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CYCLOPENTADIENYL-RUTHENIUM AND -OSMIUM CHEMISTRY

XXIV *. SOME COMPLEXES CONTAINING THE OLEFINIC TERTIARY PHOSPHINE $2\text{-}CH_2{=}CHC_6H_4PPh_2$ (sp): X-RAY STRUCTURES OF ONE ISOMER OF $OsBr(sp)(\eta\text{-}C_5H_5)$, AND OF $\overline{Ru(\eta^3\text{-}S_2CCHMeC_6H_4}PPh_2\text{-}2)(\eta\text{-}C_5H_5)$, CONTAINING AN η^3-DITHIOCARBOXYLATO GROUP

MICHAEL I. BRUCE*, TREVOR W. HAMBLEY, MICHAEL R. SNOW and A. GEOFFREY SWINCER

Jordan Laboratories, Department of Physical and Inorganic Chemistry, University of Adelaide, Adelaide, South Australia 5001 (Australia)

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Summary

Reactions between $MX(PPh_3)_2(\eta\text{-}C_5H_5)$ (M = Ru, X = Cl; M = Os, X = Br) and $2\text{-}CH_2{=}CHC_6H_4PPh_2$ afford $\overline{MX(\eta^2\text{-}CH_2{=}CHC_6H_4}PPh_2)(\eta\text{-}C_5H_5)$; the Os complex is obtained in two isomeric forms. The X-ray structure of the major isomer shows the C=C double bond (Os–C, 2.214, 2.195 Å; C=C, 1.57 Å) is almost coplanar with the Os–Br vector, with the terminal C *cis* to Br; the minor isomer is assumed to have the alternative, more sterically congested conformation, with the β-C *cis* to Br. The chlororuthenium complex reacts with NaOMe/MeOH to give the corresponding hydrido complex, which also exists as two isomers in solution; reaction of this complex with CS_2 gives the expected dithio acid derivative $\overline{Ru(S_2CCHMeC_6H_4}PPh_2)(\eta\text{-}C_5H_5)$, together with small amounts of a complex assumed to be $\overline{Ru[S_2C(CH_2)_2C_6H_4}PPh_2](\eta\text{-}C_5H_5)$. The X-ray structure of the major product reveals an unusual η^3-S_2C mode of coordination of the dithio acid fragment (Ru–S, 2.418, 2.426(1) Å; Ru–C 2.175(4) Å). Crystals of $\overline{OsBr(\eta^2\text{-}CH_2{=}CHC_6H_4}PPh_2)(\eta\text{-}C_5H_5)$ are monoclinic, space group $P2_1/n$, with *a* 12.696(2), *b* 21.719(6), *c* 15.929(3) Å, β 79.77(2)°, $Z = 8$; 2867 data ($I > 2.5\sigma(I)$) were refined to $R = 0.040$, $R_w = 0.044$. Crystals of $\overline{Ru(\eta^3\text{-}S_2CCHMeC_6H_4}PPh_2)(\eta\text{-}C_5H_5)$ are orthorhombic, space group *Pbca*, with *a* 8.921(2), *b* 15.982(9), *c* 32.216(5) Å, $Z = 8$; 1685 data ($I > 2.5\sigma(I)$) were refined to $R = 0.027$, $R_w = 0.030$.

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* For Part XXIII see ref. 13.

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Introduction

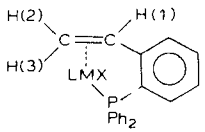
Previous papers in this series have described a considerable amount of unusual chemistry associated with complexes containing $ML_2(\eta\text{-}C_5H_5)$ (M = Ru or Os; L = tertiary phosphine) moieties, and much of this work has been summarised recently [1]. There has been relatively little work reported on complexes containing η^2-olefinic ligands: several neutral complexes having chelating en-yl ligands were described some years ago [2], and a range of cationic complexes of the types $[Ru(\eta^2\text{-un})(L)_2(\eta\text{-}C_5H_5)]^+$ (L = PMe_3; L_2 = dppe) and $[Ru(nbd)(PPh_3)(\eta\text{-}C_5H_5)]^+$ (nbd = norbornadiene) [3] have been made. More recently, the phosphine-free $RuCl(nbd)(\eta^5\text{-}C_5Me_5)$ has been obtained [4]. We have made several complexes containing the olefinic tertiary phosphine, $2\text{-}CH_2{=}CHC_6H_4PPh_2$ (sp), with a view to exploring the reactivity of the coordinated olefinic group. Some of these results are reported below.

Results

The complex $RuCl(\eta^2\text{-}CH_2{=}CHC_6H_4PPh_2)(\eta\text{-}C_5H_5)$ (**1**) is readily prepared by simple ligand exchange between sp and $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$. Complex **1** forms yellow-orange crystals, and was identified by analysis, mass spectrometry, and from its ^1H NMR spectrum (Table 1). In the latter, the olefinic protons resonate at higher field than those in the free ligand, indicating that the vinyl group is π-bonded to the metal atom as found in previous studies. The osmium bromo analogue (**2**), also orange, was prepared similarly from $OsBr(PPh_3)_2(\eta\text{-}C_5H_5)$, and in contrast with **1**, exists in solution in two isomeric forms (**2a** and **2b**, Scheme 1), as shown by ^1H NMR spectroscopy. Thus, two sets of olefinic proton resonances, accompanied by

TABLE 1

SOME NMR DATA FOR sp COMPLEXES



Compound	Chemical shifts (δ) [a]			Coupling constants (Hz)			Ref.
	H(1)	H(2)	H(3)	$J(12)$	$J(13)$	$J(23)$	
sp	[b]	4.99	5.45	11.0	17.5	1.3	12
$RuBr_2(sp)_2$	3.30	2.08	3.11	9.0	12.5	<1	12
$RuCl(sp)(\eta\text{-}C_5H_5)$ (**1**)	5.40	3.04	[c]	9.0	9.0	5.0	[e]
$OsBr(sp)(\eta\text{-}C_5H_5)$ (**2a**)	5.31	3.15	4.17	9.0	9.0	5.0	[e]
$OsBr(sp)(\eta\text{-}C_5H_5)$ (**2b**)	5.47	2.92	4.28	9.0	9.0	5.0	[e]
$HRu(sp)(\eta\text{-}C_5H_5)$ (**3a**)	[c]	1.75	2.73		[d]		[e]
$HRu(sp)(\eta\text{-}C_5H_5)$ (**3b**)	[c]	1.44	2.96		[d]		[e]

[a] The assignment of H(2) and H(3) has been made on the basis of $J(13) > J(12)$. When $J(12) = J(13)$, the resonance at lower field is arbitrarily assigned to H(3). [b] Under Ph resonance. [c] Under C_5H_5 resonance. [d] Not assigned. [e] This work.

two C_5H_5 singlets, in the ratio 9/1, are found. The two isomers can be separated by preparative TLC, the major one giving crystals suitable for X-ray study.

Structure of $OsBr(sp)(\eta\text{-}C_5H_5)$ (2)

Crystals of **2** contain two independent, discrete molecules of the complex with no contacts significantly shorter than Van der Waals distances. Figure 1 shows one of the molecules of **2** together with the atom numbering scheme employed; the other independent molecule is structurally identical.

The osmium atom is coordinated by the cyclopentadienyl group, the bromine atom, and the phosphorus and C=C double bond of the chelating sp ligand. The Os–C(Cp) distances (av. 2.223, 2.261 Å (values for the two independent molecules given)) compare well with those found in $Os(\eta\text{-}C_5H_5)_2$ (2.20(1) Å, preliminary value) [5], $OsCl(PPh_3)_2(\eta\text{-}C_5H_5)$ (2.214 Å) [6] and $[Os(NO)(PMe_3)_2(\eta\text{-}C_5H_5)]^+$ (2.25 Å) [7], and also show the symmetrical attachment of the ring. The Os–Br distance (2.545, 2.510(2) Å) can only be compared with that found in $OsBr_2(CO)(pdma)_2$ (2.567(3) Å) [8], and the Os–P separation (2.284, 2.285(4) Å) is the shortest yet recorded, previously observed values being between 2.320(2) Å in $OsCl(PPh_3)_2(\eta\text{-}C_5H_5)$ [6], and 2.46 Å, in $OsCl_2(HNO)(CO)(PPh_3)_2$ [9].

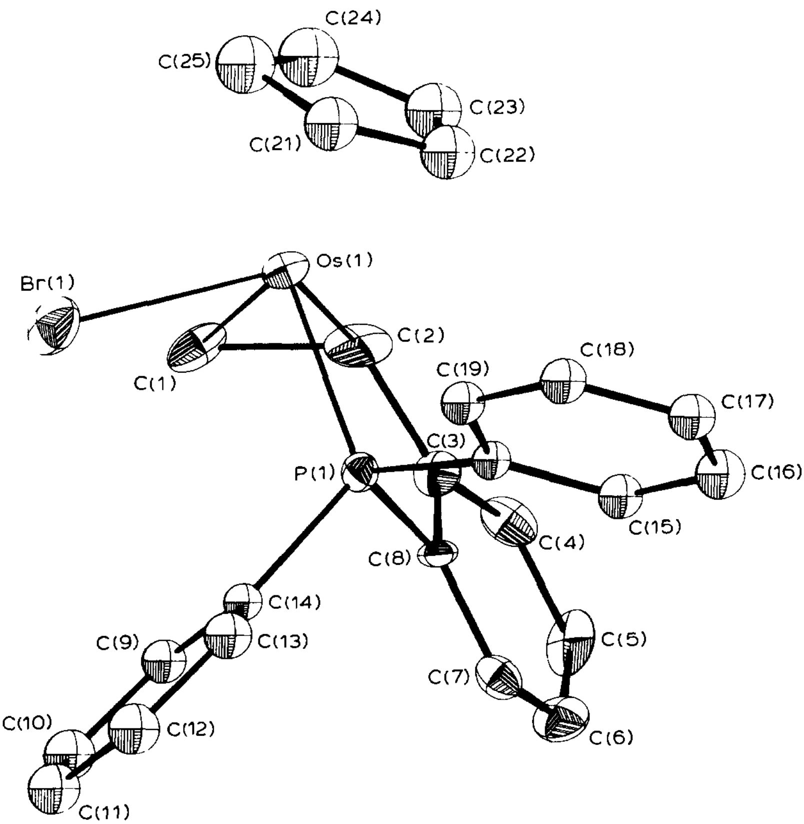
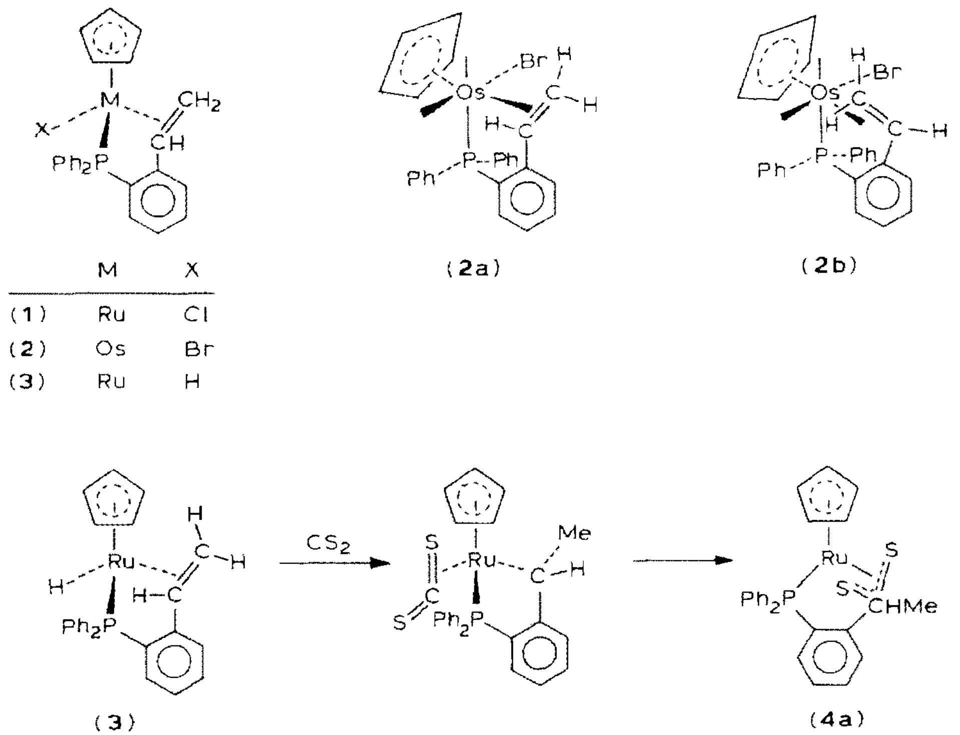


Fig. 1. ORTEP plot [26] of a molecule of $\overline{OsBr(\eta^2\text{-}CH_2{=}CHC_6H_4PPh_2})(\eta\text{-}C_5H_5)$ (**2**), showing atom numbering scheme.

The main feature of interest is the coordination of the olefinic tertiary phosphine, and this is a rare structural characterisation of this relatively uncommon subset of η^2-olefin complexes. The Os–C bonds are 2.249, 2.179(14) Å and 2.182, 2.208(14) Å to C(1) and C(2), respectively. The C(1)–C(2) separation has lengthened to 1.618, 1.521(26) Å (av. 1.57 Å), and suggests that the vinyl group is strongly bound to the metal atom. In $HOs_3(\mu\text{-SMe})(CO)_9(\eta\text{-}C_2H_4)$, Os–C (to C_2H_4) are both 2.23(4) Å, while the C=C bond is 1.42 Å [10]. The orientation of the vinyl group is such that the C=C double bond is almost coplanar with the Os–Br vector, the centre of the bond occupying a position *cis* to the Br atom in the pseudo-octahedral complex; the P atom occupies the third coordination position of this *facial* group of ligands. There is some strain in the chelate group, as indicated by the angle at C(8) (112(2)°, normally expected to be ca. 120°) (Fig. 3).

We have not been able to obtain crystals of the minor isomer suitable for X-ray study. However, we recall that similar isomerism has been noted previously for $M(CO)_4(sp)$ (M = Cr, Mo or W) in solution [11], and for the complex $Ru(CO)(sp)_2$ [12]. In these cases, the isomerism was explained by differences in the orientation of the olefinic group. Consideration of model structures suggests that the minor isomer has the conformation shown in **2b**. However, this arrangement is sterically more congested than the major isomer **2a**, but we have no evidence for any isomerisation process occurring in solution.

Treatment of **1** with NaOMe in methanol [13] afforded the hydride, $HRu(sp)(\eta\text{-}C_5H_5)$ (**3**), which also exists in two isomeric forms in solution. The ^{1}H NMR



	M	X
(1)	Ru	Cl
(2)	Os	Br
(3)	Ru	H

SCHEME 1

spectrum is complex, but indicates that there has been no addition of H^- or OMe^- to the coordinated olefin. The hydride resonances appear as two doublets of doublets at δ −8.56 and −9.60, in a 7/4 ratio. This isomeric composition was further confirmed by the ^1H resonances of the C_5H_5 group, and by appropriate resonances in the ^{13}C and ^{31}P NMR spectra. The most likely explanation of the observed isomerism is again a difference in orientation of the olefinic group. Chlorination of **3** with $CDCl_3$ regenerates **1** as a single isomer, confirming that no reaction with the coordinated vinyl group has occurred.

The reaction between hydride **3** and CS_2 gave a separable mixture of two dark red 1 : 1 adducts **4** and **5** in a 25/1 ratio. The minor isomer has not been identified unambiguously, but is probably $Ru[S_2C(CH_2)_2C_6H_4PPh_2](\eta\text{-}C_5H_5)$. The major isomer contains no Ru–*H* or SC*H*S resonances, and signals at δ 1.90 and 3.28 show that the hydride has added to the olefinic system to give a CHMe group. The ^{13}C NMR spectrum confirms the presence of a methyl group (δ 27.4), and a doublet at δ 51.3 is assigned to the methine carbon (*J*(*C*P) 11 Hz). The CS carbon gives a doublet at δ 150.6. The IR spectrum contains no bands which can be assigned to ν(C=S) modes, but absorptions at 1091, 917 and 751 cm^{-1} can be assigned to characteristic modes of a dithiocarboxylate group. The spectroscopic results are consistent with structure **4**, which has been confirmed by an X-ray study.

*Structure of $Ru(\eta^3\text{-}S_2CCHMeC_6H_4PPh_2)(\eta\text{-}C_5H_5)$ (**4**)*

Crystals of **4** contain discrete molecules of the complex with no contacts significantly shorter than the Van der Waals distances. Figure 2 shows a plot of the structure and the atom numbering scheme used.

The ruthenium atom is bonded to the cyclopentadienyl group, a phosphorus atom, and, unusually, to the two sulphur and carbon atoms of the dithiocarboxylate group. The Ru–C(Cp) distances (av. 2.215 Å, range 2.176–2.264(5) Å) show the slight tilting found previously for several $(\eta\text{-}C_5H_5)$RuABC complexes, the longer Ru–C distances being approximately *trans* to the phosphorus atom of the chelating ligand. The Ru–P bond length (2.288(1) Å) is within the range found for similar complexes.

The attachment of the S_2C portion of the ligand, with Ru–S distances of 2.418, 2.426(1) and an Ru–C separation of 2.175(4) Å, is rare, and to our knowledge, the first of its type found for ruthenium. The Ru–S interactions are comparable with those found in $[Ru(S_2CH)(PMe_2Ph)_4]^+$ (2.43(1) Å) [14] and $Ru(S_2CH)_2(PPh_3)_2$ (2.445(3) Å, *trans* to P) [15]. Other Ru^{II}–S distances are somewhat shorter, however, e.g. 2.323, 2.379(4) Å in $Ru(SC_6H_3MeSC_6H_4Me)(CO)(\eta\text{-}C_5H_5)$ [21], 2.37 Å in $[Ru\{S_2CHPMe_2(\eta^6\text{-}Ph)\}(PMe_2Ph)_3]^+$ [22], and the Ru–S bonds which are *trans* to S in $Ru(S_2CH)_2(PPh_3)_2$ (2.383(3) Å) [15]. The Ru–C separation is similar to that found for the central allylic carbons in $Ru(\eta\text{-}C_3H_5)_2(PPh_3)_2$ (2.13(1) Å) [16] or $Ru(\eta^3\text{-}C_4H_7)_2[P(OMe)_3]_2$ (2.11(2) Å) [17].

Previous examples of dithio acid ligands attached in an η^3-S_2C mode appear to be confined to three complexes of the Group VI neighbour of ruthenium, molybdenum, viz. $MoO(\eta^2\text{-}S_2CSPr^i)(\eta^3\text{-}S_2CSPr^i)$ [18], $MoO(\eta^2\text{-}S_3CPh)(\eta^3\text{-}S_2CPh)$ [19] and $[Mo(CO)_2(PEt_3)(\mu\text{-}\eta^1,\eta^3\text{-}S_2CPEt_3)]_2$ [20]. In the latter, one sulphur of the η^3-S_2C group bridges to the second Mo atom, resulting in a lengthening of the Mo–S distances. However, the isopropylxanthato complex allows a comparison of the η^2-

and η^3-bonded ligands. Characteristic features of the η^3-S_2C ligand are shorter Mo–C and Mo–S, and longer C–S separations, while angles subtended at Mo and C by the two sulphur atoms are both larger than in the η^2-bonded ligand. Similar parameters were found for the dithiobenzoate.

The RuS_2C portion of the dithio acid ligand in **4** closely resembles the MoS_2C moieties found in the two oxomolybdenum(IV) complexes. The C–S distances in **4** are equal (at 1.722, 1.728(4) Å) and are similar to those found in the Mo compounds. Angles S(1)–C(1)–S(2) and S(1)–Ru–S(2) are 121.3(2) and 76.7(1)°, respectively, with other angles at C(1) being 121.4(3) and 116.6(3)°, consistent with sp^2-hybridisation of C(1), with no direct σ-bond with ruthenium. Dithio acid ligands normally have metal–C separations $\geqslant$ 3 Å, and indeed, values for this parameter are generally not quoted, the S_2CR ligand being considered to bond only via the two sulphur atoms. In **4**, the near coplanarity of the S(1)S(2)C(1)C(2) unit (maximum deviation from the least-squares plane is C(1), +0.059 Å) is consistent with a dithio-allylic formulation for the S_2C group, which, however, still acts as a 3-electron donor.

The chelating ligand is slightly distorted at phosphorus, as evidenced by angles RuP(1)C(5) and P(1)C(5)C(6), which have opened to 116.3(3), and closed to 116.8(3)°, respectively (Fig. 3).

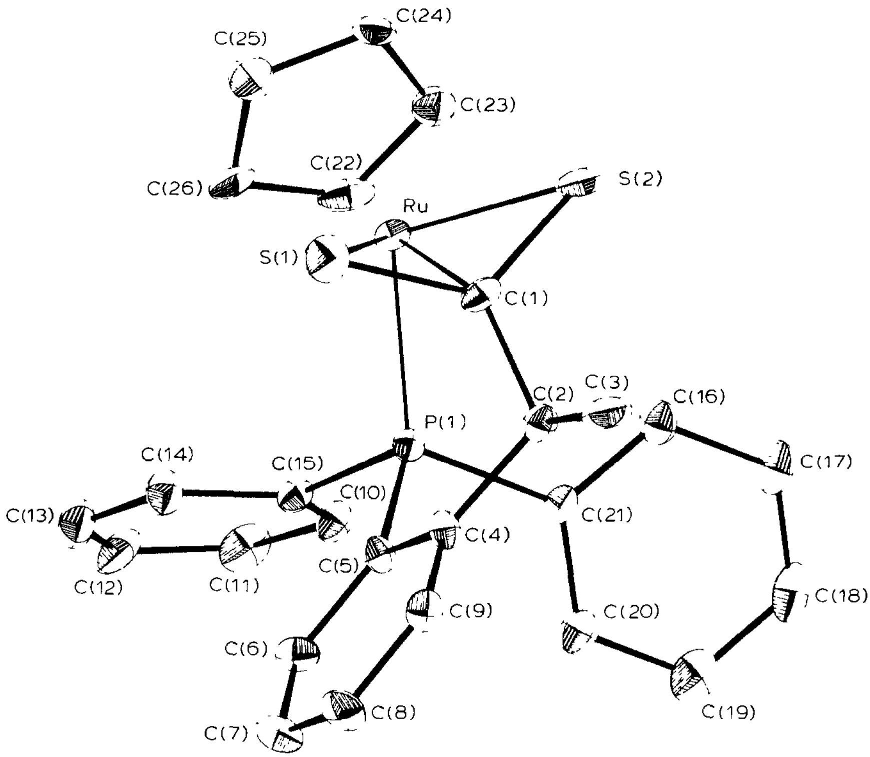
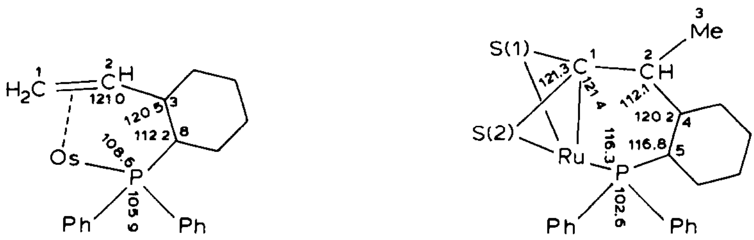


Fig. 2. ORTEP plot [26] of a molecule of $\overline{Ru(\eta^3\text{-}S_2CCHMeC_6H_4PPh_2})(\eta\text{-}C_5H_5)$ (**4**), showing atom numbering scheme.



(2) (4)

Fig. 3. Angles within the chelate rings of complexes **2** and **4**.

Discussion

Replacement of PPh_3 in $MX(PPh_3)_2(\eta\text{-}C_5H_5)$ (M = Ru, X = Cl; M = Os, X = Br) by the olefinic tertiary phosphine $2\text{-}CH_2{=}CHC_6H_4PPh_2$ (sp), gives the expected complexes **1** and **2**, in which the metal atom is chelated by the ligand phosphorus atom and vinyl group. The ruthenium complex can be converted to the corresponding hydride **3** by reaction with NaOMe in MeOH, and it is interesting that there is no addition of methoxide (or hydride) to the coordinated olefin under these conditions. Both complexes **2** and **3**, but not **1**, exist in solution as a mixture of isomers, probably as a result of differing orientations of the vinyl group. The minor isomer is the more sterically congested, and it is likely that the bulk of the chlorine atom prevents its formation in the case of **1**.

Reaction of **3** with CS_2 occurs readily to give a complex containing the $\eta^3\text{-}S_2C\text{-}CHMeC_6H_4PPh_2$ ligand. This, which is unusually bonded to ruthenium via an $\eta^3\text{-}S_2C$ group, is probably formed by insertion of a CS_2 molecule into the Ru–C bond of an intermediate, itself formed by intramolecular combination of the hydride and olefinic ligands of **3**, the hydrogen migrating to C(1) to give an RuCHMe group. Such insertions are not uncommon, and in the present case may occur as the result of initial coordination of a CS_2 molecule to **3**. No evidence was obtained for the formation of an olefinic dithioformato complex by insertion of CS_2 into the Ru–H bond of **3**.

The unprecedented attachment of the dithiocarboxylato ligand by the three atoms of the S_2C moiety, rather than the usual *S,S'* bonding, is the result of the steric constraints of the remainder of the chelate ligand, which preclude the R $\cdots$ C(1) separation of > 3.0 Å which is normally associated with the latter mode of bonding of ligands of this type [23]. The bonding must involve the π system of the CS_2 group, leading to longer C–S bonds than found in conventional dithio acid complexes; no direct Ru–C σ-bond is formed, however, and this part of the chelate ligand acts as a three-electron donor.

Experimental

General experimental conditions have been described in earlier papers. A nitrogen atmosphere was used routinely for (i) distilling solvents before use and (ii) carrying out reactions, but no special precautions were taken to exclude air during work-up procedures.

Instrumentation: Perkin–Elmer 457 and 683 double-grating IR spectrophotometers; Bruker WP80 FT NMR (^{1}H at 80 MHz, ^{13}C at 20.1 MHz) or HX90E spectrometers (^{31}P at 36.4 MHz); AEI/GEC MS 3074 mass spectrometer (direct insertion, 70 eV ionising energy, 8 kV accelerating potential).

$RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ [24] and $OsBr(PPh_3)_2(\eta\text{-}C_5H_5)$ [25] were obtained as described previously; sp was supplied by Dr M.A. Bennett (Research School of Chemistry, Australian National University).

Preparation of RuCl(sp)(η-C₅H₅) (1) (with R.C. Wallis)

A mixture of $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ (726 mg, 1.0 mmol) and sp (288 mg, 1.0 mmol) in light petroleum (100–120 °C boiling fraction, 45 ml) was heated under reflux for 2 h. Filtration of the warm reaction mixture and cooling afforded a yellow-orange powder which was recrystallized (diethyl ether) to give yellow-orange crystals of $RuCl(sp)(\eta\text{-}C_5H_5)$ (**1**) (455 mg, 93%) m.p. 252–255 °C (Found: C, 61.2; H, 4.5%; *M* (mass spectrometry) 490. $C_{25}H_{22}ClPRu$ calcd.: C, 61.3; H, 4.5%; *M* 490). Infrared: (Nujol) 1313w, 1269(sh), 1259w, 1237w, 1226w, 1190w, 1177w, 1160m, 1102(sh), 1099s, 1092m, 1088(sh), 1071m, 1027w, 997m, 990w, 835(sh), 829(sh), 822m, 813m, 783w, 771s, 758s, 750s, 745(sh), 740(sh), 728w, 699vs, 687(sh) cm^{-1}. ^{1}H NMR: δ ($CDCl_3$) (couplings in Table 1) 3.04, 1H, H(2); 4.65, s, 5H, C_5H_5 (H(3) resonance under C_5H_5); 5.40, 1H, H(1); 7.35–7.96, m, 14H, Ph. ^{13}C NMR: δ($CDCl_3$) 51.1, s, CH_2; 69.8, s, CH; 83.0, s, C_5H_5; 127.9–136.2, m, Ph. ^{31}P NMR: δ($CDCl_3$) 71.9, s (relative to PPh_3).

Preparation of OsBr(sp)(η-C₅H₅) (2)

The reaction between $OsBr(PPh_3)_2(\eta\text{-}C_5H_5)$ (300 mg, 0.35 mmol) and sp (110 mg, 0.38 mmol) in petroleum spirit (80–100 °C boiling fraction, 50 ml) in an autoclave (60 atm N_2, 200 °C, 20 h) gave an orange product. Elution on a preparative TLC plate (3/2 diethyl ether/light petroleum) gave $OsBr(PPh_3)_2(\eta\text{-}C_5H_5)$ ($R_f = 0.8$, 11 mg, 4%) and $OsBr(sp)(\eta\text{-}C_5H_5)$ (2) as two isomers:

(i) ($R_f = 0.7$) as orange crystals from dichloromethane/methanol (97 mg, 45%) m.p. 216–218 °C (Found: C, 48.4; H, 3.6; *M*(mass spectrometry), 625. $C_{25}H_{22}BrOsP$ calcd.: C, 48.2; H, 3.6%; *M*, 625). Infrared (Nujol): ν(C=C) 1587w cm^{-1}; other bands at 1714w(br), 1161w, 1156w, 1099m, 1092m, 1080w, 820w, 759m, 753m, 748m, 701(sh), 698s cm^{-1}. ^{1}H NMR: δ($CDCl_3$) (couplings in Table 1) 3.15, 1H, H(2); 4.17, 1H, H(3); 4.88, s, 5H, C_5H_5; 5.31, 1H, H(1); 7.4, m, Ph. ^{13}C NMR: δ($CDCl_3$) 32.1, s, CH_2; 51.6, s, CH; 83.1, s, C_5H_5; 126.6–134.9, m, Ph.

(ii) ($R_f = 0.6$) as orange crystals from dichloromethane/methanol (10 mg, 5%) m.p. 224–225 °C (Found: C, 49.9; H, 3.7; *M* (mass spectrometry), 625. $C_{25}H_{22}BrOsP$ calcd.: C, 48.2; H, 3.6%; *M*, 625). Infrared (Nujol): ν(C=C) 1587w cm^{-1}; other bands at 1438s, 1310w, 1248w, 1154m, 1143w, 1100w, 1092m, 1080m, 1028w, 1001w, 925w, 829w, 818w, 770m, 754m, 746w, 703s, 697s cm^{-1}; ^{1}H NMR: δ($CDCl_3$) (couplings in Table 1) 2.92, 1H, H(2); 4.28, 1H, H(3); 4.89, s, 5H, C_5H_5; 5.47, 1H, H(1); 7.4, m, Ph. ^{13}C NMR: δ($CDCl_3$) 34.3, s, CH_2; 52.7, s, CH; 83.1, s, C_5H_5; 126.6–134.9, m, Ph.

Preparation of HRu(sp)(η-C₅H₅) (3)

Sodium metal (ca. 40 mg, 2 mg atom) was added to $RuCl(sp)(\eta\text{-}C_5H_5)$ (300 mg, 0.61 mmol) in MeOH (30 ml). After 1 h, the resulting yellow solid was filtered off,

TABLE 2

POSITIONAL PARAMETERS ($\times 10^4$) FOR NON-HYDROGEN ATOMS IN $\overline{OsBr(\eta^2\text{-}CH_2{=}CHC_6H_4PPh_2)}(\eta\text{-}C_5H_5)$ (**2**)

Atom	x	y	z
Os(1)	5651(1)	1391(1)	−1445(1)
Os(2)	5949(1)	3480(1)	3197(1)
Br(1)	4812(2)	1330(1)	127(1)
P(1)	4125(3)	988(2)	−1795(2)
C(1)	5004(12)	2355(6)	−1289(11)
C(2)	5263(12)	2127(7)	−2271(13)
C(3)	4363(11)	1997(7)	−2766(9)
C(4)	4148(13)	2387(7)	−3428(11)
C(5)	3273(17)	2295(9)	−3818(10)
C(6)	2594(13)	1814(8)	−3545(11)
C(7)	2771(11)	1406(6)	−2939(9)
C(8)	3670(10)	1489(5)	−2549(8)
C(9)	2350(7)	1430(3)	−701(6)
C(10)	1453(7)	1404(3)	−70(6)
C(11)	1093(7)	845(3)	278(6)
C(12)	1631(7)	311(3)	−6(6)
C(13)	2528(7)	338(3)	−637(6)
C(14)	2887(7)	897(3)	−984(6)
C(15)	4275(7)	186(3)	−3192(5)
C(16)	4553(7)	−357(3)	−3621(5)
C(17)	4906(7)	−850(3)	−3199(5)
C(18)	4980(7)	−798(3)	−2348(5)
C(19)	4701(7)	−254(3)	−1919(5)
C(20)	4349(7)	238(3)	−2341(5)
C(21)	6796(9)	622(4)	−1386(7)
C(22)	6784(9)	750(4)	−2231(7)
C(23)	7155(9)	1341(4)	−2394(7)
C(24)	7396(9)	1579(4)	−1649(7)
C(25)	7174(9)	1135(4)	−1026(7)
Br(2)	326(2)	1726(1)	4757(1)
P(2)	−630(3)	1027(2)	3157(2)
C(26)	304(13)	2431(7)	3026(14)
C(27)	391(11)	2071(7)	2198(10)
C(28)	−604(11)	1859(6)	1917(9)
C(29)	−958(13)	2169(7)	1243(9)
C(30)	−1907(13)	1995(8)	987(9)
C(31)	−2500(12)	1532(7)	1383(10)
C(32)	−2160(12)	1232(7)	2050(10)
C(33)	−1193(9)	1375(6)	2313(3)
C(34)	−2083(7)	557(3)	4591(6)
C(35)	−2928(7)	612(3)	5263(6)
C(36)	−3491(7)	1157(3)	5392(6)
C(37)	−3209(7)	1647(3)	4849(6)
C(38)	−2364(7)	1593(3)	4177(6)
C(39)	−1801(7)	1048(3)	4047(6)
C(40)	0(7)	−163(4)	3449(5)
C(41)	266(7)	−766(4)	3239(5)
C(42)	106(7)	−1002(4)	2468(5)
C(43)	−320(7)	−635(4)	1906(5)
C(44)	−587(7)	−32(4)	2115(5)
C(45)	−427(7)	204(4)	2887(5)
C(46)	2695(8)	1730(4)	2795(7)

TABLE 2 (continued)

Atom	x	y	z
C(47)	2370(8)	1374(4)	2173(7)
C(48)	2038(8)	814(4)	2530(7)
C(49)	2159(8)	824(4)	3373(7)
C(50)	2565(8)	1390(4)	3536(7)

washed with MeOH, and dried to give pure HRu(sp)(η-C_5H_5) (**3**) (242 mg, 87%), m.p. > 140 °C (dec.) as a mixture of isomers (Found: C, 65.2; H, 5.2; *M* (mass spectrometry), 456. $C_{25}H_{23}PRu$ calcd.: C, 65.9; H, 5.1%; *M*, 456). Infrared (Nujol): ν(RuH) 1958 cm^{-1}; other bands at 1582w, 1577(sh), 1169w, 1093m, 1068w, 801w, 795(sh), 760w, 753m, 743m, 701s, 695s cm^{-1}. ^1H NMR: $\delta(C_6D_6)$ 9.60, dd, J(PH) 31 Hz, J(H(3)H) 2 Hz, RuH; −8.56, dd, J(PH) 32 Hz, J(H(3)H) 2 Hz, RuH* (* denotes the minor isomer); see Table 2 for the olefinic region; 4.36, m, 4.57, s, 4.69, s, 4.79, s, 6H, C_5H_5 + CH; 7.0–8.2, m, 14H, Ph (further assignments cannot be made at this stage). ^{13}C NMR: $\delta(C_6D_6)$ 26.2, s, CH_2; 34.9, d, J(CP) 5 Hz, CH_2*; 49.0, d, J(CP) 5 Hz, CH*; 51.1, s, CH; 82.3, s, C_5H_5*; 83.2, s, unassigned; 84.1, s, C_5H_5; 124.3–136.3, m, Ph. ^{31}P NMR: $\delta(C_6D_6)$ 76.7, s, RuP; 88.2, s, RuP* (relative to PPh_3).

Reaction between HRu(sp)(η-C_5H_5) and $CDCl_3$

A solution of **6** in C_6D_6 within an NMR tube reacted with $CDCl_3$ at room temperature. The spectrum of **3** disappeared over 1 h with concomitant formation of peaks due to RuCl(sp)(η-C_5H_5) (**1**). This crystallised from solution and was identified by its melting point (252–255 °C).

Reaction between HRu(sp)(η-C_5H_5) and CS_2

A solution of HRu(sp)(η-C_5H_5) (70 mg, 0.15 mmol) in CS_2 (20 ml) gradually changed to dark red over 2 d. Purification by separation on a preparative TLC plate gave two isomers of Ru(CS_2)[CH(CH_3)$C_6H_4PPh_2$](η-C_5H_5) (2/3 diethyl ether/cyclohexane):

(i) ($R_f \cong 0.7$) as a dark red powder (**4**) (42 mg, 51%) from dichloromethane/hexane, m.p. 202–204 °C (Found: C, 58.5; H, 4.4; *M* (mass spectrometry), 532. $C_{26}H_{23}PRuS_2$ calcd.: C, 58.7; H, 4.4%; *M*, 532). Infrared (Nujol): ν(CS) 1096(sh), 1091m, 917s, 754(sh), 751m cm^{-1}; other bands at 1312w, 1179w, 1026(sh), 1022w, 1009w, 986w, 978w, 850w, 831w, 809m, 764w, 740w, 700s cm^{-1}. ^1H NMR: $\delta(CDCl_3)$ 1.90, d, J(HH) 6.5 Hz, 3H, CH_3; 3.28, q, J(HH) 6.5 Hz, 1H, CH; 4.87, s, 5H, C_5H_5; 7.0–7.4, m, 14H, Ph. ^{13}C NMR: $\delta(CDCl_3)$ 27.4, s, CH_3; 51.3, d, J(CP) 11 Hz, CH; 84.3, s, C_5H_5; 123.2–138.4, m, Ph; 145.9, d, J(CP) 15 Hz, 150.6, d, J(CP) 6 Hz, unassigned.

(ii) ($R_f \cong 0.8$) as a red powder (**5**) (2 mg, 2%) from dichloromethane/hexane (*M* (mass spectrometry), 532. $C_{26}H_{23}PRuS_2$ calcd.: *M*, 532). (Not enough product was available for further identification.)

Crystallography

In the interest of brevity, data for complex **4** are enclosed in brackets after corresponding data for complex **2** in the following account.

A clear yellow needle-shaped crystal of **2** (red in the case of **4**) of approximate dimensions 0.11 × 0.29 × 0.09 mm (0.16 × 0.66 × 0.11 mm) was mounted on a glass fibre with epoxy resin. Lattice parameters at 23 °C were determined by a least-squares fit to the setting parameters of 25 independent reflections, measured and refined by scans performed on an Enraf-Nonius CAD4 four-circle diffractometer employing graphite monochromated Mo-K_α radiation.

Crystal data. **2**, $C_{25}H_{22}BrOsP$, mol. wt. 623.5, monoclinic, space group $P2_1/n$ (variant of No 14, $P2_1/c$); a 12.696(2), b 21.719(6), c 15.929(3) Å, β 79.77(2)°, D_m 1.92(2) g cm^{-3}, D_c 1.916 g cm^{-3}; $Z = 8$, U 4322.4 Å^3; μ(Mo-K_α) 77.64 cm^{-1}, λ(Mo-K_α) 0.7107 Å, $F(000)$ 2384 electrons.

4, $C_{26}H_{23}PRuS_2$, mol. wt. 531.6; orthorhombic, space group *Pbca*, a 8.921(2), b 15.982(9), c 32.216(5) Å; D_c 1.537 g cm^{-3}; $Z = 8$, U 4593.2 Å^3; μ(Mo-K_α) 8.89 cm^{-1}, λ(Mo-K_α) 0.7107 Å, $F(000)$ 2160 electrons.

Intensity data were collected in the range 1.2° < θ < 20° using an $\omega - n/3\theta$ scan, where n (= 2) ((= 3)) was optimised by ω/θ profile analysis of a typical reflection.

TABLE 3

BOND LENGTHS (Å) FOR ONE MOLECULE OF $\overline{OsBr(\eta^2\text{-}CH_2{=}CHC_6H_4PPh_2)}(\eta\text{-}C_5H_5)$ (**2**)

Br(1)–Os(1)	2.545(2)	P(1)–Os(1)	2.284(4)
C(1)–Os(1)	2.249(14)	C(2)–Os(1)	2.182(19)
C(21)–Os(1)	2.228(11)	C(22)–Os(1)	2.222(10)
C(23)–Os(1)	2.217(10)	C(24)–Os(1)	2.220(11)
C(25)–Os(1)	2.226(12)	C(8)–P(1)	1.792(14)
C(14)–P(1)	1.859(8)	C(20)–P(1)	1.846(8)
C(2)–C(1)	1.618(26)	C(3)–C(2)	1.526(24)
C(4)–C(3)	1.417(23)	C(8)–C(3)	1.415(18)
C(5)–C(4)	1.380(28)	C(6)–C(5)	1.376(26)
C(7)–C(6)	1.358(24)	C(8)–C(7)	1.405(21)
C(10)–C(9)	1.380(11)	C(14)–C(9)	1.380(10)
C(11)–C(10)	1.380(10)	C(12)–C(11)	1.380(10)
C(13)–C(12)	1.380(11)	C(14)–C(13)	1.380(10)
C(16)–C(15)	1.380(10)	C(20)–C(15)	1.380(12)
C(17)–C(16)	1.380(11)	C(18)–C(17)	1.380(12)
C(19)–C(18)	1.380(10)	C(20)–C(19)	1.380(11)
C(22)–C(21)	1.378(17)	C(25)–C(21)	1.378(15)
C(23)–C(22)	1.378(14)	C(24)–C(23)	1.378(17)
C(25)–C(24)	1.378(15)	C(33)–P(2)	1.798(14)
C(39)–P(2)	1.864(9)	C(45)–P(2)	1.847(9)
C(27)–C(26)	1.521(26)	C(28)–C(27)	1.487(21)
C(29)–C(28)	1.407(22)	C(33)–C(28)	1.378(18)
C(30)–C(29)	1.393(24)	C(31)–C(30)	1.345(22)
C(32)–C(31)	1.380(23)	C(33)–C(32)	1.400(21)
C(35)–C(34)	1.380(12)	C(39)–C(34)	1.380(11)
C(36)–C(35)	1.380(11)	C(37)–C(36)	1.380(11)
C(38)–C(37)	1.380(12)	C(39)–C(38)	1.380(11)
C(41)–C(40)	1.380(12)	C(45)–C(40)	1.380(12)
C(42)–C(41)	1.380(11)	C(43)–C(42)	1.380(12)
C(44)–C(43)	1.380(12)	C(45)–C(44)	1.380(11)
C(47)–C(46)	1.378(16)	C(50)–C(46)	1.378(15)
C(48)–C(47)	1.378(13)	C(49)–C(48)	1.378(17)
C(50)–C(49)	1.378(13)		

TABLE 4

BOND ANGLES (°) OF ONE MOLECULE OF $\overline{\text{OsBr}(\eta^2\text{-CH}_2\text{=CHC}_6\text{H}_4\text{P}}\text{Ph}_2)(\eta\text{-C}_5\text{H}_5)$ (**2**)

P(1)-Os(1)-Br(1)	89.7(1)	C(1)-Os(1)-Br(1)	81.9(4)
C(1)-Os(1)-P(1)	94 3(4)	C(2)-Os(1)-Br(1)	122.1(5)
C(2)-Os(1)-P(1)	80.9(4)	C(2)-Os(1)-C(1)	42.8(7)
C(21)-Os(1)-Br(1)	94.6(3)	C(21)-Os(1)-P(1)	108 1(3)
C(21)-Os(1)-C(1)	157 3(5)	C(21)-Os(1)-C(2)	142 6(5)
C(22)-Os(1)-Br(1)	129.6(3)	C(22)-Os(1)-P(1)	96 6(3)
C(22)-Os(1)-C(1)	146.5(5)	C(22)-Os(1)-C(2)	108.3(5)
C(22)-Os(1)-C(21)	36.1(4)	C(23)-Os(1)-Br(1)	145 8(3)
C(23)-Os(1)-P(1)	118 7(3)	C(23)-Os(1)-C(1)	112.0(5)
C(23)-Os(1)-C(2)	83.4(5)	C(23)-Os(1)-C(21)	60.2(4)
C(23)-Os(1)-C(22)	36 2(4)	C(24)-Os(1)-Br(1)	112.7(3)
C(24)-Os(1)-P(1)	154 6(3)	C(24)-Os(1)-C(1)	100.4(5)
C(24)-Os(1)-C(2)	96.0(5)	C(24)-Os(1)-C(21)	60 2(4)
C(24)-Os(1)-C(22)	60 3(4)	C(24)-Os(1)-C(23)	36.2(4)
C(25)-Os(1)-Br(1)	85.7(3)	C(25)-Os(1)-P(1)	142 9(3)
C(25)-Os(1)-C(1)	121.3(5)	C(25)-Os(1)-C(2)	131.8(5)
C(25)-Os(1)-C(21)	36.0(4)	C(25)-Os(1)-C(22)	60.2(4)
C(25)-Os(1)-C(23)	60.2(4)	C(25)-Os(1)-C(24)	36.1(4)
C(8)-P(1)-Os(1)	108 6(4)	C(14)-P(1)-Os(1)	121.4(3)
C(14)-P(1)-C(8)	101.3(5)	C(20)-P(1)-Os(1)	112 8(3)
C(20)-P(1)-C(8)	105.2(5)	C(20)-P(1)-C(14)	105 9(4)
C(2)-C(1)-Os(1)	66.4(8)	C(1)-C(2)-Os(1)	70.8(9)
C(3)-C(2)-Os(1)	116.5(10)	C(3)-C(2)-C(1)	121 0(12)
C(4)-C(3)-C(2)	122.3(13)	C(8)-C(3)-C(2)	120.5(13)
C(8)-C(3)-C(4)	117.1(14)	C(5)-C(4)-C(3)	121.6(15)
C(6)-C(5)-C(4)	118 6(17)	C(7)-C(6)-C(5)	123 2(17)
C(8)-C(7)-C(6)	118.7(13)	C(3)-C(8)-P(1)	112 2(10)
C(7)-C(8)-P(1)	127.1(10)	C(7)-C(8)-C(3)	120.7(13)
C(14)-C(9)-C(10)	120 0(6)	C(11)-C(10)-C(9)	120 0(7)
C(12)-C(11)-C(10)	120.0(7)	C(13)-C(12)-C(11)	120.0(6)
C(14)-C(13)-C(12)	120.0(7)	C(9)-C(14)-P(1)	116.5(5)
C(13)-C(14)-P(1)	123 4(6)	C(13)-C(14)-C(9)	120.0(7)
C(20)-C(15)-C(16)	120.0(7)	C(17)-C(16)-C(15)	120.0(8)
C(18)-C(17)-C(16)	120.0(7)	C(19)-C(18)-C(17)	120 0(7)
C(20)-C(19)-C(18)	120.0(8)	C(15)-C(20)-P(1)	120.2(6)
C(19)-C(20)-P(1)	119.5(7)	C(19)-C(20)-C(15)	120 0(7)
C(22)-C(21)-Os(1)	71.7(6)	C(25)-C(21)-Os(1)	71.9(6)
C(25)-C(21)-C(22)	108.0(9)	C(21)-C(22)-Os(1)	72.2(6)
C(23)-C(22)-Os(1)	71.7(6)	C(23)-C(22)-C(21)	108.0(10)
C(22)-C(23)-Os(1)	72.1(6)	C(24)-C(23)-Os(1)	72.0(6)
C(24)-C(23)-C(22)	108.0(10)	C(23)-C(24)-Os(1)	71.8(6)
C(25)-C(24)-Os(1)	72.2(6)	C(25)-C(24)-C(23)	108.0(9)
C(21)-C(25)-Os(1)	72.0(7)	C(24)-C(25)-Os(1)	71 7(7)
C(24)-C(25)-C(21)	108.0(11)	C(39)-P(2)-C(33)	100.9(5)
C(45)-P(2)-C(33)	106.9(5)	C(45)-P(2)-C(39)	105 1(4)
C(28)-C(27)-C(26)	119.1(12)	C(29)-C(28)-C(27)	118.9(13)
C(33)-C(28)-C(27)	121.4(13)	C(33)-C(28)-C(29)	119.7(13)
C(30)-C(29)-C(28)	120.2(14)	C(31)-C(30)-C(29)	120.5(15)
C(32)-C(31)-C(30)	119.3(15)	C(33)-C(32)-C(31)	122 5(13)
C(28)-C(33)-P(2)	114 1(10)	C(32)-C(33)-P(2)	128.1(10)
C(32)-C(33)-C(28)	117.7(13)	C(39)-C(34)-C(35)	120.0(7)
C(36)-C(35)-C(34)	120.0(7)	C(37)-C(36)-C(35)	120.0(8)
C(38)-C(37)-C(36)	120.0(7)	C(39)-C(38)-C(37)	120 0(7)
C(34)-C(39)-P(2)	122.7(6)	C(38)-C(39)-P(2)	117.2(6)

TABLE 4 (continued)

C(38)–C(39)–C(34)	120.0(8)	C(45)–C(40)–C(41)	120.0(8)
C(42)–C(41)–C(40)	120.0(8)	C(43)–C(42)–C(41)	120.0(8)
C(44)–C(43)–C(42)	120.0(8)	C(45)–C(44)–C(43)	120.0(8)
C(40)–C(45)–P(2)	117.6(6)	C(44)–C(45)–P(2)	122.1(7)
C(44)–C(45)–C(40)	120.0(8)	C(50)–C(46)–C(47)	108.0(8)
C(48)–C(47)–C(46)	108.0(10)	C(49)–C(48)–C(47)	108.0(9)
C(50)–C(49)–C(48)	108.0(9)	C(49)–C(50)–C(46)	108.0(10)

The ω scan angles and horizontal counter apertures employed were $(0.80 + 0.35 \tan \theta)^\circ$ and $(2.40 + 0.50 \tan \theta)$ mm respectively. Frequent monitoring of three standard reflections indicated that no decomposition occurred during data collection. Data reduction and application of Lorentz and polarisation corrections were performed using programme SUSCAD, while corrections for absorption effects were applied using programme ABSORB [26]. Of the 3560 [1990] independent reflections col-

TABLE 5

POSITIONAL PARAMETERS (C $\times 10^4$; all others $\times 10^5$) FOR NON-HYDROGEN ATOMS IN $Ru(\eta^3\text{-}S_2CCHMeC_6H_4PPh_2)(\eta\text{-}C_5H_5)$ (**4**)

Atom	x	y	z
Ru	72246(4)	9981(2)	43792(1)
S(1)	45306(14)	9049(8)	42877(4)
S(2)	62960(16)	21951(8)	47595(4)
P(1)	77685(11)	14745(6)	37265(4)
C(1)	5375(5)	1876(3)	4317(1)
C(2)	5130(4)	2542(3)	3980(1)
C(3)	3814(6)	3082(3)	4108(1)
C(4)	4987(4)	2158(2)	3549(1)
C(5)	6161(4)	1672(2)	3385(1)
C(6)	6034(5)	1369(3)	2982(1)
C(7)	4795(6)	1539(3)	2740(1)
C(8)	3663(5)	2014(3)	2896(1)
C(9)	3749(4)	2328(2)	3296(1)
C(10)	10467(5)	875(3)	3363(1)
C(11)	11344(5)	276(3)	3167(2)
C(12)	10733(7)	−461(3)	3041(1)
C(13)	9243(6)	−628(3)	3112(1)
C(14)	8367(5)	−43(3)	3314(1)
C(15)	8944(4)	732(3)	3431(1)
C(16)	9333(5)	2871(3)	4027(2)
C(17)	10093(5)	3634(3)	3989(2)
C(18)	10337(5)	3976(3)	3612(2)
C(19)	9857(5)	3578(3)	3252(2)
C(20)	9068(5)	2821(3)	3286(2)
C(21)	8813(4)	2467(3)	3674(1)
C(22)	9411(6)	398(4)	4416(1)
C(23)	9123(5)	811(3)	4793(1)
C(24)	7881(5)	402(3)	4987(1)
C(25)	7407(6)	−232(3)	4724(2)
C(26)	8321(7)	−236(3)	4362(1)

lected, 2867 [1685] with $I > 2.50\sigma(I)$ were considered "observed" and used in the calculations.

Solution and refinement. Both structures were solved by the heavy atom method. For **2**, the positions of the two independent osmium atoms were obtained by application of the direct methods routines of SHELX and were used to phase a difference Fourier. This map revealed the Br and P atoms while all other non-hydrogen atoms were located in a subsequent difference map. The "free" phenyl groups and the cyclopentadienyl groups were included as rigid planes (C–C, 1.380 Å) while the hydrogen atoms were included at calculated sites (C–H, 0.97 Å). The hydrogen atoms of the C_6H_4 group were not located nor included.

For **4**, the position of the ruthenium atom was determined from a Patterson map and used to phase a difference map which revealed all non-hydrogen atoms. Hydrogen atoms were included at calculated sites (C–H, 0.97 Å).

Blocked-matrix least-squares techniques were used to refine all positional and thermal parameters (anisotropic for Br, Os and P, group isotropic for H) (anisotropic for non-hydrogen, group isotropic for H). A weighting scheme was refined and converged with $w = 1.25/(\sigma^2F_o + 0.00077F_o^2)$ $(w = 1.00/(\sigma^2F_o + 0.0011F_o^2))$, while overall refinement converted with $R = 0.040$, $R_w = 0.044$ $(R = 0.027$, $R_w = 0.030)$. The final difference map was structurally featureless with the largest peaks (ca. 2 eÅ^{-3} (< 0.6 eÅ^{-3})) located near the metal atom.

All calculations were performed using the SHELX system of programmes [26], while scattering factors (neutral Os and Br (neutral Ru)) and anomalous dispersion terms were taken from the International Tables [27].

Final non-hydrogen atom coordinates for **2** and **4** are given in Tables 2 and 3, respectively. Selected bond distances and angles for these complexes are collected in Tables 4–7. Tables of thermal parameters for non-hydrogen atoms, positional and

TABLE 6

BOND LENGTHS (Å) FOR $Ru(\eta^3\text{-}S_2CCHMeC_6H_4PPh_2)(\eta\text{-}C_5H_5)$ (**4**)

S(1)–Ru	2.426(1)	S(2)–Ru	2.418(1)
P(1)–Ru	2.288(1)	C(1)–Ru	2.175(4)
C(22)–Ru	2.177(5)	C(23)–Ru	2.176(5)
C(24)–Ru	2.256(5)	C(25)–Ru	2.264(5)
C(26)–Ru	2.202(5)	C(1)–S(1)	1.728(4)
C(1)–S(2)	1.722(4)	C(5)–P(1)	1 836(4)
C(15)–P(1)	1.848(4)	C(21)–P(1)	1.847(4)
C(2)–C(1)	1.537(6)	C(3)–C(2)	1.514(6)
C(4)–C(2)	1.524(6)	C(5)–C(4)	1 406(5)
C(9)–C(4)	1.399(6)	C(6)–C(5)	1 390(6)
C(7)–C(6)	1.380(7)	C(8)–C(7)	1.360(7)
C(9)–C(8)	1.385(6)	C(11)–C(10)	1.388(7)
C(15)–C(10)	1.395(6)	C(12)–C(11)	1.360(7)
C(13)–C(12)	1.375(8)	C(14)–C(13)	1.381(7)
C(15)–C(14)	1.393(6)	C(17)–C(16)	1.399(7)
C(21)–C(16)	1.386(7)	C(18)–C(17)	1.349(9)
C(19)–C(18)	1.390(8)	C(20)–C(19)	1.403(7)
C(21)–C(20)	1.393(7)	C(23)–C(22)	1.405(7)
C(26)–C(22)	1.415(8)	C(24)–C(23)	1.431(7)
C(25)–C(24)	1.386(7)	C(26)–C(25)	1.425(7)

TABLE 7

BOND ANGLES (°) FOR $\overline{Ru(\eta^3\text{-}S_2CCHMeC_6H_4PPh_2)}(\eta\text{-}C_5H_5)$ (4)

S(2)-Ru-S(1)	76.7(1)	P(1)-Ru-S(1)	96.8(1)
P(1)-Ru-S(2)	106.0(1)	C(1)-Ru-S(1)	43.7(1)
C(1)-Ru-S(2)	43.6(1)	C(1)-Ru-P(1)	82.1(1)
C(22)-Ru-S(1)	150.1(2)	C(22)-Ru-S(2)	128.9(1)
C(22)-Ru-P(1)	90.4(1)	C(22)-Ru-C(1)	165.7(2)
C(23)-Ru-S(1)	146.8(1)	C(23)-Ru-S(2)	93.7(1)
C(23)-Ru-P(1)	116.3(1)	C(23)-Ru-C(1)	137.3(2)
C(23)-Ru-C(22)	37.7(2)	C(34)-Ru-S(1)	109.7(1)
C(24)-Ru-S(2)	89.0(1)	C(24)-Ru-P(1)	152.1(1)
C(24)-Ru-C(1)	123.3(2)	C(24)-Ru-C(22)	62.2(2)
C(24)-Ru-C(23)	37.6(2)	C(25)-Ru-S(1)	94.5(1)
C(25)-Ru-S(2)	117.6(1)	C(25)-Ru-P(1)	136.5(1)
C(25)-Ru-C(1)	131.3(2)	C(25)-Ru-C(22)	61.7(2)
C(25)-Ru-C(23)	61.6(2)	C(25)-Ru-C(24)	35.7(2)
C(26)-Ru-S(1)	112.5(2)	C(26)-Ru-S(2)	150.9(1)
C(26)-Ru-P(1)	100.4(1)	C(26)-Ru-C(1)	155.8(2)
C(26)-Ru-C(22)	37.7(2)	C(26)-Ru-C(23)	63.0(2)
C(26)-Ru-C(24)	61.9(2)	C(26)-Ru-C(25)	37.2(2)
C(1)-S(1)-Ru	60.4(1)	C(1)-S(2)-Ru	60.7(1)
C(5)-P(1)-Ru	116.3(1)	C(15)-P(1)-Ru	112.3(1)
C(15)-P(1)-C(5)	104.2(2)	C(21)-P(1)-Ru	118.4(1)
C(21)-P(1)-C(5)	101.1(2)	C(21)-P(1)-C(15)	102.6(2)
S(1)-C(1)-Ru	75.9(2)	S(2)-C(1)-Ru	75.7(2)
S(2)-C(1)-S(1)	121.3(2)	C(2)-C(1)-Ru	128.3(3)
C(2)-C(1)-S(1)	121.4(3)	C(2)-C(1)-S(2)	116.6(3)
C(3)-C(2)-C(1)	108.2(4)	C(4)-C(2)-C(1)	112.1(3)
C(4)-C(2)-C(3)	114.4(3)	C(5)-C(4)-C(2)	120.2(3)
C(9)-C(4)-C(2)	121.2(4)	C(9)-C(4)-C(5)	118.4(4)
C(4)-C(5)-P(1)	116.8(3)	C(6)-C(5)-P(1)	124.3(3)
C(6)-C(5)-C(4)	118.9(4)	C(7)-C(6)-C(5)	121.7(4)
C(8)-C(7)-C(6)	119.6(4)	C(9)-C(8)-C(7)	120.5(4)
C(8)-C(9)-C(4)	120.9(4)	C(15)-C(10)-C(11)	120.5(4)
C(12)-C(11)-C(10)	120.5(5)	C(13)-C(12)-C(11)	120.4(5)
C(14)-C(13)-C(12)	119.6(5)	C(15)-C(14)-C(13)	121.3(4)
C(10)-C(15)-P(1)	121.9(3)	C(14)-C(15)-P(1)	120.1(3)
C(14)-C(15)-C(10)	117.6(4)	C(21)-C(16)-C(17)	119.8(5)
C(18)-C(17)-C(16)	120.6(5)	C(19)-C(18)-C(17)	121.1(5)
C(20)-C(19)-C(18)	118.9(5)	C(21)-C(20)-C(19)	120.2(5)
C(16)-C(21)-P(1)	119.7(3)	C(20)-C(21)-P(1)	120.9(3)
C(20)-C(21)-C(16)	119.4(4)	C(23)-C(22)-Ru	71.1(3)
C(26)-C(22)-Ru	72.1(3)	C(26)-C(22)-C(23)	108.5(4)
C(22)-C(23)-Ru	71.2(3)	C(24)-C(23)-Ru	74.2(3)
C(24)-C(23)-C(22)	107.8(4)	C(23)-C(24)-Ru	68.2(3)
C(25)-C(24)-Ru	72.5(3)	C(25)-C(24)-C(23)	107.6(4)
C(24)-C(25)-Ru	71.8(3)	C(26)-C(25)-Ru	69.0(3)
C(26)-C(25)-C(24)	109.3(5)	C(22)-C(26)-Ru	70.2(3)
C(25)-C(26)-Ru	73.8(3)	C(25)-C(26)-C(22)	106.7(4)

thermal parameters for hydrogen atoms, and calculated and observed structure factors are available from the authors.

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