ELSEVIER

Reactions of *trans*-[RuCl$_2$(CO)$_2$(PEt$_3$)$_2$] with 1,1-dithiolates: Stepwise formation of *cis*-[Ru(CO)(PEt$_3$)(S$_2$X)] (X = CNMe$_2$, CNEt$_2$, COEt, P(OEt)$_2$, PPh$_2$)

Anthony J. Deeming, Caroline Forth, Graeme Hogarth *

Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, UK

Abstract

Trans-[RuCl$_2$(CO)$_2$(PEt$_3$)$_2$] reacts with two equivalents of a series of 1,1-dithiolate ligands to form the bis(dithiolate) complexes, *cis*-[Ru(CO)(PEt$_3$)(S$_2$X)$_2$] (X = CNMe$_2$, CNEt$_2$, COEt, P(OEt)$_2$, PPh$_2$). Two intermediates have been isolated; *trans*-[Ru(PEt$_3$)$_2$Cl-(CO){S$_2$P(OEt)$_2$}] and *trans*-[Ru(PEt$_3$)$_2$(CO)(η^1-S$_2$COEt)(η^2-S$_2$COEt)], allowing a simple reaction scheme to be postulated involving three steps; (i) initial replacement of *cis* carbonyl and chloride ligands, (ii) substitution of the second chloride, (iii) loss of a phosphine. Thermolysis of *cis*-[Ru(CO)(PEt$_3$)(S$_2$CNMe$_2$)$_2$] with Ru$_3$(CO)$_{12}$ in xylene affords trinuclear [Ru$_3$(μ$_3$-S)$_2$(PEt$_3$)(CO)$_8$] as a result of dithiocarbamate degradation. Crystal structures of *cis*-[Ru(CO)(PEt$_3$)(S$_2$X)$_2$] (X = NMe$_2$, COEt), *trans*-[Ru(PEt$_3$)$_2$Cl(CO){S$_2$P(OEt)$_2$}], *trans*-[Ru(PEt$_3$)$_2$(CO)(η^1-S$_2$COEt)(η^2-S$_2$COEt)] and [Ru$_3$(μ$_3$-S)$_2$(PEt$_3$)(CO)$_8$] are reported.
© 2005 Elsevier B.V. All rights reserved.

1. Introduction

Dithiocarbamates are a versatile class of ligand with the ability to stabilize transition metals in a wide range of oxidation states [1] and while in the vast majority of cases the ligands act in a simple spectator fashion, it is becoming increasingly apparent that this is not always the case. As early as 1973, Ricard and co-workers [2] reported that the molybdenum(IV) dimer, [Mo(μ-S)(S$_2$CNPr$_2$)(η^2-SCNPr$_2$)]$_2$, resulting from the cleavage of a carbon–sulfur bond, generating sulfido and thiocarboxamide ligands, was the product of the reaction of [Mo$_2$(μ-OAc)$_4$] with four equivalents of NaS$_2$CNPr$_2$. More recently, work in our group has shown that heating the ruthenium(II) complexes *cis*-[Ru(CO)$_2$(S$_2$CNR$_2$)$_2$] (R = Me, Et) with Ru$_3$(CO)$_{12}$ at elevated temperatures leads to the formation of novel sulfido-capped aminoalkylidyne clusters resulting from a double sulfur–carbon bond cleavage of the dithiocarbamates.

Thus, with *cis*-[Ru(CO)$_2$(S$_2$CNEt$_2$)$_2$], pentanuclear [Ru$_5$-(μ^4-S)$_2$(μ-CNEt$_2$)$_2$(CO)$_{11}$] is the major product [3], while with *cis*-[Ru(CO)$_2$(S$_2$CNMe$_2$)$_2$], octanuclear [Ru$_8$(μ^4-S)$_3$-(μ^3-S)(μ-CNMe$_2$)$_2$(CO)$_{16}$] has been isolated and crystallographically characterized [4]. The mode of formation of these clusters is unknown, but the likely initial process is one of carbonyl loss from the bis(dithiocarbamate) complexes to afford dimeric [Ru(CO)(S$_2$CNR$_2$)(μ-S$_2$CNR$_2$)]$_2$ (R = Me, Et), a process known to occur cleanly in the presence of trimethylamine N-oxide [5].

In order to explore further the potential of this method for the formation of novel aminoalkylidyne clusters and to gain more insight in to the processes involved, we sought to prepare a range of phosphine-substituted derivatives, *cis*-[Ru(CO)(PR$_3$)(S$_2$CNR$_2$)$_2$]. A number of potential routes can be envisaged to such complexes. Unfortunately, carbonyl substitution in *cis*-[Ru(CO)$_2$(S$_2$CNR$_2$)$_2$] is a very slow process and thus does not provide a viable method. Critchlow and Robinson [6] have reported the preparation of *cis*-[Ru(CO)(PPh$_3$)(S$_2$CNMe$_2$)$_2$] from the addition of two equivalents of NaS$_2$CNMe$_2$ to [Ru(NO$_3$)$_2$(CO)(PPh$_3$)$_2$],

* Corresponding author. Fax: +44 171 380 7463.
  E-mail address: g.hogarth@ucl.ac.uk (G. Hogarth).

although it is noteworthy that a similar reaction of *cis*-[RuCl$_2$(CO)$_2$ (PPh$_3$)$_2$] affords only the dicarbonyl, *cis*-[Ru-(CO)$_2$ (S$_2$CNMe$_2$)$_2$] [7]. Formation of the latter results from loss of two equivalents of phosphine and retention of both carbonyls, which might be due to the steric bulk of the phosphine and their initial *cis* disposition. *Trans*-[RuCl$_2$(CO)$_2$-(PEt$_3$)$_2$] is relatively easily prepared and has been widely utilized as a starting material for a wide range of organometallic chemistry [8]. This seemed an attractive starting material for the synthesis of *cis*-[Ru(CO)(PEt$_3$)(S$_2$CNR$_2$)$_2$] since the more basic and less sterically demanding triethylphosphine should be less readily lost, while the *trans* arrangement of ligands and the preferred *cis* arrangement of dithiocarbamates at ruthenium(II) should facilitate the loss of one carbonyl and one phosphine. We herein report that this is indeed the case, addition of two equivalents of dithiocarbamate salts to *trans*-[RuCl$_2$(CO)$_2$(PEt$_3$)$_2$] affording *cis*-[Ru(CO)(PEt$_3$)(S$_2$CNR$_2$)$_2$] (R = Me, Et), together with reactions with other 1,1-dithiolate anions, the latter leading to elucidation of the reaction mechanism.

2. Results and discussion

Heating *trans*-[RuCl$_2$(CO)$_2$(PEt$_3$)$_2$] and NaS$_2$CNR$_2$ (R = Me, Et) in ethanol for 4–7 h resulted in the clean formation of bis(dithiocarbamate) complexes *cis*-[Ru(CO)-(PEt$_3$)(S$_2$CNR$_2$)$_2$] (1a–b) as yellow crystalline solids. Characterization was straightforward, each showing a single strong carbonyl absorption in the IR spectrum and a singlet in the ^{31}P NMR spectrum, while in the ^{1}H NMR spectrum of 1a, the appearance of four methyl signals confirmed the *cis* disposition of carbonyl and phosphine ligands. In order to confirm these assignments a structural study was carried out on 1a the results of which are summarized in Fig. 1. The carbonyl and phosphine lie at right angles [C(1)–Ru(1)–P(1) 89.70(11)°] at the octahedral ruthenium(II) centre, the coordination sphere of which is completed by a *cis* disposition of the two small bite angle [S(2)–Ru(1)–S(1) 71.72(3), S(3)–Ru(1)–S(4) 72.02(3)°] dithiocarbamates. These are bound in a slightly asymmetric manner [Ru(1)–S(1) 2.4885(9), Ru(1)–S(2) 2.3937(9), Ru(1)–S(3) 2.3914(9), Ru(1)–S(4) 2.4767(9) Å], the longer distances being those *trans* to the carbonyl and phosphine; a similar *trans*-influence being exhibited by the two.

As detailed above, at room temperature all four methyl groups in 1a are inequivalent, which is consistent with the observed solid state structure, and is a consequence of the restricted rotation about the central carbon–nitrogen bond. In toluene these four signals are observed as two pairs at δ 2.61 and 2.54 and δ 2.53 and 2.49. Upon warming all signals broaden, the low field pair coalescing at 333 K, and the high field pair at 338 K. From this data, free energies of activation can be estimated as 71 ± 1 and 74 ± 1 kJ mol^{-1}, respectively. These values are slightly lower than those of 78 ± 1 and 77 ± 1 kJ mol^{-1} observed for *cis*-[Ru(CO)$_2$(S$_2$CNMe$_2$)$_2$] and *cis*-[Fe(CO)$_2$(S$_2$CNMe$_2$)$_2$], respectively [9]. The increased barrier may result from the
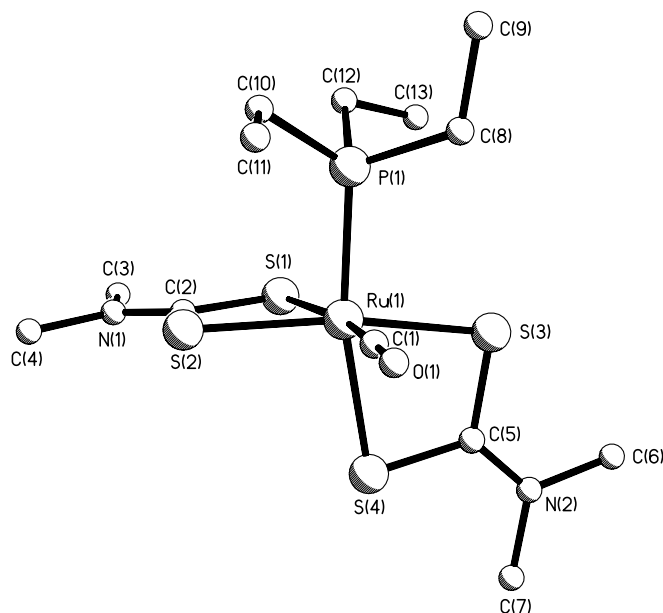

Fig. 1. Molecular structure of *cis*-[Ru(CO)(PEt$_3$)(S$_2$CNMe$_2$)$_2$] (1a) with selected bond lengths (Å) and angles (°). Ru(1)–P(1) 2.2980(9), Ru(1)–S(1) 2.4885(9), Ru(1)–S(2) 2.3937(9), Ru(1)–S(3) 2.3914(9), Ru(1)–S(4) 2.4767(9), Ru(1)–C(1) 1.835(4), C(1)–Ru(1)–P(1) 89.70(11), S(3)–Ru(1)–S(2) 164.32(3), C(1)–Ru(1)–S(1) 169.38(12), P(1)–Ru(1)–S(4) 167.88(3), S(2)–Ru(1)–S(1) 71.72(3), S(3)–Ru(1)–S(4) 72.02(3), S(1)–C(2)–S(2) 113.2(2), S(4)–C(5)–S(3) 113.2(2).

better σ-donor ability of the phosphine versus a carbonyl, which results in an increase in electron-density at the metal centre, thus disfavoring the thioureide resonance structure which has carbon–nitrogen double bond character. On this basis, it is also tempting to suggest that the lower of the two values measured in 1a is associated with the dithiocarbamate lying *trans* to the phosphine, although we have been unable substantiate this with a full assignment of the ^{1}H NMR spectrum.

Heating *trans*-[RuCl$_2$(CO)$_2$(PEt$_3$)$_2$] and KS$_2$COEt in ethanol for 6 h lead to the isolation after chromatography of two products; a small amount (5%) of the expected product, *cis*-[Ru(CO)(PEt$_3$)(S$_2$COEt)$_2$] (3) together with *trans*-[Ru(PEt$_3$)$_2$(CO)(η^1-S$_2$COEt)(η^2-S$_2$COEt)] (2) (20%). From spectroscopic data it was clear that the latter contained a carbonyl and two equivalents of phosphine and xanthate; the phosphines occupying equivalent sites while the xanthate ligands were inequivalent, suggesting mono- and bidentate coordination. In order to confirm these assignments a structural study was carried out on 2 the results of which are summarized in Fig. 2. The main structural feature is indeed the different coordination modes of the xanthates, one binding in an approximately symmetrical bidentate fashion [Ru(1)–S(1) 2.4164(8), Ru(1)–S(2) 2.4782(8) Å], while the second is monodentate [Ru(1)–S(3) 2.3915(8) Å]. The different binding modes of the two leads, as expected, to marked differences in the carbon–sulfur bonds, being approximately equivalent in the bidentate [S(1)–C(2) 1.696(4), S(2)–C(2) 1.698(4) Å] but quite different in the monodentate [S(3)–C(3)
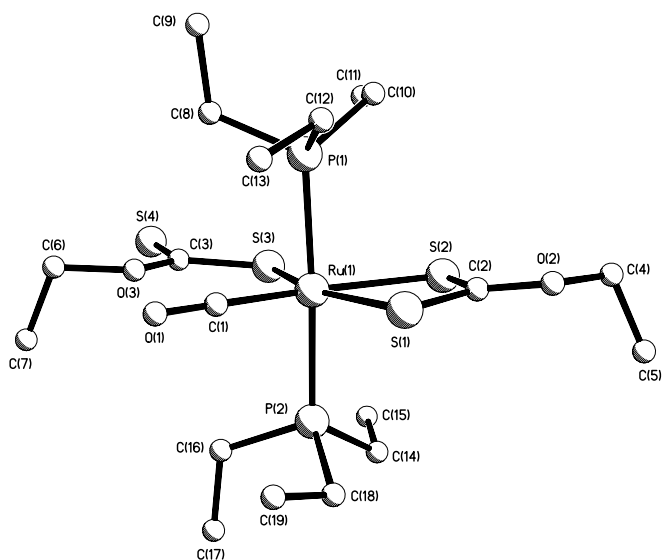
Fig. 2. Molecular structure of *trans*-[Ru(CO)(PEt$_3$)$_2$(η^1-S$_2$COEt)(η^2-S$_2$COEt)] (**2**) with selected bond lengths (Å) and angles (°). Ru(1)–P(1) 2.3758(9), Ru(1)–P(2) 2.3679(10), Ru(1)–S(1) 2.4164(8), Ru(1)–S(2) 2.4782(8), Ru(1)–S(3) 2.3915(8), Ru(1)–C(1) 1.858(3), S(1)–C(2) 1.696(4), S(2)–C(2) 1.698(4), S(3)–C(3) 1.700(4), S(4)–C(3) 1.666(4), P(2)–Ru(1)–P(1) 176.99(3), S(3)–Ru(1)–S(1) 161.03(3), C(1)–Ru(1)–S(2) 170.71(10), S(1)–Ru(1)–S(2) 71.51(3), S(1)–C(2)–S(2) 114.9(2), S(4)–C(3)–S(3) 120.6(2).

1.700(4), S(4)–C(3) 1.666(4) Å] ligand, while bond angles at the central carbon also differ significantly [S(1)–C(2)–S(2) 114.9(2)°, S(4)–C(3)–S(3) 120.6(2)°].

Heating *trans*-[RuCl$_2$(CO)$_2$(PEt$_3$)$_2$] and either NH$_4$S$_2$P-(OEt)$_2$ or NaS$_2$PPh$_2$ in ethanol for 3 h also lead to the isolation of two products. In both cases, the minor component was the expected products *cis*-[Ru(CO)(PEt$_3$){S$_2$P(OEt)$_2$}$_2$] (**5**) and *cis*-[Ru(CO)(PEt$_3$)(S$_2$PPh$_2$)$_2$] (**7**), while the major components were the monosubstituted complexes *trans*-[RuCl(CO)(PEt$_3$)$_2${S$_2$P(OEt)$_2$}] (**4**) and *trans*-[RuCl(CO)-(PEt$_3$)$_2$(S$_2$PPh$_2$)] (**6**). The latter were characterized by spectroscopic and analytical data. The presence of two equivalent phosphines and one new dithiolate ligand was easily shown by ^{31}P NMR spectroscopy; two singlets in a 2:1 ratio being observed in each case. In order to confirm these assignments a structural study was carried out on **4** the results of which are summarized in Fig. 3. There are two approximately equivalent independent molecules in the unit cell and in both the carbonyl and chloride are disordered over two sites. The dithiolate is bound approximately symmetrically to the ruthenium(II) centre [Ru(1)–S(1) 2.4879(8), Ru(1)–S(2) 2.4898(9) Å], which also supports a *trans* arrangement of the two phosphines [P(1)–Ru(1)–P(2) 175.07(2)°] and *cis* arrangement of carbonyl and chlorides [C(2)–Ru(1)–Cl(1) 93.35(18)°].

Structural characterization of **5** was also carried out in order to compare the data with that from **1a** and **4**. The results of this are summarized in Fig. 4. The bite angle of the dithiolate ligand in **4** [S(1)–Ru(1)–S(2) 79.57(3)°] is very similar to those in **5** [S(1)–Ru(1)–S(2) 80.55(2)°, S(4)–Ru(1)–S(3) 80.34(2)°], however, the ruthenium–sulfur dis-
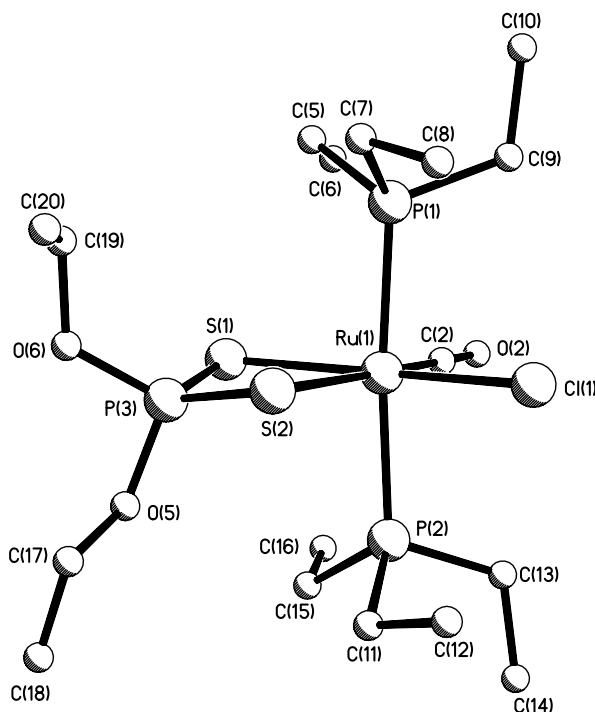

Fig. 3. Molecular structure of *trans*-[RuCl(CO)(PEt$_3$)$_2${S$_2$P(OEt)$_2$}] (**4**) with selected bond lengths (Å) and angles (°). Ru(1)–P(1) 2.3825(8), Ru(1)–P(2) 2.3844(8), Ru(1)–S(1) 2.4879(8), Ru(1)–S(2) 2.4898(9), Ru(1)–Cl(1) 2.3853(19), Ru(1)–C(2) 1.821(8), P(1)–Ru(1)–P(2) 175.07(2), C(2)–Ru(1)–Cl(1) 93.35(18), S(1)–Ru(1)–S(2) 79.57(3), Cl(1)–Ru(1)–S(1) 172.48(4), C(2)–Ru(1)–S(2) 173.59(18), S(1)–P(3)–S(2) 106.38(4).
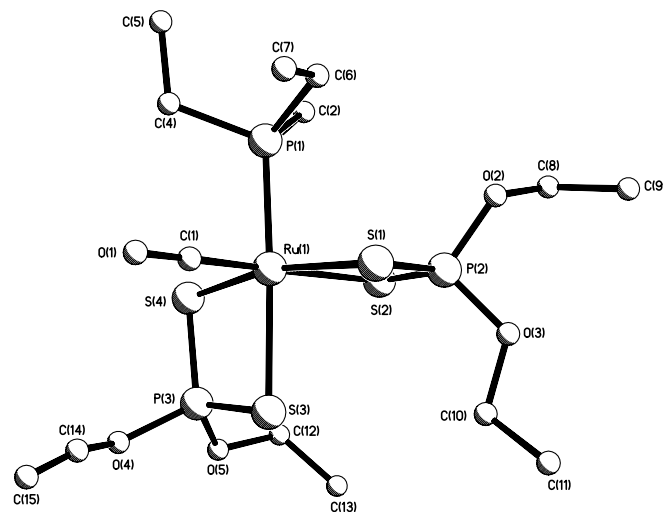

Fig. 4. Molecular structure of *cis*-[Ru(CO)(PEt$_3$){S$_2$P(OEt)$_2$}$_2$] (**5**) with selected bond lengths (Å) and angles (°). Ru(1)–P(1) 2.3050(6), Ru(1)–S(1) 2.4264(6), Ru(1)–S(2) 2.5430(7), Ru(1)–S(3) 2.5111(7), Ru(1)–S(4) 2.4305(7), Ru(1)–C(1) 1.828(3), P(1)–Ru(1)–S(3) 175.42(2), S(1)–Ru(1)–S(4) 167.32(2), C(1)–Ru(1)–S(2) 174.39(8), S(1)–Ru(1)–S(2) 80.55(2), S(4)–Ru(1)–S(3) 80.34(2), S(1)–P(2)–S(2) 107.94(4), S(3)–P(3)–S(4) 106.39(4).

tances differ appreciably. Thus in **4** the ligand is bound approximately symmetrically, [Ru(1)–S(1) 2.4879(8), Ru(1)–S(2) 2.4898(9) Å], while in **5** there is a pronounced asymmetry [Ru(1)–S(1) 2.4264(6), Ru(1)–S(2) 2.5430(7), Ru(1)–S(3) 2.5111(7), Ru(1)–S(4) 2.4305(7) Å]. As discussed above, the latter is similar to the situation found

in structurally analogous **1a** and relates to *trans*-influence of the carbonyl and phosphine ligands.

The isolation of *trans*-[Ru(PEt$_3$)$_2$(CO)(η^1-S$_2$COEt)-(η^2-S$_2$COEt)] (**2**), *trans*-[RuCl(CO)(PEt$_3$)$_2${S$_2$P(OEt)$_2$}] (**4**) and *trans*-[RuCl(CO)(PEt$_3$)$_2$(S$_2$PPh$_2$)] (**6**) allows a full picture of the course of these reactions to be elucidated as outlined in Scheme 1. Initial addition of the dithiolate results in substitution of a chloride followed by carbonyl loss to give *trans*-[RuCl(CO)(PEt$_3$)$_2$(dithiolate)]. Addition of the second dithiolate results in substitution of the second chloride to yield *trans*-[Ru(PEt$_3$)$_2$(CO)(η^1-dithiolate)(η^2-dithiolate)], which can then eliminate either a phosphine or the remaining carbonyl. The former occurs exclusively, presumably since elimination of the carbonyl would lead to the less favored *trans*-arrangement of dithiolate ligands.

As detailed in the introduction, one of our reasons for preparing dithiocarbamate complexes **1a–b** was in order to attempt to use them as sources of aminoalkylidyne clusters. Heating a xylene solution of **1a** and Ru$_3$(CO)$_{12}$ for 2 h resulted in the consumption of the former and generation of a number of products. Unfortunately, we have been unable to characterize all except one, namely triruthenium [Ru$_3$(μ_3-S)$_2$(PEt$_3$)(CO)$_8$] (**8**) isolated as a yellow crystalline solid in 10% yield (Scheme 2). In order to confirm this formulation a crystallographic study was carried out, the results of which are summarized in Fig. 5. The triruthenium centre is characterized by two short [Ru(1)–Ru(2) 2.8157(3), Ru(1)–Ru(3) 2.7230(3) Å] metal–metal interactions being capped above and below by sulfido groups. The phosphine lies in the plane of the three metal atoms, occupying a position *trans* to a ruthenium–ruthenium vector, which results in a significant elongation of this bond. This structural motif is very common for group 8 transition metals and all show the same gross structural features [10].

Formation of **8** clearly results from cleavage of one or both dithiocarbamate ligands, although disappointingly the central aminoalkylidyne fragment has been lost. The isolation of **8** does, however, shed some light onto the relationship between penta- and octaruthenium clusters [Ru$_5$(μ_4-S)$_2$(μ-CNEt$_2$)$_2$CO$_{11}$] [3] and [Ru$_8$(μ_4-S)$_3$(μ_3-S)-(μ-CNMe$_2$)$_2$(CO)$_{16}$] [4] isolated upon thermolysis of *cis*-[Ru(CO)$_2$(S$_2$CNR$_2$)$_2$] (R = Me, Et) with Ru$_3$(CO)$_{12}$. The

1a R = Me
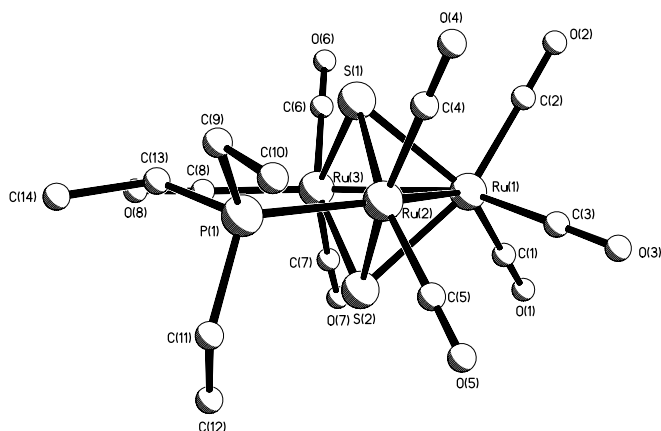**1b** R = Et

2

3

4

5

6

7
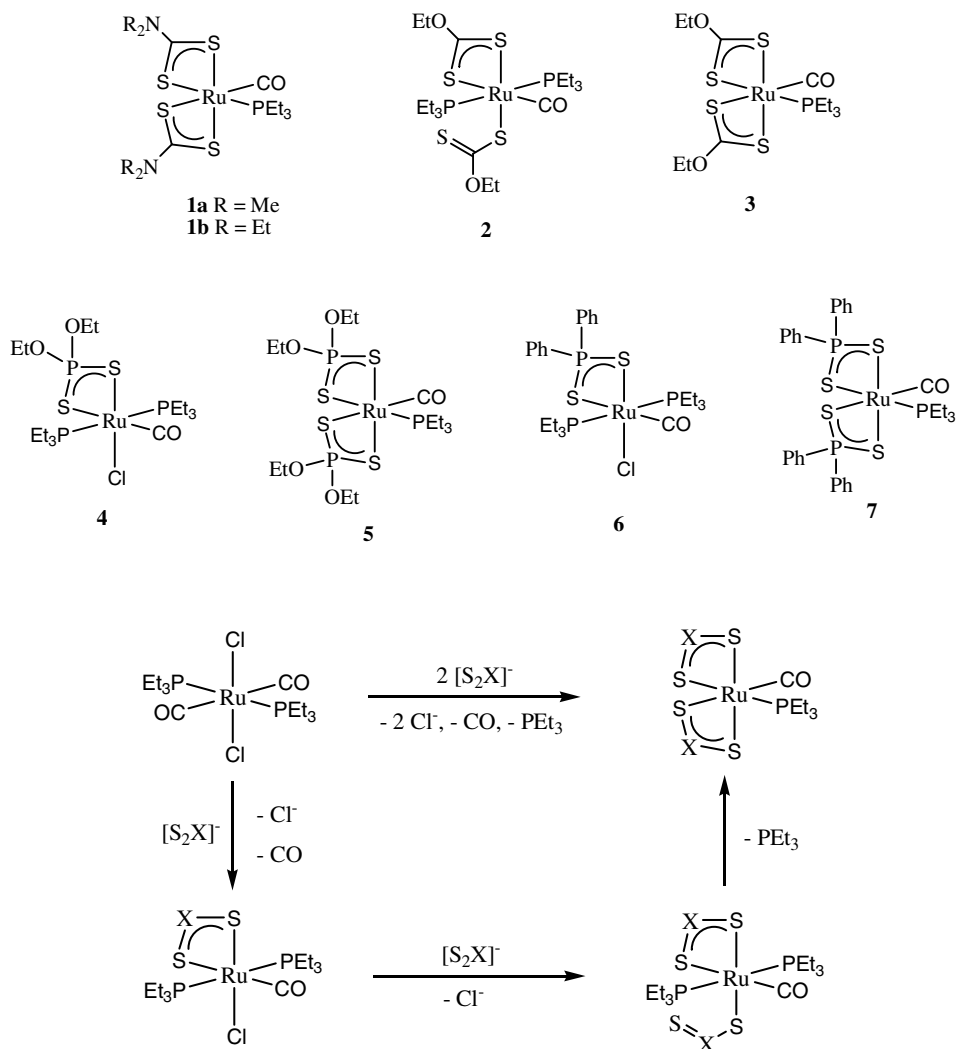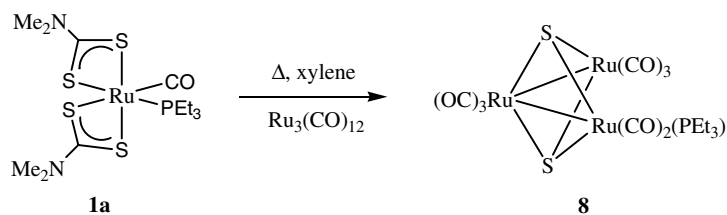
Scheme 1.

Scheme 2.

Fig. 5. Molecular structure of $[Ru_3(\mu_3\text{-S})_2(PEt_3)(CO)_8]$ (**8**) with selected bond lengths (Å) and angles (°). Ru(1)–Ru(2) 2.8157(3), Ru(1)–Ru(3) 2.7230(3), Ru(2)–P(1) 2.2956(7), Ru(1)–S(1) 2.4201(7), Ru(1)–S(2) 2.4137(7), Ru(2)–S(1) 2.3720(7), Ru(2)–S(2) 2.4006(7), Ru(3)–S(1) 2.3824(7), Ru(3)–S(2) 2.4075(7), Ru(3)–Ru(1)–Ru(2) 83.562(9), P(1)–Ru(2)–Ru(1) 147.49(2).

latter is formally related to the former by addition of an "$Ru_3(CO)_5S_2$" fragment. The source of this may well be the well known nonacarbonyl complex $[Ru_3(\mu^3\text{-S})_2(CO)_9]$ [11] which Adams and co-workers have previously shown is an excellent building block for cluster synthesis. This raises the possibility that during thermolysis of cis-$[Ru(CO)_2\text{-}(S_2CNR_2)_2]$, the nonacarbonyl is produced but reacts further and thus is not isolated. In contrast, phosphine adduct **8**, might be expected to be less reactive as a triruthenium source since the "open" ruthenium sites are less available and also the better σ-donor ligand will lead to stronger binding of the remaining carbonyls, thus hindering their loss.

In conclusion, we have shown that trans-$[RuCl_2(CO)_2\text{-}(PEt_3)_2]$ is a useful starting material for the synthesis of bis(thiolate) complexes cis-$[Ru(CO)(PEt_3)(dithiolate)_2]$, the stepwise nature of the substitution process allowing a full mechanistic scheme to be elucidated. Unfortunately, complexes cis-$[Ru(CO)(PEt_3)(S_2CNR_2)_2]$ do not seem to be useful precursors to aminoalkylidyne clusters. This is possibly due to the stronger donor ability of the phosphine rendering carbonyl loss less favorable.

3. Experimental

3.1. Synthesis of cis-[Ru(CO)(PEt₃)(S₂CNMe₂)₂] (1a)

Trans-$[RuCl_2(PEt_3)_2(CO)_2]$ (0.1032 g, 0.222 mmol) and $NaS_2CNMe_2 \cdot 3H_2O$ (0.2020 g, 1.41 mmol) were dissolved in ethanol (50 cm³) and heated under reflux for 7 h. The solvent was removed by rotary evaporation resulting in a yellow solid which was redissolved in dichloromethane (20 cm³) and filtered to give a clear yellow solution. The solvent was removed from the filtrate to give a yellow solid. Crystallization from a dichloromethane–heptane solution gave yellow crystals of cis-$[Ru(CO)(PEt_3)(S_2CNMe_2)_2]$ (**1a**) (0.1250 g, 59%). IR v(CO) (CH₂Cl₂): 1927s cm⁻¹; ¹H NMR (CDCl₃): δ 3.26 (s, 3H, NMe), 3.24 (s, 3H, NMe), 3.20 (s, 3H, NMe), 3.19 (s, 3H, NMe), 1.83 (m, 6H, PCH₂), 1.05 (dt, J 15.0, 7.6, 9H, Me); ³¹P{¹H} NMR (CDCl₃): δ 20.8 (s); mass spectrum (FAB): m/z 488 (M⁺), 460 (M⁺ – CO); Anal. Calc. for $RuPS_4ON_2C_{13}H_{27}$: C, 32.02; H, 5.58; N, 5.74. Found: C, 31.61; H, 5.37; N, 5.76%.

3.2. Synthesis of cis-[Ru(CO)(PEt₃)(S₂CNEt₂)₂] (1b)

Trans-$[RuCl_2(PEt_3)_2(CO)_2]$ (0.0993 g, 0.214 mmol) and $NaS_2CNEt_2 \cdot 3H_2O$ (0.2142 g, 1.28 mmol) were dissolved in ethanol (50 cm³) and heated under reflux for 4 h. The solvent was removed by rotary evaporation resulting in a yellow solid which was redissolved in dichloromethane (20 cm³) and filtered to give a clear yellow solution. The solvent was removed from the filtrate to give a yellow solid. Purification by TLC on silica using light petroleum and dichloromethane (10:3 by volume) gave a single yellow band characterized as cis-$[Ru(CO)(PEt_3)(S_2CNEt_2)_2]$ (**1b**) (0.0558 g, 48%). IR v(CO) (CH₂Cl₂): 1924s cm⁻¹; ¹H NMR (CDCl₃): δ 3.9–3.5 (m, 8H, NCH₂), 1.84 (m, 6H, PCH₂), 1.24 (t, J 7.1, 3H, Me), 1.23 (t, J 7.1, 3H, Me), 1.21 (t, J 7.1, 3H, Me), 1.19 (t, J 7.1, 3H, Me), 1.07 (dt, J 14.9, 7.5, 9H, Me); ³¹P{¹H} NMR (CDCl₃): δ 20.2 (s); mass spectrum (FAB): m/z 544 (M⁺), 516 (M⁺) – CO; Anal. Calc. for $RuPS_4ON_2C_{17}H_{35}$: C, 37.44; H, 6.49; N, 5.15. Found: C, 39.20; H, 6.27; N, 5.58%.

3.3. Reaction of trans-[RuCl₂(PEt₃)₂(CO)₂] and KS₂COEt

Trans-$[RuCl_2(PEt_3)_2(CO)_2]$ (0.1038 g, 0.224 mmol) and KS_2COEt (0.2152 g, 1.34 mmol) were dissolved in ethanol (50 cm³) and heated under reflux for 6 h. The solvent was removed by rotary evaporation resulting in a yellow solid which was dissolved in dichloromethane (20 cm³) and filtered. The solvent was removed from the filtrate to give a yellow solid. Purification by TLC on silica using light petroleum spirit and dichloromethane (5:1 by volume) gave three bands. The first green band band could not be

characterized. The second and third bands were yellow and shown to be *cis*-[Ru(CO)(PEt$_3$)(S$_2$COEt)$_2$] (**3**) (0.0055 g, 5%) and *trans*-[Ru(CO)(PEt$_3$)$_2$(η^1-S$_2$COEt)(η^2-S$_2$COEt)] (**2**) (0.0272 g, 20%), respectively. (**2**) IR ν(CO) (CH$_2$Cl$_2$): 1947s cm^{-1}; ^{1}H NMR (CDCl$_3$): δ 4.61 (q, *J* 7.1, 2H, OCH$_2$), 4.48 (q, 2H, *J* 7.1, OCH$_2$), 1.81 (m, 12H, PCH$_2$), 1.40 (t, *J* 7.1, 3H, Me), 1.37 (t, *J* 7.1, 3H, Me), 1.05 (tt, *J* 12.4, 7.4, 18H, Me); ^{31}P{^{1}H} NMR (CDCl$_3$): δ 21.9 (s); mass spectrum (FAB): *m/z* 608 (M$^+$), 580 (M$^+$ − CO). (**3**) IR ν(CO) (CH$_2$Cl$_2$): 1948s cm^{-1}; ^{1}H NMR (CDCl$_3$): δ 4.55 (q, *J* 7.1, 2H, OCH$_2$), 4.52 (q, *J* 7.1, 2H, OCH$_2$), 1.80 (m, 6H, PCH$_2$), 1.41 (t, *J* 7.1, 3H, Me), 1.40 (t, *J* 7.1, 3H, Me), 1.05 (dt, *J* 15.3, 7.5, 9H, Me); ^{31}P{^{1}H} NMR (CDCl$_3$): δ 0.1 (s); mass spectrum (FAB): *m/z* 490 (M$^+$), 462 (M$^+$ − CO); Anal. Calc. for RuP$_2$S$_4$O$_3$C$_{19}$H$_{40}$: C, 37.55; H, 6.63. Found: C, 37.35; H, 6.40%.

3.4. Reaction of trans-[RuCl$_2$(PEt$_3$)$_2$(CO)$_2$] and NH$_4$S$_2$P(OEt)$_2$

Trans-[RuCl$_2$(PEt$_3$)$_2$(CO)$_2$] (0.1092 g, 0.216 mmol) and NH$_4$S$_2$P(OEt)$_2$ (0.2304 g, 1.29 mmol) were dissolved in ethanol (50 cm^3) and heated under reflux for 3 h. The solvent was removed by rotary evaporation resulting in a yellow solid. This was dissolved in dichloromethane (20 cm^3), filtered and the solvent removed to give a yellow solid. Purification by TLC on silica using light petroleum and dichloromethane (5:2 by volume) gave two yellow bands. Both products were crystallized upon slow diffusion of heptane in to concentrated dichloromethane solutions to afford yellow crystals which were characterized as *trans*-[RuCl(CO)(PEt$_3$)$_2${S$_2$P(OEt)$_2$}] (**4**) (0.0468 g, 34%) and *cis*-[Ru(CO)(PEt$_3$){S$_2$P(OEt)$_2$}$_2$] (**5**) (0.0145 g, 10%), respectively. (**4**) IR ν(CO) (CH$_2$Cl$_2$): 1937s cm^{-1}; ^{1}H NMR (CDCl$_3$): δ 4.05 (dq, *J* 16.0, 8.0, 4H, OCH$_2$), 2.06 (m, 6H, PCH$_2$), 1.96 (m, 6H, PCH$_2$), 1.36 (t, J 8.0, 12H, Me), 1.61 (tt, *J* 12.0, 8.0, 18H, Me); ^{31}P{^{1}H} NMR (CDCl$_3$): δ 99.9 (s, 1P, S$_2$P), 15.2 (s, 1P, PEt$_3$); mass spectrum (FAB): *m/z* 586 (M$^+$), 550 (M$^+$ − Cl); Anal. Calc. for RuClP$_3$S$_2$O$_3$C$_{17}$H$_{40}$: C, 34.84; H, 6.88. Found: C, 32.86; H, 6.37%. (**5**) IR ν (CO) (CH$_2$Cl$_2$): 1943s cm^{-1}; ^{1}H NMR (CDCl$_3$): δ 4.26–4.07 (m, 8H, OCH$_2$), 1.89 (m, 6H, PCH$_2$), 1.36 (t, *J* 7.1, 3H, Me), 1.31 (t, *J* 7.1, 3H, Me), 1.30 (t, *J* 7.1, 3H, Me), 1.29 (t, *J* 7.1, 3H, Me), 1.06 (dt, *J* 15.4, 7.5, 9H, Me); ^{31}P{^{1}H} NMR (CDCl$_3$): δ 89.9 (d, 1P, *J* 10.7, S$_2$P), 84.0 (s, 1P, S$_2$P), 23.9 (d, 1P, *J* 10.7, PEt$_3$); mass spectrum (FAB): *m/z* 618 (M$^+$), 590 (M$^+$ − CO); Anal. Calc. for RuP$_3$S$_4$O$_5$C$_{15}$H$_{35}$: C, 29.17; H, 5.71. Found: C, 29.08; H, 5.73%.

3.5. Reaction of trans-[RuCl$_2$(PEt$_3$)$_2$(CO)$_2$] and NaS$_2$PPh$_2$

Trans-[RuCl$_2$(PEt$_3$)$_2$(CO)$_2$] (0.0841 g, 0.174 mmol) and NaS$_2$PPh$_2$ (0.0680 g, 0.349 mmol) were dissolved in ethanol (30 cm^3) and heated under reflux for 3 h. The solvent was removed by rotary evaporation resulting in an orange so-

lid. This was dissolved in dichloromethane (20 cm^3), filtered and removal of volatiles gave a dark yellow solid. Purification by TLC on silica using light petroleum and dichloromethane (5:2 by volume) gave two bands. The first was orange and was characterized as *trans*-[RuCl(CO)(PEt$_3$)$_2$(S$_2$PPh$_2$)] (**6**) (0.0577 g, 49%). The second band was yellow and shown to be *cis*-[Ru(CO)(PEt$_3$)(S$_2$PPh$_2$)$_2$] (**7**) (0.0162 g, 12%). Both products were crystallized upon slow diffusion of heptane in to concentrated dichloromethane solutions to afford yellow crystals. (**6**) IR ν(CO) (CH$_2$Cl$_2$): 1940s cm^{-1}; ^{1}H NMR (CDCl$_3$): δ 7.81–7.39 (m, 10H, Ph), 1.88 (m, 6H, PCH$_2$), 1.77 (m, 6H, PCH$_2$), 1.07 (tt, *J* 11.6, 7.4, 18H, Me); ^{31}P{^{1}H} NMR (CDCl$_3$): δ 69.2 (s, 1P, S$_2$P), −1.99 (s, 1P, PEt$_3$); mass spectrum (FAB): *m/z* 650 (M$^+$), 614 (M$^+$ − Cl); Anal. Calc. for RuClP$_3$S$_2$OC$_{25}$H$_{40}$: C, 46.18; H, 6.20. Found: C, 45.78; H, 5.99%. (**7**) IR *nu*(CO) (CH$_2$Cl$_2$): 1934s cm^{-1}; ^{1}H NMR (CDCl$_3$): δ 7.83–7.39 (m, 20H, Ph), 1.82 (m, 6H, PCH$_2$), 1.05 (dt, J 15.1, 7.5, 9H, Me); ^{31}P{^{1}H} NMR (CDCl$_3$): δ 74.6 (d, 1P, J 21.4, S$_2$P), 69.0 (s, 1P, S$_2$P), 24.0 (d, 1P, J 21.4, PEt$_3$); mass spectrum (FAB): *m/z* 746 (M$^+$), 718 (M$^+$ − CO); Anal. Calc. for RuP$_3$S$_4$OC$_{31}$H$_{35}$: C, 49.92; H, 4.73. Found: C, 49.94; H, 4.59%.

3.6. Thermolysis of 1a and Ru$_3$(CO)$_{12}$

1a (0.0450 g, 0.092 mmol) and Ru$_3$(CO)$_{12}$ (0.0590 g, 0.092 mmol) were dissolved in xylene (20 cm^3) and heated under reflux for 2 h. The solvent was removed under reduced pressure resulting in a dark orange solid. Purification by TLC on silica using light petroleum and dichloromethane (2:1 by volume) gave three bands. The first and third bands were orange and could not be characterized due to low yields. The second yellow band was crystallized from a dichloromethane–heptane solution to give yellow crystals of [Ru$_3$(μ_3-S)$_2$(PEt$_3$)(CO)$_8$] (**8**) (0.0065 g, 10%). IR ν(CO) (C$_6$H$_{12}$): 2079m, 2045vs, 2024m, 2007m, 1984w, 1972w cm^{-1}; ^{1}H NMR (CDCl$_3$): δ 2.16 (m, 6H, PCH$_2$), 1.22 (dt, *J* 17.9, 7.5, 9H, Me); ^{31}P{^{1}H} NMR (CDCl$_3$): δ 41.3 (s); mass spectrum (FAB): *m/z* 710 (M$^+$), 682 (M$^+$ − CO), 654 (M$^+$ − 2CO), 626 (M$^+$ − 3CO), 598 (M$^+$ − 4CO), 570 (M$^+$ − 5CO), 542 (M$^+$ − 5CO), 514 (M$^+$ − 6CO), 486 (M$^+$ − 7CO), 458 (M$^+$ − 8CO).

3.7. X-ray data collection and solution

Single crystals were mounted on glass fibres and all geometric and intensity data were taken from these samples using a Bruker SMART APEX CCD diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 150 ± 2 K. Data reduction was carried out with SAINT PLUS and absorption correction applied using the programme SADABS. Structures were solved by direct methods and developed using alternating alternating cycles of least-squares refinement and difference-Fourier synthesis. All non-hydrogen atoms were refined anisotropically. Hydrogens were generally placed in calculated positions

(riding model). Structure solution used SHELXTL PLUS v6.10 program package.

3.8. Crystallographic data for cis-[Ru(CO)(PEt₃)-(S₂CNMe₂)₂] (1a)

Yellow block, dimensions $0.10 \times 0.08 \times 0.08$ mm, monoclinic, space group $C2/c$, $a = 33.510(3)$, $b = 8.0715(8)$, $c = 14.8752(14)$ Å, $\beta = 93.047(2)°$, $V = 4017.7(7)$ Å³, $Z = 8$, $F(000)$ 2000, $d_{calc} = 1.612$ g cm⁻³, $\mu = 1.278$ mm⁻¹. 16 870 reflections were collected, 4775 unique [$R_{int} = 0.0370$] of which 4223 were observed [$I > 2.0\sigma(I)$]. At convergence, $R_1 = 0.0435$, $wR_2 = 0.1000$ [$I > 2.0\sigma(I)$] and $R_1 = 0.0508$, $wR_2 = 0.1035$ (all data), for 199 parameters. Crystallographic data has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 278446.

3.9. Crystallographic data for trans-[Ru(CO)(PEt₃)₂-(η¹-S₂COEt)(η²-S₂COEt)] (2)

Yellow block, dimensions $0.24 \times 0.24 \times 0.20$ mm, monoclinic, space group $P2_1/n$, $a = 9.8365(5)$, $b = 18.4937(9)$, $c = 15.4517(7)$ Å, $\beta = 97.4950(10)°$, $V = 2786.9(2)$ Å³, $Z = 4$, $F(000)$ 1264, $d_{calc} = 1.449$ g cm⁻³, $\mu = 0.995$ mm⁻¹. 7518 reflections were collected, 2689 unique [$R_{int} = 0.0356$] of which 2399 were observed [$I > 2.0\sigma(I)$]. At convergence, $R_1 = 0.0380$, $wR_2 = 0.0924$ [$I > 2.0\sigma(I)$] and $R_1 = 0.0411$, $wR_2 = 0.0941$ (all data), for 262 parameters. Crystallographic data has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 278447.

3.10. Crystallographic data for trans-[RuCl(CO)(PEt₃)₂-{S₂P(OEt)₂}] (4)

Yellow block, dimensions $0.14 \times 0.14 \times 0.12$ mm, triclinic, space group $P\bar{1}$, $a = 11.451(3)$ Å, $b = 11.717(3)$ Å, $c = 20.143(6)$ Å, $\alpha = 82.880(5)°$, $\beta = 89.830(5)°$, $\gamma = 89.885(5)°$, $V = 2681.6(14)$ Å³, $Z = 2$, $F(000)$ 1216, $d_{calc} = 1.452$ g cm⁻³, $\mu = 1.034$ mm⁻¹. 23 732 reflections were collected, 12 343 unique [$R_{int} = 0.0183$] of which 11 302 were observed [$I > 2.0\sigma(I)$]. At convergence, $R_1 = 0.0344$, $wR_2 = 0.0778$ [$I > 2.0\sigma(I)$] and $R_1 = 0.0389$, $wR_2 = 0.0799$ (all data), for 491 parameters. Crystallographic data has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 278448.

3.11. Crystallographic data for cis-[Ru(CO)(PEt₃)-{S₂P(OEt)₂}₂] (5)

Yellow block, dimensions $0.13 \times 0.12 \times 0.10$ mm, monoclinic, space group $P2_1/c$, $a = 9.4611(8)$ Å, $b = 15.0380(12)$ Å, $c = 18.7286(15)$ Å, $\beta = 97.5590(10)°$, $V = 2641.5(4)$ Å³,

$Z = 4$, $F(000)$ 1272, $d_{calc} = 1.553$ g cm⁻³, $\mu = 1.114$ mm⁻¹. 22 856 reflections were collected, 6272 unique [$R_{int} = 0.0180$] of which 5859 were observed [$I > 2.0\sigma(I)$]. At convergence, $R_1 = 0.0327$, $wR_2 = 0.0798$ [$I > 2.0\sigma(I)$] and $R_1 = 0.0350$, $wR_2 = 0.0813$ (all data), for 253 parameters. Crystallographic data has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 278449.

3.12. Crystallographic data for [Ru₃(μ₃-S)₂(PEt₃)(CO)₈] (8)

Yellow block, dimensions $0.08 \times 0.06 \times 0.05$ mm, monoclinic, space group $P2_1/n$, $a = 9.4328(5)$ Å, $b = 20.4730(12)$ Å, $c = 11.4807(7)$ Å, $\beta = 98.8390(10)°$, $V = 2190.8(2)$ Å³, $Z = 4$, $F(000)$ 1368, $d_{calc} = 2.151$ g cm⁻³, $\mu = 2.341$ mm⁻¹. 19 245 reflections were collected, 5259 unique [$R_{int} = 0.0286$] of which 4655 were observed [$I > 2.0\sigma(I)$]. At convergence, $R_1 = 0.0266$, $wR_2 = 0.0538$ [$I > 2.0\sigma(I)$] and $R_1 = 0.0328$, $wR_2 = 0.0557$ (all data), for 253 parameters. Crystallographic data has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 278450.

Acknowledgement

References

[1] G. Hogarth, Prog. Inorg. Chem. 53 (2005) 71.
[2] (a) L. Ricard, J. Estienne, R. Weiss, Inorg. Chem. 12 (1973) 2182;
(b) L. Ricard, J. Estienne, R. Weiss, J. Chem. Soc., Chem. Commun. (1972) 906.
[3] A.J. Deeming, R. Vaish, J. Organomet. Chem. 460 (1993) C8.
[4] A.J. Deeming, C.S. Forth and G. Hogarth, Can. J. Chem. (unpublished results).
[5] K.-B. Shiu, S.-J. Yu, Y. Wang, G.-H. Lee, J. Organomet. Chem. 650 (2002) 37.
[6] P.B. Critchlow, S.D. Robinson, Inorg. Chem. 17 (1978) 1902.
[7] D.J. Cole-Hamilton, T.A. Stephenson, J Chem. Soc., Dalton Trans. (1974) 739.
[8] (a) J. Chatt, B.L. Shaw, A.E. Field, J. Chem. Soc., Sect. A (1968) 40;
(b) Y. Sun, N.J. Taylor, A.J. Carty, Inorg. Chem. 32 (1993) 4457;
(c) Y. Sun, N.J. Taylor, A.J. Carty, Organometallics 11 (1992) 4293;
(d) Y. Sun, N.J. Taylor, A.J. Carty, J. Organomet. Chem. 423 (1992) C43;
(e) A.J. Deeming, G. Hogarth, M.-Y. Lee, M. Saha, S.P. Redmond, H. Phetmung, A.G. Orpen, Inorg. Chim. Acta 309 (2000) 109.
[9] C.S. Forth, Ph.D. thesis, University of London, 2003.
[10] G. Hogarth, N.J. Taylor, A.J. Carty, A. Meyer, J. Chem. Soc., Chem. Commun. (1988) 834.
[11] (a) R.D. Adams, J.E. Babin, M. Tasi, Inorg. Chem. 25 (1986) 4514;
(b) R.D. Adams, J.E. Babin, M. Tasi, Inorg. Chem. 26 (1987) 2807;
(c) R.D. Adams, J.E. Babin, J. Tanner, Organometallics 7 (1988) 2027.