

# The formation and transformation of metallacycles containing phosphorus or sulfur on molybdenum– or tungsten–cobalt mixed-metal backbones‡

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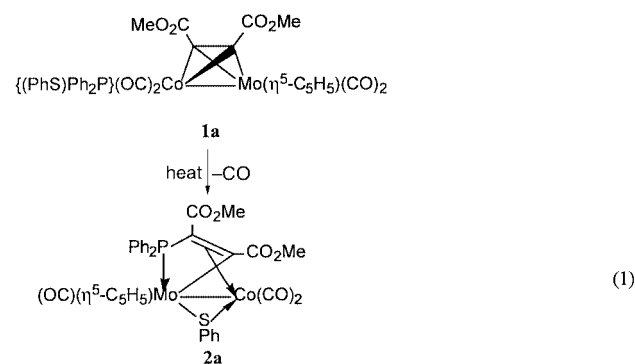
The new heterobimetallic complexes of general formula  $[(R'S)Ph_2P\{(OC)_2Co\{\mu-C_2(CO_2Me)_2\}M(\eta^5-L)(CO)_2\}]$  **1** [ $L = C_5H_5$  or  $C_5Me_5$ ;  $M = Mo$  or  $W$ ;  $R' =$  hydrocarbyl] undergo thermally induced phosphorus–sulfur bond breaking reactions. By variation of the nature of the  $R'$  substituent, the cyclopentadienyl group or the Group 6 metal centre in **1**, bimetallic complexes incorporating bridging four-membered metallacycles of the type  $M-P-C=C$  or  $M-S-C=C$  (where  $M = Co$ ,  $Mo$  or  $W$ ), are accessible. While  $[(PhS)Ph_2P\{(OC)_2Co\{\mu-C_2(CO_2Me)_2\}Mo(\eta^5-C_5H_5)(CO)_2\}]$  **1a** gives as the sole product the phosphorus-containing molybdenacyclic species  $[(OC)(\eta^5-C_5H_5)Mo\{\mu-PPh_2C(CO_2Me)C(CO_2Me)\}(\mu-SPh)Co(CO)_2]$  **2a**, the corresponding reaction of  $[(R'S)Ph_2P\{(OC)_2Co\{\mu-C_2(CO_2Me)_2\}Mo(\eta^5-C_5H_5)(CO)_2\}]$  ( $R' = Bu^n$  **1b**;  $Bu^t$  **1c**), results in the formation of both  $[(OC)(\eta^5-C_5H_5)Mo\{\mu-PPh_2C(CO_2Me)C(CO_2Me)\}(\mu-SR')Co(CO)_2]$  ( $R' = Bu^n$  **2b**;  $Bu^t$  **2c**) and  $[(OC)_2Co\{\mu-SR'C(CO_2Me)C(CO_2Me)\}(\mu-PPh_2)Mo(\eta^5-C_5H_5)(CO)]$  ( $R' = Bu^n$  **3b**;  $Bu^t$  **3c**). The latter sulfur-containing cobaltacyclic species (**3c**) has been shown to isomerise to the phosphorus-containing molybdenacyclic species **2c** on further heating. Conversely, employment of the pentamethylcyclopentadienyl complex  $[(PhS)Ph_2P\{(OC)_2Co\{\mu-C_2(CO_2Me)_2\}Mo(\eta^5-C_5Me_5)(CO)_2\}]$  **1b** gives three species,  $[(OC)(\eta^5-C_5Me_5)Mo\{\mu-PPh_2C(CO_2Me)C(CO_2Me)\}(\mu-SPh)Co(CO)_2]$  **2d** and  $[(OC)_2Co\{\mu-SPhC(CO_2Me)C(CO_2Me)\}(\mu-PPh_2)Mo(\eta^5-C_5Me_5)(CO)]$  **3d**, which are, respectively, analogues of **2a–3c** and **3b**, **3c**, and in addition the phosphorus-containing cobaltacyclic species  $[(OC)_2Co\{\mu-PPh_2C(CO_2Me)C(CO_2Me)\}(\mu-SPh)Mo(\eta^5-C_5Me_5)(CO)]$  **4d**. Thermolysis of  $[(Bu^nS)Ph_2P\{(OC)_2Co\{\mu-C_2(CO_2Me)_2\}W(\eta^5-C_5H_5)(CO)_2\}]$  **1e**, in which a tungsten centre has been introduced in place of the molybdenum in **1b**, affords only sulfur-containing metallacyclic products, which incorporate either the cobalt centre as in  $[(OC)_2Co\{\mu-SBu^nC(CO_2Me)C(CO_2Me)\}(\mu-PPh_2)W(\eta^5-C_5H_5)(CO)]$  **3e** or the tungsten centre as in  $[(OC)(\eta^5-C_5H_5)W\{\mu-SBu^nC(CO_2Me)C(CO_2Me)\}(\mu-PPh_2)Co(CO)_2]$  **5e**. The ‘flyover’ complex  $[(OC)(\eta^5-C_5H_5)W\{\mu-C(CO_2Me)CHC(OMe)O\}(\mu-SPh)Co(CO)\{PPh_2(SPh)\}]$  **6** was the only product obtained from the reaction of  $[(OC)_3Co\{\mu-C_2(CO_2Me)_2\}W(\eta^5-C_5H_5)(CO)_2]$  with  $Ph_2P(SPh)$ . Single crystal X-ray diffraction studies have been performed on complexes **1d**, **2b**, **3c'** [the  $P(OMe)_3$ -substituted derivative of **3c**], **5e** and **6**.

## 1. Introduction

The chemistry of heterobimetallic transition metal carbonyl complexes remains an area of continued interest.<sup>1–5</sup> The presence of two distinct metal centres within the same complex presents possibilities for the study of the relative reactivities of two different metal sites while cooperative interactions between the two metal centres may lead to complexes possessing unique reactivity properties.

We have been investigating the reactivity of Group 6–Group 9 alkyne-bridged carbonyl complexes  $[(OC)_3Co(\mu-C_2R_2)Mo(\eta^5-C_5H_5)(CO)_2]$  ( $R = H$ , aryl or  $CO_2Me$ ) with a variety of substituted phosphine ligands capable of undergoing intraligand bond cleavage.<sup>6,7</sup> In this earlier work we reported the reaction of  $[(OC)_3Co\{\mu-C_2(CO_2Me)_2\}Mo(\eta^5-C_5H_5)(CO)_2]$  with the thiophosphine ligand,  $Ph_2P(SPh)$ . Preferential substitution of a carbonyl group at cobalt by the phosphorus centre of the ligand gave  $[(PhS)Ph_2P\{(OC)_2Co\{\mu-C_2(CO_2Me)_2\}Mo(\eta^5-C_5H_5)(CO)_2\}]$  **1a** and subsequent cleavage of the phosphorus–sulfur bond led to the regio-specific formation of  $[(OC)(\eta^5-C_5H_5)-$

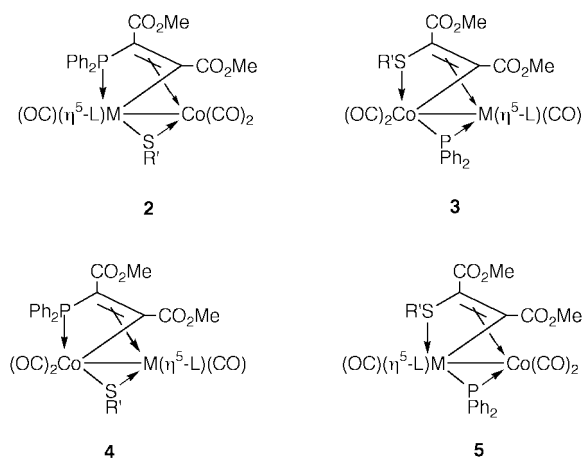
$Mo\{PPh_2C(CO_2Me)C(CO_2Me)\}(\mu-SPh)Co(CO)_2]$  **2a**, in which a  $PPh_2$  fragment had been inserted into a molybdenum–carbon bond in **1a** to form a four-membered molybdenacyclic ring while the  $SPh$  fragment bridged the metal centres (eqn. (1)).<sup>6</sup> The mechanism by which the above transformation occurs and



notably the apparent migration of the  $PPh_2$  fragment from being cobalt-bound in **1a** [as  $Ph_2P(SPh)$ ] to being molybdenum-bound in **2a** is uncertain. Furthermore the incorporation of the  $PPh_2$  rather than the  $SPh$  fragment into the four-membered

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<sup>‡</sup> Supplementary data available: rotatable 3-D crystal structure diagram in CHIME format. See <http://www.rsc.org/suppdata/dt/1999/4447/>



**Fig. 1** Four possible isomeric four-membered metallacyclic ring-bridged structures obtainable from the thermolysis of  $[(R'S)Ph_2P\{(OC)_2Co\{\mu-C_2(CO_2Me)_2\}M(\eta^5-L)(CO)_2\}]$  **1** ( $M = Mo, W$ ;  $L = C_5H_5, C_5Me_5$ ;  $R' = Ph, Bu^a, Bu^t$ ).

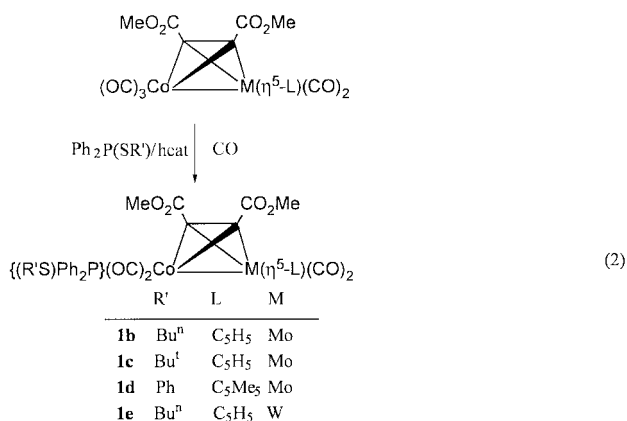
metallacycle was unexpected, given our observations in the related dicobalt chemistry that it is the  $SR'$  rather than the  $PPh_2$  fragment that is preferentially incorporated.<sup>8,9</sup>

In this paper we report the preparation of new Group 6–Group 9 alkyne-bridged complexes of the type  $[(R'S)Ph_2P\{(OC)_2Co\{\mu-C_2(CO_2Me)_2\}M(\eta^5-L)(CO)_2\}]$  ( $M = Mo, W$ ;  $L = C_5H_5, C_5Me_5$ ;  $R' = \text{alkyl}$ ) **1**. It was envisaged that changing the electronic and steric properties of **1** by varying the nature of (i) the substituent  $R'$  on the thiophosphine ligand, (ii) the cyclopentadienyl ligand or (iii) the Group 6 metal centre, could help elucidate the mechanism of formation of **2a** from **1a** (see eqn. (1)) and that thermolysis of the new complexes might also yield other metallacyclic products of the type **3–5** (Fig. 1). This expectation has been realised and we now report that all four of the isomeric four-membered ring-bridged structures shown in Fig. 1 can be obtained.

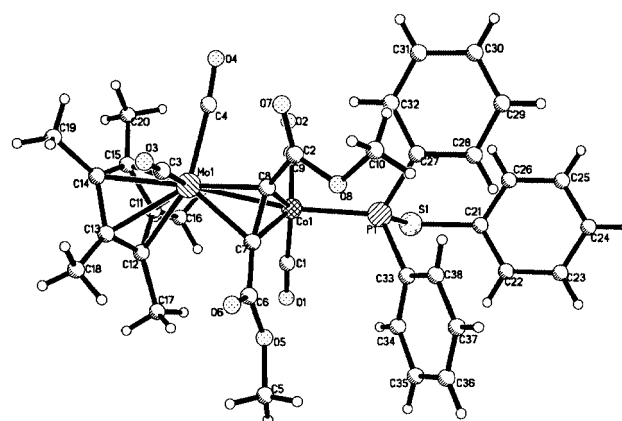
## 2. Results and discussion

### (a) Preparation of $[(R'S)Ph_2P\{(OC)_2Co\{\mu-C_2(CO_2Me)_2\}M(\eta^5-L)(CO)_2\}]$ ( $M = Mo, W$ ; $L = C_5H_5, C_5Me_5$ ; $R' = \text{hydrocarbyl}$ ) **1**

The complexes  $[(R'S)Ph_2P\{(OC)_2Co\{\mu-C_2(CO_2Me)_2\}M(\eta^5-L)(CO)_2\}]$  ( $R' = Bu^a$ ,  $M = Mo$ ,  $L = C_5H_5$  **1b**;  $R' = Bu^t$ ,  $M = Mo$ ,  $L = C_5H_5$  **1c**;  $R' = Ph$ ,  $M = Mo$ ,  $L = C_5Me_5$  **1d**;  $R' = Bu^a$ ,  $M = W$ ,  $L = C_5H_5$  **1e**) have been prepared in high yield from the reaction of  $[(OC)_3Co\{\mu-C_2(CO_2Me)_2\}M(\eta^5-L)(CO)_2]$  with  $Ph_2P(SR')$  at ca. 313 K (eqn. (2)). All the complexes have been



characterised by  $^1H$ ,  $^{13}C$ ,  $^{31}P$  NMR, IR spectroscopy and by mass spectrometry (see Table 1 and Experimental section). Complex **1d** has additionally been the subject of a single crystal X-ray diffraction study.



**Fig. 2** Molecular structure of  $[(PhS)Ph_2P\{(OC)_2Co\{\mu-C_2(CO_2Me)_2\}-Mo(\eta^5-C_5Me_5)(CO)_2\}]$  **1d**.

The molecular structure of **1d** is shown in Fig. 2; Table 2 lists selected bond distances and angles. The structure consists of a  $(OC)_2CoMo(CO)_2$  skeleton which is bridged by an unsaturated alkyne unit  $[\mu-C_2(CO_2Me)_2]$  which lies almost perpendicular to the single Co–Mo bond  $[2.715(1) \text{ \AA}]$ <sup>10,11</sup> in a manner similar to that in a number of previously reported such complexes.<sup>12</sup> The cobalt atom is further coordinated by a  $Ph_2P(SPh)$  ligand, which bonds *via* the phosphorus atom and thus completes a distorted octahedral arrangement about the cobalt centre. The molybdenum atom is additionally coordinated by a pentamethylcyclopentadienyl ligand, again completing a distorted octahedral arrangement about the molybdenum centre. The  $Ph_2P(SPh)$  and the pentamethylcyclopentadienyl groups are orientated in a ‘sawhorse’ configuration about the Co–Mo bond, occupying pseudo-axial sites on each metal centre  $[Mo-Co-P 148.81(7)^\circ, Co-Mo-(C_5Me_5)_{\text{centroid}} 122.1^\circ]$ .

The spectroscopic properties of **1** are all in accord with those of previously reported examples of mono-phosphine substituted Group 6–Group 9 alkyne-bridged complexes.<sup>6,7,12</sup> The pentamethylcyclopentadienyl species **1d** displays slightly lower frequency carbonyl absorption bands in the IR spectrum consistent with better electron donating capability of the  $C_5Me_5$  over the  $C_5H_5$  group.

### (b) Thermolysis of thiophosphine-substituted species **1**

The complexes **1** all undergo thermally induced phosphorus–sulfur bond breaking reactions. By variation of the nature of (i) the  $R'$  group of the coordinated thiophosphine group, (ii) the cyclopentadienyl ligand or (iii) the Group 6 metal centre in **1**, complexes belonging to all the structural types illustrated in Fig. 1 (**2–5**) have been identified.

The ordering of Co and Mo/W in the chemical formulae will, throughout this account, indicate the orientation of the bridging ligand. That is, when the  $\alpha$ -carbon of the substituted alkenyl ligand  $[C(CO_2Me)C(CO_2Me)SR'$  or  $C(CO_2Me)C(CO_2Me)-PPh_2]$  is  $\sigma$ -bonded to Mo/W rather than Co, then Mo/W will precede Co in the ordering of the formula and *vice versa*.

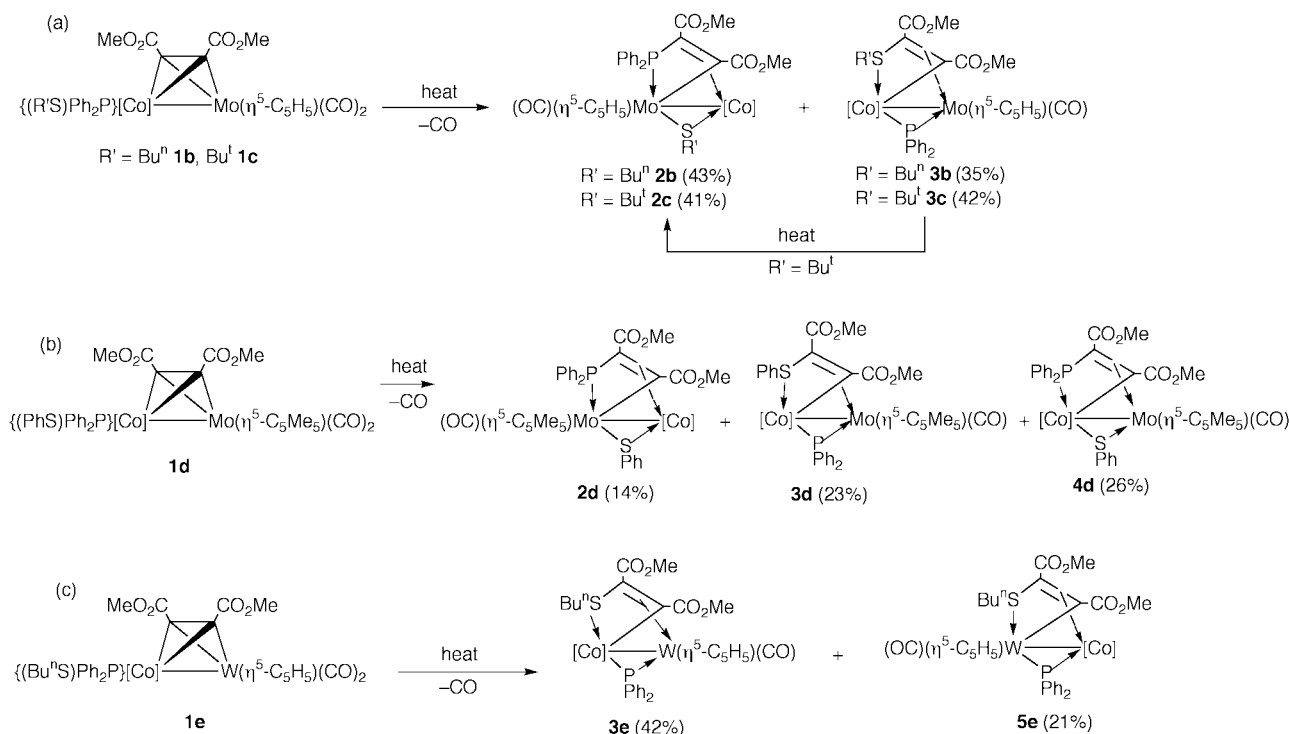
**(i) Variation of the  $R'$  group.** The thermolysis of  $[(OC)_2(\eta^5-C_5H_5)Mo\{\mu-C_2(CO_2Me)_2\}Co(CO)_2\{PPh_2(SR')\}]$  ( $R' = Bu^a$  **1b**;  $Bu^t$  **1c**) in toluene at 363 K gives  $[(OC)(\eta^5-C_5H_5)Mo\{\mu-PPh_2C(CO_2Me)C(CO_2Me)\}(\mu-SR')Co(CO)_2]$  ( $R' = Bu^a$  **2b**;  $Bu^t$  **2c**) and  $[(OC)_2Co\{\mu-SR'C(CO_2Me)C(CO_2Me)\}(\mu-PPh_2)-Mo(\eta^5-C_5H_5)(CO)]$  ( $R' = Bu^a$  **3b**;  $Bu^t$  **3c**) respectively in high combined yield (Scheme 1a). These complexes have been characterised by  $^1H$ ,  $^{13}C$ ,  $^{31}P$  NMR and IR spectroscopy, mass spectrometry and by microanalysis (see Table 1 and Experimental section). In addition complex **2b** has been the subject of a single crystal X-ray diffraction study.

The molecular structure of complex **2b** including the atom numbering scheme is depicted in Fig. 3 and selected bond dis-

**Table 1** Infrared,  $^1\text{H}$  and  $^{31}\text{P}$  NMR data for the new complexes **1–6**

| Compound   | $\nu(\text{CO})^a/\text{cm}^{-1}$         | $^1\text{H}$ NMR ( $\delta$ ) <sup>c</sup>  | $^{31}\text{P}$ NMR ( $\delta$ ) <sup>d</sup>                              |
|------------|---|---|--|
| <b>1b</b>  | 2031m, 2001vs, 1975s, 1705m               | 7.9–7.2 [m, 10H, Ph], 5.36 [s, 5H, $\text{C}_5\text{H}_5$ ], 3.34 [s, 6H, $(\text{CO}_2\text{Me})_2$ ], 2.2–0.7 [s, 9H, $\text{Bu}^n$ ]   | –65.1 [s, Co– $\text{PPh}_2(\text{SBU}^n)$ ]                               |
| <b>1c</b>  | 2030s, 1999vs, 1975s, 1708m               | 7.9–7.0 [m, 10H, Ph], 5.28 [s, 5H, $\text{C}_5\text{H}_5$ ], 3.35 [s, 6H, $(\text{CO}_2\text{Me})_2$ ], 1.28 [s, 9H, $\text{Bu}^t$ ]  | –54.7 [s, Co– $\text{PPh}_2(\text{SBU}^t)$ ]                               |
| <b>1d</b>  | 2018s, 1984s, 1954s, 1693m                | 7.6–6.8 [m, 15H, Ph], 3.43 [s, 6H, $(\text{CO}_2\text{Me})_2$ ], 1.87 [s, 15H, $\text{C}_5\text{Me}_5$ ], 1.23 [s, 9H, $\text{Bu}^t$ ]  | –50.8 [s, Co– $\text{PPh}_2(\text{SPh})$ ]                                 |
| <b>1e</b>  | 2025s, 1991vs, 1962vs, 1694m <sup>b</sup> | 7.6–7.0 [m, 10H, Ph], 5.30 [s, 5H, $\text{C}_5\text{H}_5$ ], 3.30 [s, 6H, $(\text{CO}_2\text{Me})_2$ ], 2.8 [m, 2H, $\text{CH}_2$ ], 1.9 [m, 2H, $\text{CH}_2$ ], 1.2 [m, 2H, $\text{CH}_2$ ], 0.9 [m, 3H, Me]  | –75.5 [s, Co– $\text{PPh}_2(\text{SBU}^n)$ ]                               |
| <b>2b</b>  | 2017s, 1971s, 1934w, 1693m                | 7.8–7.2 [m, 10H, Ph], 4.95 [s, 5H, $\text{C}_5\text{H}_5$ ], 3.75 [s, 3H, $\text{CO}_2\text{Me}$ ], 3.39 [s, 3H, $(\text{CO}_2\text{Me})_2$ ], 2.2–0.9 [s, 9H, $\text{Bu}^n$ ]  | –146.7 [s, Mo– $\text{PPh}_2\text{C}_2(\text{CO}_2\text{Me})_2$ ]          |
| <b>2c</b>  | 2029s, 1978s, 1935w, 1693m                | 8.0–7.2 [m, 10H, Ph], 4.89 [s, 5H, $\text{C}_5\text{H}_5$ ], 3.78 [s, 3H, $\text{CO}_2\text{Me}$ ], 3.56 [s, 3H, $\text{CO}_2\text{Me}$ ], 1.21 [s, 9H, $\text{Bu}^t$ ]   | –147.0 [s, Mo– $\text{PPh}_2\text{C}_2(\text{CO}_2\text{Me})_2$ ]          |
| <b>2d</b>  | 2001s, 1957s, 1918w, 1684m                | 7.7–7.0 [m, 15H, Ph], 3.81 [s, br, 3H, $\text{CO}_2\text{Me}$ ], 3.56 [s, br, 3H, $\text{CO}_2\text{Me}$ ], 1.63 [s, 15H, $\text{C}_5\text{Me}_5$ ]   | –146.7 [s, Mo– $\text{PPh}_2\text{C}_2(\text{CO}_2\text{Me})_2$ ]          |
| <b>3b</b>  | 2029vs, 1980vs, 1936s, 1682s, 1668m       | 7.9–7.2 [m, 10H, Ph], 5.31 [s, 5H, $\text{C}_5\text{H}_5$ ], 3.54 [s, 3H, $\text{CO}_2\text{Me}$ ], 2.79 [s, 3H, $\text{CO}_2\text{Me}$ ], 2.2–0.9 [s, 9H, $\text{Bu}^n$ ]  | 24.9 [s, $\mu$ - $\text{PPh}_2$ ]  |
| <b>3c</b>  | 2026s, 1982s, 1927m, 1682m                | 7.6–7.0 [m, 10H, Ph], 5.25 [s, 5H, $\text{C}_5\text{H}_5$ ], 3.57 [s, 3H, $\text{CO}_2\text{Me}$ ], 2.85 [s, 3H, $\text{CO}_2\text{Me}$ ], 1.38 [s, 9H, $\text{Bu}^t$ ]   | 33.6 [s, $\mu$ - $\text{PPh}_2$ ]  |
| <b>3c'</b> | 1966s, 1913s, 1675m                       | 7.9–7.2 [m, 10H, Ph], 5.31 [s, 5H, $\text{C}_5\text{H}_5$ ], 3.67 [d, $^3J(\text{PH})$ 12, 9H, $\text{P}(\text{OMe})_3$ ], 3.54 [s, 3H, Me], 2.79 [s, 3H, Me], 1.36 [s, 9H, $\text{Bu}^t$ ]   | 35.1 [s, $\mu$ - $\text{PPh}_2$ ], –1.2 [s, Co– $\text{P}(\text{OMe})_3$ ] |
| <b>3d</b>  | 2015s, 1965s, 1919w, 1676m                | not recorded  | 59.4 [s, $\mu$ - $\text{PPh}_2$ ]  |
| <b>3e</b>  | 2025s, 1981s, 1923m, 1681m                | 7.5–7.1 [m, 10H, Ph], 5.40 [s, 5H, $\text{C}_5\text{H}_5$ ], 3.61 [s, br, 3H, $\text{CO}_2\text{Me}$ ], 3.30 [s, br, 3H, $\text{CO}_2\text{Me}$ ], 2.4 [m, 2H, $\text{CH}_2$ ], 1.6 [m, 2H, $\text{CH}_2$ ], 1.4 [m, 2H, $\text{CH}_2$ ], 0.9 [m, 3H, Me] | –14.8 [s, $\mu$ - $\text{PPh}_2$ ]   |
| <b>4d</b>  | 2011s, 1970s, 1918w, 1679m                | 7.8–7.1 [m, 15H, Ph], 3.63 [s, br, 3H, $\text{CO}_2\text{Me}$ ], 2.76 [s, br, 3H, $\text{CO}_2\text{Me}$ ], 1.58 [s, 15H, $\text{C}_5\text{Me}_5$ ]   | –160.1 [s, Co– $\text{PPh}_2\text{C}_2(\text{CO}_2\text{Me})_2$ ]          |
| <b>5e</b>  | 2025s, 1981s, 1966m, 1681m                | 7.5–7.1 [m, 10H, Ph], 5.4 [s, 5H, $\text{C}_5\text{H}_5$ ], 3.6 [s, br, 3H, $\text{CO}_2\text{Me}$ ], 3.3 [s, br, 3H, $\text{CO}_2\text{Me}$ ], 2.4 [m, 2H, $\text{CH}_2$ ], 1.6 [m, 2H, $\text{CH}_2$ ], 1.4 [m, 2H, $\text{CH}_2$ ], 0.9 [m, 3H, Me]    | –32.0 [s, $\mu$ - $\text{PPh}_2$ ]   |
| <b>6</b>   | 1980s, 1923s, 1666m, 1504m <sup>b</sup>   | 7.9–7.0 [m, 20H, Ph], 5.29 [s, 5H, $\text{C}_5\text{H}_5$ ], 3.71 [s, br, $\text{CO}_2\text{Me}$ ], 3.48 [s, br, 3H, $\text{CO}_2\text{Me}$ ]   | –44.0 [s, Co– $\text{PPh}_2(\text{SPh})$ ]                                 |

<sup>a</sup> Recorded in *n*-hexane solution. <sup>b</sup> Recorded in  $\text{CH}_2\text{Cl}_2$  solution. <sup>c</sup>  $^1\text{H}$  chemical shifts ( $\delta$ ) in ppm relative to  $\text{SiMe}_4$  ( $\delta$  0.0), coupling constants in Hz in  $\text{CDCl}_3$  at 293 K. <sup>d</sup>  $^{31}\text{P}$  chemical shifts ( $\delta$ ) in ppm relative to external  $\text{P}(\text{OMe})_3$  ( $\delta$  0.0) (upfield shifts negative). Add 140.2 to tabulated values in order to reference relative to external 85%  $\text{H}_3\text{PO}_4$ . Spectra were  $\{^1\text{H}\}$ -gated decoupled and measured in  $\text{CDCl}_3$  at 293 K.

**Scheme 1** Products from the thermolysis of **1b–e**; effects of varying the nature of (a)  $\text{R}'$ , (b) the cyclopentadienyl group and (c) Group 6 metal centre.  $[\text{Co}] = \text{Co}(\text{CO})_2$ .

tances and angles are listed in Table 3. The Mo–Co single bond [2.633(1) Å]<sup>10</sup> is bridged by a *n*-butylthiolato fragment and by a vinyl-phosphide group, in which the vinyl group is  $\sigma$ -bonded to

the molybdenum [Mo–C(1) 2.183(8) Å] and asymmetrically  $\pi$ -bonded to the cobalt [Co–C(4) 2.064(8); Co–C(1) 1.917(8) Å]. The  $\beta$ -substituent of the vinyl group is a diphenylphosphide

**Table 2** Selected bond distances (Å) and angles (°) for complex  $[(\text{PhS})\text{Ph}_2\text{P}](\text{OC})_2\text{Co}\{\mu\text{-C}_2(\text{CO}_2\text{Me})_2\}\text{Mo}(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_2$  **1d**

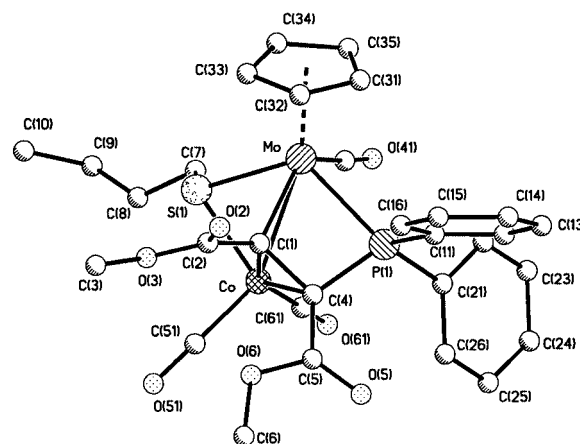
|                  |                   |                  |                   |
|------------------|-------------------|------------------|-------------------|
| Mo(1)–Co(1)      | 2.715(1)          | Mo(1)–C(8)       | 2.138(7)          |
| Mo(1)–C(7)       | 2.163(7)          | Co(1)–C(8)       | 1.970(7)          |
| Co(1)–C(7)       | 1.945(7)          | Co(1)–P(1)       | 2.227(2)          |
| P(1)–C(27)       | 1.816(7)          | P(1)–C(33)       | 1.844(8)          |
| P(1)–S(1)        | 2.129(3)          | S(1)–C(21)       | 1.808(8)          |
| C(7)–C(8)        | 1.360(9)          | C(9)–C(8)        | 1.47(1)           |
| C(6)–C(7)        | 1.46(1)           | C(9)–O(7)        | 1.210(8)          |
| C(9)–O(8)        | 1.334(8)          | C(6)–O(6)        | 1.195(8)          |
| C(6)–O(5)        | 1.346(9)          |                  |                   |
| Mo–C(carbonyl)   | 2.005(9)–2.01(1)  | C–O(Mo-carbonyl) | 1.123(9)–1.140(8) |
| Co–C(carbonyl)   | 1.776(8)–1.789(9) | C–O(Co-carbonyl) | 1.146(8)–1.148(8) |
| Co(1)–Mo(1)–C(8) | 46.0(2)           | Co(1)–Mo(1)–C(7) | 45.3(2)           |
| Co(1)–Mo(1)–C(4) | 88.3(2)           | Co(1)–Mo(1)–C(3) | 124.6(2)          |
| C(8)–Mo(1)–C(7)  | 36.9(2)           | C(8)–Mo(1)–C(4)  | 80.3(2)           |
| C(8)–Mo(1)–C(3)  | 78.8(3)           | C(7)–Mo(1)–C(4)  | 116.2(3)          |
| C(7)–Mo(1)–C(3)  | 89.8(3)           | C(4)–Mo(1)–C(3)  | 86.3(4)           |
| Mo(1)–Co(1)–C(8) | 51.3(2)           | Mo(1)–Co(1)–C(7) | 52.2(2)           |
| Mo(1)–Co(1)–P(1) | 148.81(7)         | Mo(1)–Co(1)–C(1) | 107.7(2)          |
| Mo(1)–Co(1)–C(2) | 92.1(2)           | P(1)–Co(1)–C(8)  | 97.5(2)           |
| P(1)–Co(1)–C(7)  | 107.1(2)          | P(1)–Co(1)–C(1)  | 97.6(3)           |
| P(1)–Co(1)–C(2)  | 100.0(2)          | C(8)–Co(1)–C(7)  | 40.7(3)           |
| C(8)–Co(1)–C(1)  | 138.9(3)          | C(7)–Co(1)–C(1)  | 98.3(3)           |
| C(8)–Co(1)–C(2)  | 111.8(3)          | C(7)–Co(1)–C(2)  | 142.9(3)          |
| C(1)–Co(1)–C(2)  | 102.9(4)          | C(27)–P(1)–C(33) | 107.1(4)          |
| S(1)–P(1)–C(27)  | 102.5(2)          | S(1)–P(1)–C(33)  | 103.1(3)          |
| C(7)–C(8)–Co(1)  | 68.7(4)           | C(7)–C(8)–Mo(1)  | 72.6(4)           |
| C(8)–C(7)–Co(1)  | 70.7(4)           | C(8)–C(7)–Mo(1)  | 70.6(4)           |
| Mo(1)–C(8)–Co(1) | 82.6(3)           | Mo(1)–C(7)–Co(1) | 82.6(3)           |

**Table 3** Selected bond distances (Å) and angles (°) for  $[(\text{OC})(\eta^5\text{-C}_5\text{H}_5)\text{Mo}\{\mu\text{-PPH}_2\text{C}(\text{CO}_2\text{Me})\text{C}(\text{CO}_2\text{Me})\}(\mu\text{-SBU}^n)\text{Co}(\text{CO})_2]$  **2b**

|                  |          |                  |                 |
|------------------|----------|------------------|-----------------|
| Co–Mo            | 2.633(1) | Mo–S(1)          | 2.433(3)        |
| Mo–P(1)          | 2.476(2) | Mo–C(1)          | 2.183(8)        |
| Co–S(1)          | 2.227(3) | Co–C(4)          | 2.064(8)        |
| C(4)–P(1)        | 1.775(8) | Co–C(1)          | 1.917(8)        |
| C(5)–C(4)        | 1.46(1)  | C(1)–C(2)        | 1.48(1)         |
| P(1)–C(11)       | 1.822(6) | C(1)–C(4)        | 1.46(1)         |
| C(5)–O(5)        | 1.21(1)  | P(1)–C(21)       | 1.810(6)        |
| C(5)–O(6)        | 1.33(1)  | C(6)–O(6)        | 1.43(1)         |
| C(2)–O(2)        | 1.20(1)  | C(2)–O(3)        | 1.32(1)         |
| C(3)–O(3)        | 1.46(1)  | S(1)–C(7)        | 1.81(1)         |
| Mo–C(carbonyl)   | 2.04(1)  | Co–C(carbonyl)   | 1.77(1)–1.78(1) |
| C–O(Mo-carbonyl) | 1.12(1)  | C–O(Co-carbonyl) | 1.14(1)–1.16(1) |
| Co–Mo–S(1)       | 52.0(1)  | Co–Mo–P(1)       | 70.0(1)         |
| P(1)–Mo–S(1)     | 122.0(1) | Co–Mo–C(1)       | 45.7(2)         |
| C(1)–Mo–S(1)     | 74.2(2)  | C(1)–Mo–P(1)     | 65.1(2)         |
| C(41)–Mo–Co      | 84.4(3)  | C(31)–Mo–Co      | 153.8(2)        |
| S(1)–Co–Mo       | 59.4(1)  | P(1)–Co–Mo       | 52.5(1)         |
| P(1)–Co–S(1)     | 111.9(1) | C(4)–Co–S(1)     | 125.3(2)        |
| C(1)–Co–Mo       | 54.6(2)  | C(51)–Co–Mo      | 148.0(3)        |
| C(61)–Co–Mo      | 107.8(3) | Co–S(1)–Mo       | 68.6(1)         |
| Co–P(1)–Mo       | 57.5(1)  | Co–C(4)–Mo       | 61.3(2)         |
| Co–C(1)–Mo       | 79.6(3)  |                  |                 |

group which is itself coordinated to the molybdenum [Mo–P(1) 2.476(2) Å], thus forming a four-membered metallacyclic system [Mo–C=C–P]. Similar ‘flyover’ ligands have been structurally characterised in other di- and tri-nuclear systems (Ni–Fe,<sup>13</sup> Ru–Co,<sup>14</sup> Ru<sub>3</sub>,<sup>15</sup> Mo<sub>2</sub>,<sup>16</sup> W<sub>2</sub><sup>17</sup>), and indeed in the structurally related species  $[(\text{OC})(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\mu\text{-PPH}_2\text{CPhCH})(\mu\text{-SPh})\text{Co}(\text{CO})_2]$ .<sup>7</sup>

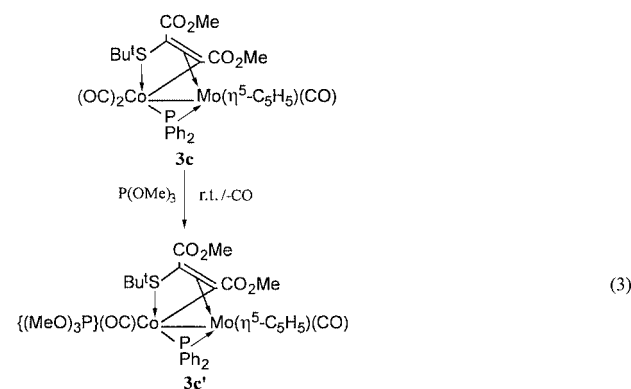
The structure of **2c** has been assigned on the basis of the close similarity in the spectroscopic data with those for the structurally characterised complex **2b**. The IR spectra of both **2b** and **2c** display, in addition to three terminal  $\nu_{\text{CO}}$  bands, a  $\nu_{\text{CO}}$  carboxylate band at *ca.* 1693 cm<sup>−1</sup>. The <sup>31</sup>P–<sup>1</sup>H NMR spectra of these complexes are in each case consistent with the presence of a diphenylphosphido group forming part of a metallacyclic

**Fig. 3** Molecular structure of  $[(\text{OC})(\eta^5\text{-C}_5\text{H}_5)\text{Mo}\{\mu\text{-PPH}_2\text{C}(\text{CO}_2\text{Me})\text{C}(\text{CO}_2\text{Me})\}(\mu\text{-SBU}^n)\text{Co}(\text{CO})_2]$  **2b**. Hydrogen atoms omitted for clarity.

system with one sharp upfield singlet resonance at  $\delta$  −146.7 for **2b** and −147.0 for **2c** [relative to P(OMe)<sub>3</sub> ( $\delta$  0.0)] indicative of the phosphorus atom of the ligand being directly bonded to the molybdenum rather than to the quadrupolar <sup>59</sup>Co atom.

The structures of complexes **3b** and **3c** have also been assigned on the basis of the spectroscopic data. The <sup>31</sup>P–<sup>1</sup>H NMR spectra are consistent with the presence of bridging phosphido groups with the breadth of the singlet downfield resonance observed in both cases [ $\delta$  24.9 **3b**, 33.6 **3c**] being due to the direct bonding of the phosphorus atom of the ligand to the quadrupolar <sup>59</sup>Co metal centre. In the <sup>13</sup>C–<sup>1</sup>H NMR spectra of **3b**, in addition to cyclopentadienyl, phenyl and butyl resonances, three carbonyl resonances are observed; one at a higher chemical shift (*ca.*  $\delta$  230) is typical of molybdenum-bound carbonyl groups<sup>4,6,7</sup> and two broad signals at lower chemical shifts (*ca.*  $\delta$  208 and 201) are characteristic of Co-bound carbonyl groups.<sup>6,7,18</sup> For **3b** and **3c** the unsaturated olefinic carbon atoms are observed as singlets between  $\delta$  100 and 90 [ $\mu\text{-SRC}(\text{CO}_2\text{Me})\text{C}(\text{CO}_2\text{Me})$ ] and between  $\delta$  50 and 30 [ $\mu\text{-SRC}(\text{CO}_2\text{Me})\text{C}(\text{CO}_2\text{Me})$ ] with the carboxylate carbonyl groups giving separate resonances at *ca.*  $\delta$  176 and 173. The inequivalence of the carboxylate substituents on the olefinic carbon atoms is further indicated by the observation of two carboxylate-methyl resonances in the <sup>1</sup>H NMR spectra [ $\delta$  3.54, 2.79 **3b**; 3.57, 2.85 **3c**].

Although single crystals of neither **3b** nor **3c** could be obtained, the P(OMe)<sub>3</sub>-substituted derivative of **3c**,  $[(\text{MeO})_3\text{P}](\text{OC})\text{Co}\{\mu\text{-SBU}^n\text{C}(\text{CO}_2\text{Me})\text{C}(\text{CO}_2\text{Me})\}(\mu\text{-PPH}_2\text{-Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{CO}))$  **3c'**, prepared by treatment of **3c** with P(OMe)<sub>3</sub> at room temperature (eqn. (3)), was crystallised and subjected to a single crystal X-ray diffraction study.

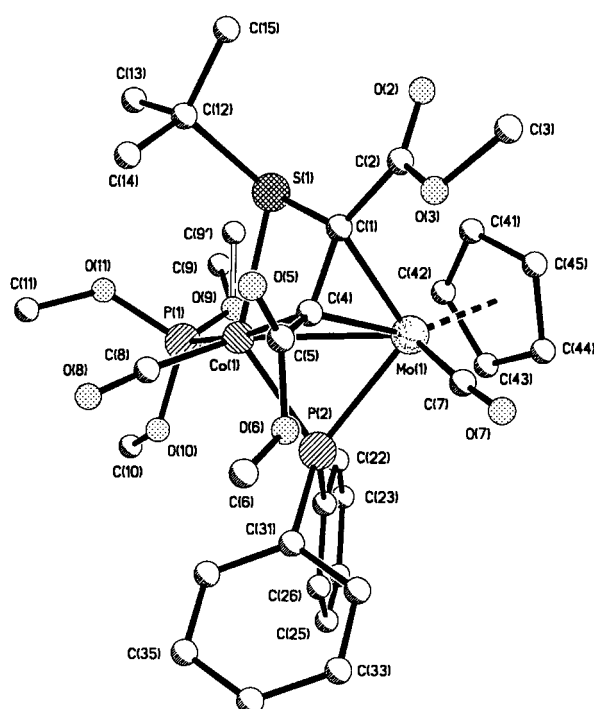


The molecular structure of **3c'** including the atom numbering scheme is illustrated in Fig. 4; Table 4 lists selected bond distances and angles. The Mo–Co single bond [2.717(1) Å],<sup>10</sup> is bridged by a diphenylphosphido group and by a vinyl group



**Table 4** Selected bond distances (Å) and angles (°) for complex  $[(\text{MeO})_3\text{P}](\text{OC})\text{Co}\{\mu\text{-SBu}^t\text{C}(\text{CO}_2\text{Me})\text{C}(\text{CO}_2\text{Me})\}(\mu\text{-PPh}_2)\text{Mo}(\eta^5\text{-C}_5\text{-H}_5)(\text{CO})\} \mathbf{3c}'$ 

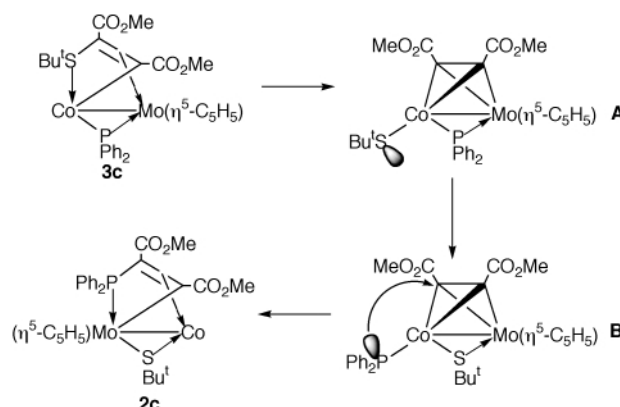
|                   |           |                   |          |
|-------------------|-----------|-------------------|----------|
| Co(1)–Mo(1)       | 2.717(1)  | Mo(1)–P(2)        | 2.401(2) |
| Mo(1)–C(1)        | 2.212(6)  | Mo(1)–C(4)        | 2.132(6) |
| Co(1)–S(1)        | 2.346(2)  | Co(1)–P(2)        | 2.209(2) |
| Co(1)–P(1)        | 2.159(2)  | Co(1)–C(4)        | 2.014(6) |
| C(1)–S(1)         | 1.800(6)  | C(1)–C(4)         | 1.434(9) |
| C(1)–C(2)         | 1.485(9)  | C(4)–C(5)         | 1.463(9) |
| P(2)–C(21)        | 1.856(6)  | P(2)–C(31)        | 1.816(6) |
| P(1)–O(9)         | 1.590(5)  | P(1)–O(10)        | 1.592(5) |
| P(1)–O(11)        | 1.613(5)  | S(1)–C(12)        | 1.903(7) |
| Mo(1)–C(carbonyl) | 1.953(8)  | Co(1)–C(carbonyl) | 1.759(7) |
| C–O(Mo-carbonyl)  | 1.154(8)  | C–O(Co-carbonyl)  | 1.145(8) |
| Co(1)–Mo(1)–P(2)  | 50.67(4)  | Co–Mo–C(1)        | 62.7(2)  |
| Co(1)–Mo(1)–C(4)  | 47.2(2)   | Co–Mo–C(7)        | 115.9(2) |
| C(7)–Mo(1)–C(4)   | 76.8(3)   | C(7)–Mo–C(1)      | 94.4(3)  |
| C(4)–Mo(1)–C(1)   | 38.5(2)   | C(4)–Mo–P(2)      | 79.0(2)  |
| C(7)–Mo(1)–P(2)   | 97.3(2)   | C(1)–Mo–P(2)      | 110.5(2) |
| Mo(1)–Co(1)–P(1)  | 122.32(6) | Mo–Co–P(2)        | 57.22(2) |
| Mo(1)–Co(1)–C(4)  | 51.0(2)   | Mo–Co–C(8)        | 137.6(2) |
| Mo(1)–Co(1)–S(1)  | 76.90(5)  | C(8)–Co–P(1)      | 96.9(2)  |
| C(8)–Co(1)–C(4)   | 92.6(3)   | C(4)–Co(1)–P(1)   | 168.7(2) |
| C(8)–Co(1)–P(2)   | 106.5(2)  | C(4)–Co(1)–P(2)   | 86.3(2)  |
| P(1)–Co(1)–P(2)   | 96.95(7)  | C(8)–Co(1)–S(1)   | 117.7(2) |
| C(4)–Co(1)–S(1)   | 74.3(2)   | P(1)–Co(1)–S(1)   | 95.70(7) |
| P(2)–Co(1)–S(1)   | 131.87(7) | O(9)–P(1)–O(10)   | 106.4(3) |
| O(9)–P(1)–O(11)   | 97.7(3)   | O(10)–P(1)–O(11)  | 103.4(3) |
| C(21)–P(2)–C(31)  | 99.0(3)   | Co(1)–P(2)–Mo(1)  | 72.11(6) |
| C(1)–S(1)–Co(1)   | 76.5(2)   | S(1)–C(1)–Mo(1)   | 103.5(3) |
| C(1)–C(4)–Co(1)   | 96.5(4)   | C(1)–C(4)–Mo(1)   | 73.7(3)  |
| Co(1)–C(4)–Mo(1)  | 81.8(2)   |                   |          |

**Fig. 4** Molecular structure of  $[(\text{MeO})_3\text{P}](\text{OC})\text{Co}\{\mu\text{-SBu}^t\text{C}(\text{CO}_2\text{Me})\text{C}(\text{CO}_2\text{Me})\}(\mu\text{-PPh}_2)\text{Mo}(\eta^5\text{-C}_5\text{-H}_5)(\text{CO})\} \mathbf{3c}'$ . Hydrogen atoms omitted for clarity. The methyl group of the disordered OMe substituent was assigned two sites of 50% occupancy.

which is  $\sigma$ -bonded to the cobalt [Co–C(4) 2.014(6) Å] and asymmetrically  $\pi$ -bonded to the molybdenum [Mo–C(1) 2.212(6), Mo–C(4) 2.132(6) Å]. The  $\beta$ -substituent of the vinyl group is a *tert*-butylthiolate group which is itself coordinated to the cobalt, forming a four-membered metallacyclic system [Co–C=C–S]. The coordination sphere of the molybdenum centre is completed by a cyclopentadienyl group and a carbonyl group while the cobalt centre is bound by a  $\text{P}(\text{OMe})_3$  group and a

carbonyl group. A noteworthy feature exhibited by the  $\text{P}(\text{OMe})_3$  ligand is its inclination away from the axial position (pseudo-*trans* to the metal–metal bond) normally adopted by phosphine ligands [Mo–Co–P(1) 122.32(6)°] in organo-bridged substituted bimetallic carbonyl complexes.<sup>7,8,19</sup> The explanation for this distortion is uncertain but it is accompanied by an elongation of the Co–S(1) bond [2.346(2) Å]<sup>20</sup> presumably to avoid any steric interaction between the *tert*-butyl substituent of the thiolate group and the methoxy substituents of the phosphite. To the knowledge of the authors there are few examples other than **3c'** of structurally characterised bimetallic complexes that incorporate a  $\mu\text{-SRCRCR}$  ligand.<sup>22</sup>

The observation that two isomeric products (**2b/3b** and **2c/3c**) are obtained respectively from the thermal reaction of **1b** or **1c** is in contrast to the outcome of the corresponding reaction of **1a** in which only **2a** was obtained. When **3c** was refluxed in toluene, **2c** was obtained in high yield (Scheme 1a), suggesting that **3** may be an intermediate in the formation of **2**. The mechanism for the transformation of **3** to **2** is uncertain but Scheme 2 shows a possible pathway. It is suggested that initial cleavage

**Scheme 2** Possible pathway for the isomerisation of **3c** to give **2c**. Terminal carbonyl groups omitted for clarity.

of the S–C bond in **3** gives intermediate **A**, which contains a pendant thiolate group and a bridging alkyne. Attack of the thiolate group at the molybdenum centre could displace the bridging phosphido group from the cobalt centre (see intermediate **B**) and insertion of the resulting pendant phosphide into an alkyne carbon–molybdenum bond would then yield complex **2**. This thermally-induced isomerisation reaction can be compared to the organophosphine-induced transformation of  $[\text{Co}_2\{\mu\text{-SPhC}(\text{O})\text{CHCH}\}(\mu\text{-PPh}_2)(\text{CO})_4]$  to  $[\text{Co}_2\{\mu\text{-PPh}_2\text{-CHCHC}(\text{O})\}(\mu\text{-SPh})(\text{CO})_2(\text{L})_2]$  (L = phosphite or phosphine) in which a five-membered thiolate-containing metallacycle is converted to a five-membered phosphide-containing metallacyclic species.<sup>8</sup>

**(ii) Variation in the cyclopentadienyl substituent.** In the previous sub-section the introduction of an alkyl-thiolate group (**1b**, **1c**) in place of the aryl-thiolate in **1a** resulted in the isolation of analogues (**3b**, **3c**) of a possible intermediate in the formation of **2a**. This effect on the reaction products of replacing an aryl substituent on sulfur with an alkyl substituent suggested that it would be worthwhile to probe the effect of changing the nature of the cyclopentadienyl substituent on the thermally induced phosphorus–sulfur bond cleavage reaction. Accordingly, the thermolysis of the pentamethylcyclopentadienyl species  $[(\text{PhS})\text{Ph}_2\text{P}](\text{OC})_2\{\mu\text{-C}_2(\text{CO}_2\text{Me})_2\}\text{Mo}(\eta^5\text{-C}_5\text{-Me}_5)(\text{CO})_2 \mathbf{1d}$  in toluene at 383 K was undertaken. Three products are isolated:  $[(\text{OC})(\eta^5\text{-C}_5\text{Me}_5)\text{Mo}\{\mu\text{-PPh}_2\text{C}(\text{CO}_2\text{Me})\text{C}(\text{CO}_2\text{Me})\}(\mu\text{-SPh})\text{Co}(\text{CO})_2] \mathbf{2d}$ ,  $[(\text{OC})_2\text{Co}\{\mu\text{-SPhC}(\text{CO}_2\text{Me})\text{C}(\text{CO}_2\text{Me})\}(\mu\text{-PPh}_2)\text{Mo}(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})] \mathbf{3d}$  and  $[(\text{OC})_2\text{Co}\{\mu\text{-PPh}_2\text{C}(\text{CO}_2\text{Me})\text{C}(\text{CO}_2\text{Me})\}(\mu\text{-SPh})\text{Mo}(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})] \mathbf{4d}$

(Scheme 1b). All three complexes have been characterised by  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{31}\text{P}$  NMR, IR spectroscopy and by mass spectrometry (see Table 1 and Experimental section).

The IR spectrum of **3d** is similar to that of other complexes of type **3** with the carbonyl absorptions in **3d** shifted to lower frequency by *ca.* 10–25  $\text{cm}^{-1}$ . The  $^{31}\text{P}$ - $\{^1\text{H}\}$  NMR spectrum of **3d** is consistent with the presence of a bridging phosphido group, displaying a single broad resonance at  $\delta$  59.4. The  $^{13}\text{C}$ - $\{^1\text{H}\}$  NMR spectrum shows, in addition to signals attributable to the phenyl and pentamethylcyclopentadienyl carbon atoms, singlet resonances corresponding to each of the carboxylate carbonyl groups [ $\mu\text{-SPhC}(\text{CO}_2\text{Me})\text{C}(\text{CO}_2\text{Me})$ ] ( $\delta$  177.6, 175.3). Additionally, the olefinic carbon  $\sigma$ -bonded to cobalt [ $\mu\text{-SPhC}(\text{CO}_2\text{Me})\text{C}(\text{CO}_2\text{Me})$ ] is observed at  $\delta$  106.2, with the inequivalent carboxylate methyl carbon resonances at  $\delta$  53.7 and  $\delta$  51.1.

For the complex  $[(\text{OC})_2\text{Co}\{\mu\text{-PPh}_2\text{C}(\text{CO}_2\text{Me})\text{C}(\text{CO}_2\text{Me})\}(\mu\text{-SPh})\text{Mo}(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})]$  **4d** the IR spectrum displays a similar pattern of  $\nu_{\text{CO}}$  absorptions to that of the phosphido-bridged cyclopentadienyl analogue  $[(\text{OC})_2\text{Co}\{\mu\text{-PPh}_2\text{C}(\text{CO}_2\text{Me})\text{C}(\text{CO}_2\text{Me})\}(\mu\text{-PPh}_2)\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})]$  **6** although the bands are shifted to lower wavenumber. The  $^{31}\text{P}$ - $\{^1\text{H}\}$  NMR spectrum of **4d** shows a broad upfield singlet [ $\delta$  -160.1] confirming that the phosphido group is incorporated into a four-membered metallacycle  $[\text{Co-P-C=C}]$  and is coordinated to the quadrupolar  $^{59}\text{Co}$  atom. The  $^{13}\text{C}$ - $\{^1\text{H}\}$  NMR spectrum of **4d** shows, in addition to pentamethylcyclopentadienyl and phenyl signals, resonances corresponding to ester groups,  $[\text{C}(\text{CO}_2\text{Me})\text{C}(\text{CO}_2\text{Me})]$ ,  $\delta$  176.0 and 171.1 and  $\text{C}(\text{CO}_2\text{Me})\text{C}(\text{CO}_2\text{Me})$ ,  $\delta$  50.9 and 50.7. In addition, a singlet at  $\delta$  106.2 [ $\mu\text{-PPh}_2\text{C}(\text{CO}_2\text{Me})\text{C}(\text{CO}_2\text{Me})$ ] and a doublet at  $\delta$  31.3 [ $^1J(\text{PC})$  42,  $\mu\text{-PPh}_2\text{C}(\text{CO}_2\text{Me})\text{C}(\text{CO}_2\text{Me})$ ] are displayed.

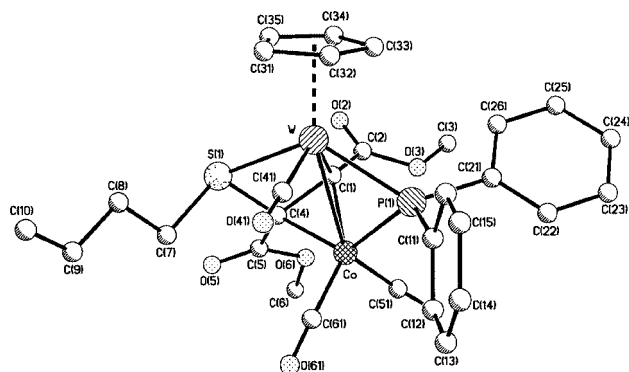
In the IR spectrum of  $[(\text{OC})(\eta^5\text{-C}_5\text{Me}_5)\text{Mo}\{\mu\text{-PPh}_2\text{C}(\text{CO}_2\text{Me})\text{C}(\text{CO}_2\text{Me})\}(\mu\text{-SPh})\text{Co}(\text{CO})_2]$  **2d** a similar pattern of  $\nu_{\text{CO}}$  absorption bands to that of the cyclopentadienyl complexes **2a–c** is observed although shifted to lower wavenumber by *ca.* 10  $\text{cm}^{-1}$ .<sup>6</sup> The  $^{31}\text{P}$ - $\{^1\text{H}\}$  NMR spectrum displays a sharp singlet at  $\delta$  -146.7, typical of a phosphide group contained within a four-membered molybdacyclic ring  $[\text{Mo-P-C=C}]$ . The  $^1\text{H}$  NMR spectrum of **2d** shows, in addition to pentamethylcyclopentadienyl and phenyl resonances, signals corresponding to the two carboxylate-methyl groups at  $\delta$  3.81 and 3.56, confirming that the two carboxylate groups are inequivalent.

While the thermolytic reaction of **1a** was found to give uniquely **2a** and that of **1b** and **1c** to give both **2b/3b** and **2c/3c**, the corresponding reaction of **1d** affords three products. Two of these products, **2d** and **3d** are analogous to the products obtained on the thermolysis of **1b** and **1c**. The third product, which is obtained in the highest yield, is the phosphorus-containing cobaltacyclic species **4d** and this has no analogue in the other reactions studied. It seems that the presence of the  $\eta^5\text{-C}_5\text{Me}_5$  group increases the tendency of the metallacycle to incorporate the Group 9 metal centre. The reason may be that the greater steric bulk of the  $\eta^5\text{-C}_5\text{Me}_5$  group on the molybdenum atom causes the bulky phenylthiolate or diphenylphosphido groups of the metallacycle to coordinate preferentially to the metal atom not bearing the  $\eta^5\text{-C}_5\text{Me}_5$  group.

**(iii) Effect of tungsten in place of molybdenum in 1.** Cobalt-tungsten systems are generally more kinetically inert and stable than their cobalt-molybdenum analogues, undergoing reactions over a longer time-scale and at higher temperatures<sup>17</sup> so it was of interest to examine the thermal reaction of  $[(\text{Bu}^n\text{S})\text{Ph}_2\text{P}](\text{OC})_2\text{Co}\{\mu\text{-C}_2(\text{CO}_2\text{Me})_2\}\text{W}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2]$  **1e**. Thermolysis of **1e** in toluene at 373 K gives the complexes  $[(\text{OC})_2\text{Co}\{\mu\text{-SBU}^n\text{C}(\text{CO}_2\text{Me})\text{C}(\text{CO}_2\text{Me})\}(\mu\text{-PPh}_2)\text{W}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})]$  **3e** and  $[(\text{OC})(\eta^5\text{-C}_5\text{H}_5)\text{W}\{\mu\text{-SBU}^n\text{C}(\text{CO}_2\text{Me})\text{C}(\text{CO}_2\text{Me})\}(\mu\text{-PPh}_2)\text{Co}(\text{CO})_2]$  **5e** in relatively high combined yield (Scheme 1c). Both complexes have been characterised by  $^1\text{H}$ ,  $^{31}\text{P}$ ,  $^{13}\text{C}$  NMR, IR spectroscopy and by mass spectrometry and micro-

**Table 5** Selected bond distances ( $\text{\AA}$ ) and angles ( $^\circ$ ) for complex  $[(\text{OC})(\eta^5\text{-C}_5\text{H}_5)\text{W}\{\mu\text{-SBU}^n\text{C}(\text{CO}_2\text{Me})\text{C}(\text{CO}_2\text{Me})\}(\mu\text{-PPh}_2)\text{Co}(\text{CO})_2]$  **5e**

|                |                 |               |                 |
|----------------|-----------------|---------------|-----------------|
| W–Co           | 2.662(2)        | W–P(1)        | 2.406(3)        |
| W–C(1)         | 2.19(1)         | W–S(1)        | 2.522(3)        |
| Co–P(1)        | 2.193(3)        | Co–C(1)       | 1.95(1)         |
| Co–C(4)        | 2.03(1)         | P(1)–C(11)    | 1.823(8)        |
| P(1)–C(21)     | 1.85(1)         | S(1)–C(4)     | 1.79(1)         |
| S(1)–C(7)      | 1.83(1)         | C(1)–C(2)     | 1.47(2)         |
| C(1)–C(4)      | 1.46(2)         | C(4)–C(5)     | 1.48(2)         |
| C(3)–O(3)      | 1.46(2)         | C(5)–O(5)     | 1.16(2)         |
| C(5)–O(6)      | 1.37(2)         | C(2)–O(2)     | 1.19(2)         |
| C(2)–O(3)      | 1.31(2)         |               |                 |
| W–C(carbonyl)  | 1.96(1)         | C–O(carbonyl) | 1.17(2)         |
| Co–C(carbonyl) | 1.78(2)–1.78(1) | C–O(carbonyl) | 1.12(2)–1.15(2) |
| P(1)–W–Co      | 51.0(1)         | S(1)–W–Co     | 75.8(1)         |
| S(1)–W–P(1)    | 126.5(1)        | C(1)–W–Co     | 46.2(3)         |
| C(1)–W–P(1)    | 79.1(3)         | C(1)–W–S(1)   | 65.4(3)         |
| C(41)–W–Co     | 82.8(4)         | P(1)–Co–W     | 58.5(1)         |
| S(1)–Co–W      | 50.1(1)         | S(1)–Co–P(1)  | 108.4(1)        |
| C(1)–Co–W      | 54.0(3)         | C(4)–Co–W     | 72.5(3)         |
| C(51)–Co–W     | 143.7(5)        | C(61)–Co–W    | 112.3(4)        |
| Co–P(1)–W      | 70.6(1)         | Co–S(1)–W     | 54.1(1)         |
| Co–C(1)–W      | 79.9(4)         |               |                 |



**Fig. 5** Molecular structure of  $[(\text{OC})_2\text{Co}\{\mu\text{-SBU}^n\text{C}(\text{CO}_2\text{Me})\text{C}(\text{CO}_2\text{Me})\}(\mu\text{-PPh}_2)\text{W}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})]$  **5e**. Hydrogen atoms omitted for clarity.

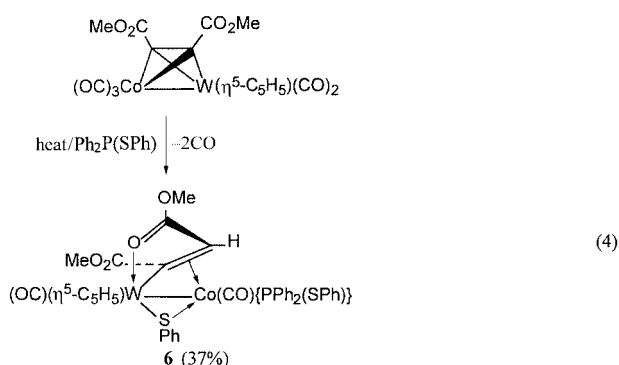
analysis (see Table 1 and Experimental section). Furthermore, complex **5e** has been the subject of a single crystal X-ray structure determination study.

The molecular structure of **5e** is shown in Fig. 5 and Table 5 lists selected bond distances and angles. The structure reveals a W–Co single bond [2.662(2)  $\text{\AA}$ ],<sup>21</sup> bridged both by a diphenylphosphido group and by a vinylthiolate ligand which is  $\sigma$ -bonded to the tungsten [W–C(1) 2.19(1)  $\text{\AA}$ ] and asymmetrically  $\pi$ -bonded to the cobalt [Co–C(1) 1.95(1), Co–C(4) 2.03(1)  $\text{\AA}$ ]. The  $\beta$ -substituent of the vinyl group is a *n*-butylthiolate group which is itself coordinated to the tungsten atom [W–S(1) 2.522(3)  $\text{\AA}$ ], thus forming a four-membered metallacyclic system [W–C=C–S]. Structurally characterised bimetallic complexes incorporating a  $\mu\text{-SRCRCR}$  ligand have been observed in only a few cases<sup>22</sup> which include **3c'** (see Fig. 4). The smaller covalent radius of cobalt compared to tungsten accounts for the asymmetric bridging of the two metal centres in **5e** by the phosphido ligand [W–P(1) 2.406(3) vs. Co–P(1) 2.193(3)  $\text{\AA}$ ].

The  $^{31}\text{P}$ - $\{^1\text{H}\}$  NMR spectrum of **5e** is consistent with a bridging diphenylphosphido group showing a broad singlet resonance [ $\delta$  -32.0] while the  $^{13}\text{C}$ - $\{^1\text{H}\}$  NMR spectrum shows, in addition to cyclopentadienyl and thiolate signals, three carbonyl resonances. One, at higher chemical shift, is split into a doublet [ $\delta$  231.4,  $^2J(\text{PC})$  9] and is typical of a tungsten-bound carbonyl<sup>3</sup> while two broad resonances at lower chemical shift [ $\delta$  210.2 and 207.2] are typical of cobalt-bound carbonyl groups.

The structure of complex **3e** is assigned on the basis of a comparison of the spectroscopic data with those of other complexes of type **3**. The  $^{31}\text{P}\{-^1\text{H}\}$  NMR spectrum shows a broad singlet resonance at  $\delta -14.8$  consistent with a bridging phosphido group. The inequivalence of the ester functionalities on the vinyl group is supported by distinct carboxylate carbonyl group resonances in the  $^{13}\text{C}\{-^1\text{H}\}$  NMR spectrum along with separate signals for the two carboxylate-methyl groups at  $\delta 3.61$  and  $3.30$  in the  $^1\text{H}$  NMR spectrum.

The products obtained from phosphorus–sulfur bond cleavage on thermolysis of the Co–W system **1e** show a notable difference from the Co–Mo system. While preferential formation of metallacycles incorporating the phosphide fragment is observed for the Co–Mo systems **1a–d** the Co–W system **1e** leads exclusively to metallacycles incorporating the thiolate fragment. More significantly, the phenylthiolate analogue of **1e**,  $[(\text{PhS})\text{Ph}_2\text{P}](\text{OC})_2\text{Co}\{\mu\text{-C}_2(\text{CO}_2\text{Me})_2\}\text{W}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2$  **1f** could not be prepared. Indeed on reaction of  $[(\text{OC})_3\text{Co}\{\mu\text{-C}_2(\text{CO}_2\text{Me})_2\}\text{W}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2]$  with  $\text{Ph}_2\text{P}(\text{SPh})$  at  $373\text{ K}$  for  $24\text{ h}$  the only product isolated was  $[(\text{OC})(\eta^5\text{-C}_5\text{H}_5)\text{W}\{\mu\text{-C}(\text{CO}_2\text{Me})\text{CHC}(\text{OMe})\text{O}\}(\mu\text{-SPh})\text{Co}(\text{CO})\{\text{PPh}_2(\text{SPh})\}]\text{6}$  in which phosphorus–sulfur bond cleavage has occurred but without coupling of either fragment with the alkyne functionality (eqn. (4)).

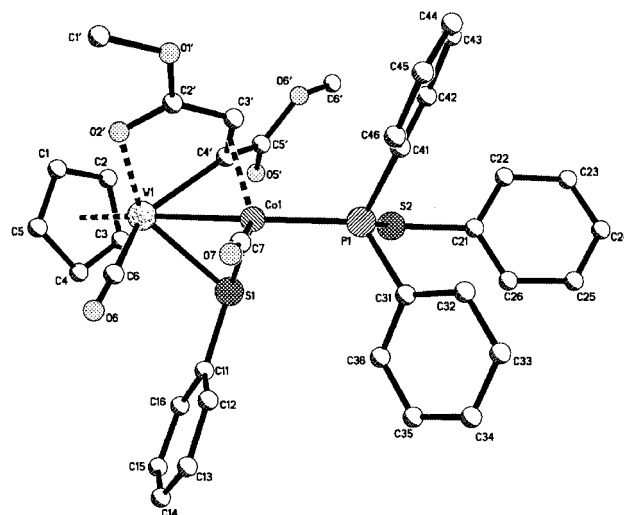


Complex **6** has been characterised by  $^1\text{H}$ ,  $^{31}\text{P}$ ,  $^{13}\text{C}$  NMR, IR spectroscopy and by mass spectrometry and microanalysis (see Table 1 and Experimental section). In addition complex **6** has been the subject of a single crystal X-ray diffraction study. The molecular structure of **6** is shown in Fig. 6 and Table 6 lists selected bond distances and angles. The complex consists of a bimetallic core with the W–Co single bond  $[2.598(2)\text{ Å}]^{23}$  bridged by a phenylthiolato ligand and by a vinyl group in which the  $\alpha$ -carbon is  $\sigma$ -bonded to tungsten  $[\text{W}–\text{C}(4')\text{ }2.14(1)\text{ Å}]$  and in which the  $\beta$ -carbon is  $\pi$ -coordinated to the cobalt atom  $[\text{Co}–\text{C}(4')\text{ }1.97(1), \text{Co}–\text{C}(3')\text{ }2.06(1)\text{ Å}]$ . In addition the  $\text{O}(2')$  atom on the ester  $\beta$ -substituent of the vinyl group is bound to the tungsten atom  $[\text{W}–\text{O}(2')\text{ }2.163(7)\text{ Å}]$  so as to form a five-membered metallacycle  $[\text{W}–\text{C}=\text{C}=\text{O}]$ . Similar bonding of the  $\mu\text{-CRCHC}(\text{OMe})\text{O}$  ligand has been observed in a number of homo- and hetero-bimetallic complexes  $[\text{Fe}_2,^{24}\text{ Mo}_2,^{25}\text{ Ru}_2,^{26}\text{ Mn}_2,^{27}\text{ Co}_2,^{28}\text{ CoFe},^{29}\text{ CoMo}^6]$ . The coordination sphere at tungsten is completed by a  $\eta^5\text{-C}_5\text{H}_5$  group and a carbonyl group while that around the cobalt centre is completed by an equatorial carbonyl group and an axially bound thiophosphine ligand, which coordinates *via* the phosphorus donor. The spectroscopic properties of **6** are consistent with the solid-state structure being maintained in solution.

It is uncertain why a complex of the type  $[(\text{PhS})\text{Ph}_2\text{P}](\text{CO})_2\text{Co}\{\mu\text{-C}_2(\text{CO}_2\text{Me})_2\}\text{W}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2$  **1f** could not be isolated and indeed why four-membered metallacyclic products like **2–5** (Fig. 1) are not produced in the attempted preparation. A possible reason may be the prolonged thermolysis conditions necessary when tungsten is present compared to those when molybdenum is present. The formation of complex **6** probably involves the formation of a hydride at some point, which may

**Table 6** Selected bond distances (Å) and angles (°) for complex  $[(\text{OC})(\eta^5\text{-C}_5\text{H}_5)\text{W}\{\mu\text{-C}(\text{CO}_2\text{Me})\text{CHC}(\text{OMe})\text{O}\}(\mu\text{-SPh})\text{Co}(\text{CO})\{\text{PPh}_2(\text{SPh})\}]\text{6}$

|                   |          |                   |          |
|-------------------|----------|-------------------|----------|
| W(1)–Co(1)        | 2.598(2) | W(1)–O(2')        | 2.163(7) |
| W(1)–C(4')        | 2.14(1)  | W(1)–S(1)         | 2.443(3) |
| Co(1)–S(1)        | 2.244(3) | Co(1)–P(1)        | 2.202(3) |
| Co(1)–C(4')       | 1.97(1)  | Co(1)–C(3')       | 2.06(1)  |
| O(1')–C(1')       | 1.46(1)  | O(1')–C(2')       | 1.34(1)  |
| O(2')–C(2')       | 1.27(1)  | O(5')–C(5')       | 1.23(1)  |
| O(6')–C(5')       | 1.34(1)  | O(6')–C(6')       | 1.42(2)  |
| C(2')–C(3')       | 1.40(2)  | C(3')–C(4')       | 1.43(1)  |
| C(4')–C(5')       | 1.47(2)  | P(1)–C(31)        | 1.83(1)  |
| P(1)–C(41)        | 1.82(1)  | P(1)–S(2)         | 2.118(4) |
| S(1)–C(11)        | 1.79(1)  | S(2)–C(21)        | 1.79(1)  |
| W–C(carbonyl)     | 1.98(2)  | C–O(W-carbonyl)   | 1.15(2)  |
| Co–C(carbonyl)    | 1.75(1)  | C–O(Co-carbonyl)  | 1.15(1)  |
| Co(1)–W(1)–S(1)   | 52.76(9) | Co(1)–W(1)–O(2')  | 83.1(2)  |
| Co(1)–S(1)–C(4')  | 48.0(3)  | Co(1)–W(1)–C(6)   | 80.1(3)  |
| C(6)–W(1)–C(4')   | 126.0(4) | C(6)–W(1)–O(5)    | 85.7(4)  |
| C(4')–W(1)–O(5)   | 75.6(3)  | C(4')–W(1)–S(1)   | 75.7(3)  |
| W(1)–Co(1)–S(1)   | 60.07(8) | W(1)–Co(1)–P(1)   | 154.1(1) |
| W(1)–Co(1)–C(3')  | 76.9(3)  | W(1)–Co(1)–C(4')  | 53.8(3)  |
| W(1)–Co(1)–C(7)   | 109.0(4) | S(1)–Co(1)–P(1)   | 102.7(1) |
| S(1)–Co(1)–C(3')  | 124.7(3) | S(1)–Co(1)–C(4')  | 83.8(4)  |
| S(1)–Co(1)–C(7)   | 117.9(4) | P(1)–Co(1)–C(3')  | 102.3(3) |
| P(1)–Co(1)–C(3)   | 108.6(3) | P(1)–Co(1)–C(7)   | 96.0(4)  |
| C(3)–Co(1)–C(4)   | 41.4(4)  | C(4)–Co(1)–C(8)   | 107.5(5) |
| C(4')–C(3')–Co(1) | 66.2(6)  | C(3')–C(4')–Co(1) | 72.4(6)  |
| C(3')–C(4')–W(1)  | 108.5(8) | C(2)–C(3)–W(1)    | 129.4(9) |
| Co(1)–C(4')–W(1)  | 78.2(4)  | C(11)–S(1)–S(1)   | 109.5(4) |
| C(11)–S(1)–Co(1)  | 118.9(4) | Co(1)–S(1)–W(1)   | 67.16(9) |



**Fig. 6** Molecular structure of  $[(\text{OC})(\eta^5\text{-C}_5\text{H}_5)\text{W}\{\mu\text{-C}(\text{CO}_2\text{Me})\text{CHC}(\text{OMe})\text{O}\}(\mu\text{-SPh})\text{Co}(\text{CO})\{\text{PPh}_2(\text{SPh})\}]\text{6}$ . Hydrogen atoms omitted for clarity.

then add to the bridging alkyne. The origin of this hydride is unknown but may come from impurities in the starting material or from decomposition products. An alternative possibility is that the hydrogen atom in **6** is scavenged from the solvent.

### 3. Conclusions

The regiospecific formation of heterobimetallic complexes of type **2** first observed when complex **1a** was thermolysed<sup>6</sup> has now been shown to be only one possible outcome of a complicated reaction sequence influenced by (i) the nature of the  $\text{R}'$  substituent, (ii) the cyclopentadienyl group and (iii) the identity of the Group 6 metal centre in  $[(\text{R}'\text{S})\text{Ph}_2\text{P}](\text{OC})_2\text{Co}\{\mu\text{-C}_2(\text{CO}_2\text{Me})_2\}\text{M}(\eta^5\text{-L})(\text{CO})_2$  ( $\text{M} = \text{Mo}, \text{W}$ ;  $\text{L} = \text{C}_5\text{H}_5, \text{C}_5\text{Me}_5$ ;  $\text{R}' = \text{aryl or alkyl}$ ) **1**. The facile movement of the thermally generated thiolate or phosphide fragments around the mixed



metal back-bone has been demonstrated by the isolation of species **2–5** in which either thiolate or phosphide can be incorporated into four-membered metallacycles, which contain either of the two different metal centres. In one case a kinetic product (**3c**) has been isolated and converted to its thermodynamically more stable isomer (**2c**).

## 4. Experimental

### (a) General techniques

All reactions were carried out under a nitrogen atmosphere using standard Schlenk techniques. Solvents were distilled under nitrogen from appropriate drying agents and degassed prior to use. Preparative thin-layer chromatography (TLC) was carried out on commercial Merck plates with a 0.25 mm layer of silica, or on 1 mm silica plates prepared at the University Chemical Laboratory, Cambridge. Column chromatography was performed on Kieselgel 60 (70–230 or 230–400 mesh). Products are given in order of decreasing  $R_f$  values.

The instrumentation used to obtain spectroscopic data has been described previously.<sup>30</sup> Unless otherwise stated all reagents were obtained from commercial suppliers while  $\text{Ph}_2\text{P}(\text{SR}')$  ( $\text{R}' = \text{Bu}^t, \text{Bu}^n, \text{Ph}$ ),<sup>9,31</sup>  $[(\text{OC})_3\text{Co}\{\mu\text{-C}_2(\text{CO}_2\text{Me})_2\}\text{Mo}(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_2]$ ,  $[(\text{OC})_3\text{Co}\{\mu\text{-C}_2(\text{CO}_2\text{Me})_2\}\text{W}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2]$ , and  $[(\text{OC})_3\text{Co}\{\mu\text{-C}_2(\text{CO}_2\text{Me})_2\}\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2]$  were prepared by literature methods.<sup>11b,32</sup>

### (b) The reaction of $[(\text{OC})_3\text{Co}\{\mu\text{-C}_2(\text{CO}_2\text{Me})_2\}\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2]$ with $\text{Ph}_2\text{P}(\text{SR}')$

To a solution of  $[(\text{OC})_3\text{Co}\{\mu\text{-C}_2(\text{CO}_2\text{Me})_2\}\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2]$  (1.00 g, 1.99 mmol) in toluene (70 cm<sup>3</sup>) was added solutions of the thiophosphines  $\text{L}$  ( $\text{L} = \text{Ph}_2\text{P}(\text{SBU}^n)$  (1.00 g, 3.6 mmol) or  $\text{Ph}_2\text{P}(\text{SBU}^t)$  (1.00 g, 3.6 mmol)) in toluene (20 cm<sup>3</sup>). The solutions were stirred at 298 K for 24 h and after removal of the solvents under reduced pressure the mixtures were absorbed onto a minimum amount of silica, added to the top of chromatography columns and eluted with hexane–dichloromethane (10:1). This gave, in addition to a small amount of unreacted starting material, orange crystalline  $[(\text{OC})_2\{\text{R}'\text{S}\}\text{Ph}_2\text{P}\{\text{Co}\{\mu\text{-C}(\text{CO}_2\text{Me})_2\}\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\}]$  ( $\text{R}' = \text{Bu}^n$  **1b** (1.176 g, 79%);  $\text{Bu}^t$  **1c** (1.101 g, 74%)). Complex **1b**: FAB mass spectrum,  $m/z$  748 ( $\text{M}^+$ ) and  $\text{M}^+ - n\text{CO}$  ( $n = 1-3$ ). NMR ( $\text{CDCl}_3$ ):  $^{13}\text{C}$  ( $^1\text{H}$  composite pulse decoupled),  $\delta$  223.5 [s, Mo–CO], 205.6 [s, Co–CO], 172.6 [s,  $\text{C}_2(\text{CO}_2\text{Me})_2$ ], 134–128 [m, Ph], 90.4 [s,  $\text{C}_5\text{H}_5$ ], 70.8 [s,  $\text{C}_2(\text{CO}_2\text{Me})_2$ ], 51.6 [s,  $\text{C}_2(\text{CO}_2\text{Me})_2$ ] and 32.5 [s,  $\text{Bu}^t$ ]. Complex **1c**: FAB mass spectrum,  $m/z$  748 ( $\text{M}^+$ ) and  $\text{M}^+ - n\text{CO}$  ( $n = 1-3$ ). NMR ( $\text{CDCl}_3$ ):  $^{13}\text{C}$  ( $^1\text{H}$  composite pulse decoupled),  $\delta$  222.6 [s, Mo–CO], 204.9 [s, Co–CO], 172.5 [s,  $\text{C}_2(\text{CO}_2\text{Me})_2$ ], 134–128 [m, Ph], 90.6 [s,  $\text{C}_5\text{H}_5$ ], 70.8 [s,  $\text{C}_2(\text{CO}_2\text{Me})_2$ ], 51.7 [s,  $\text{C}_2(\text{CO}_2\text{Me})_2$ ], 32.3 [s,  $\text{CH}_2$ ], 31.5 [s,  $\text{CH}_2$ ], 21.7 [s,  $\text{CH}_2$ ] and 13.4 [s, Me].

### (c) Thermolysis of $[(\text{R}'\text{S})\text{Ph}_2\text{P}\{\text{OC}\}_2\text{Co}\{\mu\text{-C}_2(\text{CO}_2\text{Me})_2\}\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2]$ ( $\text{R}' = \text{Bu}^n$ **1b**, $\text{Bu}^t$ **1c**)

Solutions of  $[(\text{R}'\text{S})\text{Ph}_2\text{P}\{\text{OC}\}_2\text{Co}\{\mu\text{-C}_2(\text{CO}_2\text{Me})_2\}\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2]$  ( $\text{R}' = \text{Bu}^n$  **1b**, 0.300 g, 0.40 mmol;  $\text{Bu}^t$  **1c**, 0.300 g, 0.40 mmol) in toluene (50 cm<sup>3</sup>) were thermolysed at 363 K for 2–3 h. After removal of the solvent under reduced pressure, the mixtures were separated using preparative TLC with hexane–ethyl acetate (2:1) as eluent. This gave, in addition to a small amount of unreacted starting material, yellow crystalline  $[(\text{OC})_2\text{Co}\{\mu\text{-SR}'\text{C}(\text{CO}_2\text{Me})\text{C}(\text{CO}_2\text{Me})\}(\mu\text{-PPh}_2)\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})]$  ( $\text{R}' = \text{Bu}^n$  **3b** (0.101 g, 35%),  $\text{Bu}^t$  **3c** (0.121 g, 42%)) and red-green crystalline  $[(\text{OC})(\eta^5\text{-C}_5\text{H}_5)\text{Mo}\{\mu\text{-PPh}_2\text{C}(\text{CO}_2\text{Me})\text{C}(\text{CO}_2\text{Me})\}(\mu\text{-SR}')\text{Co}(\text{CO})_2]$  ( $\text{R}' = \text{Bu}^n$  **2b** (0.124 g, 43%),  $\text{Bu}^t$  **2c** (0.118 g, 41%)) complexes. Complex **3b** (Found: C, 50.11; H, 4.10.  $\text{C}_{30}\text{H}_{30}\text{O}_7\text{PSCoMo}$  requires C, 50.00; H, 4.17%). FAB mass spectrum,  $m/z$  720 ( $\text{M}^+$ ) and  $\text{M}^+ - n\text{CO}$  ( $n = 1-3$ ).

NMR ( $\text{CDCl}_3$ ):  $^{13}\text{C}$  ( $^1\text{H}$  composite pulse decoupled),  $\delta$  230.3 [d,  $^2J(\text{PC})$  9, Mo–CO], 208.2 [s, Co–CO], 201.7 [s, Co–CO], 175.3 [s,  $\text{CO}_2\text{Me}$ ], 173.4 [s,  $\text{CO}_2\text{Me}$ ], 144–127 [m, Ph], 98.4 [d,  $^2J(\text{PC})$  39,  $\text{SBU}^n\text{C}(\text{CO}_2\text{Me})\text{C}(\text{CO}_2\text{Me})$ ], 91.2 [s,  $\text{C}_5\text{H}_5$ ], 51.5 [s, Me], 51.2 [s, Me], 47.8 [s,  $\text{SBU}^n\text{C}(\text{CO}_2\text{Me})$ ], 45.0 [s,  $\text{CH}_2$ ], 28.9 [s,  $\text{CH}_2$ ], 22.1 [s,  $\text{CH}_2$ ] and 13.7 [s, Me]. Complex **3c**: FAB mass spectrum,  $m/z$  720 ( $\text{M}^+$ ) and  $\text{M}^+ - n\text{CO}$  ( $n = 1-3$ ). NMR ( $\text{CDCl}_3$ ):  $^{13}\text{C}$  ( $^1\text{H}$  composite pulse decoupled),  $\delta$  175.8 [s,  $\text{CO}_2\text{Me}$ ], 173.5 [s,  $\text{CO}_2\text{Me}$ ], 145–125 [m, Ph], 93.2 [s,  $\text{SBU}^t\text{C}(\text{CO}_2\text{Me})\text{C}(\text{CO}_2\text{Me})$ ], 92.5 [s,  $\text{C}_5\text{H}_5$ ], 51.5 [s, Me], 50.7 [s, Me], 33.4 [s,  $\text{SBU}^t\text{C}(\text{CO}_2\text{Me})$ ] and 29.0 [s,  $\text{Bu}^t$ ]. Complex **2b**: FAB mass spectrum,  $m/z$  720 ( $\text{M}^+$ ) and  $\text{M}^+ - n\text{CO}$  ( $n = 1-3$ ). NMR ( $\text{CDCl}_3$ ):  $^{13}\text{C}$  ( $^1\text{H}$  composite pulse decoupled),  $\delta$  242.1 [d,  $^2J(\text{PC})$  12, Mo–CO], 208.2 [s, Co–CO], 207.8 [s, Co–CO], 177.7 [s,  $\text{CO}_2\text{Me}$ ], 172.3 [s,  $\text{CO}_2\text{Me}$ ], 143–127 [m, Ph], 109.6 [d,  $^2J(\text{PC})$  27,  $\text{PPh}_2\text{C}(\text{CO}_2\text{Me})\text{C}(\text{CO}_2\text{Me})$ ], 90.8 [s,  $\text{C}_5\text{H}_5$ ], 51.7 [s, Me], 51.1 [s, Me], 43.5 [s,  $\text{CH}_2$ ], 29.2 [s,  $\text{CH}_2$ ], 22.3 [s,  $\text{CH}_2$ ] and 13.6 [s, Me]. Complex **2c**: (Found: C, 49.63; H, 4.06.  $\text{C}_{30}\text{H}_{30}\text{O}_7\text{PSCoMo}$  requires C, 50.00; H, 4.17%). FAB mass spectrum,  $m/z$  720 ( $\text{M}^+$ ) and  $\text{M}^+ - n\text{CO}$  ( $n = 1-3$ ). NMR ( $\text{CDCl}_3$ ):  $^{13}\text{C}$  ( $^1\text{H}$  composite pulse decoupled),  $\delta$  240.5 [d,  $^2J(\text{PC})$  40, Mo–CO], 210.0 [s, Co–CO], 206.0 [s, Co–CO], 179.5 [s,  $\text{CO}_2\text{Me}$ ], 170.5 [s,  $\text{CO}_2\text{Me}$ ], 135–125 [m, Ph], 107.4 [d,  $^2J(\text{PC})$  40,  $\text{PPh}_2\text{C}(\text{CO}_2\text{Me})\text{C}(\text{CO}_2\text{Me})$ ], 91.3 [s,  $\text{C}_5\text{H}_5$ ], 52.9 [s,  $\text{PPh}_2\text{C}(\text{CO}_2\text{Me})\text{C}(\text{CO}_2\text{Me})$ ], 51.7 [s, Me], 51.5 [s, Me] and 34.0 [s,  $\text{Bu}^t$ ].

### (d) Reaction of $[(\text{OC})_3\text{Co}\{\mu\text{-C}_2(\text{CO}_2\text{Me})_2\}\text{Mo}(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_2]$ with $\text{Ph}_2\text{P}(\text{SPh})$

To a solution of  $[(\text{OC})_3\text{Co}\{\mu\text{-C}_2(\text{CO}_2\text{Me})_2\}\text{Mo}(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_2]$  (1.00 g, 1.75 mmol) in toluene (50 cm<sup>3</sup>) was added excess  $\text{Ph}_2\text{P}(\text{SPh})$  (0.70 g, 2.38 mmol) in toluene (50 cm<sup>3</sup>). The solution was stirred at 298 K for 24 h and after removal of the solvent under reduced pressure the residue was dissolved in the minimum quantity of  $\text{CH}_2\text{Cl}_2$  and absorbed onto a minimum amount of silica, added to the top of chromatography column and eluted with hexane–ethyl acetate (2:1). This gave, in addition to a small amount of unreacted starting material, the orange crystalline complex  $[(\text{PhS})\text{Ph}_2\text{P}\{\text{OC}\}_2\text{Co}\{\mu\text{-C}_2(\text{CO}_2\text{Me})_2\}\text{Mo}(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_2]$  **1d** (0.983 g, 67%). Complex **1d**: FAB mass spectrum,  $m/z$  838 ( $\text{M}^+$ ) and  $\text{M}^+ - n\text{CO}$  ( $n = 1-3$ ). NMR ( $\text{CDCl}_3$ ):  $^{13}\text{C}$  ( $^1\text{H}$  composite pulse decoupled),  $\delta$  226.5 [s, W–CO], 208.4 [s, Co–CO], 172.4 [s,  $\text{C}_2(\text{CO}_2\text{Me})_2$ ], 135–127 [m, Ph], 103.7 [s,  $\text{C}_5\text{Me}_5$ ], 72.2 [s,  $\text{C}_2(\text{CO}_2\text{Me})_2$ ], 51.4 [s,  $\text{C}_2(\text{CO}_2\text{Me})_2$ ] and 10.7 [s,  $\text{C}_5\text{Me}_5$ ].

### (e) Thermolysis of $[(\text{PhS})\text{Ph}_2\text{P}\{\text{OC}\}_2\text{Co}\{\mu\text{-C}_2(\text{CO}_2\text{Me})_2\}\text{Mo}(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_2]$ **1d**

A solution of  $[(\text{PhS})\text{Ph}_2\text{P}\{\text{OC}\}_2\text{Co}\{\mu\text{-C}_2(\text{CO}_2\text{Me})_2\}\text{Mo}(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_2]$  **1d** (0.500 g, 0.60 mmol) in toluene (50 cm<sup>3</sup>) was thermolysed at 383 K for 2 h. After removal of the solvent under reduced pressure, the mixture was separated using preparative TLC with hexane–ethyl acetate (2:1) as eluent. This gave, in addition to a small amount of unreacted starting material, the orange crystalline complexes  $[(\text{OC})_2\text{Co}\{\mu\text{-SPhC}(\text{CO}_2\text{Me})\text{C}(\text{CO}_2\text{Me})\}(\mu\text{-PPh}_2)\text{Mo}(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})]$  **3d** (0.111 g, 23%),  $[(\text{OC})_2\text{Co}\{\mu\text{-PPh}_2\text{C}(\text{CO}_2\text{Me})\text{C}(\text{CO}_2\text{Me})\}(\mu\text{-SPh})\text{Mo}(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})]$  **4d** (0.126 g, 26%) and  $[(\text{OC})(\eta^5\text{-C}_5\text{Me}_5)\text{Mo}\{\mu\text{-PPh}_2\text{C}(\text{CO}_2\text{Me})\text{C}(\text{CO}_2\text{Me})\}(\mu\text{-SPh})\text{Co}(\text{CO})_2]$  **2d** (0.068 g, 14%). Complex **3d**: FAB mass spectrum,  $m/z$  810 ( $\text{M}^+$ ) and  $\text{M}^+ - n\text{CO}$  ( $n = 1-3$ ). NMR ( $\text{CDCl}_3$ ):  $^{13}\text{C}$  ( $^1\text{H}$  composite pulse decoupled),  $\delta$  177.6 [s,  $\text{CO}_2\text{Me}$ ], 175.3 [s,  $\text{CO}_2\text{Me}$ ], 139–128 [m, Ph], 106.2 [s,  $\text{SPhC}(\text{CO}_2\text{Me})\text{C}(\text{CO}_2\text{Me})$ ], 102.5 [s,  $\text{C}_5\text{Me}_5$ ], 53.7 [s,  $\text{CO}_2\text{Me}$ ], 51.1 [s,  $\text{CO}_2\text{Me}$ ] and 10.7 [s,  $\text{C}_5\text{Me}_5$ ]. Complex **4d**: FAB mass spectrum,  $m/z$  810 ( $\text{M}^+$ ) and  $\text{M}^+ - n\text{CO}$  ( $n = 1-3$ ). NMR ( $\text{CDCl}_3$ ):  $^{13}\text{C}$  ( $^1\text{H}$  composite pulse decoupled),  $\delta$  176.0 [s,  $\text{CO}_2\text{Me}$ ], 171.1 [s,  $\text{CO}_2\text{Me}$ ], 137–128 [m, Ph], 106.2 [s,  $\text{PPh}_2\text{C}(\text{CO}_2\text{Me})\text{C}(\text{CO}_2\text{Me})$ ], 102.6 [s,  $\text{C}_5\text{Me}_5$ ], 50.9 [s,  $\text{CO}_2\text{Me}$ ], 50.7 [s,  $\text{CO}_2\text{Me}$ ], 31.1 [d,  $^1J(\text{PC})$  42,  $\text{PPh}_2\text{C}(\text{CO}_2\text{Me})\text{C}(\text{CO}_2\text{Me})$ ] and



10.7 [s, C<sub>5</sub>Me<sub>5</sub>]. Complex **2d**: FAB mass spectrum, *m/z* 810 (M<sup>+</sup>) and M<sup>+</sup> – *n*CO (*n* = 1–3). NMR (CDCl<sub>3</sub>): <sup>13</sup>C (1H composite pulse decoupled), δ 242.0 [s, Mo–CO], 206.9 [s, Co–CO], 176.1 [s, CO<sub>2</sub>Me], 171.1 [s, CO<sub>2</sub>Me], 138–126 [m, Ph], 51.1 [s, CO<sub>2</sub>Me], 50.8 [s, CO<sub>2</sub>Me], 30.0 [d, PPh<sub>2</sub>C(CO<sub>2</sub>Me)C(CO<sub>2</sub>Me)] and 10.5 [s, C<sub>5</sub>Me<sub>5</sub>].

**(f) Thermolysis of [(OC)<sub>2</sub>Co{μ-SBu<sup>n</sup>C(CO<sub>2</sub>Me)C(CO<sub>2</sub>Me)}-(μ-PPh<sub>2</sub>)Mo(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(CO)] **3c****

A solution of [(OC)<sub>2</sub>Co{μ-SBu<sup>n</sup>C(CO<sub>2</sub>Me)C(CO<sub>2</sub>Me)}-(μ-PPh<sub>2</sub>)Mo(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(CO)] **3c** (0.100 g, 0.14 mmol) in toluene (50 cm<sup>3</sup>) was thermolysed at 383 K for 4 h. After removal of the solvent under reduced pressure, the mixture was separated using preparative TLC with hexane–ethyl acetate (2:1) as eluent. This gave, in addition to a small amount of unreacted starting material, the red-green crystalline complex [(OC)-(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)Mo{μ-PPh<sub>2</sub>C(CO<sub>2</sub>Me)C(CO<sub>2</sub>Me)}(μ-SBu<sup>n</sup>)Co(CO)<sub>2</sub>] **2c** (0.830 g, 83%).

**(g) Reaction of [(OC)<sub>2</sub>Co{μ-SBu<sup>n</sup>C(CO<sub>2</sub>Me)C(CO<sub>2</sub>Me)}-(μ-PPh<sub>2</sub>)Mo(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(CO)] **3c** with P(OMe)<sub>3</sub>**

To a solution of [(OC)<sub>2</sub>Co{μ-SBu<sup>n</sup>C(CO<sub>2</sub>Me)C(CO<sub>2</sub>Me)}-(μ-PPh<sub>2</sub>)Mo(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(CO)] **3c** (0.100 g, 0.14 mmol) in toluene (50 cm<sup>3</sup>) was added P(OMe)<sub>3</sub> (0.10 cm<sup>3</sup>, 0.85 mmol). The solution was stirred at 298 K for 24 h and after removal of the solvent under reduced pressure, the mixture was separated using preparative TLC with hexane–ethyl acetate (2:1) as eluent. This gave the orange crystalline complex [(MeO)<sub>3</sub>P-(OC)Co{μ-SBu<sup>n</sup>C(CO<sub>2</sub>Me)C(CO<sub>2</sub>Me)}(μ-PPh<sub>2</sub>)Mo(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(CO)] **3c'** (0.952 g, 84%). Complex **3c'**: FAB mass spectrum, *m/z* 816 (M<sup>+</sup>) and M<sup>+</sup> – *n*CO (*n* = 1–3). NMR (CDCl<sub>3</sub>): <sup>13</sup>C (1H composite pulse decoupled), δ 235.1 [s, Mo–CO], 206.3 [s, Co–CO], 177.2 [s, CO<sub>2</sub>Me], 174.1 [s, CO<sub>2</sub>Me], 145–125 [m, Ph], 96.3 [s, SBu<sup>n</sup>C(CO<sub>2</sub>Me)C(CO<sub>2</sub>Me)], 93.0 [s, C<sub>5</sub>H<sub>5</sub>], 51.3 [s, Me], 50.6 [s, Me], 34.0 [s, SBu<sup>n</sup>C(CO<sub>2</sub>Me)] and 29.8 [s, Bu<sup>n</sup>].

**(h) The reaction of [(OC)<sub>3</sub>Co{μ-C<sub>2</sub>(CO<sub>2</sub>Me)<sub>2</sub>}W(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(CO)<sub>2</sub>] with Ph<sub>2</sub>P(SBu<sup>n</sup>)**

To a solution of [(OC)<sub>3</sub>Co{μ-C<sub>2</sub>(CO<sub>2</sub>Me)<sub>2</sub>}W(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(CO)<sub>2</sub>] (0.500 g, 0.85 mmol) in toluene (50 cm<sup>3</sup>) excess Ph<sub>2</sub>P(SBu<sup>n</sup>) (1.0 cm<sup>3</sup>, 5.75 mmol) was added. This solution was stirred at 298 K for 24 h and after removal of the solvents under reduced pressure the mixture was absorbed onto a minimum amount of silica, added to the top of chromatography column and eluted with hexane–ethyl acetate (2:1). This gave, in addition to a small amount of unreacted starting material, orange crystalline [(Bu<sup>n</sup>S)Ph<sub>2</sub>P}(OC)<sub>2</sub>Co{μ-C<sub>2</sub>(CO<sub>2</sub>Me)<sub>2</sub>}W(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(CO)<sub>2</sub>] **1e** (0.473 g, 65%). Complex **1e** (Found: C, 44.60; H, 3.64. C<sub>31</sub>H<sub>30</sub>O<sub>8</sub>PSCoW requires C, 43.46; H, 3.50%): FAB mass spectrum, *m/z* 856 (M<sup>+</sup>) and M<sup>+</sup> – *n*CO (*n* = 1–3). NMR (CDCl<sub>3</sub>): <sup>13</sup>C (1H composite pulse decoupled), δ 235.2 [s, W–CO], 210.2 [s, Co–CO], 173.5 [s, C<sub>2</sub>(CO<sub>2</sub>Me)<sub>2</sub>], 133–128 [m, Ph], 88.4 [s, C<sub>5</sub>H<sub>5</sub>], 50.9 [s, C<sub>2</sub>(CO<sub>2</sub>Me)<sub>2</sub>], 32.2 [s, CH<sub>2</sub>], 31.6 [s, CH<sub>2</sub>], 21.8 [s, CH<sub>2</sub>] and 13.5 [s, CH<sub>3</sub>].

**(i) The reaction of [(OC)<sub>3</sub>Co{μ-C<sub>2</sub>(CO<sub>2</sub>Me)<sub>2</sub>}W(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(CO)<sub>2</sub>] with Ph<sub>2</sub>P(SPh)**

To a solution of [(OC)<sub>3</sub>Co{μ-C<sub>2</sub>(CO<sub>2</sub>Me)<sub>2</sub>}W(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(CO)<sub>2</sub>] (0.500 g, 0.85 mmol) in toluene (50 cm<sup>3</sup>) was added Ph<sub>2</sub>P(SPh) (0.300 g, 1.02 mmol). After thermolysis at 373 K for 7 h and removal of the solvent under reduced pressure, the mixture was separated using preparative TLC with hexane–ethyl acetate (2:1) as eluent. This gave, in addition to a small amount of uncharacterised product, the orange crystalline complex [(OC)(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)W{μ-C(CO<sub>2</sub>Me)=CHC(OMe)O}(μ-SPh)-Co(CO){PPh<sub>2</sub>(SPh)}] **6** (0.286 g, 37%). Complex **6** (Found: C, 48.65; H, 3.49. C<sub>37</sub>H<sub>32</sub>O<sub>6</sub>PS<sub>2</sub>CoW requires C, 48.81; H, 3.54%).

FAB mass spectrum, *m/z* 910 (M<sup>+</sup>) and M<sup>+</sup> – *n*CO (*n* = 1–3). NMR (CDCl<sub>3</sub>): <sup>13</sup>C (1H composite pulse decoupled), δ 243.4 [d, <sup>2</sup>J(PC) 11, W–CO], 212.1 [s, Co–CO], 188.2 [d, <sup>2</sup>J(PC) 10, CO<sub>2</sub>Me], 180.8 [s, CO<sub>2</sub>Me], 141–128 [m, Ph], 120.4 [s, C(CO<sub>2</sub>Me)], 91.6 [s, C<sub>5</sub>H<sub>5</sub>], 53.7 [s, CO<sub>2</sub>Me] and 50.9 [s, CO<sub>2</sub>Me].

**(j) Thermolysis of [(Bu<sup>n</sup>S)Ph<sub>2</sub>P}(OC)<sub>2</sub>Co{μ-C<sub>2</sub>(CO<sub>2</sub>Me)<sub>2</sub>}W(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(CO)<sub>2</sub>] **1e****

A solution of [(Bu<sup>n</sup>S)Ph<sub>2</sub>P}(OC)<sub>2</sub>Co{μ-C<sub>2</sub>(CO<sub>2</sub>Me)<sub>2</sub>}W(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(CO)<sub>2</sub>] **1e** (0.300 g, 0.36 mmol) in toluene (50 cm<sup>3</sup>) was thermolysed at 383 K for 8 h. After removal of the solvent under reduced pressure, the mixture was separated using preparative TLC with hexane–ethyl acetate (2:1) as eluent. This gave, in addition to a small amount of unreacted starting material and uncharacterised products, the brown crystalline complexes [(CO)(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)W{μ-SBu<sup>n</sup>C(CO<sub>2</sub>Me)C(CO<sub>2</sub>Me)}-(μ-PPh<sub>2</sub>)Co(CO)<sub>2</sub>] **5e** (0.061 g, 21%) and [(CO)<sub>2</sub>Co{μ-SBu<sup>n</sup>-C(CO<sub>2</sub>Me)C(CO<sub>2</sub>Me)}(μ-PPh<sub>2</sub>)W(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(CO)] **3e** (0.122 g, 42%). Complex **5e** (Found: C, 44.42; H, 3.63. C<sub>30</sub>H<sub>30</sub>O<sub>7</sub>PS<sub>2</sub>-CoW requires C, 44.55; H, 3.71%): FAB mass spectrum, *m/z* 808 (M<sup>+</sup>) and M<sup>+</sup> – *n*CO (*n* = 1–3). NMR (CDCl<sub>3</sub>): <sup>13</sup>C (1H composite pulse decoupled), δ 231.4 [d, <sup>2</sup>J(PC) 9, W–CO], 210.2 [s, Co–CO], 207.2 [s, Co–CO], 177.9 [s, CO<sub>2</sub>Me], 174.4 [s, CO<sub>2</sub>Me], 143–128 [m, Ph], 95.9 [d, <sup>2</sup>J(PC) 24, SBu<sup>n</sup>C(CO<sub>2</sub>Me)C(CO<sub>2</sub>Me)], 88.2 [s, C<sub>5</sub>H<sub>5</sub>], 51.7 [s, CO<sub>2</sub>Me], 51.0 [s, CO<sub>2</sub>Me], 45.5 [s, CH<sub>2</sub>], 35.2 [d, <sup>2</sup>J(PC) 10, SBu<sup>n</sup>C(CO<sub>2</sub>Me)-C(CO<sub>2</sub>Me)] and 29–13 [m, Bu<sup>n</sup>]. Complex **3e** (Found: C, 44.40; H, 3.65. C<sub>30</sub>H<sub>30</sub>O<sub>7</sub>PSCoW requires C, 44.55; H, 3.71%): FAB mass spectrum, *m/z* 808 (M<sup>+</sup>) and M<sup>+</sup> – *n*CO (*n* = 1–3). NMR (CDCl<sub>3</sub>): <sup>13</sup>C (1H composite pulse decoupled), δ 232.5 [s, W–CO], 209.2 [s, Co–CO], 207.2 [s, Co–CO], 177.1 [s, CO<sub>2</sub>Me], 174.1 [s, CO<sub>2</sub>Me], 134–128 [m, Ph], 90.5 [s, C<sub>5</sub>H<sub>5</sub>], 51.6 [s, CO<sub>2</sub>Me], 51.3 [s, CO<sub>2</sub>Me], 48.9 [s, CH<sub>2</sub>], 28.8 [s, CH<sub>2</sub>], 22.2 [s, CH<sub>2</sub>] and 13.8 [s, Me].

**(k) Crystal structure determinations of complexes **1d**, **2b**, **3c'**, **5e** and **6****

X-Ray intensity data were collected on a Phillips PW1100 four-circle diffractometer for **2b** and **5e**, on a Stöe four-circle diffractometer for **3c'** and **6** and for **1d** on a Rigaku AFC5R four-circle diffractometer. Details of the data collection, refinement and crystal data are given in Table 7. The data were corrected for Lorentz polarisation factors. Absorption corrections based on  $\psi$ -scans<sup>33</sup> were applied to the data of **1d**, **3c'** and **6**. After refinement with isotropic displacement parameters for all atoms, empirical corrections<sup>34</sup> were applied to the data of **2b** and **5e**.

For **2b** and **5e**, the metal positions were deduced from Patterson syntheses and the remaining non-hydrogen atoms were located from subsequent difference-Fourier syntheses. Refinement was based on *F*<sup>2</sup>.

For **1d**, **3c'** and **6**, the positions of the metal atoms and most of the non-hydrogen atoms were located from direct methods,<sup>36</sup> and the remaining non-hydrogen atoms were revealed from subsequent difference-Fourier syntheses. Refinement was based on *F*<sup>2</sup>.

In **2b** and **5e** the phenyl and cyclopentadienyl rings were constrained to refine with idealised geometries. Hydrogen atoms for these structures were placed in calculated positions with displacement parameters of 0.1 Å<sup>2</sup>, except those of the cyclopentadienyl ring in **2b**.

For **1d**, **3c'** and **6**, hydrogen atoms were placed in calculated positions with displacement parameters equal to 1.5 *U*<sub>eq</sub> of the parent carbon atoms (1.2 *U*<sub>eq</sub> of parent atoms for phenyl hydrogen atoms in **1d**). All non-hydrogen atoms were assigned anisotropic displacement parameters except the phenyl carbon atoms in **2b**. Some disorder of one OMe substituent of the P(OMe)<sub>3</sub> ligand was noted in **3c'** and the methyl carbon atom was assigned two sites of *ca.* 50% occupancy.

**Table 7** Crystallographic and data processing parameters for complexes **1d**, **2b**, **3c'**, **5e** and **6**

| Complex   | <b>1d</b>   | <b>2b</b>   | <b>3c'</b>  | <b>5e</b>  | <b>6</b>  |
|---|---|---|---|--|---|
| Empirical formula   | C <sub>38</sub> H <sub>36</sub> CoMoO <sub>8</sub> PS               | C <sub>30</sub> H <sub>30</sub> CoMoO <sub>7</sub> PS | C <sub>32</sub> H <sub>30</sub> CoMoO <sub>9</sub> P <sub>2</sub> S | C <sub>30</sub> H <sub>30</sub> CoWO <sub>7</sub> PS | C <sub>37</sub> H <sub>32</sub> CoWO <sub>6</sub> PS <sub>2</sub>   |
| Formula weight  | 838.57  | 720.38  | 816.50  | 808.35   | 910.50  |
| Crystal system  | Monoclinic  | Monoclinic  | Monoclinic  | Triclinic  | Triclinic   |
| Space group   | <i>P</i> 2 <sub>1</sub> / <i>n</i>                                  | <i>P</i> 2 <sub>1</sub> / <i>n</i>                    | <i>P</i> 2 <sub>1</sub> / <i>n</i>                                  | <i>P</i> $\bar{1}$ (no. 2)                           | <i>P</i> $\bar{1}$ (no. 2)  |
| <i>a</i> /Å   | 9.517(2)  | 12.823(3)   | 11.148(2)   | 8.997(2)   | 9.555(2)  |
| <i>b</i> /Å   | 9.699(2)  | 15.293(4)   | 18.141(4)   | 12.386(3)  | 10.419(2)   |
| <i>c</i> /Å   | 40.567(8)   | 16.643(4)   | 17.411(3)   | 13.955(3)  | 19.358(4)   |
| $\alpha$ /°   | —   | —   | —   | 85.13(3)   | 76.22(3)  |
| $\beta$ /°  | 91.39(3)  | 103.19(3)   | 94.33(3)  | 77.88(3)   | 76.57(3)  |
| $\gamma$ /°   | —   | —   | —   | 88.51(3)   | 73.19(3)  |
| <i>U</i> /Å <sup>3</sup>                                  | 3744(1)   | 3178(1)   | 3511(1)   | 1515(1)  | 1763.8(6)   |
| <i>Z</i>  | 4   | 4   | 4   | 2  | 2   |
| <i>D</i> <sub>c</sub> /g cm <sup>-3</sup>                 | 1.488   | 1.510   | 1.545   | 1.772  | 1.714   |
| $\mu$ (Mo-K $\alpha$ )/mm <sup>-1</sup>                   | 0.927   | 0.818   | 1.031   | 4.510  | 3.937   |
| <i>F</i> (000)  | 1712  | 1464  | 1672  | 760  | 900   |
| Reflections collected                                     | 10498   | 6024  | 4725  | 5562   | 4918  |
| Independent reflections                                   | 4896 [ <i>R</i> <sub>int</sub> = 0.1335]                            | 2915 [ <i>I</i> > 3 $\sigma$ ( <i>I</i> )]            | 4557 [ <i>R</i> <sub>int</sub> = 0.0263]                            | 4005 [ <i>I</i> > 3 $\sigma$ ( <i>I</i> )]           | 4618 [ <i>R</i> <sub>int</sub> = 0.0492]                            |
| Final <i>R</i> indices <i>I</i> > 2 $\sigma$ ( <i>I</i> ) | <i>R</i> <sub>1</sub> = 0.0481,<br>w <i>R</i> <sub>2</sub> = 0.0814 | <i>R</i> = 0.0521,<br><i>R</i> ' = 0.0552             | <i>R</i> <sub>1</sub> = 0.0410,<br>w <i>R</i> <sub>2</sub> = 0.1150 | <i>R</i> = 0.0584,<br><i>R</i> ' = 0.0617            | <i>R</i> <sub>1</sub> = 0.0509,<br>w <i>R</i> <sub>2</sub> = 0.1078 |
| All data  | <i>R</i> <sub>1</sub> = 0.1603,<br>w <i>R</i> <sub>2</sub> = 0.5203 | —   | <i>R</i> <sub>1</sub> = 0.0623,<br>w <i>R</i> <sub>2</sub> = 0.1455 | —  | <i>R</i> <sub>1</sub> = 0.0824,<br>w <i>R</i> <sub>2</sub> = 0.1224 |

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See <http://www.rsc.org/suppdata/dt/1999/4447/> for crystallographic files in .cif format.

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