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**PAPER** Wilton-Ely *et al.* Bimetallic complexes based on carboxylate and xanthate ligands: Synthesis and electrochemical investigations

#### PERSPECTIVE

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## Bimetallic complexes based on carboxylate and xanthate ligands: Synthesis and electrochemical investigations<sup>†</sup>

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The homobimetallic ruthenium(II) and osmium(II) complexes  $[{RuR(CO)(PPh_3)_2}_2]$  $(S_2COCH_2C_6H_4CH_2OCS_2)]$  (R = CH=CHBu<sup>t</sup>, CH=CHC\_6H\_4Me-4, C(C=CPh)=CHPh, CH=CHCPh<sub>2</sub>OH) and [{Os(CH=CHC<sub>6</sub>H<sub>4</sub>Me-4)(CO)(PPh<sub>3</sub>)<sub>2</sub>}<sub>2</sub>(S<sub>2</sub>COCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>OCS<sub>2</sub>)] form readily from the reactions of  $[MRCl(CO)(BTD)(PPh_3)_3]$  (M = Ru or Os; BTD = 2,1,3-benzothiadiazole) with the dixanthate KS<sub>2</sub>COCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>OCS<sub>2</sub>K. Addition of KS<sub>2</sub>COCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>OCS<sub>2</sub>K to two equivalents of *cis*-[RuCl<sub>2</sub>(dppm)<sub>2</sub>] leads to the formation of [{(dppm)<sub>2</sub>Ru}<sub>2</sub>- $(S_2COCH_2C_6H_4CH_2OCS_2)^{2+}$ . The benzoate complexes  $[RuR\{O_2CC_6H_4(CH_2OH)-4\}(CO)(PPh_3)_2]$  $(R = CH = CHBu^{t}, CH = CHC_{6}H_{4}Me-4, C(C = CPh) = CHPh)$  are obtained by treatment of [RuRCl(CO)-(BTD)(PPh<sub>3</sub>)<sub>2</sub>] with 4-(hydroxymethyl)benzoic acid in the presence of base. Reaction of [RuHCl-(CO)(PPh<sub>3</sub>)<sub>3</sub>] or [RuRCl(CO)(BTD)(PPh<sub>3</sub>)<sub>2</sub>] with 4-(hydroxymethyl)benzoic acid in the absence of base leads to formation of the chloride analogue [RuCl{O<sub>2</sub>CC<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>OH)-4}(CO)(PPh<sub>3</sub>)<sub>2</sub>]. The unsymmetrical complex [{ $Ru(CH=CHC_6H_4Me-4)(CO)(PPh_3)_2$ }\_2(O<sub>2</sub>CC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>OCS<sub>2</sub>)] forms from the sequential treatment of  $[Ru(CH=CHC_6H_4Me-4){O_2CC_6H_4(CH_2OH)-4}(CO)(PPh_3)_2]$  with base, CS<sub>2</sub> and  $[Ru(CH=CHC_6H_4Me-4)Cl(CO)(BTD)(PPh_3)_2]$ . The new mixed-donor xanthate-carboxylate ligand, KO<sub>2</sub>CC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>OCS<sub>2</sub>K is formed by treatment of 4-(hydroxymethyl)benzoic acid with excess KOH and two equivalents of carbon disulfide. This ligand reacts with two equivalents of  $[Ru(CH=CHC_6H_4Me-4)Cl(BTD)(CO)(PPh_3)_2]$  or *cis*- $[RuCl_2(dppm)_2]$  to yield  $[{(dppm)_2Ru}_2 (O_2CC_6H_4CH_2OCS_2)^{2+}$  or [{Ru(CH=CHC\_6H\_4Me-4)(CO)(PPh\_3)\_2}\_2(O\_2CC\_6H\_4CH\_2OCS\_2)], respectively. Electrochemical experiments are also reported in which communication between the metal centres is investigated.

#### Introduction

While a huge range of transition metal dithiocarbamate complexes is known,<sup>1</sup> xanthate complexes have received far less attention despite the ready accessibility of these ligands from the reaction between alkoxides/aryloxides and carbon disulfide. A few reviews cover these species along with other dithio ligands.<sup>2</sup> Our recent research has concentrated on the extraordinary potential of piperazine dithiocarbamate ligands,<sup>3</sup> which allow the sequential and controlled complexation of a wide variety of metal units. More recently this has been extended to the functionalisation of gold nanoparticles.<sup>4</sup> Building on an investigation of xanthate complexes of ruthenium, including a parent xanthate complex [Ru( $\kappa^2$ -S<sub>2</sub>COH)(dppm)<sub>2</sub>)]<sup>+</sup>,<sup>5</sup> we decided to explore the potential offered by bifunctional xanthate ligands for the preparation of multimetallic compounds. An additional interest was the possibility of electronic communication between the metal centres *via* the linker. Previous studies on complexes of the piperazine bis(dithiocarbamate) ligand  $[S_2CNC_4H_8NCS_2]^{2-}$ , showed no communication due to the saturation of the linkage.<sup>3b</sup>

Our overall aim is to use simple organic linkers which display reliable reactivity in order to construct multimetallic arrays of increasing complexity. Furthermore, their potential as components for metal–organic framework (MOF) systems and nanoscale materials is also under investigation.

While not common, xanthate complexes of ruthenium and osmium are known. The compounds  $[M(S_2COR)_2(PR_3)_2]$ (M = Ru, Os) were reported almost forty years ago,<sup>6d</sup> while the hydride complexes  $[MH(S_2COR)(CO)(PR_3)_2]$  (M = Ru, Os) were prepared more recently.<sup>6b,7</sup> An example bearing both xanthate and dithiocarbamate ligands,  $[Os(S_2COEt)(S_2CNMe_2)(PMe_2Ph)_2]$ , was synthesised by Cole-Hamilton and Stephenson in 1976.<sup>8</sup> Organometallic complexes bearing xanthate ligands are less well known,<sup>9</sup> with cyclopentadienyl donors being typical co-ligands, such as  $[Ru(Cp^*)(S_2COPr^i)(PEt_3)]$ .<sup>9b</sup>

Dixanthate ligands are known but have seen little use. One example is the ligand  $KS_2COCH_2C_6H_4CH_2OCS_2K$ , for which only one report exists aimed at its use in the analysis of mercury(II).<sup>10</sup> Although this and other metals were complexed using this ligand to form polymers, none of the metal species was characterised. Moreover, only one paper reports the preparation of (mononuclear) ruthenium vinyl complexes bearing a xanthate ligand,<sup>9c</sup> and no previous examples exist for osmium vinyl species. An additional

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Scheme 1 General scheme for generation of bimetallic complexes. (i)  $2M^{1}L_{n}$ ; (ii)  $M^{1}L_{n}$ ; (iii) Excess KOH, excess  $CS_{2}$ ; (iv) Base,  $CS_{2}$ ,  $M^{2}L_{n}$ .

interest is the route to unsymmetrical species and hybrid xanthate ligands were identified as having potential for this application. In order to explore this aspect, 4-(hydroxymethyl)benzoic acid was chosen to bond first as a carboxylate and then, *via* deprotonation and addition of carbon disulfide (to afford a xanthate donor unit), it was envisaged that a second metal could then be attached (Scheme 1).

Thus, simple, commercially available organic molecules can be used to form the building blocks for multimetallic systems which can be tailored for their geometric, electrochemical or catalytic properties in simple steps.

Relatively few bimetallic complexes with vinyl or other  $\sigma$ organyl ligands are known and almost all are symmetrical in nature.<sup>11</sup> In some cases the vinyl functionality has been used to link the metal centres<sup>12</sup> or, alternatively, diamine and diisocyanide units<sup>12a</sup> have provided the bridging unit. Recently it has been reported that bidentate dicarboxylate ligands can also act as the bridge between the metals.<sup>13</sup> Apart from [{RuCl(CO)-(PPh<sub>3</sub>)<sub>2</sub>}<sub>2</sub>(SCCH=CHC<sub>6</sub>H<sub>4</sub>CH=CHCS)]<sup>13</sup> and an unusual example by Shaver,<sup>14</sup> in which a diruthenium complex is isolated from the reaction of two equivalents of [CpRu(PPh<sub>3</sub>)<sub>2</sub>SH] with *para*phenylenediisothiocyanate, sulfur-based ligands are rarely used to link organometallic centres. Bimetallic organo-osmium complexes are also rare, with only a few vinyl complexes known.<sup>3c,15</sup> Very few mixed ruthenium–osmium vinyl complexes exist<sup>3e,16</sup>

This report employs dixanthate and mixed carboxylate– xanthate ligands to prepare bimetallic organometallic species of the heavier congeners of group 8. The electrochemical investigations extend the very few studies carried out on ruthenium and osmium xanthate complexes.

#### **Results and discussion**

Hydrometallation of alkynes by the divalent ruthenium and osmium hydride complexes  $[RuHCl(CO)L_{2/3}]$  (L = P<sup>i</sup>Pr<sub>3</sub>,<sup>17</sup> PPh<sub>3</sub><sup>18</sup>) provides a valuable and much used route to the vinyl complexes  $[Ru(CR^1=CHR^2)Cl(CO)L_{2/3}]$ .<sup>19</sup> These vinyl species have been explored in fundamental work by the groups of Werner,<sup>20</sup> Esteruelas<sup>21</sup> Santos,<sup>22</sup> Caulton,<sup>23</sup> Jia,<sup>11,12a-12f,15</sup> Hill,<sup>24</sup> as well as by ourselves.<sup>25</sup> The most convenient triphenylphosphine-stabilised vinyl complexes to use as starting materials are those of the form  $[Ru(CR^1=CHR^2)Cl(CO)(PPh_3)_2]^{18}$  or  $[Ru(CR^1=CHR^2)Cl(CO)(BTD)(PPh_3)_2]$  (BTD = 2,1,3-benzothiadiazole),<sup>24a</sup> where BTD is a labile ligand. A significant

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advantage of the latter is that it avoids contamination with tris(phosphine) material.

Decolorisation of an initially bright yellow dichloromethane solution of [Ru(CH=CHBu<sup>1</sup>)Cl(CO)(BTD)(PPh<sub>3</sub>)<sub>2</sub>] was observed on addition of a methanolic solution of KS<sub>2</sub>COCH<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>OCS<sub>2</sub>K. Analysis of the pale yellow product by <sup>31</sup>P NMR spectroscopy revealed the presence of a new singlet resonance at 39.8 ppm. Broadened doublets for the  $\alpha$ - and  $\beta$ -protons of the vinyl ligand at 5.95 and 4.21 ppm ( $J_{HH} = 16.0$  Hz) were observed in the <sup>1</sup>H NMR spectrum along with a singlet at 0.00 ppm corresponding to the methyl protons. The symmetrical nature of the complex was indicated by two singlet resonances for the dixanthate ligand at 3.96 (OCH<sub>2</sub>) and 6.53 (C<sub>6</sub>H<sub>4</sub>) ppm. A molecular ion at m/z = 1762 in the Fast Atom Bombardment (FAB) mass spectrum confirmed the overall formulation as [{Ru(CH=CHBu<sup>t</sup>)(CO)(PPh<sub>3</sub>)<sub>2</sub>]<sub>2</sub>(S<sub>2</sub>COCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>OCS<sub>2</sub>)] (1) and this composition was also supported by elemental analysis.

To complete the characterisation of the compound, single crystals were grown and a structural study undertaken (Fig. 1). The geometry at the ruthenium centre is a slightly distorted octahedral arrangement. The aromatic ring in the linker is found to be slightly disordered and occupies a number of positions (at 150 K). As can be seen from Table 1, the Ru-S distances in dixanthate complex 1 are longer than those reported for the few other structurally characterised ruthenium xanthate complexes. It is also noteworthy that both the xanthate and the related dithiocarbamate ligand  $(R_2NCS_2)$  often bond to the metal in an asymmetric fashion. This asymmetry can be traced to the trans influence of the other equatorial ligands. In the dithiocarbamate complex,  $[Ru(C(C \equiv CPh) = CHPh)(S_2CNC_4H_8NH_2)(CO)(PPh_3)_2]^+, ^{3c}$ and complex 1, the Ru-S bond *trans* to the vinyl ligand is longer than that *trans* to the carbonyl ligand, illustrating the superior trans influence of the vinyl relative to the carbonyl ligand. In contrast, the two Ru-S values in the symmetrical complexes, [Ru(S<sub>2</sub>COMe)(dppm)<sub>2</sub>]<sup>+ 5</sup> and [Cp\*Ru(S<sub>2</sub>COPr<sup>i</sup>)(PEt<sub>3</sub>)]<sup>9b</sup> are essentially the same. The C-S values of 1.687(5) and 1.674(5) Å are significantly shorter than typically found in thiolate ligands (1.744 Å)<sup>26</sup> indicating the multiple bond character present. While the S-Ru-S bite angle in complex 1 is smaller than that in the other xanthate complexes listed in Table 1, both the C-O distance and the C–O–C angle are similar.

Table 2 compares the data for the vinyl group with literature examples and shows that the Ru– $C_{\alpha}$  distance of complex 1 is similar to that for [Ru(CH=CH<sub>2</sub>)(O<sub>2</sub>CC<sub>5</sub>H<sub>4</sub>FeC<sub>5</sub>H<sub>5</sub>)(CO)(PPh<sub>3</sub>)<sub>2</sub>] but greater than the other two examples, while the vinyl C<sub> $\alpha$ </sub>–C<sub> $\beta$ </sub>

#### **Table 1** Distances in Å, angles in degrees; $L = PPh_3$

Complex	Ru–S	C–O	S–Ru–S	C–O–C
$[Ru(C(C \equiv CPh) = CHPh)(S_2CNC_4H_8NH_2)(CO)L_2]^{+3c}$	2.466(1)		70.33(4)	
	2.508 (1)			
[Ru(S <sub>2</sub> COMe)(dppm) <sub>2</sub> ] <sup>+ 5</sup>	2.435(1)	1.320(3)	71.72(2)	118.3(2)
	2.440(1)	1.447(3)		
$trans-[Ru(S_2COEt)_2(PMe_2Ph)_2]^{6c}$	2.380(2)	1.317(8)	72.04(8)	117.1(6)
	2.404(2)	1.452(9)		
$[Ru(Cp^*)(S_2COPr^i)(PEt_3)]^{9b}$	2.393(2)	1.315(6)	71.45(6)	119.6(4)
	2.406(2)	1.474(7)		
$\textit{cis-}[Ru(S_2COEt)_2(PMe_2Ph)_2]^{6c}$	2.463(2)		71.81(9)	
	2.452(2)		71.39(6)	
	2.397(2)			
	2.385(2)			
$[{Ru(CH=CHBu^{t})(CO)L_{2}}_{2}{S_{2}COCH_{2}C_{6}H_{4}CH_{2}OCS_{2}}](1)$	2.474(1)	1 339(5)	70 13(4)	118 2(3)
	2.516(1)	1.451(6)		11012(0)

**Table 2** Distances in Å, angles in degrees;  $L = PPh_3$ 

Complex	Ru–C <sub>a</sub>	$C_{\alpha}$ – $C_{\beta}$	Ru– $C_{\alpha}$ – $C_{\beta}$
$[Ru(CH=CHPh)(O_2CMe)(CO)L_2]^{27}$	2.030(15)	1.294(14)	125.6(8)
$[Ru(CH=CHPh)(O_2CH)(CO)L_2]^{28}$	2.036(8)	1.35(1)	124.4(7)
$[Ru(CH=CH_2)(O_2CFc)(CO)L_2]^{29}$	2.073(7)	1.159(11)	122.4(7)
$[\{Ru(CH=CHBu^{t})(CO)L_{2}\}_{2}(S_{2}COCH_{2}C_{6}H_{4}CH_{2}OCS_{2})](1)$	2.077(4)	1.336(6)	127.8(3)
$[Ru(C(C \equiv CPh) = CHPh)(S_2CNC_4H_8NH_2)(CO)L_2]^{+3c}$	2.109(5)	1.351(7)	127.6(4)



**Fig. 1** Molecular structure of compound **1**. Selected bond distances (Å) and angles (°) other than those provided in Tables 1 and 2: Ru1–C57 = 1.837(4), C3–S2 = 1.687(5), C3–S4 = 1.674(5), C3–O5 = 1.339(5), P13–Ru–P32 = 173.78(4). Atoms labelled with a prime were generated using symmetry code 1 - x, y, 1/2 - z.

distance is comparable to that for other substituted vinyl ligands. The Ru– $C_{\alpha}$ – $C_{\beta}$  angle is greatest for 1 however this feature could easily be influenced by intermolecular packing requirements.

The homobimetallic ruthenium complexes [{RuR(CO)-(PPh<sub>3</sub>)<sub>2</sub>}<sub>2</sub>(S<sub>2</sub>COCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>OCS<sub>2</sub>)] (R = CH=CHC<sub>6</sub>H<sub>4</sub>Me-4 (**2**), CH=CHCPh<sub>2</sub>OH (**3**), C(C≡CPh)=CHPh (**4**)) were prepared by the same method. All showed similar spectroscopic data for the dixanthate ligand and characteristic resonances for the vinyl ligands in the <sup>1</sup>H NMR spectrum (Scheme 2). The <sup>13</sup>C NMR spectrum of **2** displayed triplets for the carbonyl (206.1 ppm,  $J_{PC} = 15.6$  Hz) and both the C<sub>a</sub> (149.3 ppm,  $J_{PC} = 12.8$  Hz) and C<sub>β</sub> (134.5 ppm,  $J_{PC} = 3.5$  Hz) carbon nuclei of the vinyl ligand. The CS<sub>2</sub> nuclei resonated at 221.8 (t,  $J_{PC} = 2.9$  Hz) ppm while the spacer unit appeared as singlets at 139.2 (*ipso*) and 128.5 (*ortho/meta*) ppm for the aromatic carbons and at 71.4 ppm for the methylene nuclei. An osmium example [ $\{Os(CH=CHC_6H_4Me-4)(CO)(PPh_3)_2\}_2(S_2COCH_2C_6H_4CH_2OCS_2)$ ] (5) was also prepared, demonstrating similar spectroscopic features.

In order to provide an additional comparison (structure, electrochemistry) with the piperazine bis(dithiocarbamate) complexes reported in earlier work,<sup>3</sup> the dicationic dixanthate complex [{(dppm)<sub>2</sub>Ru}<sub>2</sub>(S<sub>2</sub>COCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>OCS<sub>2</sub>)](PF<sub>6</sub>)<sub>2</sub> (**6**) was prepared from the reaction of two equivalents of *cis*-[RuCl<sub>2</sub>(dppm)<sub>2</sub>] with KS<sub>2</sub>COCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>OCS<sub>2</sub>K (Scheme 2). The symmetrical nature of the complex was indicated by two pseudotriplets in the <sup>31</sup>P NMR spectrum. However, in the <sup>1</sup>H NMR spectrum, four doublets were observed for the methylene protons of the dixanthate ligand at 5.06 (d,  $J_{HH} = 11.7$  Hz), 5.07 (d,  $J_{HH} = 11.7$  Hz),



Scheme 2 General scheme for generation of homobimetallic ruthenium complexes. M = Ru,  $R^1 = H$ ,  $R^2 = Bu^t$  (1),  $C_6H_4Me$ -4 (2), CPh<sub>2</sub>OH (3); M = Ru,  $R^1 = C \equiv CPh$ ,  $R^2 = Ph$  (4); M = Os,  $R^1 = H$ ,  $R^2 = C_6H_4Me$ -4 (5); (i) KS<sub>2</sub>COCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>OCS<sub>2</sub>K.

5.45 (d × 2,  $J_{\text{HH}}$  = 12.0 Hz) ppm. This inequivalence was ascribed to the position of the phenyl rings of the dppm ligands, which extend above the linker ligand in an orientation that depends also on the chirality of the metal centre ( $\Delta$  or  $\Lambda$ ). Due to this effect the methylene protons couple and pairs of doublets are observed for both optical isomers. A good model for this is the crystal structure of the complex [(dppm)<sub>2</sub>Ru(S<sub>2</sub>CNC<sub>4</sub>H<sub>8</sub>NCS<sub>2</sub>)Ru(dppm)<sub>2</sub>]<sup>2+, 3</sup> which displays distinct axial and equatorial environments for the piperazine unit in the <sup>1</sup>H NMR spectrum. The resonance for the protons of the C<sub>6</sub>H<sub>4</sub> moiety was found to be obscured by features attributed to the phenyl protons of the diphosphine ligands. Overall composition was assigned on the basis of these data, the appearance of a molecular ion at m/z = 1965 in the FAB mass spectrum and good agreement of elemental analysis values.

As outlined in Scheme 1, it was envisaged that unsymmetrical bimetallic species could be accessed by functionalising a pendant hydroxy group on a ligand already coordinated to the first metal centre. Accordingly, commercially available 4-(hydroxymethyl)benzoic acid was chosen for this purpose. Direct treatment of  $[RuHCl(CO)(PPh_3)_3]$  with this compound led to a product with resonances in the <sup>1</sup>H NMR spectrum at 4.49 (s, OCH<sub>2</sub>) ppm and 6.86 (s,  $C_6H_4$ ) ppm for the carboxylate ligand but no high field resonance. An absorption attributable to a hydride was also absent in the solid state infrared spectrum (KBr/nujol) though new  $v_{\rm CO}$  absorptions were observed at 1943 cm<sup>-1</sup> and 1519 cm<sup>-1</sup>. On the basis of these data and mass spectrometry and elemental analysis, the structure was formulated as the carboxylate complex  $[RuCl{O_2CC_6H_4(CH_2OH)-4}(CO)(PPh_3)_2]$ (7) shown in Scheme 3. It is likely that the hydride is replaced by the HCl effectively generated by the addition of the 4-(hydroxymethyl)benzoic acid to the complex. The same product was obtained on treatment of [Ru(CH=CHC<sub>6</sub>H<sub>4</sub>Me-4)(CO)(BTD)(PPh<sub>3</sub>)<sub>2</sub>] with HO<sub>2</sub>CC<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>OH)-4 directly, illustrating the sensitivity of the vinyl group to HCl. However, reaction of  $[Ru(CH=CHR)(CO)(BTD)(PPh_3)_2]$  (R = C<sub>6</sub>H<sub>4</sub>Me-4, Bu<sup>t</sup>) with a solution of HO<sub>2</sub>CC<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>OH)-4 pre-stirred with NaOMe yielded the compounds  $[Ru(CH=CHR) \{O_2CC_6H_4(CH_2OH)\}$ -4{(CO)(PPh<sub>3</sub>)<sub>2</sub>] (R = C<sub>6</sub>H<sub>4</sub>Me-4 (8), Bu<sup>t</sup> (9)). The new resonances in the <sup>1</sup>H NMR spectrum for **9** arose from the  $C_6H_4$ ,  $CH_2$  and OHprotons, which gave rise to an AB system (6.55, 6.63 ppm,  $J_{AB} =$ 8.2 Hz), a doublet (4.17 ppm,  $J_{\rm HH} = 5.5$  Hz) and a multiplet at 1.13 ppm, respectively.

The incorporation of the pendant hydroxy unit was designed to allow the formation of the xanthate complexes, [RuCl-



Scheme 3 Preparation of carboxylate-xanthate complexes.  $R = C_6H_4Me$ -4; (i)  $HO_2CC_6H_4CH_2OH$ ; (ii)  $HC\equiv CC_6H_4Me$ -4; (iii)  $HO_2CC_6-H_4CH_2OH$ , NaOMe; (iv) 0.5  $KO_2CC_6H_4CH_2OCS_2K$ ; (v) DBU, CS<sub>2</sub>, [Ru(CH=CHC<sub>6</sub>H<sub>4</sub>Me-4)Cl(CO)(BTD)(PPh\_3)<sub>2</sub>]; (vi) 0.5  $KO_2CC_6H_4CH_2-OCS_2K$ , NH<sub>4</sub>PF<sub>6</sub>.

 $\{O_2CC_6H_4(CH_2OCS_2)-4\}(CO)(PPh_3)_2$  or  $[Ru(vinyl)] \{O_2CC_6H_4 (CH_2OCS_2)-4$  (CO)(PPh\_3)<sub>2</sub>, *in situ* by reaction with CS<sub>2</sub> and then, on treatment with another metal fragment, to provide the heterobimetallic species,  $[L_n Ru \{O_2 CC_6 H_4 CH_2 OCS_2\} ML_n]$ . Deprotonation of the hydroxy proton in 7-9 under sufficiently mild conditions to allow retention of the other co-ligands did not prove straightforward. However, overall, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) provided the best results. Complex 8 was stirred overnight with excess DBU followed by addition of CS<sub>2</sub> and then addition of the vinyl complex [Ru(CH=CHC<sub>6</sub>H<sub>4</sub>Me-4)Cl(CO)(BTD)(PPh<sub>3</sub>)<sub>2</sub>] (BTD = 2,1,3-benzothiadiazole). Analysis of the reaction mixture showed a number of products in addition to the unsymmetrical bimetallic divinyl complex [Ru(CH=CHC<sub>6</sub>H<sub>4</sub>Me- $4)(CO)(PPh_3)_2 \{O_2CC_6H_4(CH_2OCS_2)-4\}$  (10). Repeated recrystallisation allowed a pure sample to be obtained in low yield.

This difficulty was addressed by developing an alternative route to this complex. Treatment of 4-(hydroxymethyl)benzoic acid with two equivalents of  $CS_2$  and excess KOH for 5 h led to the formation of the new carboxylate–xanthate ligand,  $KO_2CC_6H_4CH_2OCS_2K$ 

(11). This was used to prepare compound 10 cleanly, and in high yield. The success of the reaction was indicated by the observation of two equal intensity singlets in the <sup>31</sup>P NMR spectrum at 37.2 and 39.3 ppm. In the <sup>1</sup>H NMR spectrum, two AB systems were observed at 6.38, 6.79 and 6.45, 6.79 ppm ( $J_{\rm HH} = 8.1$  Hz,  $J_{\rm HH} = 7.9$  Hz) for the aromatic section of the linker, along with a singlet at 4.52 ppm for the methylene unit. The subtle difference in the environments of the tolylvinyl ligands could also be discerned from the pairs of  $H_{\scriptscriptstyle\beta}$  doublet resonances at 5.62 ( $J_{\rm HH} = 17.2$  Hz) and 5.91 ( $J_{\rm HH} = 15.1$  Hz) and doublets of triplets for the H<sub> $\alpha$ </sub> protons at 7.83 ( $J_{\rm HH}$  = 17.2 Hz,  $J_{\rm HP}$  = 3.4 Hz) and 7.85 ( $J_{HH} = 15.1$  Hz,  $J_{HP} = 2.8$  Hz). From comparison of these data with those recorded for [{Ru(CH=CHC<sub>6</sub>H<sub>4</sub>Me-4)(CO)- $(PPh_3)_2$ }2(S<sub>2</sub>COCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>OCS<sub>2</sub>)] (2) and [Ru(CH=CHC<sub>6</sub>H<sub>4</sub>-Me-4) $\{O_2CC_6H_4(CH_2OH)-4\}(CO)(PPh_3)_2\}$  (8), reasonably confident assignments of these resonances could be made. The solid state infrared spectrum showed a single, broad  $v_{co}$  absorption at 1923 cm<sup>-1</sup> and a medium intensity  $v_{C-0}$  band at 1507 cm<sup>-1</sup> for the carboxylate moiety.

In order to explore the reactivity of the dixanthate ligand with other related metal-ligand sets, and to extend our earlier work with xanthates,6 KO2CC6H4CH2OCS2K was treated with two equivalents of cis-[RuCl<sub>2</sub>(dppm)<sub>2</sub>] in the presence of  $NH_4PF_6$  to provide [{ $Ru(dppm)_2$ }\_{2}{ $O_2CC_6H_4CH_2OCS_2$ }]( $PF_6$ )<sub>2</sub> (12). Two pairs of pseudotriplets were observed in the <sup>31</sup>P NMR spectrum at -17.8, -5.8 (assigned to the phosphorus nuclei of the metal-xanthate moiety) and -11.9, -8.7 ppm (assigned to the phosphorus nuclei of the metal-carboxylate unit). The assignments were based on data for the dixanthate complex  $[(dppm)_2Ru(S_2COCH_2C_6H_4CH_2OCS_2)Ru(dppm)_2](PF_6)_2$  (6). In the <sup>1</sup>H NMR spectrum, the aromatic protons of the linker were obscured by the resonances of the dppm ligands. As found in complex 6, the methylene protons were observed as two pairs of doublets at 5.05 (two superimposed) and 5.47, 5.49 ppm, all with coupling of  ${}^{2}J_{\rm HH} = 12.7$  Hz. Again this can be explained by the steric encroachment of one phenyl ring of a dppm ligand rendering these protons mutually inequivalent (hence their coupling). Resonances are present for both  $\Lambda$  and  $\Delta$  isomers, leading to the observed features. This was further supported by measurement of the spectrum at 500 MHz. Solid state infrared spectroscopy gave rise to bands attributed to the carboxylate-xanthate bridge at 1516 cm<sup>-1</sup> for the  $v_{C-O}$  absorption as well as an absorption at 1238 cm<sup>-1</sup> attributed to  $v_{\rm SCS}$  on the basis of literature assignments.<sup>9c</sup> Elemental analysis and mass spectrometry confirmed the overall formulation (Scheme 3).

#### Electrochemistry

Our previous electrochemical investigations concentrated on the complexes  $[Ru(S_2CNC_4H_8NH_2)(dppm)_2]^{2+}$  and  $[\{(dppm)_2Ru\}_2-(S_2CNC_4H_8NCS_2)]^{2+}$ .<sup>3b</sup> The latter was shown to display a Ru(II/III) couple at 0.72 V and to show no significant electronic communication between the metal centres through the largely unsaturated dithiocarbamate linker.

Fig. 2a shows overlaid cyclic voltammograms (CV) for the complex  $[{(dppm)_2Ru}_2(S_2COCH_2C_6H_4CH_2OCS_2)]^{2+}$  (6) and the mononuclear complex  $[Ru(S_2COMe)(dppm)_2]^+$ , both at concentration 0.64 mM, along with a background CV for the electrolyte solution 0.1 M [TBA]PF<sub>6</sub> in DCM. For both mono- and binuclear



**Fig. 2** (a) CV of 0.64 mM complex **6** (thick black); 0.64 mM mononuclear  $[Ru(S_2COMe)(dppm)_2]^+$  (thin black) and background electrolyte, 0.1 M [TBA]PF<sub>6</sub> in DCM only (grey); scan rate 100 mV s<sup>-1</sup>, glassy carbon electrode. (b) CV of 0.64 mM complex **6** (thick black) and 0.64 mM mononuclear  $[Ru(S_2COMe)(dppm)_2]^+$  (thin black) cycling to 1.15 V vs. Fc/Fc<sup>+</sup> only, scan rate 100 mV s<sup>-1</sup>, glassy carbon electrode. (c) Plot of oxidation peak height,  $i_p^{ox}$ , vs. square root scan rate for complex **6** (black diamonds) and mononuclear  $[Ru(S_2COMe)(dppm)_2]^+$  (open diamonds). Lines show best linear fit of data through the origin.

species a quasi-reversible response centred at 0.97 V vs. Fc/Fc<sup>+</sup> was observed and attributed to the Ru(II/III) couple of the complexes. Further irreversible oxidation processes at 1.25 V and 1.40 V were assumed to be due to redox chemistry of the ligands.<sup>30</sup> A reduction response observed at 0.6 V for **6** was not present when the potential was cycled below 1.15 V and so can be attributed to a decomposition product resulting from the oxidation process at 1.25 V. The reversibility of the Ru(II/III) couple was investigated at different scan rates between 20–500 mV s<sup>-1</sup>. At rates above 100 mV s<sup>-1</sup> the response was quasi-reversible for both **6** and the mononuclear complex, as shown in Fig. 2b. The oxidation peak current for the binuclear species was between one and two times higher than that of the mononuclear complex.

Comparison with previous studies<sup>3b</sup> shows that oxidation of 6 takes place at a considerably higher potential than the related complex [{(dppm)<sub>2</sub>Ru}<sub>2</sub>(S<sub>2</sub>CNC<sub>4</sub>H<sub>8</sub>NCS<sub>2</sub>)]<sup>2+</sup> which exhibits a reversible couple at 0.72 V. The greater potential required for oxidation of the metal centres of 6 must be due to the  $[S_2COCH_2C_6H_4CH_2OCS_2]^2$  ligand, as the remaining ligand set is identical to that in  $[{(dppm)_2Ru}_2(S_2CNC_4H_8NCS_2)]^{2+.3b}$  Dithiocarbamates are known for their ability to stabilise high oxidation states, a propensity attributed to the contribution of the thioureide resonance form.<sup>1</sup> The provision of less electron density from the dixanthate ligand (compared to dithiocarbamates) could result in a less electron-rich metal centre, thus making removal of an electron more difficult. Similar behaviour has previously been reported for mononuclear  $[Ru(S_2COEt)_2(dppe)]$  and  $[Ru{S_2CN(CH_2)_4}_2(dppe)]$ , where  $E^\circ$  for the xanthate complex was found to be ~0.35 V higher than that for the dithiocarbamate complex.<sup>6c</sup> This was attributed to the greater  $\sigma$ -donor ability of the dithiocarbamate ligand. Despite the conjugation of the dixanthate linker, there is no evidence of facilitative electronic interaction between the two ruthenium centres. The conjugation in  $[{(dppm)_2Ru}_2(S_2COCH_2C_6H_4CH_2OCS_2)]^{2+}$  should potentially allow communication between the metals through the linker. However, it is interesting to note that the crystal structure obtained of  $[{Ru(CH=CHBu^{t})(CO)(PPh_{3})_{2}}_{2}(S_{2}COCH_{2}C_{6}H_{4}CH_{2}OCS_{2})]$  (1) showed the aromatic unit to exist in a number of different positions (causing significant disorder in the structure). Rotation around this axis would occur in solution and could lead to interruption of the conjugation between the metal centres, contributing to the lack of observed communication.

The CVs of  $[{(dppm)_2Ru}_2(S_2COCH_2C_6H_4CH_2OCS_2)]^{2+}$  (6) and  $[{(dppm)_2Ru}_2(O_2CC_6H_4CH_2OCS_2)]^{2+}$  (12) were also compared (see ESI†). The potential of the quasireversible Ru(II/III) couple is identical for the two complexes, despite the latter having the carboxylate–xanthate linker, which is shorter, more conjugated and has different donor combinations at either end.

In contrast to the electrochemical behaviour of 6, the CV for  $[{Ru(CH=CHC_6H_4Me-4)(CO)(PPh_3)_2}_2(S_2COCH_2C_6H_4-CO)(PPh_3)_2]_2(S_2COCH_2C_6H_4-CO)(PPh_3)_2]_2(S_2COCH_2C_6H_4-CO)(PPh_3)_2]_2(S_2COCH_2C_6H_4-CO)(PPh_3)_2]_2(S_2COCH_2C_6H_4-CO)(PPh_3)_2]_2(S_2COCH_2C_6H_4-CO)(PPh_3)_2]_2(S_2COCH_2C_6H_4-CO)(PPh_3)_2]_2(S_2COCH_2C_6H_4-CO)(PPh_3)_2]_2(S_2COCH_2C_6H_4-CO)(PPh_3)_2]_2(S_2COCH_2C_6H_4-CO)(PPh_3)_2]_2(S_2COCH_2C_6H_4-CO)(PPh_3)_2]_2(S_2COCH_2C_6H_4-CO)(PPh_3)_2]_2(S_2COCH_2C_6H_4-CO)(PPh_3)_2]_2(S_2COCH_2C_6H_4-CO)(PPh_3)_2]_2(S_2COCH_2C_6H_4-CO)(PPh_3)_2]_2(S_2COCH_2C_6H_4-CO)(PPh_3)_2]_2(S_2COCH_2C_6H_4-CO)(PPh_3)_2]_2(S_2COCH_2C_6H_4-CO)(PPh_3)_2]_2(S_2COCH_2C_6H_4-CO)(PPh_3)_2]_2(S_2COCH_2C_6H_4-CO)(PPh_3)_2(S_2COCH_2C_6H_4-CO)(PPh_3)_2(S_2COCH_2C_6H_4-CO)(PPh_3)_2(S_2COCH_2C_6H_4-CO)(PPh_3)_2(S_2COCH_2C_6H_4-CO)(PPh_3)_2(S_2COCH_2C_6H_4-CO)(PPh_3)_2(S_2COCH_2C_6H_4-CO)(PPh_3)_2(S_2COCH_2C_6H_4-CO)(PPh_3)_2(S_2COCH_2C_6H_4-CO)(PPh_3)_2(S_2COCH_2C_6H_4-CO)(PPh_3)_2(S_2COCH_2C_6H_4-CO)(PPh_3)_2(S_2COCH_2C_6H_4-CO)(PPh_3C_6H_4 (CH_2OCS_2)$  (2) showed a significantly less positive potential for the Ru(II/III) couple, at 0.23 V, as shown in Fig. 3a. Oxidation of the corresponding mononuclear complex, [Ru(CH=CHC<sub>6</sub>H<sub>4</sub>Me-4)(S<sub>2</sub>COMe)(CO)(PPh<sub>3</sub>)<sub>2</sub>],<sup>31</sup> occurred at the same potential and the irreversible oxidation peaks observed for both compounds at 0.85 V and 1.25 V were thus assigned to redox chemistry of the ligands. It was found that if the potential is cycled above 1 V, the response for the Ru(II/III) couple at 0.23 V became significantly less reversible (not shown) indicating that irreversible chemical reaction of the complex can take place on further oxidation. However, when cycled in the region below 0.5 V the Ru(II/III) couple of both 2 and the mononuclear complex showed excellent reversibility and stability in comparison to complex 6 discussed above. This is further illustrated in Fig. 3b where the CV at 100 mV s<sup>-1</sup> for 0.64 mM of complex 2 and 0.64 mM [Ru(CH=CHC<sub>6</sub>H<sub>4</sub>Me-4)(S<sub>2</sub>COMe)(CO)(PPh<sub>3</sub>)<sub>2</sub>] complex are shown. Fig. 3c shows a plot of  $i_p^{ox}$  vs. square root of scan rate for both bi- and mononuclear complexes, where both complexes exhibit model behaviour for reversible, diffusion controlled electron transfer processes.

The ease of oxidation of 2 relative to the dppm complex 6 and the increased stability of the oxidised product could be related



**Fig. 3** (a) CV of 0.64 mM complex **2** (thin black, cycling to 1.4 V; thick black, cycling to 0.5 V) and 0.64 mM mononuclear [Ru(CH=CHC<sub>6</sub>H<sub>4</sub>Me-4)(S<sub>2</sub>COMe)(CO)(PPh<sub>3</sub>)<sub>2</sub>], (grey) scan rate 100 mV s<sup>-1</sup>, glassy carbon electrode. (b) CV of 0.64 mM complex **2** (thick black) and 0.64 mM mononuclear [Ru(CH=CHC<sub>6</sub>H<sub>4</sub>Me-4)(S<sub>2</sub>COMe)(CO)(PPh<sub>3</sub>)<sub>2</sub>], (thin black) cycling to 0.5 V vs. Fc/Fc<sup>+</sup> only, scan rate 100 mV s<sup>-1</sup>, glassy carbon electrode. (c) Plot of oxidation peak height,  $i_p^{\alpha x}$ , vs. square root scan rate for complex **2** (black diamonds) and mononuclear [Ru(CH=CHC<sub>6</sub>H<sub>4</sub>Me-4)(S<sub>2</sub>COMe)(CO)(PPh<sub>3</sub>)<sub>2</sub>] (open diamonds). Lines show best linear fit of data through the origin.

to the neutral nature of compound **2** compared to dication **6**, in which a tetracation must be formed on oxidation of each centre to Ru(III). The stability of the complex to oxidation may also be due to the  $\sigma$ -donation and unsaturated nature of the tolylvinyl ligand permitting accommodation of the accumulated positive charge and hence stabilisation of the higher oxidation state of the metal centre.

The CVs of  $[{Ru(CH=CHC_6H_4Me-4)(CO)(PPh_3)_2}_2$ (S<sub>2</sub>COCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>OCS<sub>2</sub>)] (2) and  $[{Ru(CH=CHC_6H_4Me-4)-(CO)(PPh_3)_2}_2{O_2CC_6H_4CH_2OCS_2}]$  (10) were also compared (see ESI†). In a similar way to the comparison of the CV of complexes 6 and 12 discussed above,  $E^{\circ}$  of the Ru(II/III) couple was identical for complexes 2 and 10, despite the latter having the shorter, more conjugated carboxylate-xanthate linker. It therefore must be the co-ligands which dominate the electrochemical behaviour of these species rather than the dixanthate or carboxylate-xanthate linkage.

#### Conclusion

The work described here illustrates the potential for xanthate donors to be used in the construction of binuclear organometallic complexes. This approach involves the possibility of introducing a second, different metal in this manner—something usually not possible using conventional bifunctional linkages without employing protection strategies. A new hybrid carboxylate–xanthate ligand has been prepared and shown to form unsymmetrical bimetallic species. The conjugated nature of both linkages between the metal units might be expected to allow electronic communication, however, little evidence of this was observed, possibly due to the orientation of the linker and its rapid rotation in solution. These electrochemical studies augment the very small number of investigations of this kind to address xanthate complexes.

#### Experimental

#### General

All experiments were carried out under aerobic conditions and the majority of the complexes appear indefinitely stable towards the atmosphere in solution or in the solid state. The following compounds have been described elsewhere: [RuHCl(CO)(PPh<sub>3</sub>)<sub>3</sub>],<sup>32</sup>  $[OsHCl(BTD)(CO)(PPh_3)_2]^{24h}$   $[Ru(CR^1 = CHR^2)Cl(CO)(PPh_3)_2],$  $(R^{1} = H, R^{2} = Bu^{1}, 2h^{2h} \text{ and } R^{1} = C \equiv CPh, R^{2} = Ph^{24a,b}),$  $[Ru(CR^{1}=CHR^{2})Cl(BTD)(CO)(PPh_{3})_{2}], (R^{1}=H, R^{2}=C_{6}H_{4}Me^{-1})$ 4, CPh<sub>2</sub>OH),<sup>24c</sup> [Os(CH=CHC<sub>6</sub>H<sub>4</sub>Me-4)Cl(CO)(BTD)(PPh<sub>3</sub>)<sub>2</sub>],<sup>24h</sup> cis-[RuCl<sub>2</sub>(dppm)<sub>2</sub>],<sup>33</sup> KS<sub>2</sub>COCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>OCS<sub>2</sub>K.<sup>10</sup> Solvents and compounds not mentioned above were used as received from commercial sources. MALDI-MS and FAB-MS data were obtained using Micromass TofSpec and Autospec Q instruments, respectively. The FAB mass spectrum for 6 was obtained at the EPSRC National Mass Spectrometry Service Centre, University of Wales, Swansea. The peak for the most abundant isotopomer is reported in all cases. The notation [M]+ refers to the molecular ion without counter anion(s). Infrared data were obtained using a Perkin Elmer Paragon 1000 FT-IR spectrometer, KBr plates were used for solid state IR spectroscopy, and characteristic phosphineassociated infrared data are not reported. NMR spectroscopy was performed at 25 °C using a Varian Mercury 300 spectrometer in CDCl<sub>3</sub> unless otherwise indicated. All couplings are in Hz and <sup>31</sup>P NMR spectra are proton decoupled. Elemental analysis data were obtained from London Metropolitan University. The procedures given provide materials of sufficient purity for synthetic and spectroscopic purposes. Samples were recrystallised from a mixture of dichloromethane and ethanol for elemental analysis. Solvates were confirmed by integration of the <sup>1</sup>H NMR spectrum. The electrochemical behaviour of selected complexes was investigated using cyclic voltammetry (CV) in dichloromethane (DCM) with 0.1 M tetrabutylammonium hexafluorophosphate ([TBA]PF<sub>6</sub>) as

the background electrolyte. Measurements were taken with a PSTAT 10 potentiostat (Autolab, Ecochemie) and a three electrode cell comprising a glassy carbon disk working electrode (area =  $0.03141 \text{ cm}^2$ ), a platinum wire coil counter electrode and a silver wire quasi-reference electrode. All potentials are reported with respect to the reversible ferrocene (Fc/Fc<sup>+</sup>) couple. CVs were carried out at different scan rates, *v*, of 10–500 mV s<sup>-1</sup>.

 $[{Ru(CH=CHBu^{t})(CO)(PPh_{3})_{2}}_{2}(S_{2}COCH_{2}C_{6}H_{4}CH_{2}OCS_{2})]$ (1).  $[Ru(CH=CHBu^{t})Cl(CO)(BTD)(PPh_{3})_{2}]$ (150)mg. 0.165 mmol) in dichloromethane (40 mL) was stirred with KS<sub>2</sub>COCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>OCS<sub>2</sub>K (30.3 mg, 0.083 mmol) in methanol (20 mL) at room temperature for 1 h. After removal of all solvent, the crude product was dissolved in the minimum volume of dichloromethane and filtered through a plug of diatomaceous earth (Celite) to remove precipitated KCl. Ethanol (30 mL) was added and a light yellow solid was obtained by slow concentration under reduced pressure on the rotary evaporator. The product was filtered, washed with cold ethanol (10 mL), hexane (10 mL) and dried under vacuum. Yield: 112 mg (76%). IR (CH<sub>2</sub>Cl<sub>2</sub>): 1915 (v<sub>co</sub>) cm<sup>-1</sup>. IR (KBr/Nujol): 1917 (v<sub>co</sub>), 1600, 1581, 1331, 1257, 1189, 1081 cm<sup>-1</sup>. NMR <sup>1</sup>H:  $\delta$  0.01 (s, 18 H, Bu<sup>t</sup>), 3.96 (s, 4 H, CH<sub>2</sub>), 4.21 (d, 2 H, H<sub> $\beta$ </sub>,  $J_{HH}$  = 16.0 Hz), 5.95 (d(br), 2 H,  $H_{\alpha}$ ,  $J_{HH} = 16.0$  Hz), 6.53 (s, 4 H,  $C_6H_4$ ), 6.87–7.19 (m, 60 H,  $C_6H_5$ ) ppm. <sup>31</sup>P:  $\delta$  39.8 (s, PPh<sub>3</sub>) ppm. MS (FAB) m/z (%) = 1762 (1) [M]<sup>+</sup>, 1499 (1) [M – PPh<sub>3</sub>]<sup>+</sup>. Analysis: Found C, 65.4; H, 5.0%. Calculated for C<sub>96</sub>H<sub>90</sub>O<sub>4</sub>P<sub>4</sub>Ru<sub>2</sub>S<sub>4</sub>: C, 65.4; H, 5.2%.

 $[{Ru(CH=CHC_6H_4Me-4)(CO)(PPh_3)_2}_2(S_2COCH_2C_6H_4CH_2 OCS_2$  (2). The same procedure was followed as for compound 1 using  $[Ru(CH=CHC_6H_4Me-4)Cl(CO)(BTD)(PPh_3)_2]$ (170 mg, 0.180 mmol) and KS<sub>2</sub>COCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>OCS<sub>2</sub>K (33.1 mg, 0.090 mmol) to yield 141 mg of pale yellow product (86%). IR (CH<sub>2</sub>Cl<sub>2</sub>): 1922 (v<sub>co</sub>) cm<sup>-1</sup>. IR (KBr/Nujol): 1924 (v<sub>co</sub>), 1559, 1505, 1323, 1272, 1173 cm<sup>-1</sup>. NMR <sup>1</sup>H (CD<sub>2</sub>Cl<sub>2</sub>, 500 MHz): δ 2.17 (s, 6 H, CH<sub>3</sub>), 4.52 (s, 4 H, CH<sub>2</sub>), 5.53 (dt, 2 H, H<sub> $\beta$ </sub>,  $J_{HH} = 16.9$  Hz,  $J_{\rm HP} = 1.7$  Hz), 6.42, 6.82 (AB, 8 H, C<sub>6</sub>H<sub>4</sub>,  $J_{\rm AB} = 7.9$  Hz), 7.01 (s, 4 H,  $C_6H_4$ ), 7.30–7.38, 7.53–7.58 (m × 2, 60 H,  $C_6H_5$ ), 7.80 (dt, 2 H, H<sub> $\alpha$ </sub>,  $J_{HH}$  = 16.9 Hz,  $J_{HP}$  = 3.3 Hz) ppm. <sup>13</sup>C (CD<sub>2</sub>Cl<sub>2</sub>, 500 MHz)  $\delta$  = 221.8 (t, CS<sub>2</sub>,  $J_{PC}$  = 2.9 Hz), 206.1 (t, CO,  $J_{PC}$  = 15.6 Hz), 149.3 (t,  $C_{\alpha}$ ,  $J_{PC} = 12.8$  Hz), 139.3 (s,  $C^{1/4}$ (tolyl)), 139.2 (s, C<sup>1/4</sup>(C<sub>6</sub>H<sub>4</sub>) spacer), 135.1 (s, C<sup>1/4</sup>(tolyl)), 134.8 (t<sup>v</sup>, o/m-C<sub>6</sub>H<sub>5</sub>,  $J_{PC} = 4.7$  Hz), 134.5 (t, C<sub> $\beta$ </sub>,  $J_{PC} = 3.5$  Hz), 133.8 (s, ipso-C<sub>6</sub>H<sub>5</sub>,  $J_{PC} = 22.0$  Hz), 129.9 (s, para-C<sub>6</sub>H<sub>5</sub>), 128.8 (s, C<sup>2/3/5/6</sup>(tolyl)), 128.5 (s,  $C^{2/3/5/6}(C_6H_4)$  spacer), 128.0 (t<sup>v</sup>, o/m-C<sub>6</sub>H<sub>5</sub>,  $J_{PC} = 4.7$  Hz), 124.5 (s, C<sup>2/3/5/6</sup>(tolyl)), 71.4 (s, OCH<sub>2</sub>), 21.0 (s, CH<sub>3</sub>) ppm. <sup>31</sup>P: δ 39.4 (s, PPh<sub>3</sub>) ppm. MS (FAB) m/z (%) = 1830 (1) [M]<sup>+</sup>, 1566 (1) [M - PPh<sub>3</sub>]<sup>+</sup>. Analysis: Found C, 66.9; H, 4.8%. Calculated for C102H86O4P4Ru2S4: C, 66.9; H, 4.7%.

[{**Ru**(CH=CHCPh<sub>2</sub>OH)(CO)(PPh<sub>3</sub>)<sub>2</sub>}<sub>2</sub>(S<sub>2</sub>COCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>-OCS<sub>2</sub>)] (3). The same procedure was followed as for compound 1 using [Ru(CH=CHCPh<sub>2</sub>OH)Cl(CO)(BTD)(PPh<sub>3</sub>)<sub>2</sub>] (200 mg, 0.193 mmol) and KS<sub>2</sub>COCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>OCS<sub>2</sub>K (35.4 mg, 0.097 mmol) to yield 117 mg of yellow product (60%). IR (CH<sub>2</sub>Cl<sub>2</sub>): 1919 ( $v_{co}$ ) cm<sup>-1</sup>. IR (KBr/Nujol): 1919 ( $v_{co}$ ), 1906, 1557, 1309, 1219, 1195 cm<sup>-1</sup>. NMR (CD<sub>2</sub>Cl<sub>2</sub>)<sup>-1</sup>H: δ 4.31 (s, 4 H, CH<sub>2</sub>), 4.66 (d, 2 H, H<sub>β</sub>,  $J_{HH} = 15.8$  Hz), 6.82 (dt, 2 H, H<sub>α</sub>,  $J_{HH} = 15.8$  Hz,  $J_{HP} = 2.0$  Hz), 6.94 (s, 4 H, C<sub>6</sub>H<sub>4</sub>), 7.36–7.60 (m, 80 H, C<sub>6</sub>H<sub>5</sub>) ppm. <sup>31</sup>P: δ 40.8 (s, PPh<sub>3</sub>) ppm. MS (FAB) = not diagnostic. Analysis: Found

C, 67.9; H, 4.7%. Calculated for  $C_{114}H_{94}O_6P_4Ru_2S_4{:}$  C, 68.0; H, 4.7%.

[{**Ru**(**C**(**C**≡**CPh**)=**CHPh**)(**CO**)(**PPh**<sub>3</sub>)<sub>2</sub>]<sub>2</sub>(**S**<sub>2</sub>**COCH**<sub>2</sub>**C**<sub>6</sub>**H**<sub>4</sub>**CH**<sub>2</sub>-**OCS**<sub>2</sub>)] (4). The same procedure was followed as for compound **1** using [**Ru**(**C**(**C**≡**CPh**)=**CHPh**)**C**](**CO**)(**PPh**<sub>3</sub>)<sub>2</sub>] (100 mg, 0.112 mmol) in dichloromethane (20 mL) and **KS**<sub>2</sub>**COCH**<sub>2</sub>**C**<sub>6</sub>**H**<sub>4</sub>**CH**<sub>2</sub>**OCS**<sub>2</sub>**K** (20.5 mg, 0.056 mmol) in methanol (10 mL) to yield 68 mg of yellow product (60%). **IR** (**CH**<sub>2</sub>**C**]<sub>2</sub>): 1931 ( $v_{co}$ ) cm<sup>-1</sup>. **IR** (**KB**r/**Nu**jol): 2147 ( $v_{c=c}$ ), 1930 ( $v_{co}$ ), 1603, 1323, 1179 cm<sup>-1</sup>. **NMR** <sup>1</sup>H: δ 4.47 (s, 4 H, CH<sub>2</sub>), 6.93 (s, 4 H, **C**<sub>6</sub>**H**<sub>4</sub>), 7.05 (m, 11 H, **CC**<sub>6</sub>**H**<sub>5</sub>), 7.16–7.32 (m, 60 H + 9 H, **PC**<sub>6</sub>**H**<sub>5</sub> + **CC**<sub>6</sub>**H**<sub>5</sub>) ppm. <sup>31</sup>P: δ 38.0 (s, **PPh**<sub>3</sub>) ppm. **MS** (**FAB**) *m/z* (%) = 2004 (1) [**M**]<sup>+</sup>, 1741 (1) [**M** – **PPh**<sub>3</sub>]<sup>+</sup>. Analysis: Found **C**, 69.4; H, 4.5%. Calculated for **C**<sub>116</sub>**H**<sub>90</sub>**O**<sub>4</sub>**P**<sub>4</sub>**Ru**<sub>2</sub>**S**<sub>4</sub>: **C**, 69.5; H, 4.5%.

[{Os(CH=CHC<sub>6</sub>H<sub>4</sub>Me-4)(CO)(PPh<sub>3</sub>)<sub>2</sub>}<sub>2</sub>(S<sub>2</sub>COCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>-OCS<sub>2</sub>)] (5). The same procedure was followed as for compound 1 using [Os(CH=CHC<sub>6</sub>H<sub>4</sub>Me-4)Cl(CO)(BTD)(PPh<sub>3</sub>)<sub>2</sub>] (90 mg, 0.087 mmol) in dichloromethane (20 mL) and KS<sub>2</sub>COCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>OCS<sub>2</sub>K (16 mg, 0.044 mmol) in methanol (10 mL) to yield 63 mg of product (72%). IR (CH<sub>2</sub>Cl<sub>2</sub>): 1956 ( $v_{co}$ ) cm<sup>-1</sup>. IR (KBr/Nujol): 1910 ( $v_{co}$ ), 1544, 1505, 1261, 1228, 1185 cm<sup>-1</sup>. NMR <sup>1</sup>H:  $\delta$  2.21 (s, 6 H, CH<sub>3</sub>), 4.54 (s, 4 H, CH<sub>2</sub>), 5.47 (d, 2 H, Hβ,  $J_{HH}$  = 16.8 Hz), 6.37, 6.82 (AB, 8 H, C<sub>6</sub>H<sub>4</sub>,  $J_{AB}$  = 7.5 Hz), 6.96 (s, 4 H, C<sub>6</sub>H<sub>4</sub>), 7.29–7.53 (m, 60 H, C<sub>6</sub>H<sub>5</sub>), 8.35 (dt, 2 H, H<sub>α</sub>,  $J_{HH}$  = 16.8 Hz,  $J_{HP}$  = 2.3 Hz) ppm. <sup>31</sup>P:  $\delta$  8.2 (s, PPh<sub>3</sub>) ppm. MS (FAB) m/z (%) = 2008 (1) [M]<sup>+</sup>. Analysis: Found C, 60.9; H, 4.3%. Calculated for C<sub>102</sub>H<sub>86</sub>O<sub>4</sub>Os<sub>2</sub>P4S<sub>4</sub>: C, 61.0; H, 4.3%.

 $[{(dppm)_2Ru}_2(S_2COCH_2C_6H_4CH_2OCS_2)](PF_6)_2$  (6). A solution of KS<sub>2</sub>COCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>OCS<sub>2</sub>K (20 mg, 0.053 mmol) and NH<sub>4</sub>PF<sub>6</sub> (35 mg, 0.213 mmol) in methanol (10 mL) was added to a yellow solution of *cis*-[RuCl<sub>2</sub>(dppm)<sub>2</sub>] (100 mg, 0.106 mmol) in dichloromethane (20 mL). The solution was stirred for 2 h. All volatiles were removed and the crude solid was dissolved in dichloromethane (10 mL) and filtered through diatomaceous earth (Celite) to remove NH<sub>4</sub>Cl and excess NH<sub>4</sub>PF<sub>6</sub>. Ethanol (20 mL) was added to the yellow solution and the product was precipitated out under reduced pressure. The yellow solid was filtered and washed with cold ethanol (5 mL) and hexane (10 mL). Yield: 87 mg (85%). IR (KBr/Nujol): 1586, 1573, 1484, 1309, 1237, 1197, 1068, 1026, 1000, 920, 840 (v<sub>P-F</sub>) cm<sup>-1</sup>. NMR <sup>1</sup>H (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  4.52, 4.98 (m × 2, 2 × 4 H, PCH<sub>2</sub>P), 5.06 (d, 1 H, OCH<sub>2</sub>, J<sub>HH</sub> = 12.0 Hz), 5.07 (d, 1 H, OCH<sub>2</sub>,  $J_{\rm HH}$  = 11.7 Hz), 5.45 (d × 2, 2 × 1 H, OCH<sub>2</sub>,  $J_{\rm HH} = 12.0$  Hz), 6.49, 7.00, 7.11, 7.18–7.53, 7.62  $(m \times 5, 84 \text{ H}, C_6 \text{H}_5 \text{ and } C_6 \text{H}_4) \text{ ppm.} {}^{31}\text{P} (\text{CD}_2 \text{Cl}_2): \delta = -17.6$ (td, dppm,  $J_{PP} = 36.0$  Hz,  $J_{PP} = 6.3$  Hz), -5.4 (td, dppm,  $J_{PP} =$ 35.7 Hz,  $J_{PP} = 3.2$  Hz) ppm. MALDI-MS m/z (%): 2175 (14) [M + PF<sub>6</sub>]<sup>+</sup>, 1084 (14) [M - Ru(dppm)<sub>2</sub>(S<sub>2</sub>C)]<sup>+</sup>. Analysis: Calculated for  $C_{110}H_{96}F_{12}O_2P_{10}Ru_2S_4$ : C, 57.0; H, 4.2%. Found: C, 57.0; H, 4.2%.

[RuCl{ $O_2CC_6H_4(CH_2OH)-4$ }(CO)(PPh\_3)\_2] (7). 4-(Hydroxymethyl)benzoic acid (35.1 mg, 0.231 mmol) was added to a dichloromethane (60 mL) solution of [RuHCl(CO)(PPh\_3)\_3] (200 mg, 0.210 mmol) and the reaction stirred for 2 h. Ethanol (60 mL) was added and slow concentration under reduced pressure provided a light orange product. This was washed with ethanol (20 mL), hexane (10 mL) and dried. Yield 103 mg (58%). IR (CH<sub>2</sub>Cl<sub>2</sub>): 1946 ( $v_{co}$ ), 1521 ( $v_{c-0}$ ) cm<sup>-1</sup>. IR (KBr/Nujol): 1943 ( $v_{CO}$ ), 1519 ( $v_{C-O}$ ) cm<sup>-1</sup>. NMR <sup>1</sup>H:  $\delta$  4.49 (s, 2 H, CH<sub>2</sub>), 6.86 (s, 4 H, C<sub>6</sub>H<sub>4</sub>), 7.19–7.49 (m, 30 H, C<sub>6</sub>H<sub>5</sub>) ppm. <sup>31</sup>P:  $\delta$  35.2 (s, PPh<sub>3</sub>) ppm. MS (ES+) *m/z* (%) = 842 (5) [M]<sup>+</sup>. Analysis: Found C, 64.2; H, 4.4%. Calculated for C<sub>45</sub>H<sub>37</sub>ClO<sub>4</sub>P<sub>2</sub>Ru: C, 64.3; H, 4.4%.

 $[Ru(CH=CHC_6H_4Me-4)\{O_2CC_6H_4(CH_2OH)-4\}(CO)(PPh_3)_2]$ (8). 4-(Hydroxymethyl)benzoic acid (88.8 mg, 0.584 mmol) and NaOMe (94.6 mg, 1.750 mmol) were stirred together in a mixture of dichloromethane (50 mL) and methanol (50 mL) for 30 min. Solid  $[Ru(CH=CHC_6H_4Me-4)Cl(CO)(BTD)(PPh_3)_2]$  (500 mg, 0.531 mmol) was added to the reaction and the reaction stirred for 2 h. Slow concentration under reduced pressure provided a light yellow product. This was washed with ethanol (20 mL), hexane (10 mL) and dried. Yield: 451 mg (92%). IR (CH<sub>2</sub>Cl<sub>2</sub>): 1919 ( $v_{CO}$ ), 1510 ( $v_{C-0}$ ) cm<sup>-1</sup>. IR (KBr/Nujol): 1915 ( $v_{C0}$ ), 1544, 1506 ( $v_{C-0}$ ), 1164 cm<sup>-1</sup>. NMR <sup>1</sup>H:  $\delta$  2.21 (s, 3 H, CH<sub>3</sub>), 4.57 (d, 2 H, CH<sub>2</sub>,  $J_{\rm HH} = 4.4$  Hz), 5.75 (d, H<sub> $\beta$ </sub>, 1 H,  $J_{\rm HH} = 15.6$  Hz), 6.31, 6.81 (AB, 4 H,  $C_6H_4Me$ ,  $J_{AB} = 8.1$  Hz), 6.97, 7.07 (AB, 4 H,  $O_2CC_6H_4$ ,  $J_{AB} = 8.2$  Hz), 7.23–7.48 (m, 30 H, C<sub>6</sub>H<sub>5</sub>), 7.78 (dt, H $\alpha$ , 1 H,  $J_{\rm HH} = 15.6$  Hz,  $J_{\rm HP} = 2.8$  Hz) ppm. <sup>31</sup>P:  $\delta$  37.7 (s, PPh<sub>3</sub>) ppm. MS  $(FAB) m/z (\%) = 922 (13) [M]^+$ . Analysis: Found C, 70.4; H, 4.9%. Calculated for C<sub>54</sub>H<sub>46</sub>O<sub>4</sub>P<sub>2</sub>Ru: C, 70.4; H, 5.0%.

[Ru(CH=CHBu'){O<sub>2</sub>CC<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>OH)-4}(CO)(PPh<sub>3</sub>)<sub>2</sub>] (9). The same procedure was followed as for compound **8** using 4-(hydroxymethyl)benzoic acid (92.1 mg, 0.605 mmol), NaOMe (98.1 mg, 1.820 mmol) and [Ru(CH=CHBu')Cl(CO)-(BTD)(PPh<sub>3</sub>)<sub>2</sub>] (500 mg, 0.551 mmol) in methanol (50 mL) and dichloromethane (50 mL), yielding 431 mg of yellow product (88%). IR (CH<sub>2</sub>Cl<sub>2</sub>): 1921 ( $v_{co}$ ), 1517 ( $v_{c-0}$ ) cm<sup>-1</sup>. IR (KBr/Nujol): 1911 ( $v_{co}$ ), 1613, 1589, 1507 ( $v_{c-0}$ ), 1309, 1254 cm<sup>-1</sup>. NMR <sup>1</sup>H: δ 0.00 (s, 9 H, Bu'), 1.13 (m, 1 H, OH), 4.17 (d, 2 H, CH<sub>2</sub>,  $J_{HH}$  = 5.5 Hz), 4.65 (d, Hβ, 1 H,  $J_{HH}$  = 15.3 Hz), 5.98 (dt, Hα, 1 H,  $J_{HH}$  = 15.3 Hz,  $J_{HP}$  = 2.1 Hz), 6.55, 6.63 (AB, 4 H, C<sub>6</sub>H<sub>4</sub>,  $J_{AB}$  = 8.2 Hz), 6.84–7.06 (m, 30 H, C<sub>6</sub>H<sub>5</sub>) ppm. <sup>31</sup>P: δ 37.9 (s, PPh<sub>3</sub>) ppm. MS (MALDI) m/z (%) = 888 (95) [M]<sup>+</sup>. Analysis: Found C, 69.1; H, 5.5%. Calculated for C<sub>51</sub>H<sub>48</sub>O<sub>4</sub>P<sub>2</sub>Ru: C, 69.0; H, 5.5%.

 $[{Ru(CH=CHC_6H_4Me-4)(CO)(PPh_3)_2}_2(O_2CC_6H_4CH_2OCS_2)]$ (10). (a) The same procedure was followed as for compound 1 using  $[Ru(CH=CHC_6H_4Me-4)Cl(CO)(BTD)(PPh_3)_2]$  (80 mg, 0.085 mmol) in dichloromethane (20 mL) and KO<sub>2</sub>CC<sub>6</sub>H<sub>4</sub>-CH<sub>2</sub>OCS<sub>2</sub>K (11) (12.9 mg, 0.042 mmol) in methanol (10 mL) to yield 49 mg of product (65%) after recrystallisation. (b) Compound 8 (50 mg, 0.054 mmol) in dichloromethane (20 mL) was stirred with a few drops of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) overnight. A few drops of CS<sub>2</sub> were added and the mixture stirred for 45 min. [Ru(CH=CHC<sub>6</sub>H<sub>4</sub>Me-4)Cl(CO)(BTD)(PPh<sub>3</sub>)<sub>2</sub>] (56.2 mg, 0.060 mmol) was added and the orange solution stirred for a further 2 h. Ethanol (20 mL) was added and an orange solid was obtained by slow concentration under reduced pressure on the rotary evaporator. The product was filtered, washed with cold ethanol (10 mL) and hexane (10 mL). The product was recrystallised twice from dichloromethane/ethanol and dried under vacuum. Yield: 37 mg (39%) IR (CH<sub>2</sub>Cl<sub>2</sub>): 1921 ( $v_{CO}$ ), 1507 ( $v_{C-0}$ ) cm<sup>-1</sup>. IR (KBr/Nujol): 1923 ( $v_{C0}$ ), 1545, 1507 ( $v_{C-0}$ ), 1183, 999 cm<sup>-1</sup>. NMR (acetone-d<sub>6</sub>) <sup>1</sup>H:  $\delta$  2.15, 2.16 (s × 2, 2 × 3 H, CH<sub>3</sub>), 4.52 (s, 2 H, CH<sub>2</sub>), 5.62 (d, 1 H, H $\beta_{xanthate}$ ,  $J_{HH}$  = 17.2 Hz), 5.91 (d, 1 H, H $\beta_{carboxylate}$ ,  $J_{HH} = 15.1$  Hz), 6.38, 6.79 (AB, 4 H, C<sub>6</sub>H<sub>4</sub>Me<sub>xanthate</sub>,  $J_{AB} = 8.1$  Hz), 6.45, 6.79 (AB, 4 H, C<sub>6</sub>H<sub>4</sub>Me<sub>carboxylate</sub>,  $J_{AB} = 7.9$  Hz), 6.77, 7.11 (AB, 4 H, C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>,  $J_{AB} = 7.9$  Hz), 7.33–7.60 (m, 60 H, C<sub>6</sub>H<sub>5</sub>), 7.83 (dt, 1 H, H<sub> $\alpha$ </sub>,  $J_{HH} = 17.2$  Hz,  $J_{HP} = 3.4$  Hz), 7.85 (dt, 1 H, H<sub> $\alpha$ </sub>,  $J_{HH} = 15.1$  Hz,  $J_{HP} = 2.8$  Hz) ppm. <sup>31</sup>P:  $\delta$  37.2, 39.3 (s × 2, PPh<sub>3</sub>) ppm. MS (FAB) m/z (%) = 1770 (1) [M]<sup>+</sup>. Analysis: Found C, 68.7; H, 4.8%.

**KO**<sub>2</sub>**CC**<sub>6</sub>**H**<sub>4</sub>**CH**<sub>2</sub>**OCS**<sub>2</sub>**K** (11). Carbon disulfide (450 mg, 5.91 mmol) was added to an aqueous solution (7 mL) of 4-(hydroxymethyl)benzoic acid (450 mg, 2.96 mmol) and KOH (830 mg, 14.80 mmol), and the reaction mixture stirred in an ice bath for 5 h. Some crystalline solid appeared in the deep yellow solution but disappeared after ethanol (20 mL) was added. Slow concentration under reduced pressure provided a yellow product. This was filtered, washed with cold ethanol (20 mL) and dried under vacuum. Yield: 840 mg (93%). IR (KBr/Nujol): 1547 ( $v_{C-0}$ ), 1319, 1254, 1216, 1144 ( $v_{SCS}$ ), 1048 ( $v_{SCS}$ ), 876 ( $v_{C-S}$ ) cm<sup>-1</sup>. NMR <sup>1</sup>H (D<sub>2</sub>O) :  $\delta$  5.54 (s, 2 H, CH<sub>2</sub>), 7.42, 7.81 (AB, 4 H, C<sub>6</sub>H<sub>4</sub>,  $J_{AB}$  = 8.7 Hz) ppm. MS (ES–) *m/z* (%) = 227 (98) [M]<sup>2–</sup>. Analysis: Found C, 35.4; H, 1.9%. Calculated for C<sub>9</sub>H<sub>6</sub>K<sub>2</sub>O<sub>3</sub>S<sub>2</sub>: C, 35.5; H, 2.0%.

 $[{(dppm)_2Ru}_2(O_2CC_6H_4CH_2OCS_2)](PF_6)_2$  (12). A solution of K<sub>2</sub>[O<sub>2</sub>CC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>OCS<sub>2</sub>] (16 mg, 0.053 mmol) and NH<sub>4</sub>PF<sub>6</sub> (52 mg, 0.319 mmol) in methanol (20 mL) was added to a vellow solution of *cis*-[RuCl<sub>2</sub>(dppm)<sub>2</sub>] (100 mg, 0.106 mmol) in chloroform (30 mL). The solution was heated under reflux for 5 min then left to stir for 2 h during which time it turned pale yellow. All volatiles were removed and the crude solid was dissolved in chloroform (10 mL) and filtered through diatomaceous earth (Celite) to remove NH<sub>4</sub>Cl and excess NH<sub>4</sub>PF6. Ethanol (20 mL) was added to the yellow solution and the product was precipitated out under reduced pressure. The yellow solid was filtered and washed with cold ethanol (5 mL) and hexane (10 mL). Yield: 78 mg (65%). IR (KBr/nujol): 1613, 1586, 1573, 1516 (v<sub>C-O</sub>), 1483, 1311, 1238, 1191, 1067, 1000, 840 ( $v_{P-F}$ ) cm<sup>-1</sup>. NMR <sup>1</sup>H (CDCl<sub>3</sub>):  $\delta = 4.02$ , 5.00 (m × 2, 2 × 2 H, PCH<sub>2</sub>P), 4.64 (m, 4 H, PCH<sub>2</sub>P), 5.05 (d, 1 H, OCH<sub>2</sub>,  $J_{HH} = 12.7$  Hz), 5.47, 5.49  $(d \times 2, 1 H, OCH_2, J_{HH} = 12.7 Hz), 6.19, 6.53, 6.84-7.78 (m \times 10^{-1})$ 3, 84 H, C<sub>6</sub>H<sub>5</sub> and C<sub>6</sub>H<sub>4</sub>) ppm. <sup>31</sup>P:  $\delta = -17.8$ , -5.8 (m × 2,  $(dppm)_2RuS_2$ , -11.9, 8.7 (m × 2, (dppm)\_2RuO<sub>2</sub>) ppm. FAB-MS *m/z* (%): 1965 (2) [M]<sup>+</sup>, 1004 (7) [M - Ru(dppm)<sub>2</sub>S<sub>2</sub>CO]<sup>+</sup>, 869 (6)  $[M - Ru(dppm)_2(S_2COCH_2C_6H_4CO_2)]^+$ . Analysis: Calculated for C<sub>109</sub>H<sub>94</sub>F<sub>12</sub>O<sub>3</sub>P<sub>10</sub>Ru<sub>2</sub>S<sub>2</sub>: C, 58.0; H, 4.2%. Found: C, 57.9; H, 4.2%.

#### Crystallographic section

Crystals of 1 were grown by slow diffusion of ethanol into a chloroform solution of the complex and subsequent slow evaporation. A typical crystal was mounted using the oil drop technique, in perfluoropolyether oil at 150(2) K with a Cryostream N<sub>2</sub> open-flow cooling device<sup>34</sup> Single crystal X-ray diffraction data were collected using graphite monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å) on an Enraf-Nonius KappaCCD diffractometer. A series of  $\omega$ -scans were performed in such a way as to cover a sphere of data to a maximum resolution of 0.77 Å.

Cell parameters and intensity data for **1** were processed and intensities corrected for absorption effects by the multi-scan method, using the DENZO-SMN package.<sup>35</sup> The structure was

 Table 3
 Crystal data and structure refinement parameters for 1

	<b>1</b> ·4(CHCl <sub>3</sub> )
Chemical Formula	$C_{100}H_{94}Cl_{12}O_4P_4Ru_2S_4$
Fw	2239.58
Crystal system	Monoclinic
Crystal colour	Yellow
Crystal size (mm)	$0.22 \times 0.17 \times 0.02$
Space group	C2/c
a (Å)	35.8614(5)
$b(\mathbf{A})$	12.3470(2)
<i>c</i> (Å)	26.4338(4)
$\alpha$ (°)	90
$\beta$ (°)	119.6973(6)
γ (°)	90
$V(Å^3)$	10167.1(3)
Ζ	4
$D_{\text{calcd}} (\text{g/cm}^3)$	1.463
$T(\mathbf{K})$	150(2)
$\mu$ (Mo K $\alpha$ ) (mm <sup>-1</sup> )	0.807
F(000)	4568
Reflections collected	66391
Unique reflns $(R_{int})$	11512 (0.061)
$R_1 (I > 2\sigma(I))$	0.0571
$wR_2$ (all data)	0.0742

solved by direct methods using SIR92<sup>36</sup> and refined by full-matrix least-squares on F using the CRYSTALS suite.<sup>37</sup>

Where possible, non-hydrogen atoms were refined with anisotropic displacement parameters, however, where there is disorder in the central  $C_6H_4$  unit and the solvent, it was necessary to model refined atoms as isotropic. The bridging aromatic ring was refined with constraints to ensure that it retained a sensible geometry and the total occupancy of the disordered chloroform was constrained to unity with the restraints to ensure the minor, isotropic component maintained a feasible shape. Hydrogen atoms were visible in the difference map and were refined using soft restraints to generate positions for a riding model. Crystal data and structure refinement parameters are included in Table 3.

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by a peak on the forward scan but with no corresponding peak on the reverse scan.

- 31 Prepared in the same manner as [Ru(CH=CHPh)(S<sub>2</sub>COMe)(CO)-(PPh<sub>3</sub>)<sub>2</sub>] reported in reference 9c.
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