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Stabilisation of alkynyl dithiocarboxylates at a ruthenium centre: X-ray crystal structures of [Ru(H)(CO)($S_2CC{\equiv}CPh$)(PPh_3)$_2$], [Ru(CO)(CPh=CHPh)($S_2CC{\equiv}CPh$)(PPh_3)$_2$] and [Ru(CO)(C≡CMes)($S_2CC{\equiv}CPh$)(PPh_3)$_2$]

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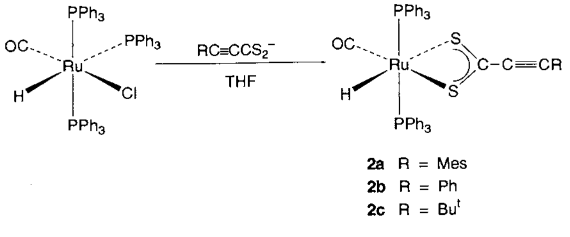
Abstract

Solutions of the alkynyldithiocarboxylate anions RC≡C–CS_2^- (R = Mes, Ph, Bu^t), generated by treatment of the acetylides LiC≡CR with carbon disulfide, are sufficiently stable to allow reaction with haloruthenium(II) complexes. In this way, the complexes [Ru(H)(CO)($S_2CC{\equiv}CR$)(PPh_3)$_2$] and [Ru(CO)(CPh=CHPh)($S_2CC{\equiv}CR$)(PPh_3)$_2$] (R = Mes, Ph, Bu^t) have been prepared and characterised. The vinyl complexes react with additional terminal alkynes $R^1C{\equiv}CH$ at room temperature to afford the acetylide complexes [Ru(CO)($C{\equiv}CR^1$)($S_2CC{\equiv}CR$)(PPh_3)$_2$]. The crystal structures of [Ru(H)(CO)($S_2CC{\equiv}CPh$)(PPh_3)$_2$], [Ru(CO)(CPh=CHPh)($S_2CC{\equiv}CPh$)(PPh_3)$_2$] and [Ru(CO)(C≡CMes)($S_2CC{\equiv}CPh$)(PPh_3)$_2$] have been determined. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Ruthenium; Alkyne; Hydride; Vinyl; Crystal structures

1. Introduction

Addition of an anion X^- to carbon disulfide affords species of the type XCS_2^- which can be coordinated to metal centres as uninegative didentate ligands, the most common examples being dithiocarbamates (X = NR_2), xanthates (X = OR) and dithiocarboxylates (X = alkyl, aryl, etc.) [1]. Given that terminal alkynes RC≡CH have relatively acidic protons, we were intrigued to discover that there are very few reports dealing with alkynyl dithiocarboxylates, RC≡C–CS_2^-, or their derivatives. In 1973 Brandsma and co-workers mentioned that in contrast to alkyl and aryl Grignard reagents, alkynyl Grignards are insufficiently nucleophilic to add to CS_2 [2]. More recently, Hartke reported the preparation of several dithioesters of the type RC≡C–CS_2Me, mainly by indirect methods from acetylenic thioamides, and showed that unless R was a bulky aryl group, these compounds decomposed at room temperature within a few hours. Only in the case of R = Mes was it possible to prepare a stable dithioester by deprotonation of MesC≡CH, addition of CS_2 and alkylation with MeI, and even then the intermediate anion MesC≡C–CS_2^- was described as unstable [3]. Moreover, only one transition metal complex of such a ligand is known: [Ru($S_2CC{\equiv}CPh$)(PPh_3)(η-C_5H_5)] was prepared by insertion of carbon disulfide into the metal–carbon bond of the corresponding acetylide complex [Ru(C≡CPh)(PPh_3)$_2$(η-C_5H_5)] [4]. We therefore set out to discover



Scheme 1. Synthesis of complexes **2a–c**.

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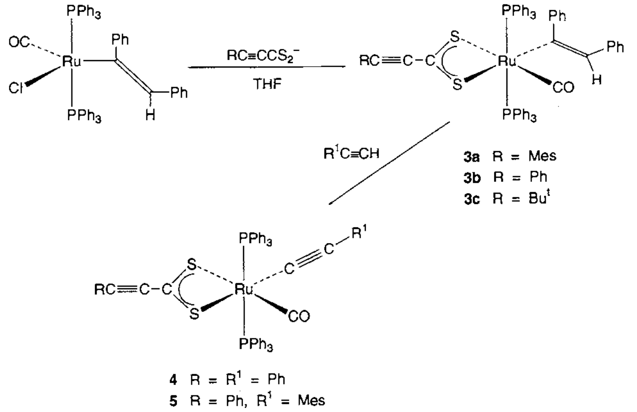

Scheme 2. Synthesis of complexes **3–5**.

whether alkynyl dithiocarboxylates could be prepared by addition of acetylide anions to CS_2 and stabilised by coordination to ruthenium.

2. Results and discussion

In order to maximise kinetic stabilisation of the intermediate species, we initially followed the lead of Hartke et al. by preparing MesC≡CH (**1a**). We were able to confirm that deprotonation of **1a** with one equivalent of BuLi followed by addition of CS_2 gave a dark red solution containing MesC≡C–CS_2^- which yielded the stable dithioester MesC≡C–CS_2Me on alkylation with MeI [3]. We then investigated coordination of the same anion to ruthenium, in the form of [Ru(H)(Cl)(CO)$(PPh_3)_3$]. This compound was chosen because it is known to react readily with dithiocarbamates by replacement of the chloride ligand and loss of one labile PPh_3 to give [Ru(H)(CO)(S_2CNR_2)$(PPh_3)_2$] [5].

Addition of one equivalent of the MesC≡C–CS_2^- solution to a suspension of [Ru(H)(Cl)(CO)$(PPh_3)_3$] in THF caused the rapid dissolution of the complex and a colour change from grey to red. The new complex [Ru(H)(CO)(S_2CC≡CMes)$(PPh_3)_2$] (**2a**) could be isolated by column chromatography as an air- and moisture-stable red powder in 63% yield (Scheme 1). Its solution IR spectrum showed a carbonyl absorption at 1936 cm^{-1} and a weaker peak due to the alkyne functionality at 2176 cm^{-1}. The ^1H-NMR spectrum showed aryl protons and the methyl groups of the mesityl substituent, together with a characteristic triplet ($J = 20.2$ Hz) at δ −10.48 due to the hydride ligand, thus also confirming the presence of two *trans*-PPh_3 groups. In the ^{13}C-NMR spectrum, two low field triplets were observed, at 218.0 ppm ($J = 6$ Hz) and 204.7 ppm ($J = 13$ Hz) which are assigned to the CS_2 carbon and the CO ligand respectively on the basis of the size of the coupling constant and also by comparison with related complexes, e.g. the starting material. Peaks due to the alkyne carbons were observed at 105.5 and 87.8 ppm, similar to their position in the stable dithioester.

We next attempted the same reaction sequence with phenylacetylene. Gratifyingly, treatment of [Ru(H)(Cl)(CO)$(PPh_3)_3$] with the red solution prepared by stirring CS_2 with LiC≡CPh produced an analogous complex [Ru(H)(CO)(S_2CC≡CPh)$(PPh_3)_2$] (**2b**) in 51% yield, proving that the PhC≡C–CS_2^- anion is sufficiently stable in solution at room temperature for 1 h to enable the reaction to proceed in the same way. The spectroscopic data of **2b** are very similar to those of **2a**. Moreover, the synthesis of analogous **2c** from Bu^{t}C≡CH was also successful, showing that the presence of an aryl substituent is not necessary. We did not observe any interaction between the hydride ligand and the alkynyl portion of the dithiocarboxylate, in contrast to the reactions of **1** with alkynecarboxylic acids which gave compexes containing alkenylcarboxylate ligands [6].

It is known that [Ru(H)(Cl)(CO)$(PPh_3)_3$] readily hydroruthenates alkynes to produce vinyl complexes of the type [RuCl(CR^1=CHR^2)(CO)$(PPh_3)_n$] where n can be 2 or 3 depending on the steric bulk of the alkyne [7]. The chloride ligands in these products can also be readily replaced by dithiocarbamates [8]. Treatment of the red diphenylacetylene derivative [RuCl(CPh=CHPh)(CO)$(PPh_3)_2$] with the red solutions of RC≡CCS_2^- (R = Mes, Ph, Bu^t) described above gave green–brown solutions from which the compounds [Ru(CO)(CPh=CHPh)(S_2CC≡CR)$(PPh_3)_2$] (**3a–c**) (Scheme 2) could be isolated by chromatographic workup in yields of 78, 72 and 25%, respectively. Their IR spectra showed the presence of the alkynyldithiocarboxylate ligand, and the continued presence of the vinyl group was indicated by a broad signal at approximately δ 5.85 in the ^1H-NMR spectrum due to the CPh=CHPh proton.

Small amounts of orange products were also isolated from these reactions. Based on the fact that their IR spectra showed two alkyne peaks in addition to the CO stretch, we assigned their formulae as [Ru(CO)(C≡CR)(S_2CC≡CR)$(PPh_3)_2$] and postulated that they arose through reaction of **3a** and **3b** with the small excess of alkyne present. Indeed, stirring isolated **3b** with an excess of phenylacetylene in THF at room temperature for 4 d led to a 61% yield of [Ru(CO)(C≡CPh)(S_2CC≡CPh)$(PPh_3)_2$] (**4**). To confirm that the added alkyne was the source of the alkynyl group, the mixed complex [Ru(CO)(C≡CMes)(S_2CC≡CPh)$(PPh_3)_2$] (**5**) was made from **3b** and mesityl acetylene. The reaction presumably proceeds by an oxidative addition and reductive elimination sequence with loss of stilbene (not detected). Analogous reactions were recently reported in the carboxylate species

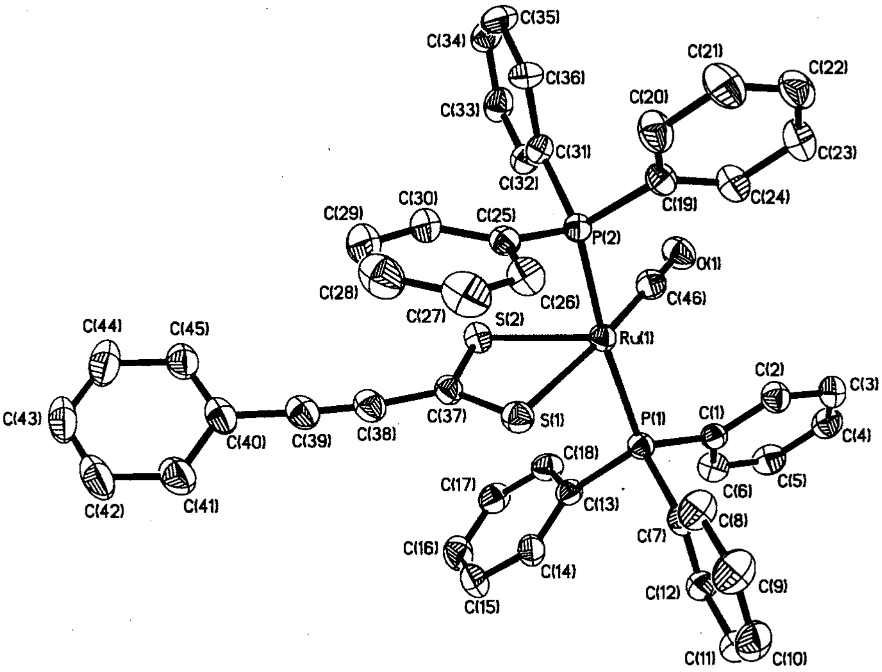

Fig. 1. Molecular structure of [Ru(H)(CO)($S_2CC{\equiv}CPh$)(PPh_3)$_2$] (**2b**) in the crystal showing the atomic numbering scheme. The dichloromethanes of solvation have been omitted.

[Ru(CO)(CPh=CHPh)(O_2CR)(PPh_3)$_2$] [9] and in the dithiocarbamate analogues of **3** [10].

Since the reactions here were all carried out at room temperature or below with stoichiometric quantities of alkyne, we did not observe any enynyl complexes containing the Ru–{C(C≡CR)=CHR)} group, which are known to be produced by extended reaction of [Ru(H)(Cl)(CO)(PPh_3)$_3$] and related compounds with terminal alkynes at elevated temperature.

2.1. Crystal structure determinations

In order to define some structural parameters for the alkynyldithiocarboxylate ligands, the crystal structure of one example of each of the three types of complex was determined. Well-formed red blocks of **2b** were obtained by crystallisation from CH_2Cl_2 and light petroleum; the structure is shown in Fig. 1, with selected bond lengths and angles collected in Table 1. As expected the ruthenium(II) centre is octahedrally coordinated with the two PPh_3 ligands occupying *trans* positions [the P(1)–Ru(1)–P(2) angle is 169.62(4)°]. The hydride ligand was not located directly but is presumably situated in the vacant region *trans* to S(2). The dithiocarboxylate ligand is asymmetrically coordinated, with the Ru(1)–S(1) bond [2.4855(12) Å] being significantly longer than Ru(1)–S(2) [2.4527(11) Å]. The same asymmetry is observed in the related carboxylate complexes [11]. The bite angle of the didentate ligand is 70.14(4)°. The presence of the alkynyl portion of the ligand is confirmed, with C(37), C(38), C(39) and C(40) displaying virtually linear geometry and the C(38)–C(39) bond length being 1.204(7) Å, typical of a C≡C bond.

The structures of complexes **3b** and **5** are shown in Figs. 2 and 3, respectively; the numbering scheme is the same for both complexes, and their selected bond lengths and angles are collected in Table 2 for ease of comparison. The arrangement of dithiocarboxylate, PPh_3 and carbonyl ligands is the same as in **2b**, and the sixth position is occupied either by a 1,2-diphenylvinyl group in **3b** or by a mesitylethynyl ligand in **5**. In **3b**, the two phenyl substituents occupy *cis* positions on the vinyl group and the C(11)–C(12) bond length is 1.320(8) Å. Again the dithiocarboxylate is coordinated

Table 1
Selected bond lengths (Å) and angles (°) for **2b**·$2CH_2Cl_2$

Ru(1)–C(46)	1.854(5)	Ru(1)–P(1)	2.3329(11)
Ru(1)–P(2)	2.3512(11)	Ru(1)–S(2)	2.4527(11)
Ru(1)–S(1)	2.4855(12)	S(1)–C(37)	1.681(5)
S(2)–C(37)	1.685(4)	O(1)–C(46)	1.147(6)
C(37)–C(38)	1.430(6)	C(38)–C(39)	1.204(7)
C(39)–C(40)	1.450(6)		
C(46)–Ru(1)–P(1)	92.38(14)	C(46)–Ru(1)–P(2)	91.10(14)
P(1)–Ru(1)–P(2)	169.62(4)	C(46)–Ru(1)–S(2)	101.18(14)
P(1)–Ru(1)–S(2)	97.59(4)	P(2)–Ru(1)–S(2)	91.32(4)
C(46)–Ru(1)–S(1)	170.56(14)	P(1)–Ru(1)–S(1)	85.32(4)
P(2)–Ru(1)–S(1)	92.76(4)	S(2)–Ru(1)–S(1)	70.14(4)
C(37)–S(1)–Ru(1)	86.91(15)	C(37)–S(2)–Ru(1)	87.91(15)
C(38)–C(37)–S(1)	125.1(3)	C(38)–C(37)–S(2)	119.9(3)
S(1)–C(37)–S(2)	114.9(2)	C(39)–C(38)–C(37)	173.6(5)
C(38)–C(39)–C(40)	176.4(6)	O(1)–C(46)–Ru(1)	179.7(5)

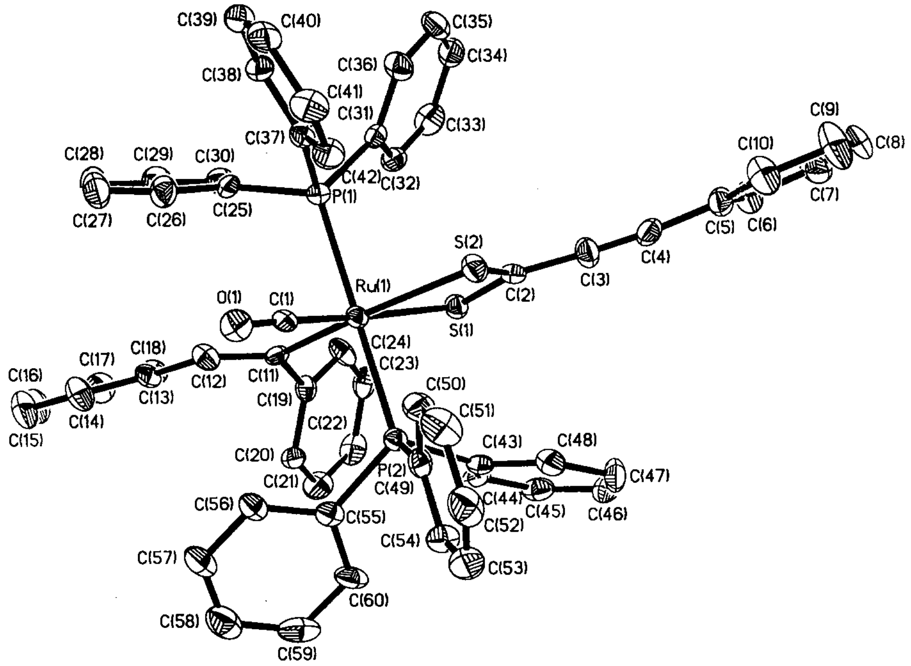

Fig. 2. Molecular structure of [Ru(CO)(CPh=CHPh)($S_2CC{\equiv}CPh$)($(PPh_3)_2$)] (**3b**) in the crystal showing the atomic numbering scheme.

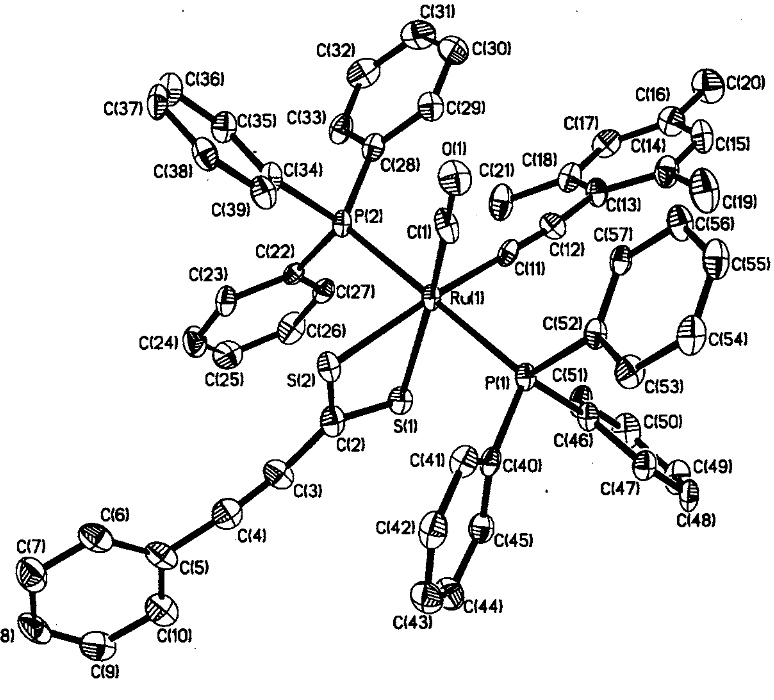

Fig. 3. Molecular structure of [Ru(CO)($C{\equiv}CMes$)($S_2CC{\equiv}CPh$)($(PPh_3)_2$)] (**5**) in the crystal showing the atomic numbering scheme.

slightly asymmetrically, with a bite angle of 69.67(5)°, and the alkynyl portion of the ligand is linear with a C≡C bond length of 1.199(8) Å. These structural features are largely reproduced in **5**, except that the presence of the bulky mesityl substituent causes a slight distortion around the central ruthenium, manifested by changes in bond angles of up to 4°. The geometrical parameters of the mesitylethynyl ligand are very similar to those found in the carboxylate complex [Ru(CO)($C{\equiv}CPh$)(O_2CR)($(PPh_3)_2$)] (R = CH=CHCH=CHMe) [9].

3. Conclusions

From the work described here, it is clear that alkynyl lithium reagents are sufficiently nucleophilic to add to carbon disulfide to produce dithiocarboxylates, and that these are sufficiently stable in solution to undergo coordination to a variety of ruthenium complexes. Future work will examine the coordination of these ligands to other metal centres and their potential for linking centres together to form 'molecular wires'.

4. Experimental

4.1. General

General experimental techniques were as described in recent papers from this laboratory [12,13]. Infrared (IR) spectra were recorded in dichloromethane solution on a Perkin–Elmer 1600 FTIR machine. ^{1}H-, ^{13}C- and ^{31}P-NMR spectra were obtained in $CDCl_3$ solution on a Bruker AC250 machine with automated sample-changer or an AMX400 spectrometer. Chemical shifts are given on the δ scale relative to $SiMe_4 = 0.0$ ppm; the $^{31}P\{^1H\}$-NMR spectra were referenced to 85% $H_3PO_4 = 0.0$ ppm with downfield shifts reported as positive. The $^{13}C\{^1H\}$-NMR spectra were routinely recorded using an attached proton test technique (JMOD pulse sequence). Mass spectra were recorded on a Fisons/BG Prospec 3000 instrument operating in fast atom bombardment mode with *m*-nitrobenzyl alcohol as matrix, except the electrospray mass spectrum of **4** which was run on a Micromass Platform in MeCN–H_2O (3:1). Elemental analyses were carried out by the Microanalytical Service of the Department of Chemistry.

Table 2
Selected bond lengths (Å) and angles (°) for **3b** and **5**

Bond	**3b**	**5**
Ru(1)–C(1)	1.840(5)	1.861(6)
Ru(1)–C(11)	2.141(6)	2.039(5)
Ru(1)–P(2)	2.3773(17)	2.4029(14)
Ru(1)–P(1)	2.3938(17)	2.3626(14)
Ru(1)–S(1)	2.4730(15)	2.4940(15)
Ru(1)–S(2)	2.5010(17)	2.4244(14)
S(1)–C(2)	1.699(6)	1.696(5)
S(2)–C(2)	1.687(6)	1.678(6)
O(1)–C(1)	1.157(6)	1.153(6)
C(2)–C(3)	1.418(8)	1.415(8)
C(3)–C(4)	1.199(8)	1.206(8)
C(4)–C(5)	1.415(8)	1.466(9)
C(11)–C(12)	1.320(8)	1.214(7)
C(1)–Ru(1)–C(11)	90.0(2)	91.8(2)
C(1)–Ru(1)–P(2)	89.34(18)	90.98(18)
C(11)–Ru(1)–P(2)	92.26(15)	89.97(15)
C(1)–Ru(1)–P(1)	86.55(17)	92.72(18)
C(11)–Ru(1)–P(1)	91.58(15)	87.62(15)
P(2)–Ru(1)–P(1)	174.37(5)	175.65(5)
C(1)–Ru(1)–S(1)	173.13(16)	168.53(17)
C(11)–Ru(1)–S(1)	96.81(15)	99.08(16)
P(2)–Ru(1)–S(1)	90.75(5)	92.54(5)
P(1)–Ru(1)–S(1)	92.88(5)	84.26(5)
C(1)–Ru(1)–S(2)	103.47(17)	99.11(17)
C(11)–Ru(1)–S(2)	166.45(15)	168.84(16)
P(2)–Ru(1)–S(2)	88.90(5)	87.61(5)
P(1)–Ru(1)–S(2)	88.32(5)	94.06(5)
S(1)–Ru(1)–S(2)	69.67(5)	70.16(5)
C(2)–S(1)–Ru(1)	88.4(2)	86.6(2)
C(2)–S(2)–Ru(1)	87.8(2)	89.3(2)
O(1)–C(1)–Ru(1)	177.9(5)	178.2(5)
C(3)–C(2)–S(2)	122.4(5)	120.7(4)
C(3)–C(2)–S(1)	123.4(4)	125.3(4)
S(2)–C(2)–S(1)	114.1(3)	113.9(3)
C(4)–C(3)–C(2)	174.9(7)	172.6(6)
C(3)–C(4)–C(5)	174.9(7)	174.9(6)
C(12)–C(11)–Ru(1)	124.9(4)	177.9(5)
C(11)–C(12)–C(13)	131.9(5)	172.8(6)

Mesityl acetylene was prepared in 55% overall yield from 2,4,6-trimethylacetophenone by chlorination with PCl_5 to give MesC(Cl)=CH_2 followed by elimination with KOH in ethanol, according to a combination of literature procedures [14]. The complexes [Ru(H)(Cl)(CO)$(PPh_3)_3$] and [RuCl(CPh=CHPh)(CO)$(PPh_3)_2$] were prepared by the literature methods [7,15].

*4.2. Preparation of [Ru(H)(CO)(S_2C≡CMes)$(PPh_3)_2$] (**2a**)*

Mesityl acetylene (1.0 ml, 1.28 g, 8.88 mmol) was dissolved in THF (10 ml) in a Schlenk tube and treated dropwise with BuLi (5.56 ml of 1.6M solution) at − 10°C. After stirring for 30 min, the solution was cannulated into a second Schlenk tube containing THF (9 ml) and carbon disulfide (4.45 ml) and washed in with a further 1 ml of THF. An immediate colour change to dark red occurred. The solution was allowed to stir at room temperature (r.t.) for 2 h. In a separate Schlenk tube, [Ru(H)(Cl)(CO)$(PPh_3)_3$] (0.5 g, 0.525 mmol) was suspended in THF (50 ml). To this suspension was added 1.83 ml of the dark red Li[S_2CC≡CMes] solution (the remaining solution was used for other purposes) [16]. The suspended solid rapidly dissolved to give a dark red solution. After stirring for 2 h the solvent was removed. The remaining red oil was absorbed onto silica and loaded onto a chromatography column. Elution with light petroleum–dichloromethane (7:3) afforded a large red band which yielded a red powder of [Ru(H)(CO)(S_2CC≡CMes)$(PPh_3)_2$] on removal of the solvent. Yield 0.2881 g, 63%. M.p. 110°C (dec.). IR (CH_2Cl_2): 2176 w (C≡C), 1936 s (CO); IR (KBr): 2170, 1942 cm^{-1}. ^{1}H-NMR: δ 7.77–7.38 (m, 30 H, Ph of PPh_3), 6.80 (s, 2 H, Mes), 2.22 (s, 3 H, 4-Me of Mes), 2.20 (s, 6 H, 2,6-Me of Mes), − 10.48 (t, $J_{PH} = 20.2$ Hz, 1 H, RuH). ^{13}C-NMR: δ 218.0 (t,

$J_{PC} = 6$ Hz, S_2C), 204.7 (t, $J_{PC} = 13$ Hz, CO), 141.1 (s, 2,6-C of Mes), 139.3 (s, 4-C of Mes), 135.4 (apparent t, $J_{PC} = 22$ Hz, C_{ipso} of Ph), 134.0–127.7 (m, aryl), 118.8 (s, C_{ipso} of Mes), 105.5 (s, $C{\equiv}C$), 87.8 (s, $C{\equiv}C$), 21.6 (s, 4-Me of Mes), 21.0 (s, 2,6-Me of Mes). ^{31}P-NMR: δ 51.7. Anal. Found: C, 62.63; H, 4.55; S, 6.77. Calc. for $C_{49}H_{42}OP_2RuS_2\cdot CH_2Cl_2$: C, 62.62; H, 4.62; S, 6.69%. Mass spectrum: *m*/*z* 873 (M^+), 846 ($M{-}CO^+$).

4.3. Preparation of $[Ru(H)(CO)(S_2C{\equiv}CPh)(PPh_3)_2]$ (**2b**)

Phenylacetylene (0.29 ml, 0.27 g, 2.64 mmol) was dissolved in THF (9 ml) in a Schlenk tube and treated dropwise with BuLi (1.65 ml of 1.6 M soln) at −78°C. After stirring for 30 min, the solution was cannulated into a second Schlenk tube containing THF (8.9 ml) and carbon disulfide (0.16 ml), also held at −78°C, and washed in with a further 5 ml of THF. The pale yellow solution was then allowed to warm to r.t. and then stir for 1 h, producing a further colour change to dark red. In a separate Schlenk tube, $[Ru(H)(Cl)(CO)(PPh_3)_3]$ (0.5 g, 0.525 mmol) was suspended in THF (50 ml). To this suspension was added 5.0 ml of the dark red $Li[S_2CC{\equiv}CPh]$ solution (the remaining solution was used for other purposes). The suspended solid rapidly dissolved to give a dark red solution. After stirring for 2 h the solvent was removed. The remaining solid was absorbed onto silica and loaded onto a chromatography column. Elution with light petroleum–dichloromethane (7:3) afforded a large red band which yielded a red powder of $[Ru(H)(CO)(S_2CC{\equiv}CPh)(PPh_3)_2]$ on removal of the solvent. Yield 0.2313 g, 53%. M.p. 160°C (dec.). IR (CH_2Cl_2): 2183 w ($C{\equiv}C$), 1934 s (CO) cm^{-1}. ^{1}H-NMR: δ 7.76–7.30 (m, 35 H, Ph), −10.47 (t, $J_{PH} = 19.9$ Hz, 1 H, RuH). ^{13}C-NMR: 217.4 (t, $J = 6$ Hz, S_2C), 204.6 (t, $J = 13$ Hz, CO), 135.4 (apparent t, $J = 22$ Hz, C_{ipso} of PPh_3), 133.9–127.6 (m, Ph), 122.1 (s, C_{ipso} of Ph), 97.4 (s, $C{\equiv}C$), 89.1 (s, $C{\equiv}C$). ^{31}P-NMR: δ 51.3. Anal. Found: C, 63.39; H, 4.29; S, 7.29. Calc. for $C_{46}H_{36}OP_2RuS_2\cdot 0.5CH_2Cl_2$: C, 63.87; H, 4.26; S, 7.33%. Mass spectrum: *m*/*z* 832 (M^+), 804 ($M{-}CO^+$).

4.4. Preparation of $[Ru(H)(CO)(S_2CC{\equiv}CBu^t)(PPh_3)_2]$ (**2c**)

In a similar manner to the above, $Bu^tC{\equiv}CH$ (0.31 ml, 0.205 g, 2.5 mmol) was dissolved in THF (17.96 ml) in a Schlenk tube and treated dropwise with BuLi (1.58 ml of 1.6 M solution) at −78°C. After stirring for 30 min at r.t. the solution was cooled again to −78°C and carbon disulfide (0.15 ml, 2.5 mmol) added dropwise. The pale yellow solution was allowed to warm to r.t. and then stir for 1 h, causing a change to dark orange. In a separate Schlenk tube $[Ru(H)(Cl)(CO)(PPh_3)_3]$ (0.5 g, 0.525 mmol) was suspended in THF (50 ml). To this suspension was added 4.2 ml of the dark orange $Li(S_2CC{\equiv}CBu^t)$ solution. The suspended solid rapidly dissolved and a light orange–red solution was obtained on stirring overnight. The solvent was removed and the remaining solid was absorbed onto silica and loaded onto a chromatography column. Elution with light petroleum–dichloromethane (3:2) afforded a large orange-red band, which yielded a bright orange powder of $[Ru(H)(CO)(S_2CC{\equiv}CBu^t)(PPh_3)_2]$ on removal of the solvent. Yield 0.3105 g, 73%. M.p. 149–151°C. IR(CH_2Cl_2): 2197 w ($C{\equiv}C$), 1936 s (CO) cm^{-1}. ^{1}H-NMR: δ 7.75–7.25 (m, 30 H, Ph), 1.10 (s, 9 H, Me), −10.55 (t, $J = 20.0$ Hz, 1 H, RuH). ^{13}C-NMR: δ 220.6 (t, $J = 6$ Hz, S_2C), 205.1 (t, $J = 13$ Hz, CO), 135.7 (apparent t, $J = 22$ Hz, C_{ipso}), 134.3–127.9 (m, Ph), 100.2, 89.4 (both s, $C{\equiv}C$), 30.6 (s, Me), 28.3 (CMe_3). ^{31}P-NMR δ 51.7. Anal. Found: C, 60.41; H, 4.59; S, 7.97. Calc. for $C_{44}H_{40}OP_2RuS_2\cdot CH_2Cl_2$: C, 60.30; H, 4.69; S, 7.81%. Mass spectrum: *m*/*z* 812 ($M + H^+$).

4.5. Preparation of $[Ru(CO)(CPh{=}CHPh)(S_2CC{\equiv}CMes)(PPh_3)_2]$ (**3a**)

A red solution of $Li[S_2CC{\equiv}CMes]$ was prepared as above from $MesC{\equiv}CH$ (0.25 ml, 0.32 g, 2.22 mmol) and BuLi (1.40 ml of 1.6 M solution) in 18.2 ml of THF, followed by addition of CS_2 (0.15 ml, 2.5 mmol). The total volume was therefore 20 ml. In a separate Schlenk tube $[Ru(Cl)(CO)(CPh{=}CHPh)(PPh_3)_2]$ (0.5 g, 0.576 mmol) was suspended in THF (50 ml), and to this was added 5.2 ml of the $Li[S_2CC{\equiv}CMes]$ solution. Overnight stirring produced a brown–red solution which was stripped to dryness. Column chromatography, eluting with light petroleum–dichloromethane (1:1) afforded a large brown-green band, which yielded a dark brown powder of $[Ru(CO)(CPh{=}CHPh)(S_2CC{\equiv}CMes)(PPh_3)_2]$ on removal of the solvent. Yield 0.4667 g, 78%. M.p. 178–180°C. IR (CH_2Cl_2): 2175 w ($C{\equiv}C$), 1930 s (CO) cm^{-1}. ^{1}H-NMR: δ 7.47–6.78 (m, Ph + Mes), 6.44 (d br, Ph), 5.83 (s br, CH), 2.24 (s, 3 H, Me), 2.15 (s, 6 H, 2 Me). ^{13}C-NMR: δ 215.3 (t, $J = 5$ Hz, S_2C), 205.9 (t, $J = 15$ Hz, CO), 166.5 (br s, CPh of vinyl), 152.9 (br s, CHPh of vinyl), 141.0–123.0 (m, Ph + Mes), 118.3 (s, C_{ipso} of Mes), 104.1, 90.6 (both s, $C{\equiv}C$), 21.4 (s, Me), 21.0 (s, 2 Me). ^{31}P-NMR: δ 37.8. Anal. Found: C, 71.81; H, 5.52; S, 6.01. Calc. for $C_{63}H_{52}OP_2RuS_2$: C, 71.93; H, 4.95; S, 6.09%. Mass spectrum: *m*/*z* 1053 (M^+), 873, 762.

4.6. Preparation of $[Ru(CO)(CPh{=}CHPh)(S_2CC{\equiv}CPh)(PPh_3)_2]$ (**3b**)

A red solution of $Li[S_2CC{\equiv}CPh]$ (2.64 mmol in 20 ml of THF) was prepared as described in Section 4.3, and 8.72 ml of this solution was added to a suspension of $[Ru(Cl)(CO)(CPh{=}CHPh)(PPh_3)_2]$ (1 g, 1.153 mmol) in

THF (50ml). The solid dissolved and a red–green solution was obtained after overnight stirring. After absorption onto a small amount of silica, the residue was chromatographed. Elution with light petroleum–dichloromethane (3:2) afforded a large brown-green band, which yielded a dark green powder of $[Ru(CO)(CPh{=}CHPh)(S_2CC{\equiv}CPh)(PPh_3)_2]$ on removal of the solvent. Yield 0.8357 g, 72%. M.p. 194–196°C. IR (CH_2Cl_2): 2184 w ($C{\equiv}C$), 1931 s (CO) cm^{-1}. ^1H-NMR: δ 7.45–6.76 (m, H, Ph), 6.36 (br s, Ph), 5.85 (br s, CH). ^{13}C-NMR: δ 215.0 (t, $J = 5$ Hz, S_2C), 205.7 (t, $J = 16$ Hz, CO), 166.3 (s, CPh of vinyl), 140.8 (s, CHPh of vinyl), 135.0–123.1 (m, Ph), 121.6 (s, C_{ipso} of Ph), 96.1, 92.0 (both s, $C{\equiv}C$). ^{31}P-NMR: δ 37.3. Anal. Found: C, 69.29; H, 4.70; S, 6.69. Calc. for $C_{60}H_{46}OP_2RuS_2{\cdot}0.5CH_2Cl_2$: C, 69.04; H, 4.47; S, 6.09%. Mass spectrum: m/z 1011 (M^+), 983 ($M{-}CO^+$), 831, 803.

4.7. Preparation of $[Ru(CO)(CPh{=}CHPh)(S_2CC{\equiv}CBu^t)(PPh_3)_2]$ (**3c**)

A dark orange solution of $Li[S_2CC{\equiv}CBu^t]$ (2.5 mmol in 20 ml of THF) was prepared as described in Section 4.4, and 4.61 ml of this solution was added to a suspension of $[Ru(Cl)(CO)(CPh{=}CHPh)(PPh_3)_2]$ (0.5 g, 0.576 mmol) in THF (50 ml). A dark red solution was obtained after stirring overnight. Chromatography as above, eluting with light petroleum–dichloromethane (3:2) afforded a large brown–green band, which yielded a dark brown powder of $[Ru(CO)(CPh{=}CHPh)(S_2CC{\equiv}CBu^t)(PPh_3)_2]$ on removal of the solvent. Yield 0.1446 g, 25%. M.p. 194–197°C. IR(CH_2Cl_2): 2200 w ($C{\equiv}C$), 1930 s (CO) cm^{-1}. ^1H-NMR: δ 7.45–6.78 (m, Ph), 6.35 (br s, Ph), 5.78 (br s, 1 H, CH of vinyl), 1.05 (s, 9 H, Me). ^{13}C-NMR: δ 217.6 (t, $J = 5$ Hz, S_2C), 205.8 (t, $J = 16$ Hz, CO), 166.7 (br s, CPh), 140.9 (s, CHPh), 134.8–123.0 (m, Ph), 102.6, 87.8 (both s, $C{\equiv}C$), 29.9 (s, Me), 27.9 (s, CMe_3). ^{31}P-NMR: 37.8. Anal. Found: C, 68.45; H, 5.02; S, 7.07. Calc. for $C_{58}H_{50}OP_2RuS_2{\cdot}0.5CH_2Cl_2$: C, 68.05; H, 4.94; S, 6.20%. Mass spectrum: m/z 991 ($M + H^+$).

4.8. Preparation of $[Ru(CO)(C{\equiv}CPh)(S_2CC{\equiv}CPh)(PPh_3)_2]$ (**4**)

A suspension of $[Ru(CO)(CPh{=}CHPh)(S_2CC{\equiv}CPh)(PPh_3)_2]$ (0.18 g, 0.178 mmol) in THF (50 ml) was treated with an excess of phenylacetylene (0.1 ml, 0.093 g, 0.91mmol). The green–red solution had turned red after stirring for 4 days. The solvent was removed and the remaining solid was absorbed onto silica and loaded onto a chromatography column. Elution with light petroleum–dichloromethane (3:2) afforded a large red band, which yielded a bright red powder of $[Ru(CO)(C{\equiv}CPh)(S_2CC{\equiv}CPh)(PPh_3)_2]$ on removal of solvent. Yield: 0.1009 g, 61%. M.p. 208–211°C (dec.). IR (CH_2Cl_2): 2185 w ($C{\equiv}C$), 2100 w ($C{\equiv}C$), 1955 s (CO) cm^{-1}. ^1H-NMR: δ 7.95–6.60 (m, Ph). ^{13}C-NMR: δ 217.0 (t, $J = 5$ Hz, S_2C), 203.7 (t, $J = 13$ Hz, CO), 134.8–128.0 (m, Ph), 124.7, 122.0 (both s, C_{ipso} of $C{\equiv}CPh$), 118.5 (s, $C{\equiv}C$ of acetylide), 110.5 (t, $J = 19$ Hz, $Ru{-}C{\equiv}C$ of acetylide), 96.9, 92.5 (both s, $C{\equiv}C$). ^{31}P-NMR: δ 38.8. Anal. Found: C, 64.71; H, 4.31; S, 7.36. Calc. for $C_{54}H_{40}OP_2RuS_2{\cdot}CH_2Cl_2$: C, 64.96; H, 4.13; S, 6.29%. Mass spectrum (electrospray): m/z 830 ($M{-}C_2Ph)^+$.

4.9. Preparation of $[Ru(CO)(C{\equiv}CMes)(S_2CC{\equiv}CPh)(PPh_3)_2]$ (**5**)

In the same manner, $[Ru(CO)(CPh{=}CHPh)(S_2CC{\equiv}CPh)(PPh_3)_2]$ (0.5 g, 0.496 mmol) in THF (50 ml) reacted with mesityl acetylene (0.2 ml, 0.256 g, 1.78 mmol) to give a red solution after stirring for 4 days. The solvent was removed and the remaining solid was absorbed onto silica and chromatograped as above. Elution with light petroleum–dichloromethane (3:2) afforded a large red band, which yielded a dark red powder of $[Ru(CO)(C{\equiv}CMes)(S_2CC{\equiv}CPh)(PPh_3)_2]$ on removal of solvent. Yield 0.1977 g, 41%. M.p. 194–198°C. IR (CH_2Cl_2): 2184 w ($C{\equiv}C$), 2086 w ($C{\equiv}C$), 1951 s (CO) cm^{-1}. ^1H-NMR: δ 7.96–6.68 (m, 17H, Ph + Mes), 2.20 (s, 3 H, Me), 2.18 (s, 6 H, 2 Me). ^{13}C-NMR: δ 215.7 (t, $J = 5$ Hz, S_2C), 203.5 (t, $J = 13$ Hz, CO), 140.4–121.1 (m, Ph + Mes), 115.3 (s, $C{\equiv}C$ of acetylide), 113.8 (t, $J = 19$ Hz, $Ru{-}C{\equiv}C$ of acetylide), 96.3 (t, $J = 3$ Hz, $C{\equiv}C$), 91.9 (s, $C{\equiv}C$), 20.7 (s, 2 Me), 14.9 (s, Me). ^{31}P-NMR: δ 37.1. Anal. Found: C, 68.44; H, 4.81; S, 6.87. Calc. for $C_{57}H_{46}OP_2RuS_2{\cdot}0.5CH_2Cl_2$: C, 67.95; H, 4.53; S, 6.30%. Mass spectrum: m/z 975 (M^+), 947, 831, 684.

4.10. Crystal structure determinations of **2b**, **3b** and **5**

Details of the crystal structure determinations are given in Table 3. Data collected were measured on a Bruker SMART CCD area detector with Oxford Cryosystems low temperature system. Reflections were measured from a hemisphere of data collected of frames each covering 0.3° in omega. Of the reflections measured, all of which were corrected for Lorentz and polarisation effects and for absorption by semi empirical methods based on symmetry-equivalent and repeated reflections, those independent reflections which exceeded the significance level $|F|/\sigma(|F|) > 4.0$ were used in refinement. The structure was solved by direct methods and refined by full-matrix least-squares methods on F^2. Hydrogen atoms were placed geometrically and refined with a riding model (including torsional freedom for methyl groups) and with U_{iso} constrained to be 1.2 (1.5 for methyl groups) times U_{eq} of the carrier

Table 3
Summary of crystallographic data for complexes **2b**·$2CH_2Cl_2$, **3b** and **5**

	2b·$2CH_2Cl_2$	**3b**	**5**
Identification code	ims10m	ims17a	ims20m
Empirical formula	$C_{48}H_{39}Cl_4OP_2RuS_2$	$C_{60}H_{46}OP_2RuS_2$	$C_{57}H_{46}OP_2RuS_2$
Formula weight	1000.72	1010.10	974.07
Temperature (K)	150(2)	150(2)	150(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	$P2(1)/n$	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions			
a (Å)	11.451(3)	12.270(4)	11.3531(12)
b (Å)	33.727(10)	14.297(4)	11.8388(12)
c (Å)	11.879(4)	16.115(5)	18.3351(18)
α (°)	90	86.004(6)	72.229(2)
β (°)	100.372(6)	69.513(5)	85.892(2)
γ (°)	90	64.738(5)	79.352(2)
Volume (Å^3)	4512(2)	2384.2(12)	2306.1(4)
Z	4	2	2
D_{calc} (Mg m^{-3})	1.473	1.407	1.403
Absorption coefficient (mm^{-1})	0.784	0.526	0.541
$F(000)$	2036	1040	1004
Crystal size (mm)	$0.25 \times 0.10 \times 0.10$	$0.19 \times 0.08 \times 0.03$	$0.24 \times 0.20 \times 0.18$
θ Range for data collection (°)	1.21–28.34	1.35–28.34	1.83–28.30
Index ranges	$-15 \leq h \leq 9$, $-44 \leq k \leq 44$, $-15 \leq l \leq 15$	$-16 \leq h \leq 10$, $-18 \leq k \leq 19$, $-20 \leq l \leq 19$	$-15 \leq h \leq 10$, $-14 \leq k \leq 15$, $-21 \leq l \leq 24$
Reflections collected	29 075	14 820	14 063
Independent reflections	10 700 [$R_{int} = 0.1530$]	10 872 [$R_{int} = 0.0911$]	10364 [$R_{int} = 0.1066$]
Completeness to θ (%)	95.1	91.4	90.3
Absorption correction	Semi-empirical	Semi-empirical from equivalents	None
Max. and min. transmission	0.9257 and 0.8281	0.9844 and 0.9066	0.9089 and 0.8811
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	10 700/9/522	10 872/0/590	10 364/0/568
Goodness-of-fit on F^2	1.096	0.910	0.902
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0733$, $wR_2 = 0.1910$	$R_1 = 0.0578$, $wR_2 = 0.1391$	$R_1 = 0.0698$, $wR_2 = 0.1550$
R indices (all data)	$R_1 = 0.0850$, $wR_2 = 0.1995$	$R_1 = 0.1199$, $wR_2 = 0.1921$	$R_1 = 0.1199$, $wR_2 = 0.1764$
Largest difference peak and hole (e Å^{-3})	1.643 and −1.563	0.868 and −0.979	1.053 and −2.296

atom. Refinement converged at the final R values shown with allowance for the thermal anisotropy of all non-hydrogen atoms. Weighting schemes $w = 1/[\sigma^2(F_o^2) + (0.0939P)^2 + 12.70P]$ (for **2b**), $w = 1/[\sigma^2(F_o^2) + (0.1019P)^2 + 0.00P]$ (for **3b**) and $w = 1/[\sigma^2(F_o^2) + (0.0850P)^2 + 0.00P]$ (for **5**) where $P = (F_o^2 + 2F_c^{2)}/3$ were used in the latter stages of refinement. Complex scattering factors were taken from the program package SHELXTL [17] as implemented on the Viglen Pentium computer.

5. Supplementary material

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 147705, 147706 and 147707 for complexes **2b**, **3b** and **5**, respectively. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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