^2:\eta^1\text{-CS}_2)\text{Cr}(\text{CO})_4(\text{PEt}_3)]$  **9a**

$[\text{Fe}(\text{CO})_2(\text{PMe}_3)(\text{PPh}_3)(\eta^2\text{-CS}_2)]$ ,<sup>10</sup> where the bond lengths for co-ordinated and unco-ordinated C–S bonds are 1.676 and 1.615 Å, respectively (*cf.* C–S bond length of 1.56 Å in free  $\text{CS}_2$ <sup>31</sup>). On donation from the unco-ordinated sulfur, as seen in **3a**, to osmium, as seen in **8a**, back-donation from the iron centre to the  $\pi^*$  orbitals of the C–S bond to osmium is increased and that to the  $\pi^*$  set of the C–S bond to iron decreased. Overall this gives an increase in the electron density donated to the orbitals related to the C–S bond to osmium and hence a lengthening of that bond, this equating the two C–S bond lengths. Alternatively, there may be some donation from filled non-bonding orbitals on the sulfur co-ordinated to the iron to the  $\pi^*$  orbitals of the C–S bond to osmium. This would increase the strength of the bond co-ordinated to iron and decrease that of the other.

This confirms the postulation made for **8a** that donation from the unco-ordinated sulfur of a  $\pi$   $\text{CS}_2$  ligand to a metal centre surrounded by good  $\pi$ -acceptor ligands removes electron density from the sulfur leaving it relatively  $\delta^+$ . This leads to an electron drift towards that sulfur from the carbon of the disulfide unit. To compensate for this either back donation from iron to  $\pi^*$  orbitals of the C(1)–S(1) bond is reduced or electron density is donated from the filled non-bonding orbitals S(1) to C(1). This increases the carbene character of the Fe(1)–C(1) bond; this being less marked in **9a** [Fe(1)–C(1) = 1.934(3) Å] as compared to **8a**.

Of interest is the *cis* disposition of the  $\text{CS}_2$  and  $\text{PEt}_3$  ligands at the Cr centre in **9a**. Steric arguments would favour a *trans* arrangement as is observed in all the crystallographically characterised  $\text{S-Cr}(\text{CO})_4\text{-P}$  fragments published to date<sup>32</sup> with the exception of those with a bidentate S–P containing ligand where *cis* geometry is forced. However, the *cis* disposition of the S and P ligands about the metal centre has the advantage that these  $\sigma$ -donor ligands are then both *trans* to  $\pi$ -accepting carbonyls. This has a co-operative effect, the strength of the M–S and M–P bonds being increased as does that of the *trans* situated carbonyl groups.

The phosphine-substituted complexes  $[(\text{PEt}_3)_2(\text{CO})_2\text{Fe}(\mu\text{-}\eta^2:\eta^1\text{-CS}_2)\text{M}(\text{CO})_4(\text{PEt}_3)]$  can also be prepared thermally. In refluxing methanol,  $[(\text{PEt}_3)_2(\text{CO})_2\text{Fe}(\mu\text{-}\eta^2:\eta^1\text{-CS}_2)\text{M}(\text{CO})_5]$  reacts with  $\text{PEt}_3$  to give moderate yields of  $[(\text{PEt}_3)_2(\text{CO})_2\text{Fe}(\mu\text{-}\eta^2:\eta^1\text{-CS}_2)\text{M}(\text{CO})_4(\text{PEt}_3)]$  (**9a** or **10b**) together with  $[\text{Fe}(\text{CO})_2(\text{PEt}_3)_2(\eta^2\text{-CS}_2)]$  **3a**. The reaction times varied from 2½ h for Cr to 54 h for W, this being a measure of the relative kinetic stability of the reactants. For thermolysis, like photolysis, the reaction must be performed in a co-ordinating solvent; reaction in refluxing hexane leads to decomposition. This is a situation where photolysis is the synthetic method of

choice for substitution since yields are higher and reaction times shorter. This gives credence to our assertion that photochemistry not only offers a route to novel complexes but also to known products both faster and in higher yields than the analogous thermolytic pathways.

## Conclusion

Photochemistry has been used to generate a number of hetero-bimetallic complexes containing  $\pi + \sigma$   $\text{CS}_2$  bridging groups. Unlike thermolysis reactions in which often the  $\text{CS}_2$  moiety is broken, in the case of photolysis the  $\text{CS}_2$  unit remains intact. Broad-band UV photolysis of thf solutions of  $[\text{M}(\text{CO})_6]$  ( $\text{M} = \text{Cr}, \text{Mo}$  or  $\text{W}$ ) and acetonitrile solutions of  $[\text{Os}_3(\text{CO})_{12}]$  with  $[\text{Fe}(\text{CO})_2(\text{PR}_3)_2(\eta^2\text{-CS}_2)]$  ( $\text{R} = \text{Et}$  **3a** or  $\text{Ph}$  **3b**) leads to the formation of the bimetallic complexes  $[(\text{PR}_3)_2(\text{CO})_2\text{Fe}(\mu\text{-}\eta^2:\eta^1\text{-CS}_2)\text{M}(\text{CO})_5]$  ( $\text{R} = \text{Et}$ ,  $\text{M} = \text{Cr}$  **5a**,  $\text{Mo}$  **6a** or  $\text{W}$  **7a**;  $\text{R} = \text{Ph}$ ,  $\text{M} = \text{Cr}$  **5b**,  $\text{Mo}$  **6b** or  $\text{W}$  **7b**) and  $[(\text{PR}_3)_2(\text{CO})_2\text{Fe}(\mu\text{-}\eta^2:\eta^1\text{-CS}_2)\text{Os}_3(\text{CO})_{11}]$  ( $\text{R} = \text{Et}$  **3a** or  $\text{Ph}$  **3b**) respectively. The reaction chemistry of  $[(\text{PEt}_3)_2(\text{CO})_2\text{Fe}(\mu\text{-}\eta^2:\eta^1\text{-CS}_2)\text{M}(\text{CO})_5]$  (**5a–7a**) has been investigated and it is found that these complexes are not susceptible to nucleophilic attack either at the  $\text{CS}_2$  moiety or at the Group 6 metal centre. Broad-band UV photolysis of a thf solution of  $[(\text{PEt}_3)_2(\text{CO})_2\text{Fe}(\mu\text{-}\eta^2:\eta^1\text{-CS}_2)\text{M}(\text{CO})_5]$  (**5a–7a**) with  $\text{PEt}_3$  leads to the formation of the phosphine-substituted complexes  $[(\text{PPh}_3)_2(\text{CO})_2\text{Fe}(\mu\text{-}\eta^2:\eta^1\text{-CS}_2)\text{M}(\text{CO})_4(\text{PEt}_3)]$  ( $\text{M} = \text{Cr}$  **9a** or  $\text{Mo}$  **10b**).

## Experimental

### General

Unless stated otherwise, all syntheses were performed under an inert atmosphere of dry nitrogen using standard Schlenk techniques. All photochemical reactions were performed in a specially designed glass reaction vessel fitted with a nitrogen bubbler, reflux condenser and dry-ice cooling finger. A 125 W mercury arc broad-band UV lamp was used as the irradiation source and reflectors placed around the reaction vessel to maximise efficiency. The reaction mixtures were maintained at low temperature by means of a dry-ice cooling finger. Routine separation of products was performed by thin-layer chromatography (TLC), using commercially prepared glass plates, pre-coated to a thickness of 0.25 mm with Merck Kieselgel 60  $\text{F}_{254}$  as supplied by Merck. Alternatively laboratory prepared glass plates, coated to a thickness of 1.0 mm with Merck Kieselgel 60  $\text{F}_{254}$ , were used. All reagents were purchased from commercial sources and used as received unless noted otherwise. Literature methods were used to prepare  $[\text{Os}_3(\text{CO})_{12}]$ .<sup>33</sup>

### Physical measurements

Infrared spectra were recorded using a Perkin-Elmer PE 1710 Fourier-transform infrared spectrometer, solution spectra in NaCl solution cells (path length 0.5 mm) and solid-state spectra in compressed KBr pellets. All values quoted are in wavenumbers ( $\text{cm}^{-1}$ ). The  $^1\text{H}$  NMR spectra were recorded using Bruker AM400, WM250 or WP80SY Fourier-transform NMR spectrometers and data reported using the chemical shift scale in units of ppm relative to the solvent resonance. Fast atom bombardment (FAB) mass spectra were recorded using a KRATOS MS-50 spectrometer, with either 3-nitrobenzyl alcohol or thioglycerol as a matrix and CsI as calibrant. Microanalyses were performed by the Department of Chemistry microanalysis section. Infrared and NMR data are collected in Table 4 and yields, mass spectral and microanalytical data in Table 5.

### Photolyses

**[Fe(CO)<sub>5</sub>] 1 with CS<sub>2</sub> in thf.** A thf solution of  $[\text{Fe}(\text{CO})_5]$  **1**

**Table 4** Infrared and NMR data for the carbon disulfide complexes

Compound	$\nu(\text{CO})^a/\text{cm}^{-1}$	$\nu(\text{CS})^b/\text{cm}^{-1}$	$\delta(\text{H})^c$
<b>3a</b> $[\text{Fe}(\text{CO})_2(\text{PEt}_3)_2(\eta^2\text{-CS}_2)]$	1982s, 1921vs	1116	1.60 (m, CH <sub>2</sub> ), 1.18 (m, CH <sub>3</sub> )
<b>3b</b> $[\text{Fe}(\text{CO})_2(\text{PPh}_3)_2(\eta^2\text{-CS}_2)]$	1992s, 1932vs	1143	7.55 (m, Ph)
<b>4a</b> $[\text{Fe}(\text{CO})_2(\text{PEt}_3)_2(\eta^2\text{-CS}_2\text{Me})]^+$	2035s, 1973vs	1140	3.13 (s, SCH <sub>3</sub> ), 1.64 (m, CH <sub>2</sub> ), 1.12 (m, CH <sub>3</sub> )
<b>5a</b> $[(\text{PEt}_3)_2(\text{CO})_2\text{Fe}(\mu\text{-}\eta^2\text{:}\eta^1\text{-CS}_2)\text{Cr}(\text{CO})_5]$	2054m, 1996s, 1982s, 1934 (sh), 1926vs, 1879m	1132	1.67 (m, CH <sub>2</sub> ), 1.21 (m, CH <sub>3</sub> )
<b>6a</b> $[(\text{PEt}_3)_2(\text{CO})_2\text{Fe}(\mu\text{-}\eta^2\text{:}\eta^1\text{-CS}_2)\text{Mo}(\text{CO})_5]$	2064m, 1996s, 1981s, 1933 (sh), 1928vs, 1885m	1131	1.70 (m, CH <sub>2</sub> ), 1.18 (m, CH <sub>3</sub> )
<b>7a</b> $[(\text{PEt}_3)_2(\text{CO})_2\text{Fe}(\mu\text{-}\eta^2\text{:}\eta^1\text{-CS}_2)\text{W}(\text{CO})_5]$	2062m, 1999s, 1983s, 1935 (sh), 1920vs, 1880m	1111	1.68 (m, CH <sub>2</sub> ), 1.19 (m, CH <sub>3</sub> )
<b>5b</b> $[(\text{PPh}_3)_2(\text{CO})_2\text{Fe}(\mu\text{-}\eta^2\text{:}\eta^1\text{-CS}_2)\text{Cr}(\text{CO})_5]$	2055m, 2002m, 1982s, 1940 (sh), 1928s, 1884s	<sup>d</sup>	7.45 (m, Ph)
<b>6b</b> $[(\text{PPh}_3)_2(\text{CO})_2\text{Fe}(\mu\text{-}\eta^2\text{:}\eta^1\text{-CS}_2)\text{Mo}(\text{CO})_5]$	2069m, 2005m, 1984s, 1948 (sh), 1923s, 1884s	<sup>d</sup>	7.60 (m, Ph)
<b>7b</b> $[(\text{PPh}_3)_2(\text{CO})_2\text{Fe}(\mu\text{-}\eta^2\text{:}\eta^1\text{-CS}_2)\text{W}(\text{CO})_5]$	2064m, 2004m, 1986s, 1943 (sh), 1926s, 1887s	1141	7.45 (m, Ph)
<b>8a</b> $[(\text{PEt}_3)_2(\text{CO})_2\text{Fe}(\mu\text{-}\eta^2\text{:}\eta^1\text{-CS}_2)\text{Os}_3(\text{CO})_{11}]$	2098w, 2045s, 2027m, 2009s, 1998 (sh), 1986w, 1977m, 1964w, 1949m	1099	1.77 (m, CH <sub>2</sub> ), 1.18 (m, CH <sub>3</sub> )
<b>8b</b> $[(\text{PPh}_3)_2(\text{CO})_2\text{Fe}(\mu\text{-}\eta^2\text{:}\eta^1\text{-CS}_2)\text{Os}_3(\text{CO})_{11}]$	2098w, 2044s, 2023m, 2008s, 2002 (sh), 1974w, 1964m, 1940m	1129	7.47 (m, Ph)
<b>9a</b> $[(\text{PEt}_3)_2(\text{CO})_2\text{Fe}(\mu\text{-}\eta^2\text{:}\eta^1\text{-CS}_2)\text{Cr}(\text{CO})_4(\text{PEt}_3)]$	2003 (sh), 2000w, 1990s, 1934m, 1900m, 1889s, 1864s	<sup>d</sup>	1.72 (m, CH <sub>2</sub> ), 1.12 (m, CH <sub>3</sub> )
<b>10a</b> $[(\text{PEt}_3)_2(\text{CO})_2\text{Fe}(\mu\text{-}\eta^2\text{:}\eta^1\text{-CS}_2)\text{Mo}(\text{CO})_4(\text{PEt}_3)]$	2010 (sh), 2008w, 1991s, 1924m, 1900m, 1889s, 1865s	<sup>d</sup>	1.69 (m, CH <sub>2</sub> ), 1.15 (m, CH <sub>3</sub> )
<b>11a</b> $[(\text{PEt}_3)_2(\text{CO})_2\text{Fe}(\mu\text{-}\eta^2\text{:}\eta^1\text{-CS}_2)\text{W}(\text{CO})_4(\text{PEt}_3)]$	2010 (sh), 2005w, 1990s, 1934s, 1897m, 1886s, 1861s	<sup>d</sup>	1.70 (m, CH <sub>2</sub> ), 1.09 (m, CH <sub>3</sub> )

<sup>a</sup> Hexane solution. <sup>b</sup> Nujol mull. <sup>c</sup> In CDCl<sub>3</sub>. <sup>d</sup> Not unambiguously assigned.

**Table 5** Yields, mass spectral and microanalytical data for the carbon disulfide complexes

Compound	Yield (%)	<i>m/z</i>	Analyses <sup>a</sup> (%)			
			C	H	P	S
<b>3a</b> $[\text{Fe}(\text{CO})_2(\text{PEt}_3)_2(\eta^2\text{-CS}_2)]$	80	424	—	—	—	—
<b>3b</b> $[\text{Fe}(\text{CO})_2(\text{PPh}_3)_2(\eta^2\text{-CS}_2)]$	75	712	—	—	—	—
<b>4a</b> $[\text{Fe}(\text{CO})_2(\text{PEt}_3)_2(\eta^2\text{-CS}_2\text{Me})]^+$	95	—	—	—	—	—
<b>5a</b> $[(\text{PEt}_3)_2(\text{CO})_2\text{Fe}(\mu\text{-}\eta^2\text{:}\eta^1\text{-CS}_2)\text{Cr}(\text{CO})_5]$	65	616	39.17 (38.97)	4.97 (4.91)	10.32 (10.05)	10.09 (10.40)
<b>6a</b> $[(\text{PEt}_3)_2(\text{CO})_2\text{Fe}(\mu\text{-}\eta^2\text{:}\eta^1\text{-CS}_2)\text{Mo}(\text{CO})_5]$	60	622	36.61 (36.38)	4.75 (4.58)	9.22 (9.38)	10.91 (9.71)
<b>7a</b> $[(\text{PEt}_3)_2(\text{CO})_2\text{Fe}(\mu\text{-}\eta^2\text{:}\eta^1\text{-CS}_2)\text{W}(\text{CO})_5]$	50	750	31.91 (32.11)	4.06 (4.04)	8.39 (8.28)	8.51 (8.57)
<b>5b</b> $[(\text{PPh}_3)_2(\text{CO})_2\text{Fe}(\mu\text{-}\eta^2\text{:}\eta^1\text{-CS}_2)\text{Cr}(\text{CO})_5]$	60	<i>b</i>	59.10 (58.42)	3.41 (3.34)	6.14 (6.85)	7.62 (7.09)
<b>6b</b> $[(\text{PPh}_3)_2(\text{CO})_2\text{Fe}(\mu\text{-}\eta^2\text{:}\eta^1\text{-CS}_2)\text{Mo}(\text{CO})_5]$	50	<i>b</i>	56.47 (55.71)	3.42 (3.19)	6.59 (6.53)	6.94 (6.76)
<b>7b</b> $[(\text{PPh}_3)_2(\text{CO})_2\text{Fe}(\mu\text{-}\eta^2\text{:}\eta^1\text{-CS}_2)\text{W}(\text{CO})_5]$	50	<i>b</i>	51.05 (50.99)	2.87 (2.92)	6.07 (5.98)	5.63 (6.19)
<b>8a</b> $[(\text{PEt}_3)_2(\text{CO})_2\text{Fe}(\mu\text{-}\eta^2\text{:}\eta^1\text{-CS}_2)\text{Os}_3(\text{CO})_{11}]$	80	<i>b</i>	22.91 (23.97)	2.40 (2.32)	4.56 (4.75)	4.48 (4.92)
<b>8b</b> $[(\text{PPh}_3)_2(\text{CO})_2\text{Fe}(\mu\text{-}\eta^2\text{:}\eta^1\text{-CS}_2)\text{Os}_3(\text{CO})_{11}]$	50	<i>b</i>	38.05 (37.74)	2.07 (1.90)	3.95 (3.89)	4.06 (4.03)
<b>9a</b> $[(\text{PEt}_3)_2(\text{CO})_2\text{Fe}(\mu\text{-}\eta^2\text{:}\eta^1\text{-CS}_2)\text{Cr}(\text{CO})_4(\text{PEt}_3)]$	60 <sup>c</sup> /18 <sup>d</sup>	<i>b</i>	—	—	—	—
<b>10a</b> $[(\text{PEt}_3)_2(\text{CO})_2\text{Fe}(\mu\text{-}\eta^2\text{:}\eta^1\text{-CS}_2)\text{Mo}(\text{CO})_4(\text{PEt}_3)]$	50 <sup>c</sup> /21 <sup>d</sup>	<i>b</i>	—	—	—	—
<b>11a</b> $[(\text{PEt}_3)_2(\text{CO})_2\text{Fe}(\mu\text{-}\eta^2\text{:}\eta^1\text{-CS}_2)\text{W}(\text{CO})_4(\text{PEt}_3)]$	40 <sup>c</sup> /10 <sup>d</sup>	<i>b</i>	—	—	—	—

<sup>a</sup> Calculated values in parentheses. <sup>b</sup> Decomposes in mass spectrometer. <sup>c</sup> Photochemical. <sup>d</sup> Thermochemical.

(1 ml in 150 ml) containing excess CS<sub>2</sub> (1 ml) was irradiated using the broad-band UV source, the reaction mixture maintained at low temperature by means of the dry-ice cooling finger. A brown precipitate was formed, this being insoluble in common organic solvents and consequently characterisation of the photolysis products was not possible.

**[Fe(CO)<sub>3</sub>(PR<sub>3</sub>)<sub>2</sub>] (R = Et **2a** or Ph **2b**) with CS<sub>2</sub> in dichloromethane.** In a typical reaction, a dichloromethane solution of [Fe(CO)<sub>3</sub>(PR<sub>3</sub>)<sub>2</sub>] (R = Et **2a** or Ph **2b**) (30 mg in 150 ml) containing excess CS<sub>2</sub> (1 ml) was irradiated (3 h) using the broad-band UV source. From comparison with literature data<sup>7</sup> it was proposed that the yellow complex [Fe(CO)<sub>3</sub>(PR<sub>3</sub>)<sub>2</sub>(η<sup>2</sup>-CS<sub>2</sub>)] (R = Et **3a** or Ph **3b**) was formed. The product was purified by TLC (diethyl ether–hexane, 20:80, as eluent).

**[Fe(CO)<sub>3</sub>(PEt<sub>3</sub>)<sub>2</sub>(η<sup>2</sup>-CS<sub>2</sub>)] **3a** with methyl iodide in dichloromethane.** A dichloromethane solution of [Fe(CO)<sub>3</sub>(PEt<sub>3</sub>)<sub>2</sub>(CS<sub>2</sub>)] (30 mg in 100 ml) was stirred with methyl iodide (1 ml) at room temperature for 2 h. The product [Fe(CO)<sub>3</sub>(PEt<sub>3</sub>)<sub>2</sub>(η<sup>2</sup>-CS<sub>2</sub>Me)]<sup>+</sup> was obtained as an orange crystalline material on addition of hexane.

**[M(CO)<sub>6</sub>] (M = Cr, Mo or W) with [Fe(CO)<sub>3</sub>(PR<sub>3</sub>)<sub>2</sub>(η<sup>2</sup>-CS<sub>2</sub>)] (R = Me **3a** or Ph **3b**) in thf.** In a typical reaction, a thf solution

of [M(CO)<sub>6</sub>] (30 mg in 150 ml) containing a stoichiometric equivalent of [Fe(CO)<sub>3</sub>(PR<sub>3</sub>)<sub>2</sub>(η<sup>2</sup>-CS<sub>2</sub>)] (**3a** or **3b**) was irradiated (4 h) using the broad-band UV source. From analysis of the spectral data it was proposed that the yellow complex [(PR<sub>3</sub>)<sub>2</sub>(CO)<sub>2</sub>Fe(μ-η<sup>2</sup>:η<sup>1</sup>-CS<sub>2</sub>)M(CO)<sub>5</sub>] was formed. The product was purified by TLC (diethyl ether–hexane, 15:85, as eluent).

**[Os<sub>3</sub>(CO)<sub>12</sub>] with [Fe(CO)<sub>3</sub>(PR<sub>3</sub>)<sub>2</sub>(η<sup>2</sup>-CS<sub>2</sub>)] (R = Me **3a** or Ph **3b**) in acetonitrile.** In a typical reaction, an acetonitrile solution of [Os<sub>3</sub>(CO)<sub>12</sub>] (40 mg in 150 ml) containing a stoichiometric equivalent of [Fe(CO)<sub>3</sub>(PR<sub>3</sub>)<sub>2</sub>(η<sup>2</sup>-CS<sub>2</sub>)] (**3a** or **3b**) was irradiated (4 h) using the broad-band UV source. From analysis of the spectral data it was proposed that the dark red complex [(PR<sub>3</sub>)<sub>2</sub>(CO)<sub>2</sub>Fe(μ-η<sup>2</sup>:η<sup>1</sup>-CS<sub>2</sub>)Os<sub>3</sub>(CO)<sub>11</sub>] (**8a** or **8b**) was formed. The product was purified by TLC (dichloromethane–hexane, 20:80, as eluent).

**[(PEt<sub>3</sub>)<sub>2</sub>(CO)<sub>2</sub>Fe(μ-η<sup>2</sup>:η<sup>1</sup>-CS<sub>2</sub>)M(CO)<sub>5</sub>] (M = Cr **5a**, Mo **6a** or W **7a**) with PEt<sub>3</sub> in thf.** A thf solution of [(PEt<sub>3</sub>)<sub>2</sub>(CO)<sub>2</sub>Fe(μ-η<sup>2</sup>:η<sup>1</sup>-CS<sub>2</sub>)M(CO)<sub>5</sub>] (**5a**, **6a** or **7a**) (30 mg in 150 ml) containing excess PEt<sub>3</sub> (1 ml) was irradiated (2 h) using the broad-band UV source. From analysis of the spectral data it was proposed that the orange complex [(PEt<sub>3</sub>)<sub>2</sub>(CO)<sub>2</sub>Fe(μ-η<sup>2</sup>:η<sup>1</sup>-CS<sub>2</sub>)M(CO)<sub>4</sub>(PEt<sub>3</sub>)] was formed. The product was purified by TLC (diethyl ether–hexane, 20:80, as eluent).

**Table 6** Crystal data and structure refinement parameters for [(PPh<sub>3</sub>)<sub>2</sub>(CO)<sub>2</sub>Fe(μ-η<sup>2</sup>:η<sup>1</sup>-CS<sub>2</sub>)W(CO)<sub>5</sub>] **7b**, [(PEt<sub>3</sub>)<sub>2</sub>(CO)<sub>2</sub>Fe(μ-η<sup>2</sup>:η<sup>1</sup>-CS<sub>2</sub>)Os<sub>3</sub>(CO)<sub>11</sub>] **8a** and [(PEt<sub>3</sub>)<sub>2</sub>(CO)<sub>2</sub>Fe(μ-η<sup>2</sup>:η<sup>1</sup>-CS<sub>2</sub>)Cr(CO)<sub>4</sub>(PEt<sub>3</sub>)] **9a**<sup>a</sup>

Compound	<b>7b</b>	<b>8a</b>	<b>9a</b>
Molecular formula	C <sub>44</sub> H <sub>30</sub> FeO <sub>7</sub> P <sub>2</sub> S <sub>2</sub> W	C <sub>26</sub> H <sub>30</sub> FeO <sub>13</sub> Os <sub>3</sub> P <sub>2</sub> S <sub>2</sub>	C <sub>25</sub> H <sub>45</sub> CrFeO <sub>6</sub> P <sub>3</sub> S <sub>2</sub>
<i>M</i>	1036.62	1304.23	704.45
Crystal habit	Yellow needles	Dark brown needles	Orange blocks
Crystal size/mm	0.38 × 0.19 × 0.11	0.23 × 0.16 × 0.14	0.27 × 0.24 × 0.23
<i>a</i> /Å	12.024(3)	10.496(3)	8.522(3)
<i>b</i> /Å	13.029(4)	13.532(4)	12.320(4)
<i>c</i> /Å	16.412(5)	14.625(5)	18.386(6)
<i>α</i> /°	101.47(3)	89.19(3)	102.09(3)
<i>β</i> /°	103.46(3)	74.11(3)	99.88(3)
<i>γ</i> /°	115.70(3)	72.55(3)	106.53(3)
<i>U</i> /Å <sup>3</sup>	2117	1901	1754
<i>Z</i>	2	2	2
<i>D<sub>c</sub></i> /Mg m <sup>-3</sup>	1.626	2.278	1.334
<i>F</i> (000)	1024	1212	740
μ/mm <sup>-1</sup>	3.297	10.590	0.962
Maximum, minimum transmission	0.948, 0.779	0.931, 0.451	0.577, 0.551
Index ranges	-14 ≤ <i>h</i> ≤ 14, -16 ≤ <i>k</i> ≤ 16, 0 ≤ <i>l</i> ≤ 20	-10 ≤ <i>h</i> ≤ 11, -16 ≤ <i>k</i> ≤ 17, 0 ≤ <i>l</i> ≤ 18	-8 ≤ <i>h</i> ≤ 8, -15 ≤ <i>k</i> ≤ 15, 0 ≤ <i>l</i> ≤ 23
Reflections measured	4687	3354	4825
Independent reflections ( <i>R</i> <sub>int</sub> )	4175 (0.0167)	3015 (0.0076)	4138 (0.0054)
Parameters, restraints	257, 8	299, 0	344, 0
<i>R</i> 1 <sup>b</sup>	0.0590	0.0512	0.0337
<i>wR</i> 1 <sup>b</sup>	0.0589	0.0467	0.0347
<i>P</i> <sup>b</sup>	0.001	0.000	0.0003
Observed reflections	3769 [ <i>F</i> > 4σ( <i>F</i> )]	2436 [ <i>F</i> > 4σ( <i>F</i> )]	4059 [ <i>F</i> > 3σ( <i>F</i> )]
Peak, hole in final difference map/e Å <sup>-3</sup>	1.890, -1.836	1.529, -1.151	0.624, -0.337

<sup>a</sup>Details in common: crystal system triclinic; space group *P* $\bar{1}$  (no. 2); data collection range 3.0 < 2θ < 55.0°. <sup>b</sup>*R*1 = Σ||*F*<sub>o</sub>| - *F*<sub>c</sub>||/Σ|*F*<sub>o</sub>|, *wR*1 = [Σ*w*<sup>2</sup>(||*F*<sub>o</sub>| - |*F*<sub>c</sub>||)/Σ*w*<sup>2</sup>*F*<sub>o</sub>], *w* = 1/[σ<sup>2</sup>(*F*<sub>o</sub>)<sup>2</sup> + *PF*<sup>2</sup>].

### X-Ray crystallography

Structural determinations were undertaken on single crystals of [(PPh<sub>3</sub>)<sub>2</sub>(CO)<sub>2</sub>Fe(μ-η<sup>2</sup>:η<sup>1</sup>-CS<sub>2</sub>)W(CO)<sub>5</sub>] **7b**, [(PEt<sub>3</sub>)<sub>2</sub>(CO)<sub>2</sub>Fe(μ-η<sup>2</sup>:η<sup>1</sup>-CS<sub>2</sub>)Os<sub>3</sub>(CO)<sub>11</sub>] **8a** and [(PEt<sub>3</sub>)<sub>2</sub>(CO)<sub>2</sub>Fe(μ-η<sup>2</sup>:η<sup>1</sup>-CS<sub>2</sub>)Cr(CO)<sub>4</sub>(PEt<sub>3</sub>)] **9a** using X-ray diffraction analyses. All measurements were made at 298 K with graphite-monochromated radiation (λ = 0.71073 Å) in the ω-θ scan mode on a Stoe-Siemens AED diffractometer. Crystal data and data acquisition details are summarised in Table 6. Cell parameters were obtained by least-squares refinement on diffractometer angles from 25 centred reflections (20 < 2θ < 22.5°). Semiempirical absorption corrections based on ψ-scan data were applied for **7b**, **8a** and **9a**.<sup>34</sup>

The structures were solved by direct (**8a** and **9a**) and Patterson methods (**7b**) followed by Fourier-difference syntheses and refined by blocked-cascade (**8a** and **9a**) or full-matrix (**7b**) least-squares fits on *F* (SHELXL 76).<sup>35</sup> All non-hydrogen atoms in **9a**, W, Fe, P, S, and C and O atoms of ordered CO ligands in **7b** and Os, Fe, P, S, and C and O atoms of CO ligands on Fe and some C atoms of Et groups in **8a** were treated anisotropically. Some of the ethyl groups in **8a** were subject to slight thermal libration which could not be described successfully with a two-fold disorder model. The hydrogen atoms were placed in idealised positions and allowed to ride on the relevant carbon atom. In the final cycles of refinement a weighting scheme was introduced which produced a flat analysis of variance. The phenyl rings on the triphenylphosphine moieties in **7b** were refined as rigid groups. The CS<sub>2</sub> group and one of the carbonyl groups in **7b** are disordered over two orientations about the C(1)-S(1) and C(22)-O(22) bonds with relative occupancies 0.67 and 0.33 and were refined isotropically with restraints to the Fe-S(1), Fe-S(1'), Fe-C(1), Fe-C(1'), C(1)-S(2), C(1')-S(2'), Fe-C(22') and C(22')-O(22') distances and thermal parameters of atoms S(1), S(1'), C(1), C(1'), C(22), O(22), C(22'), O(22'). Those atoms of the minor contribution are annotated with a prime ('). As a further check, alternative settings of the cell were checked for the presence of a twin, but no reasonable alternatives could be found. The final

difference syntheses revealed two peaks of weight ≥ 1 e Å<sup>-3</sup> at distances of ca. 1 Å from W in **7b**, these and similar peaks in the vicinity of the Os atoms in **8a** have no chemical significance and may be ascribed to absorption effects.

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