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Ruthenium(II) dihalogeno-complexes with $(C_6H_5)_2P(CH_2)_2SR$ ligands ($R = CH_3$, C_2H_5, and *cyclo*-C_6H_{11}) and their reactions with carbon monoxide and acetonitrile. The crystal structure of *trans,cis,cis* [1]-$[RuCl_2\{(C_6H_5)_2P(CH_2)_2S(\textit{cyclo}\text{-}C_6H_{11})\text{-}P,S\}_2]$

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Abstract

The reaction between *cis*-$[RuCl_2(dmso)_4]$ (dmso = dimethylsulfoxide) and the phosphine-thioether ligands $Ph_2P(CH_2)_2SR$ (PSR, R = Me PSMe, R = Et PSEt, or R = *cyclo*-C_6H_{11} PSCy) affords the ruthenium(II) six-coordinate derivatives $[RuCl_2(PSR\text{-}P,S)_2]$. All complexes have been characterised by means of UV–Vis, IR and ^1H, ^{13}C and ^{31}P NMR spectroscopy. Three of the five possible isomers (*cis,cis,cis*, *cis,cis,trans* and *trans,cis,cis*) of the octahedral complexes have been obtained. The crystal structure of *trans,cis,cis*-$[RuCl_2(PSCy\text{-}P,S)_2]$ has been determined by single-crystal X-ray diffraction analysis. Also *cis,cis,trans*-$[RuI_2(PSR\text{-}P,S)_2]$ derivatives have been prepared from the corresponding dichloro-compounds by halide metathesis. The reaction of $[RuCl_2(PSR\text{-}P,S)_2]$ with carbon monoxide gives cationic $[RuCl(CO)(PSR\text{-}P,S)_2]^+$ or neutral $[RuCl_2(CO)(PSCy\text{-}P)(PSCy\text{-}P,S)]$ derivatives via Ru–Cl or Ru–S bond cleavage, respectively. In the case of the diiodo-derivatives the corresponding monocarbonyls $[RuI(CO)(PSR\text{-}P,S)_2]^+$ are obtained. The reaction of *cis,cis,cis*- and *cis,cis,trans*-$[RuCl_2(PSMe\text{-}P,S)_2]$ isomers with acetonitrile has also been investigated, and both *cis,cis*- and *cis,trans*-$[Ru(MeCN)_2(PSMe\text{-}P,S)_2]^{2+}$ have been obtained. Both diacetonitrile compounds slowly react with CO yielding the corresponding $[Ru(CO)(MeCN)(PSMe\text{-}P,S)_2]^{2+}$ derivatives with retention of configuration.

Properties, structural features, and reactivity of $[RuX_2(PSR\text{-}P,S)_2]$ compounds are compared with that of the ruthenium(II) analogues with phosphine-ether ligands.

Keywords: Ruthenium(II) complexes; Bidentate P,S ligands complexes; Carbonyl complexes; Acetonitrile complexes; Crystal structures

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1. Introduction

Ruthenium(II) complexes with tertiary and ditertiary phosphines have been extensively studied in particular with respect to their application in homogeneous catalysis [1]. In the last few years there has been also growing interest in ruthenium(II) species with unsymmetrical bidentate ligands containing P and a second weaker donor function such as N [2] or O [2c,3].

The combination of strong and weak donor atoms in the ligand leads to very interesting structural features and reactivity patterns of their transition-metal complexes. The major work has been done with P,O-donor ligands containing different oxygen donor functions such as ethers [2c,3c–j,4], esters [3c,5], carboxylic acids [6] aldehydes [7], ketones and enolates [3b,k]. In the ruthenium(II) complexes the P,O-donor molecule can act either as bidentate or P-bound monodentate ligand. Moreover, when both donor atoms are coordinated to the metal centre, the oxygen arm of the ligand can easily dissociate leaving an empty coordination site at the ruthenium centre. This can be suitable for substrate binding, thus allowing the complex to act as an effective catalyst. A similar behaviour has been reported also for ruthenium(II) complexes with P,N-donor ligands [2].

In contrast, the coordination chemistry of ruthenium(II) with bidentate ligands containing phosphorus and sulfur donor atoms has received much less attention, though the chemistry of these species is as potentially interesting as that of the P,O-derivatives and its investigation may lead to the discovery of novel catalysts. Among the P,S-donor ligands,

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[1] Throughout this paper the *cis* and *trans* notation refers to the pairs of X, P or S atoms.

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the thioether-phosphines appear the most promising, as it is well known that they behave either as P-bound mono- or bidentate ligands, depending upon the transition metal and its environment [8].

Therefore, we decided to study the complexation between ruthenium(II) and thioether-phosphines of the type $Ph_2P(CH_2)_2SR$ (PSR; R = Me PSMe, R = Et PSEt, R = *cyclo*-C_6H_{11} PSCy), in which the alkyl group R possess different electronic and steric properties. Indeed, Sanger [9] has investigated the chemistry of ruthenium(II) with the analogous ligand $Ph_2P(CH_2)_2SPh$ (PSPh), reporting the synthesis of the pink product $[RuCl_2(PSPh)_2]_x$, but its very low solubility in common solvents precluded any investigation. The carbonyl derivatives $[RuCl_2(CO)_3(PSPh\text{-}P)]$ and $[RuCl_2(CO)_2(PSPh\text{-}P)_2]$, in which the PSPh ligand acts as P-bound monodentate, and $[RuCl_2(CO)(PSPh\text{-}P)(PSPh\text{-}P,S)]$, where both chelated and P-bound monodentate PSPh molecules are present, were also described.

In contrast, we succeeded in preparing the soluble six-coordinate complexes $[RuX_2(PSR\text{-}P,S)_2]$ with all the PSR ligands employed. Three different geometries have been observed for these species, which have been probed with the help of UV–Vis, IR and NMR spectroscopy. The structure of the complex *trans,cis,cis*-$[RuCl_2(PSCy\text{-}P,S)_2]$ in the solid state has been determined by single-crystal X-ray crystallography.

Since the corresponding P,O-donor ligands $Ph_2P(CH_2)_2OR$ (POR) give similar $[RuCl_2(POR\text{-}P,O)_2]$ species [2c,3c–e,g,4], we were interested to establish whether the substitution of the ether with a thioether function in the hybrid ligand would affect stereochemistry, properties and chemical behaviour of the ruthenium(II) derivative. The coordination chemistry of the ruthenium(II)–PSR derivatives can be compared also with that of complexes formed with $RS(CH_2)_2SR$ ligands previously reported by Chatt and coworkers [10].

The reactivity of the octahedral complexes $[RuX_2(PSR\text{-}P,S)_2]$ towards carbon monoxide was investigated and, depending on the nature of both X and R, the formation of either neutral $[RuX_2(CO)(PSR\text{-}P)(PSR\text{-}P,S)]$ or cationic $[RuX(CO)(PSR\text{-}P,S)_2]^+$ derivatives, via rupture of the Ru–S or Ru–X bond, respectively, has been observed. The cleavage of both Ru–X bonds in $[RuX_2(PSR\text{-}P,S)_2]$ complexes was also achieved by reaction with acetonitrile, in the presence of Ag^+ ion as halide scavenger. Two isomeric forms of the diacetonitrile complex $[Ru(MeCN)_2(PSMe\text{-}P,S)_2]^{2+}$ have been prepared and characterised, and also their reactions with carbon monoxide have been investigated.

2. Experimental

2.1. General procedures

Solvents were purified by standard methods and stored over molecular sieves under argon atmosphere. All chemicals used were of reagent grade or comparable purity. The starting complex *cis*-$[RuCl_2(dmso)_4]$ was prepared as previously described [11]. The ligands PSMe and PSEt were synthesised according to a published method [8a]. Infrared and UV–Vis spectra (Nujol mulls on CsI plates) were recorded on Nicolet Magna FT 550 and Cary 2300 spectrophotometers, respectively. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker AC 200 F QNP spectrometer equipped with a variable temperature probe, temperatures were calibrated with methanol. Positive ^{31}P chemical shifts are downfield from 85% H_3PO_4 external standard; ^1H and ^{13}C chemical shifts are referenced to $SiMe_4$. The ^{13}C spectral simulation for complex **10a** was performed with the program PANIC [12]. Conductance data, obtained at 293 K in 10^{-3} M nitromethane solutions of the complexes, were measured with a Metrohm E 518 conductivity bridge. Elemental analyses were performed by the Microanalytical Laboratory of our Department.

2.2. Preparation of compounds

All manipulations were performed under argon with rigorous exclusion of atmospheric oxygen and moisture.

2.2.1. $Ph_2P(CH_2)_2S$(*cyclo*-C_6H_{11})

Freshly distilled Ph_2PCl (22.06 g, 0.1 mol) and Li (1.39 g, 0.2 mol) in THF (150 ml) were refluxed for 8 h. After the mixture had been cooled to 0°C, $Cl(CH_2)_2S$(*cyclo*-C_6H_{11}) (17.87 g, 0.1 mol) in THF (50 ml) was added dropwise. The reaction mixture was stirred for 4 h at 0°C, allowed to warm to room temperature, and left to stir for 2 h. After evaporation of the THF, deoxygenated water (100 ml) was added and the organic material extracted with dichloromethane (3 × 50 ml). The organic layer was separated and dried on Na_2SO_4. After evaporation in vacuo of the dichloromethane, the residual yellow viscous oil was distilled under reduced pressure (b.p. 188–90°C at 0.5 hPa) to give $Ph_2P(CH_2)_2S$(*cyclo*-C_6H_{11}) as a colourless oil. Yield: 17.78 g, 54%. $^{31}P\{^1H\}$NMR (CD_2Cl_2): δ − 16.2. *m/z*: 328 (M^+, 0.13%), 246 (13), 245 (100), 186 (31), 183 (37), 108 (43).

2.2.2. *Cis,cis,cis*-$[RuCl_2(PSMe\text{-}P,S)_2]$ (**1a**)

Cis-$[RuCl_2(dmso)_4]$ (0.485 g, 1 mmol) and PSMe (0.547 g, 2.1 mmol) were suspended in 20 ml of toluene and the slurry was refluxed for 2 h. Upon cooling to 0°C the solution deposited yellow *crystals* which were filtered off, washed with diethyl ether and vacuum dried. Yield: 0.534 g, 77%. *Anal.* Calc. for $C_{30}H_{34}P_2S_2Cl_2Ru$: C, 52.00; H, 4.95. Found: C, 51.30; H, 4.95%.

2.2.3. *Cis,cis,trans*-$[RuCl_2(PSMe\text{-}P,S)_2]$ (**2a**)

Complex **1a** (0.346 g, 0.5 mmol) was stirred in a dichloromethane (10 ml) propan-2-ol (10 ml) mixture for 1 h. Evaporation of the dichloromethane gave a yellow product, which was filtered off, washed with diethyl ether and dried in vacuo. Yield: 0.315 g, 91%. *Anal.* Calc. for $C_{30}H_{34}P_2S_2Cl_2Ru$: C, 52.00; H, 4.95. Found: C, 52.10; H, 4.90%.

2.2.4. *Cis,cis,trans-[RuCl$_2$(PSEt-P,S)$_2$]* (**2b**)

Cis-[RuCl$_2$(dmso)$_4$] (0.485 g, 1 mmol) and PSEt (0.576 g, 2.1 mmol) were suspended in toluene (20 ml) and the suspension was refluxed for 2 h. The yellow product obtained on cooling to room temperature was recrystallised from dichloromethane–propan-2-ol. Yield: 0.564 g, 78%. *Anal.* Calc. for $C_{32}H_{38}P_2S_2Cl_2Ru$: C, 53.35; H, 5.30. Found: C, 53.10; H, 5.25%.

2.2.5. *Cis,cis,trans-[RuI$_2$(PSMe-P,S)$_2$]* (**2Ia**)

Complex **2a** (0.346 g, 0.5 mmol) was refluxed in acetone (20 ml) with NaI (1.50 g, 10 mmol) for 5 days. Upon cooling to room temperature from the solution yellow *crystals* precipitated which were filtered off and dried in vacuum. Recrystallisation from dichloromethane–propan-2-ol. Yield: 0.403 g, 96%. *Anal.* Calc. for $C_{30}H_{34}P_2S_2I_2Ru$: C, 41.15; H, 3.90. Found: C, 41.35; H, 3.80%.

2.2.6. *Cis,cis,trans-[RuI$_2$(PSEt-P,S)$_2$]* (**2Ib**)

This yellow complex was prepared from **2b** using the method developed for **2Ia**. Yield: 0.427 g, 94%. *Anal.* Calc. for $C_{32}H_{38}P_2S_2I_2Ru$: C, 42.55; H, 4.25. Found: C, 42.50; H, 4.20%.

2.2.7. *Cis,cis,trans-[RuI$_2$(PSCy-P,S)$_2$]* (**2Ic**)

This yellow complex was prepared from **3c** using the method developed for **2Ia**. Yield: 0.469 g, 93%. *Anal.* Calc. for $C_{40}H_{50}P_2S_2I_2Ru$: C, 47.50; H, 5.00. Found: C, 46.95; H, 4.80%.

2.2.8. *Trans,cis,cis-[RuCl$_2$(PSCy-P,S)$_2$]* (**3c**)

Cis-[RuCl$_2$(dmso)$_4$] (0.485 g, 1 mmol) and PSCy (0.690 g, 2.1 mmol) were suspended in 20 ml of toluene and the slurry was refluxed for 2 h. Upon cooling to 0°C, addition of *n*-hexane (20 ml) gave an orange product, which was filtered off, washed with diethyl ether and *n*-hexane and dried in vacuo. Recrystallisation from dichloromethane–propan-2-ol. Yield: 0.565 g, 68%. *Anal.* Calc. for $C_{40}H_{50}P_2S_2Cl_2Ru$: C, 57.95; H, 6.10. Found: C, 57.25; H, 6.05%.

2.2.9. *Cis,cis-[RuCl(CO)(PSMe-P,S)$_2$]PF$_6$* (**4a**)

Complex **1a** (0.346 g, 0.5 mmol) was stirred in dichloromethane (20 ml) under CO atmosphere for 2 days. NH_4PF_6 (0.326 g, 2 mmol) in ethanol (20 ml) was then added, and the dichloromethane pumped off until a pale yellow product formed, which was filtered off and dried in vacuo. Recrystallisation from dichloromethane–propan-2-ol. Yield: 0.345 g, 83%. Λ_M (10^{-3} M, CH_3NO_2) = 82 Ω^{-1} cm^2 mol^{-1}. *Anal.* Calc. for $C_{31}H_{34}OF_6P_3S_2ClRu$: C, 44.85 H, 4.15. Found: C, 44.35; H, 4.10%.

2.2.10. *Cis,trans-[RuCl(CO)(PSR-P,S)$_2$]PF$_6$ (R=Me (**5a**) or Et (**5b**))*

These pale yellow complexes were prepared from **2a** and **2b**, respectively, by the method used to prepare **4a**. Yield: 0.358 g, 86% (**5a**); 0.374 g, 87% (**5b**). Λ_M (10^{-3} M, CH_3NO_2, Ω^{-1} cm^2 mol^{-1}): 84 (**5a**), 81 (**5b**). *Anal.* Calc. for $C_{31}H_{34}OF_6P_3S_2ClRu$ (**5a**): C, 44.85; H, 4.15. Found: C, 44.55; H, 4.35%. Calc. for $C_{33}H_{38}OF_6P_3S_2ClRu$ (**5b**): C, 46.20; H, 4.45. Found: C, 45.85; H, 4.55%.

2.2.11. *Cis,trans-[RuI(CO)(PSR-P,S)$_2$]PF$_6$ (R=Me (**5Ia**), Et (**5Ib**), Cy (**5Ic**))*

Complex *cis,cis,trans*-[RuI$_2$(PSR-*P,S*)$_2$] (R=Me **2Ia**, Et **2Ib** or Cy **2Ic**) (0.5 mmol) was stirred in dichloromethane under a CO atmosphere. After 30 min, NH_4PF_6 (0.326 g, 2 mmol) in ethanol (20 ml) was added to the resulting solution and the dichloromethane pumped off. The yellow precipitate formed was filtered off and dried in vacuo. Recrystallisation from dichloromethane–propan-2-ol. Yield: 0.360 g, 78% (**5Ia**); 0.375 g, 79% (**5Ib**); 0.392 g, 75% (**5Ic**). Λ_M (10^{-3} M, CH_3NO_2, Ω^{-1} cm^2 mol^{-1}): 79 (**5Ia**), 81 (**5Ib**), 78 (**5Ic**). *Anal.* Calc. for $C_{31}H_{34}OF_6P_3S_2IRu$ (**5Ia**): C, 40.40; H, 3.70. Found: C, 40.25; H, 3.90%. Calc. for $C_{33}H_{38}OF_6P_3S_2IRu$ (**5Ib**): C, 41.75; H, 4.05. Found: C, 41.60; H, 4.15%. Calc. for $C_{41}H_{50}OF_6P_3S_2IRu$ (**5Ic**): C, 46.55; H, 4.75. Found: C, 46.95; H, 4.85%.

2.2.12. *Trans,trans-[RuCl(CO)(PSCy-P,S)(PSCy-P)]* (**6c**)

Complex **3c** (0.166 g, 0.2 mmol) was suspended in toluene (10 ml) and stirred under CO atmosphere for 6 h at 60°C. After cooling to room temperature, the yellow product was precipitated by addition of *n*-hexane (30 ml), filtered off, washed with *n*-hexane, and dried in vacuo. Yield: 0.144 g, 84%. *Anal.* Calc. for $C_{41}H_{50}OP_2S_2ClRu$: C, 57.45; H, 5.90. Found: C, 57.75; H, 6.05%.

2.2.13. *Cis,cis-[Ru(MeCN)$_2$(PSMe-P,S)$_2$](PF$_6$)$_2$* (**9a**)

A mixture of **1a** (0.346 g, 0.5 mmol) and $AgPF_6$ (0.303 g, 1.2 mmol) was stirred in acetonitrile (20 ml) for 1 h. The suspension was filtered on Celite to remove any solid. The cream-white complex **9a** precipitated after concentration of the solution to ca. 5 ml and subsequent addition of diethyl ether (30 ml). Yield: 0.421 g, 85%. Λ_M (10^{-3} M, CH_3NO_2) = 167 Ω^{-1} cm^2 mol^{-1}. *Anal.* Calc. for $C_{34}H_{40}N_2F_{12}P_4S_2Ru$: C, 41.10; H, 4.05; N, 2.80. Found: C, 41.20; H, 4.00; N, 2.90%.

2.2.14. *Cis,trans-[Ru(MeCN)$_2$(PSMe-P,S)$_2$](PF$_6$)$_2$* (**10a**)

This cream-white derivative was obtained from **2a** by the same procedure described above for **9a**. Yield: 88%. Λ_M (10^{-3} M, CH_3NO_2) = 163 Ω^{-1} cm^2 mol^{-1}. *Anal.* Calc. for $C_{34}H_{40}N_2F_{12}P_4S_2Ru$: C, 41.10; H, 4.05; N, 2.80. Found: C, 41.00; H, 4.15; N, 2.75%.

2.2.15. *Cis,cis-[Ru(CO)(MeCN)(PSMe-P,S)$_2$](PF$_6$)$_2$ (11a)*

Complex **9a** (0.199 g, 0.2 mmol) was stirred in acetone (10 ml) for 2 days under a CO atmosphere. The volume of the solution was concentrated to approximately 2 ml and a white solid precipitated from solution by addition of propan-2-ol (10 ml). The white solid was filtered off and dried in vacuo. Yield: 0.165 g, 84%. Λ_M (10^{-3} M, CH_3NO_2) = 171 Ω^{-1} cm^2 mol^{-1}. *Anal.* Calc. for $C_{33}H_{37}NOF_{12}P_4S_2Ru$: C, 40.40; H, 3.80; N, 1.45. Found: C, 40.10; H, 4.00; N, 1.35%.

2.2.16. *Cis,trans-[Ru(CO)(MeCN)(PSMe-P,S)$_2$](PF$_6$)$_2$ (12a)*

Starting with complex **10a**, the white complex **12a** was obtained in analogy to **11a**. Yield: 86%. Λ_M (10^{-3} M, CH_3NO_2) = 168 Ω^{-1} cm^2 mol^{-1}. *Anal.* Calc. for $C_{33}H_{37}NOF_{12}P_4S_2Ru$: C, 40.40; H, 3.80; N, 1.45. Found: C, 39.95; H, 3.90; N, 1.45%.

2.3. *X-ray data collection and structure refinement*

2.3.1. *Crystal data of 3c·0.5propan-2-ol*

$C_{40}H_{50}RuCl_2P_2S_2 \cdot 0.5C3H_7OH$, M = 858.95, monoclinic, space group $P2_1/n$ (alternative setting of No. 14), a = 17.252(3), b = 13.351(2), c = 20.362(3) Å, β = 114.49(6)°, U = 4267(1) Å^3, Z = 4, D_c = 1.34 g cm^{-3}, approximate crystal dimensions 0.30×0.30×0.40 mm, μ(Mo Kα) = 6.8 cm^{-1}, λ = 0.71073 Å, $F(000)$ = 1788.

2.3.2. *Structure determination*

Unit cell parameters were obtained by least squares treatment of 25 reflections in the θ range 12–19°, Enraf–Nonius CAD4 diffractometer, graphite-monochromated. ω–2θ scan method, $2\theta_{max}$ = 56°, Mo Kα radiation. Scan angle (°) 0.70 + 0.35 tan θ, T = 293 K, three standard reflections measured every 4000 s showed no significant variation in intensity. A total of 9936 independent reflections collected, of which 5550 with $I > 3\sigma(I)$, corrected for Lorentz-polarisation effects, used for structure determination. No absorption correction was applied. Secondary extinction coefficient 6.2×10^{-8}.

Structure solved by conventional Patterson and Fourier methods. A molecule of propan-2-ol with an occupancy factor of 0.5 was located on the ΔF map. The contribution of these atoms as well as that of the H atoms was included in final cycles of refinements (C–H bond length 0.95 Å, isotropic $B = 1.3B_{eq}$ of corresponding bonded atoms), excluding those of the propan-2-ol molecule. Anisotropic temperature factors for all non-H atoms of the complex. The final residuals were $R(F_o)$ = 0.047, $Rw(F_o)$ = 0.057 for 441 variables and weighting scheme $w = 1/[\sigma(F)^2 + (0.02F)^2 + 4.0]$ [13].

The cyclohexyl group bound to S(2) presents a considerably thermal motion (see Fig. 2 and Table 6), but no attempt was made to resolve this disorder by splitting the C atoms over two positions. Refinement of the assigned atom positions in the region of the disordered solvent leads to high displacements parameters. There are no observed close contacts in the structure.

The scattering neutral factors were taken into account [14]. Calculations were carried out on a μVAX 2000 computer using the Enraf–Nonius CAD4 system of programs [15].

3. Results and discussion

3.1. *Preparation of [RuX$_2$(PSR-P,S)$_2$] complexes*

The reaction between *cis*-[RuCl$_2$(dmso)$_4$] (dmso = dimethylsulfoxide) and the ligands $Ph_2P(CH_2)_2SR$ (PSR; R = Me, PSMe; R = Et, PSEt; R = *cyclo*-C_6H_{11}, PSCy) in 1:2 molar ratio in refluxing toluene yields non-ionic products which analyse as [RuCl$_2$(PSR)$_2$]. These complexes could have potentially the five different structures which are shown in Fig. 1. The isomeric composition of the crude products isolated in the solid state depends on the nature of the alkyl group R of the PSR ligand. Thus, when R is Me, the yellow complex *cis,cis,cis*-[RuCl$_2$(PSMe-*P,S*)$_2$] **1a** is obtained pure and in near quantitative yields. On the contrary, the reaction between the ruthenium(II) precursor and the ligand PSEt yields a mixture of *cis,cis,cis*-[RuCl$_2$(PSEt-*P,S*)$_2$] **1b** and *cis,cis,trans*-[RuCl$_2$(PSEt-*P,S*)$_2$] **2b** isomers in ca. 2:1 ratio, respectively (from the ^{31}P NMR spectrum recorded on freshly prepared dichloromethane solution of the crude product). Complex **1b** can be readily and quantitatively converted into **2b** by dissolving the mixture of the two isomers in dichloromethane, followed by addition of propan-2-ol to cause precipitation of the product. A pure sample of *cis,cis,trans*-[RuCl$_2$(PSMe-*P,S*)$_2$] **2a** has been obtained from **1a** by adopting the same procedure. In contrast, any attempt to prepare complex **1b** in pure form failed. In the case of the reaction between *cis*-[RuCl$_2$(dmso)$_4$] and PSCy, the crude product is a mixture of three isomers, *cis,cis,cis*-[RuCl$_2$(PSCy-*P,S*)$_2$] **1c** (ca. 15%), *cis,cis,trans*-[RuCl$_2$(PSCy-*P,S*)$_2$] **2c** (ca. 40%), and *trans,cis,cis*-[RuCl$_2$(PSCy-*P,S*)$_2$] **3c** (ca. 45%). A quantitative conversion into **3c** was achieved by recrystallisation of the crude mixture from dichloromethane–

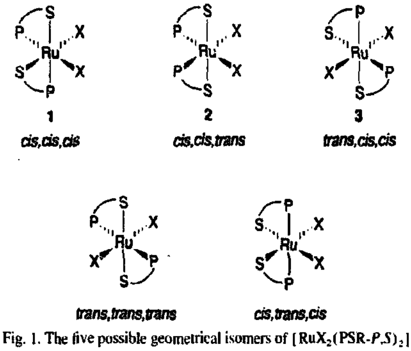


Fig. 1. The five possible geometrical isomers of [RuX$_2$(PSR-*P,S*)$_2$].

Table 1
$^{31}P\{^1H\}$ and selected ^1H NMR data for complexes **1a**–**3c** [a]

Complex	^1H	$^{31}P\{1H\}$	
	$\delta(SCH_3)$	δ	$^2J(P–P')$ (Hz)
1a	2.26(s), 2.65(d) [b]	51.7(d), 56.4(d)	27.8
1b [c]		51.6(d), 55.7(d)	28.0
1c [c]		50.5(d), 53.5(d)	29.5
2a	2.73(s)	53.1(s)	
2b		52.8(s)	
2c [c]		50.1(s)	
2Ia	3.11(s)	48.1(s)	
2Ib		47.0(s)	
2Ic		44.0(s)	
3c		54.8(s)	

[a] In CD_2Cl_2 solution, at 293 K. Multiplicity given in parentheses: s = singlet, d = doublet.
[b] $^4J(^1H–^{31}P) = 3.1$ Hz.
[c] Complex not isolated in the solid state.

propan-2-ol. The rates of isomerisation are rather slow in dichloromethane solution, but they considerably increase if polar solvents such as alcohols are added. This seems to suggest that the isomerisation process proceeds via dissociation of the Ru–Cl bond. Apparently, the thermodynamically stable isomer exhibit the *cis,cis,trans* geometry **2** when R is Me or Et, while if R is the bulky cyclohexyl group, the stable complex shows the *trans,cis,cis* stereochemistry **3** with mutually *trans* Cl atoms.

It should be emphasised that, of the five possible isomers for $[RuX_2(PSR\text{-}P,S)_2]$ compounds (Fig. 1), those with mutually *trans* P atoms have not been observed. Probably because of electronic considerations, strong *trans* directors prefer not to be *trans* each other [16].

Moreover, complexes **2a**,**b** react with an excess of NaI in refluxing acetone yielding the diiodo-derivatives *cis,cis,trans*-$[RuI_2(PSR\text{-}P,S)_2]$ (R = Me **2Ia** or Et **2Ib**) by halogen metathesis. It is noteworthy that, in the same experimental conditions, also **3c** yields the isostructural compound *cis,cis,trans*-$[RuI_2(PSCy\text{-}P,S)_2]$ **2Ic**.

3.2. Stereochemistry of $[RuX_2(PSR\text{-}P,S)_2]$ complexes

The stereochemistry of the dihalogeno-complexes has been inferred from a combination of UV–Vis, IR, and ^1H, ^{13}C, and ^{31}P NMR spectroscopy (Tables 1–3).

Table 2
$^{13}C\{^1H\}$ NMR data (δ) for complexes **1a**–**3c** [a]

	1a	**2a**	**2b**	**3c** [b]	
				293 K	183 K
C_{ipso}	134.0(d) 135.0(d) 135.2(dd) 138.9(dd)	136.9(q) 138.7(q)	136.8(q) 138.8(q)	136.4(br s)	132.5(q) 137.9(q)
C_{ortho}	131.9(d) 132.5(d) 133.4(d) 135.2(d)	129.5(t) 132.0(t)	129.5(t) 132.0(t)	134.4(t)	132.4(t) 133.6(t)
C_{meta}	127.6(d) 127.7(d) 127.9(d) 128.3(d)	127.9(t) 128.6(t)	127.8(t) 128.7(t)	127.5(t)	127.0(br s)
C_{para}	129.4(d) 129.6(d) 129.6(d) 129.8(d)	128.8(s) 129.1(s)	128.8(s) 129.0(s)	129.4(s)	128.8(br s)
PCH_2	25.0(d) 34.6(d)	25.3(q)	25.2(q)	28.8(t)	28.7(br t)
SCH_2	33.4(d) 36.5(d)	35.1(t)	32.3(t)	32.7(t)	31.8(br s)
CH_2 [c]			29.5(s)		
CH_3	15.8(d) [d] 17.9(s)	17.9(s)	14.0(s)		

[a] In CD_2Cl_2 solution at 293 K, unless otherwise stated. Multiplicity given in parentheses, s = singlet, d = doublet, t: non-binomial triplet, dd = doublet of doublets, q = non-binomial quintet, br s = broad singlet, br t = broad triplet.
[b] Signals (singlets) of the *cyclo*-C_6H_{11} carbon atoms: δ 25.5 (C_4), 26.1 ($C_{3,5}$), 32.1 ($C_{2,6}$), and 43.2 (C_1) (293 K); δ 25.1 (C_4), 25.4 ($C_{3,5}$), 30.5 ($C_{2,6}$), and 42.4 (C_1) (183 K).
[c] Methylene carbons of the ethyl groups.
[d] $^3J(^{31}P–^{13}C) = 2.7$ Hz.

Table 3
UV–Vis data for complexes **1a**–**3c**

Complex	Dichloromethane solution λ_{max} (nm) [ε(dm^3 mol^{-1} cm^{-1})]	Nujol mull λ_{max} (nm)
1a	415 (sh), 355 (sh)	420 (sh), 350 (sh)
2a	375 (1340), 330 (sh)	370
2b	375 (1450), 335 (sh)	370
2Ia	405 (1590), 350 (sh)	415 (sh), 350 (sh)
2Ib	400 (1880), 350 (sh)	410 (sh), 355 (sh)
2Ic	405 (1850), 350 (sh)	410 (sh), 360 (sh)
3c	475 (170), 370 (sh)	480, 380 (sh)

3.2.1. *Cis,cis,cis isomers 1*

The all-*cis* geometry of **1a** has been established on the basis of its ${}^{31}P\{{}^1H\}$ NMR spectrum, which shows the two doublets expected for inequivalent phosphorus atoms [${}^2J$(P–P′) = 27.8 Hz]. It is noteworthy that the two P nuclei are chemically and magnetically inequivalent only in structure **1** (Fig. 1). The presence of a SMe group *trans* to a P atom is confirmed by the ${}^1H$ NMR spectrum, which shows a methyl signal (δ 2.65) split by spin–spin coupling with the *trans* P atom [${}^4J({}^{31}P–{}^1H)$ = 3.1 Hz]. The other SMe group, which is in a *cis* arrangement with respect to both P atoms, exhibits a singlet at δ 2.26. The isostructural derivatives **1b**,**c**, which were not isolated pure in the solid state, display ${}^{31}P\{{}^1H\}$ NMR spectra similar to that of **1a**, with ${}^2J$(P–P′) of 28.0 and 29.5 Hz, respectively. The ${}^{13}C\{{}^1H\}$ NMR spectra of **1a** confirms the lack of symmetry elements in the complex. In particular, each phenyl group lies in a different environment and distinct doublets arising from spin–spin coupling with a ${}^{31}P$ nucleus are shown by each of the four C_{para} and by the four pairs of C_{ortho} and C_{meta} carbon atoms. Moreover, the resonances of two of the four inequivalent C_{ipso} carbon atoms appear as doublets, while doublets of doublets are shown by the remaining two C_{ipso} carbon atoms. In addition, four doublets in the region δ 25–37 are assigned to the methylene carbon atoms of two inequivalent PCH_2CH_2S moieties. The whole spectral pattern is consistent with a mutual *cis* arrangement of inequivalent P atoms (Table 2). Finally, a singlet at δ 17.9 and a doublet at δ 15.8 [${}^3J({}^{31}P–{}^{13}C)$ = 2.7 Hz] are assigned to the methyl carbon atoms, the latter being in agreement with the presence of a *trans* P–Ru–SMe framework.

3.2.2. *Cis,cis,trans isomers 2*

The UV–Vis spectra of the yellow complexes **2a**,**b** and of the three iodo-derivatives **2Ia**–**c** are similar to each other, both in solution and in the solid state, with a band in the 375–405 nm region and a shoulder at higher frequency (Table 3). The energies of the maximum are in accord with the spectrochemical series, Cl > I. The ${}^{31}P\{{}^1H\}$ NMR spectra of these species exhibit a sharp singlet in agreement with the presence of equivalent P nuclei. For complexes **2a**,**b** the mutual *cis* arrangement of the P atoms is inferred from their ${}^{13}C\{{}^1H\}$ NMR spectra. Two pairs of equivalent phenyl rings are present in the molecule. In particular, each C_{ipso} carbon resonance appears as a symmetric non-binomial quintet due to coupling with two equivalent mutually *cis* P atoms [2f] (Table 2). The ${}^{13}C$ NMR spectra of complexes **2Ia**–**c** were not obtained as the solubility of these compounds in common solvents is too low. It should be noted that complexes **2a**,**b** are expected to display two IR absorptions in the Ru–Cl stretching region. Unfortunately, several very weak bands are shown in the region below 350 cm^{-1}, thus preventing the *cis* or *trans* geometry of the Cl–Ru–Cl moiety to be established.

3.2.3. *The trans,cis,cis isomer 3c*

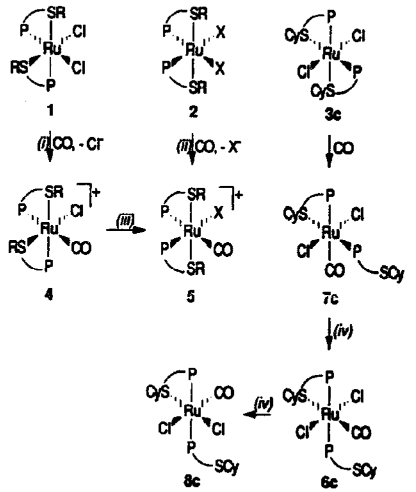
The solid-state structure of the orange complex **3c·0.5propan-2-ol** has been assessed by means of a single-crystal X-ray analysis (see below). Moreover, the UV–Vis spectrum in dichloromethane solution is similar to that shown by the Nujol mull sample (Table 3), thus indicating that **3c** possesses the same structure in solution and in the solid state.

As expected for a *trans,cis,cis* stereochemistry, the room temperature ${}^{31}P\{{}^1H\}$ NMR spectrum of **3c** shows a singlet at δ 54.8, and no appreciably changes are observed on cooling the sample. On the contrary, the ${}^{13}C\{{}^1H\}$ NMR spectra show in the aromatic region a remarkable temperature dependence of the signals, thus suggesting that a dynamic exchange process does occur in solution. At room temperature an average resonance is observed for each type of phenyl carbon atom, which on cooling broadens and then eventually splits into two equivalent signals. At 183 K, the lowest available temperature, the slow exchange limit spectrum is still not achieved (Table 2). Nevertheless, the two *pseudo*-quintets exhibited by the C_{ipso} carbons are in agreement with the presence of equivalent *cis* P atoms as in structure **3** [2]f. On the other hand, the resonances of the carbon atoms of both PCH_2CH_2S and *cyclo*-C_6H_{11} groups are not significantly affected by temperature. At present, the effective nature of the process which takes place in solution is not clear.

3.3. *Carbonyl derivatives*

The carbonylation reactions of complexes **1a**–**3c** have been investigated by means of IR and multinuclear NMR spectroscopy. Monocarbonyl derivatives of the types **4**–**8** are formed depending on the nature of the PSR ligand (Scheme 1). These species have been either isolated in the solid state or observed in solution. The spectroscopic data have been collected in Table 4 (IR, ${}^1H$ and ${}^{31}P\{{}^1H\}$ NMR) and Table 5 (${}^{13}C\{{}^1H\}$ NMR).

The *cis,cis,cis* isomer **1a** reacts slowly with CO in dichloromethane solution to give the cationic monocarbonyl *cis,cis*-$[RuCl(CO)(PSMe\text{-}P,S)_2]^+$ **4a**, which has been isolated in the solid state as its hexafluorophosphate salt. The geometry of the cation is that expected in which the CO group has replaced in **1a** the Cl$^-$ ion labilised by the *trans* P atom. The ${}^{31}P\{{}^1H\}$ NMR spectrum of **4a** shows two doublets with a ${}^2J$(P–P′) of 28.0 Hz typical of two inequivalent mutually *cis* P atoms. Moreover, its ${}^{13}C\{{}^1H\}$ NMR spectrum displays in the carbonyl region a doublet of doublets centred at δ 195.0



Scheme 1. Carbonylation reactions of complexes **1**–**3** in dichloromethane solution: (*i*) R = Me, Et or Cy; (*ii*) R = Me, Et or Cy; X = Cl or I; (*iii*) R = Et or Cy; (*iv*) on standing in solution.

indicative that the ^{13}CO group is *cis* to a P atom and *trans* to the other one [$^2J(^{31}P–^{13}C)_{trans} = 100.8 \gg {}^2J(^{31}P–^{13}C)_{cis} = 14.2$ Hz]. The spectral patterns of the phenyl carbons also confirm the asymmetric structure of **4a**. Each phenyl ring of the PPh_2 moiety lies in a magnetically different environment, thus the C_{ipso} carbon resonances appear as four distinct doublets of doublets in the range δ 127–135 (Table 5). Finally, the ^{1}H NMR spectrum of **4a** exhibits two methyl protons resonances. The doublet at δ 2.66 [$^4J(^{31}P–^1H) = 2.7$ Hz] is attributed to the protons of the SMe group spin–spin coupled to the *trans* P atom, while the resonance of the protons of the other thiomethyl group, which is *cis* to both P atoms, appears as a singlet at δ 2.26.

A dichloromethane solution of the *cis,cis,trans* isomer **2a** saturated with carbon monoxide yields *cis,trans*-$[RuCl(CO)(PSMe\text{-}P,S)_2]^+$ **5a**. Consistent with structure **5** (SMe groups mutually *trans*), no ^{31}P–^{1}H coupling constants are observed in high field region of the ^{1}H NMR spectrum. The ^{31}P–{^{1}H} NMR spectrum shows the expected two doublets, and in the ^{13}C{^{1}H} NMR spectrum the resonance of the ^{13}CO group appears as a doublet of doublets indicative that the carbonyl group is *cis* to a P atom and *trans* to the second one [$^2J(^{31}P–^{13}C)_{trans} = 103.1 \gg {}^2J(^{31}P–^{13}C)_{cis} = 11.5$ Hz] (Table 5). The strong absorption at ca. 2000 cm^{-1} [ν(CO)] in the Nujol mull IR spectra of both **4a** and **5a**, typical of a *trans* P–Ru–CO arrangement, ulteriorly confirms the assigned geometry.

The PSEt derivative **2b** also reacts slowly with carbon monoxide to give *cis,trans*-$[RuCl(CO)(PSEt\text{-}P,S)_2]^+$ **5b**, whose NMR spectral features are very similar to those of the isostructural **5a**. As pointed out above, the PSEt all-*cis* derivative **1b** was not obtained pure in the solid state. However,

Table 4
IR and ^{1}H (selected) and ^{1}P{^{1}H} NMR data for complexes **4a**–**12a**

	IR [a]		^{1}H [b]	^{31}P{^{1}H} [b]	
	ν(CO)	Other (cm^{-1})	δ(SCH$_3$)	δ	^2J(P–P′) (Hz)
4a	1998		2.26(s), 2.66(d) [c]	27.4(d), 48.2(d)	28.0
4b [d]				26.0(d), 48.3(d)	28.0
4c [d]				30.2(d), 43.6(d)	27.9
5a	2000		2.81(s), 2.83(s)	27.0(d), 45.4(d)	26.3
5b	1995			26.1(d), 45.1(d)	26.3
5c [d]				23.4(d), 43.1(d)	26.6
5Ia	1999		2.98(s), 2.99(s)	17.0(d), 45.4(d)	25.0
5Ib	2003			15.8(d), 43.1(d)	25.1
5Ic	2001			12.9(d), 39.4(d)	25.7
6c	1950	301 [e]		15.3(d), 43.8(d)	347.3
7c [d]	1972 [f]			25.4(d), 31.3(d)	29.4
8c [d]				18.7(d), 35.1(d)	324.2
9a		2290, 2320 [g]	2.34(s), 2.66(d) [h]	53.2(d), 54.5(d)	27.3
10a		2290, 2325 [g]	2.62(s)	47.3(s)	
11a	2034	2295 [g]	2.50(s), 2.90(d) [i]	34(d), 49.9(d)	25.7
12a	2038	2295 [g]	3.00(s), 3.03(s)	27.1(d), 42.4(d)	29.2

[a] In Nujol mull, unless otherwise stated.
[b] In CD_2Cl_2 solution, at 293 K. Multiplicity given in parentheses: s = singlet, d = doublet.
[c] $^4J(^{31}P–^1H) = 2.7$ Hz.
[d] Complex not isolated in the solid state.
[e] ν(Ru–Cl).
[f] In CH_2Cl_2 solution.
[g] ν(CN).
[h] $^4J(^{31}P–^1H) = 3.2$ Hz.
[i] $^4J(^{31}P–^1H) = 3.0$ Hz.

Table 5
Selected $^{13}C\{^1H\}$ NMR data for complexes **4a–12a** [a]

Complex	$\delta(C_{ipso})$	$\delta(CO)$	$\delta(CN)$
4a	127.8(dd) 130.0(dd) 133.4(dd) 134.5(dd)	195.0(dd) [14.2, 100.8]	
5a	132.0(dd) [b] 132.2(dd) 135.8(dd)	194.8(dd) [11.5, 103.1]	
5b	132.1(dd) [c] 136.0(dd)	195.2(dd) [11.7, 103.2]	
5Ia	132.4(dd) [b] 133.8(dd) 135.4(dd)	195.8(dd) [11.0, 99.6]	
5Ib	132.4(dd) [b] 133.8(dd) 135.4(dd)	196.1(dd) [10.9, 100.3]	
5Ic	132.2(dd) [b] 134.1(dd) 135.8(dd)	197.6(dd) [11.1, 102.2]	
6c	130.9(dd) [b] 132.4(dd) 134.6(dd)	199.3(t) [12.2]	
9a	127.1(d) 129.9(dd) 130.3(dd) 133.4(dd)		128.3(br s) 128.6(br s)
10a	131.8(q) 131.9(q)		127.2(q) [11.8, 1.9] [d]
11a	124.8(d) [c] 128.1(d)	193.1(dd) [93.5, 13.0]	[e]
12a	131.2(dd) [c] 134.5(dd)	192.7(dd) [92.6, 12.8]	129.6(s)

[a] In CD_2Cl_2 solution, at 293 K. Multiplicity given in parentheses: s = singlet, br s = broad singlet, d = doublet, dd = doublet of doublets, t = *pseudo*-triplet, q = non-binomial quintet; ^{13}C–^{31}P coupling constants (Hz) are reported in square brackets.

[b] The fourth C_{ipso} signal is partially overlapped by the resonances of phenyl carbons.

[c] Two C_{ipso} signals are partially overlapped by the resonances of phenyl carbons.

[d] ^{31}P–^{13}C coupling constants obtained from computer simulation, $^2J(P–P')$ = 28.4 Hz.

[e] Not assigned.

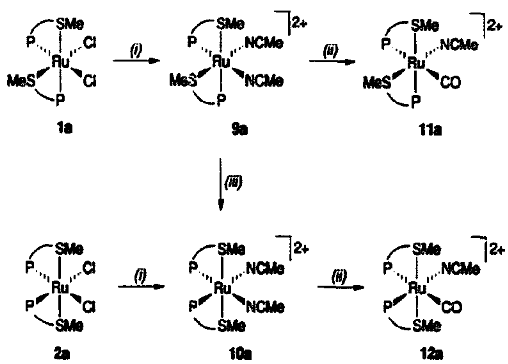
the carbonylation reaction of the mixture of **1b** (67%) and **2b** (33%), isolated from the reaction of *cis*-[$RuCl_2(dmso)_4$] and PSEt, has been monitored by ^{31}P NMR. After saturation with CO of a CH_2Cl_2 solution of the mixture, the spectrum shows the signals attributed to **5b** along with two doublets [δ 26.0 and 48.3; $^2J(P–P')$ = 28.0 Hz], which can be assigned to the isomer *cis,cis*-[RuCl(CO)(PSEt-*P,S*)$_2$]$^+$ **4b**. Complex **4b** very slowly isomerises into the more stable **5b**, and its complete conversion has been observed within 8 days. It should be noted that the isostructural complex **4a** does not isomerise at room temperature in dichloromethane solution.

In the case of the ligand PSCy no complexes of the type **1** and **2** have been obtained in pure form, and therefore the reaction between CO and a mixture of **1c**, **2c** and **3c** has been investigated. The ^{31}P NMR data suggest that both **1c** (*via* the intermediate *cis,cis*-[RuCl(CO)(PSCy-*P,S*)$_2$]$^+$ **4c**) and **2c** react with CO to give as final product the monocarbonyl derivative *cis,trans*-[RuCl(CO)(PSCy-*P,S*)$_2$]$^+$ **5c**, as found for complexes with the ligand PSEt. Complex **5c** was not isolated pure in the solid state.

Analogously, the three diiodo-derivatives **2Ia–c** react stereoselectively and quantitatively with CO in dichloromethane solution to afford *cis,trans*-[RuI(CO)(PSR-*P,S*)$_2$]$^+$ (R = Me **5Ia**, Et **5Ib**, and Cy **5Ic**). The carbonylation reaction is faster for the iodo- than for the corresponding chloro-derivatives and, independently from the nature of the ligand PSR, the formation of the iodo-carbonyls is completed within 30 min. Both IR and NMR data of complexes **5Ia–c** closely resemble that of **5a–c**.

On the contrary, **3c** reacts with carbon monoxide to yield neutral complexes of the type [$RuCl_2$(CO)(PSCy-*P*)(PSCy-*P,S*)], which contain one dangling P-bound monodentate PSCy ligand. The isomer *trans,trans*-[$RuCl_2$(CO)(PSCy-*P*)(PSCy-*P,S*)] **6c** has been prepared by warming at 60°C a CO-saturated toluene suspension of **3c** for 6 h. The mutual *trans* arrangement of the P atoms in **6c** is inferred by its $^{31}P\{^1H\}$ NMR spectrum, which shows an AX spin system with a $^2J(P–P')$ value of 347.3 Hz. Furthermore, both IR and $^{13}C\{^1H\}$ NMR spectra seem to confirm structure **6**. The single band at 301 cm^{-1} observed in the IR spectrum, which can be assigned to the Ru–Cl stretching mode, indicates the presence of a *trans* arrangement of the chloro atoms, while the ^{13}CO pattern, a *pseudo*-triplet centred at δ 199.3 [$^2J(^{31}P–^{13}C)$ = 12.2 Hz], reveals the presence of a meridional P,P′,CO arrangement. These data indicate that the coordination of CO [$\nu(CO)$ = 1950 cm^{-1}] involves dissociation of the thioether arm of one PSCy ligand, with cleavage of one Ru–S bond and formation of a carbonyl adduct in which one ligand acts as P-bound monodentate, while the second one is chelated to the metal centre.

The reaction between **3c** and carbon monoxide has been studied by means of IR and ^{31}P NMR spectroscopy. When CO gas is bubbled into a CH_2Cl_2 solution of **3c**, the orange colour fades, and a strong absorption appears in the IR spectrum at 1972 cm^{-1}. With time this band is slowly replaced by a new strong band at 1950 cm^{-1}. The stepwise formation of the two species can be more conveniently monitored by $^{31}P\{^1H\}$ NMR spectroscopy. An AX spin system [$^2J(P–P')$ = 29.4 Hz] is initially observed, which is attributed to the kinetic isomer *trans,cis*-[$RuCl_2$(CO)(PSCy-*P*)(PSCy-*P,S*)] **7c**. With time its intensity decreases, while a new AX spin system [$^2J(P–P')$ = 347.3 Hz] due to the formation of isomer **6c** appears and gains in intensity. The rate of conversion of **7c** into **6c** in dichloromethane solution is comparable with the rate of carbonylation of complex **3c**, therefore we



Scheme 2. Syntheses of complexes **9a**–**12a**: (*i*) $AgPF_6$ in MeCN solution; (*ii*) 1 atm CO in CH_2Cl_2 solution; (*iii*) in boiling acetone.

were not able to isolate pure **7c** in the solid state. We have also observed that complex **6c** is very slowly transformed into a new product, as shown by the appearance in the $^{31}P\{^1H\}$ NMR spectra of its aged solutions of two doublets at δ 18.7 and 35.1, with a $^2J(P–P')$ value (324.2 Hz) typical of mutually *trans* P atoms. This final product is most probably the *cis,trans*-[$RuCl_2(CO)$(PSCy-*P*)(PSCy-*P,S*)] isomer **8c**, in which the chloro atoms are mutually *cis*. However, attempts to prepare pure samples of **8c** resulted in the formation of mixtures of products. It should be stressed that, during the whole carbonylation process from **3c** to **8c**, no conductivity was shown by the solution. The carbonyl complex *cis,trans*-[$RuCl_2(CO)$(PSPh-*P*)(PSPh-*P,S*)], with a geometry of the type **8**, has been obtained by Sanger by refluxing a mixture of $RuCl_3 \cdot 3H_2O$ and PSPh in ethanol under CO atmosphere [9].

With the aim of preparing cationic carbonyls with the ligand PSCy, the reaction between **3c** and CO was carried out also in boiling alcohols and in the presence of NH_4PF_6. Almost all the starting material decomposed and only the formation of a small amount of **5c** was observed.

The different behaviour of complexes **1**–**3** in the reaction with CO is consistent with their geometry (Scheme 1). In the case of isomers **1** and **2** the cleavage of the Ru–X bond *trans* to P occurs with formation of cationic derivatives, while for **3c** the *trans* effect of the P atom favours the formation of neutral species with dissociation of the thioether arm of a PSCy ligand.

3.4. Acetonitrile and carbonyl–acetonitrile derivatives

The reactivity of complexes **1**–**3** towards other neutral molecules such as acetonitrile has been also investigated. Whereas **3c** is inert at room temperature towards MeCN, complexes **1** and **2** readily react affording cationic derivatives via cleavage of one or both Ru–Cl bonds. It should be noted that complexes of the type *trans,cis,cis*-[$RuCl_2$(POR-*P,O*)$_2$], isostructural with **3c**, react with MeCN in CH_2Cl_2 solution to give the neutral *cis,cis*-[$RuCl_2$(MeCN)(POR-*P*)(POR-*P,O*)] derivatives with cleavage of a Ru–O bond [3g]. Complexes **1a** and **2a** dissolve in acetonitrile with formation of equilibrium mixtures of [RuCl(MeCN)(PSMe-*P,S*)$_2$]$^+$ and [Ru(MeCN)$_2$(PSMe-*P,S*)$_2$]$^{2+}$, as suggested by ^{31}P NMR measurements. Attempts to isolate in the solid state the [RuCl(MeCN)(PSMe-*P,S*)$_2$]$^+$ isomers led to impure products. On the contrary, a complete scavenging of the Cl^- ions from the dichloro-precursors was achieved by treatment with soluble silver(I) salts with consequent precipitation of AgCl. Thus, when the *cis,cis,cis* isomer **1a** is stirred with an excess of $AgPF_6$ in acetonitrile, cream-white crystals of *cis,cis*-[Ru(MeCN)$_2$(PSMe-*P,S*)$_2$](PF_6)$_2$ **9a** can be isolated. By means of the same procedure, the *cis,cis, trans* isomer **2a** gave *cis,trans*-[Ru(MeCN)$_2$(PSMe-*P,S*)$_2$](PF_6)$_2$ **10a** (Scheme 2).

Also complexes **9a** and **10a**, which behave as 1:2 electrolytes in nitromethane solution, have been characterised by a combination of IR and multinuclear NMR spectroscopy. The $^{31}P\{^1H\}$ NMR spectrum of **9a** in dichloromethane solution shows two doublets at δ 53.2 and 54.5 (AB spin system) with a $^2J(P–P')$ of 27.3 Hz typical of P atoms in mutually *cis* position. Moreover, the IR spectrum in Nujol mull exhibits two weak absorptions at 2290 and 2320 cm^{-1}, which can be assigned to the CN stretching mode of the MeCN ligands. In agreement with the asymmetric structure of **9a**, the $^{13}C\{^1H\}$ NMR spectrum in the aromatic carbons region shows patterns indicative of the presence of four different phenyl rings. The ^{13}CN resonances appear as broad signals at δ ca. 128.

The *cis,trans* geometry of **10a** has been inferred from the appearance in the $^{31}P\{^1H\}$ NMR spectrum of a singlet at δ 47.3, while in the $^{13}C\{^1H\}$ NMR spectrum the ^{13}CN carbons resonance appears as a *pseudo*-quintet at δ 127.2 arising from spin–spin coupling with two chemically but not magnetically equivalent P atoms mutually *cis* [17]. In agreement with the presence of mutually *cis* MeCN ligands, the IR spectrum in Nujol mull of **10a** exhibits two weak ν(CN) absorptions at 2290 and 2325 cm^{-1}.

Apparently, the substitution of both Cl^- ions with MeCN molecules occurs with retention of configuration around the metal centre of the starting complex. The *cis,cis* derivative **9a**, which is fairly stable in common solvents at room tem-

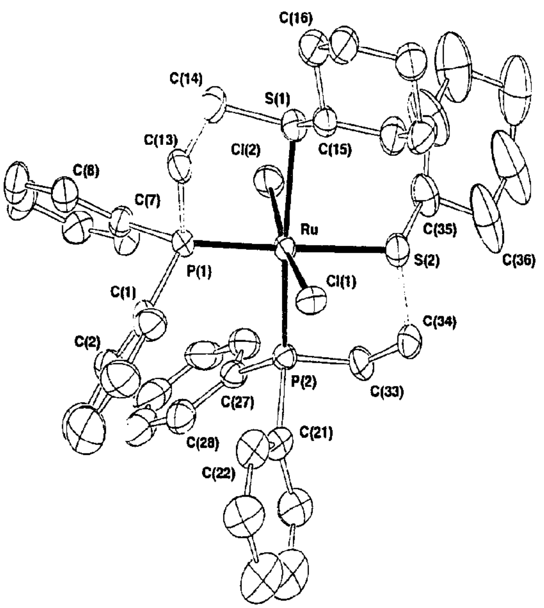


Fig. 2. ORTEP drawing and atom-labelling scheme of complex **3c·0.5 propan-2-ol**. Thermal ellipsoids are drawn at 40% probability.

perature, can be thermally converted in acetone solution into the thermodynamically preferred isomer **10a**.

The diacetonitrile derivatives were found to be a convenient starting material for the synthesis of other ruthenium(II) dicationic species by substitution of one MeCN ligand with other neutral molecules such as, for example, carbon monoxide. Thus, **9a** and **10a** react with CO to give *cis,cis*-[Ru(CO)(MeCN)(PSMe-*P,S*)$_2$](PF$_6$)$_2$ **11a** and *cis,trans*-[Ru(CO)(MeCN)(PSMe-*P,S*)$_2$](PF$_6$)$_2$ **12a**, respectively (Scheme 2). The IR spectra in Nujol mull of both complexes show a strong absorption at ca. 2035 cm^{-1} together with a weak band at 2295 cm^{-1}, which can be attributed to ν(CO) and ν(CN) vibrations, respectively. The ^{31}P{^{1}H} spectra of both complexes exhibit AX spin systems with ^{2}J(P–P′) values indicative of the presence of *cis* P atoms (Table 4). The ^{13}CO multiplet in the ^{13}C{^{1}H} spectra is the typical doublet of doublets characteristic of a CO group *trans* to a P atom and *cis* to the second one [$^{2}J(^{31}\mathrm{P}-^{13}\mathrm{C})_{trans}$ ca. 93 $\gg$ $^{2}J(^{31}\mathrm{P}-^{13}\mathrm{C})_{cis}$ ca. 13 Hz] (Table 5). Furthermore, in the case of **11a**, the presence of a *trans* P–Ru–SMe arrangement is confirmed by the appearance in the ^{1}H NMR spectrum of a doublet at δ 2.90, which can be assigned to the protons of a SMe group coupled with the *trans* P atom [$^{4}J(^{31}\mathrm{P}-^{1}\mathrm{H})$ = 3.0 Hz]. The protons of the other SMe group give a singlet at higher field.

3.5. Description of the molecular structure of 3c·0.5propan-2-ol

The ORTEP drawing [18] of the structure of complex **3c·0.5propan-2-ol** is shown in Fig. 2, along with the associated atom labelling scheme. Atomic positional parameters are presented in Table 6, while a selection of relevant bond lengths and angles is reported in Table 7. The crystal structure consists of discrete monomeric molecular units which possess an approximately C$_2$ symmetry about the axis bisecting the P(1)–Ru–P(2) and S(1)–Ru–S(2) angles. A distorted octahedral geometry is observed about the Ru atom with *trans* chloro-atoms and two PSCy chelating ligands in such a way that like donor atoms are in *cis* position. There are significant in-plane angular distortions from the ideal interligand angles of 90°, owing to the restricted chelate bite of 86.00(5) and 85.52(6)°. The P(1)–Ru–P(2) angle of 99.74(6)° is larger than the S(1)–Ru–S(2) of 89.45(6)°, possibly in order to reduce non-bonded interactions among the phenyl rings. The P and S donors present a slight tetrahedral distortion of ±0.13 Å from the coordination mean plane RuP$_2$S$_2$.

The Cl atoms are significantly bent away from the P atoms, presenting a Cl(1)–Ru–Cl(2) bond angle of 170.80(6)°, thereby minimising a possible steric interaction with the phenyl rings. This geometrical feature has already been detected in related *trans,cis,cis*-[RuCl$_2$(P–O)$_2$] complexes, P–O = (diphenylphosphino)acetophenone [3k], *o*-(diphenylphosphino)anisole [4a] or 1-(diphenylphosphino)-2-(methoxy)ethane [4c] where the values of the Cl–Ru–Cl angle are 172.0(1), 165.67(3) and 166.0(1), respectively. Comparable values of the Cl–Ru–Cl angle are shown also by other ruthenium(II) complexes with a *trans,cis,cis*-Cl$_2$P$_2$O$_2$ set around the metal centre. This is the case of *trans,cis,cis*-[RuCl$_2$\{Bu^{t}P(CH$_2$CO$_2$Me)$_2$\}$_2$] [19] and of the isostructural complex with (2,6-dimethoxyphenyl)diphenylphosphine [20], in which the potentially tridentate O–P–O ligands are

Table 6
Atomic fractional coordinates and equivalent isotropic temperature factors and their e.s.d.s for **3c·0.5propan-2-ol**

Atom	*x*	*y*	*z*	*B* (Å^2)
Ru	0.43180(3)	0.50880(3)	0.66544(2)	2.487(8)
Cl(1)	0.56795(9)	0.5702(1)	0.67616(9)	3.78(3)
Cl(2)	0.28649(9)	0.4712(1)	0.64330(9)	4.16(4)
S(1)	0.37871(9)	0.6815(1)	0.65859(8)	3.33(3)
S(2)	0.3986(1)	0.5153(1)	0.53625(7)	3.66(3)
P(1)	0.47480(9)	0.5228(1)	0.78812(7)	2.86(3)
P(2)	0.46311(9)	0.3430(1)	0.65824(8)	2.86(3)
C(1)	0.5823(4)	0.4881(5)	0.8528(3)	3.6(1)
C(2)	0.5949(4)	0.3940(6)	0.8850(4)	4.4(2)
C(3)	0.6753(5)	0.3626(7)	0.9331(4)	5.8(2)
C(4)	0.7435(5)	0.4270(9)	0.9499(5)	7.3(3)
C(5)	0.7312(5)	0.5206(8)	0.9186(5)	6.7(2)
C(6)	0.6519(4)	0.549686)	0.8699(4)	5.1(2)
C(7)	0.4131(4)	0.4718(5)	0.8351(3)	3.3(1)
C(8)	0.4218(4)	0.5095(6)	0.9010(3)	4.4(2)
C(9)	0.3787(4)	0.4662(7)	0.9385(3)	5.2(2)
C(10)	0.3290(4)	0.3841(7)	0.9122(4)	5.5(2)
C(11)	0.3197(5)	0.3448(7)	0.8467(4)	5.3(2)
C(12)	0.3615(4)	0.3882(6)	0.8085(3)	4.2(2)
C(13)	0.4708(4)	0.6584(5)	0.8035(3)	3.9(2)
C(14)	0.3889(4)	0.6980(5)	0.7502(3)	4.0(1)
C(15)	0.4510(4)	0.7783(5)	0.6518(3)	3.5(1)
C(16)	0.4277(5)	0.8818(5)	0.6678(4)	5.4(2)
C(17)	0.4858(6)	0.9605(6)	0.6574(4)	6.4(2)
C(18)	0.4846(6)	0.9562(6)	0.5832(4)	5.7(2)
C(19)	0.5068(5)	0.8513(6)	0.5673(4)	5.8(2)
C(20)	0.4468(5)	0.7745(5)	0.5766(4)	5.4(2)
C(21)	0.5719(4)	0.2979(5)	0.6877(3)	3.5(1)
C(22)	0.6402(4)	0.3495(6)	0.7370(4)	4.6(2)
C(23)	0.7229(5)	0.3110(7)	0.7634(5)	6.2(2)
C(24)	0.7368(5)	0.2197(7)	0.7395(5)	6.8(2)
C(25)	0.6711(5)	0.1673(7)	0.6900(5)	7.1(2)
C(26)	0.5880(5)	0.2044(6)	0.6650(4)	5.3(2)
C(27)	0.4178(4)	0.2429(4)	0.6931(3)	3.3(1)
C(28)	0.4675(4)	0.1966(5)	0.7583(4)	4.4(2)
C(29)	0.4316(5)	0.1233(6)	0.7864(4)	5.5(2)
C(30)	0.3479(5)	0.0966(6)	0.7503(4)	6.3(2)
C(31)	0.2993(5)	0.1400(6)	0.6865(5)	6.0(2)
C(32)	0.3336(4)	0.2146(6)	0.6[illegible]0(4)	4.5(2)
C(33)	0.4172(4)	0.3136(5)	0.5612(3)	4.0(2)
C(34)	0.4388(4)	0.3962(5)	0.5223(3)	3.9(1)
C(35)	0.2854(4)	0.5072(7)	0.4773(3)	5.0(2)
C(36)	0.2652(6)	0.468(1)	0.4024(5)	10.2(3)
C(37)	0.1756(8)	0.477(1)	0.3548(6)	13.1(4)
C(38)	0.1429(7)	0.585(1)	0.3521(5)	10.2(4)
C(39)	0.1617(7)	0.622(1)	0.4265(5)	10.0(4)
C(40)	0.2497(6)	0.6126(8)	0.4747(6)	8.5(3)
O	−0.0664(6)	0.6032(8)	0.3938(5)	5.3(3)
C(50)	−0.0107(7)	0.7185(9)	0.5079(5)	3.2(3)
C(51)	−0.1331(9)	0.649(1)	0.4801(7)	5.4(4)
C(52)	−0.0849(8)	0.669(1)	0.4522(8)	6.3(4)

η^2-P,O bonded. For these species the values of the Cl–Ru–Cl angle are 169.59(9) and 167.13(5)°, respectively. A comparable value of the Cl–Ru–Cl angle (166.89(9)°) has been found for [$RuCl_2(PPh_3)(L)$] [21], also showing a *trans,cis,cis*-$Cl_2P_2O_2$ octahedral geometry, in which L is a potentially tetradentate amphiphilic phosphine-polyether ligand η^3-P,O,O coordinated to the metal centre.

Table 7
Selected bond lengths (Å) and angles (°) for complex **3c·0.5propan-2-ol** with e.s.d.s in parentheses

Ru–Cl(1)	2.411(2)	Cl(1)–Ru–Cl(2)	170.80(6)
Ru–Cl(2)	2.409(2)	Cl(1)–Ru–S(1)	90.69(6)
Ru–S(1)	2.464(2)	Cl(1)–Ru–S(2)	82.55(6)
Ru–S(2)	2.451(2)	Cl(1)–Ru–P(1)	90.61(6)
Ru–P(1)	2.300(2)	Cl(1)–Ru–P(2)	95.02(6)
Ru–P(2)	2.298(2)	Cl(2)–Ru–S(1)	81.43(6)
S(1)–C(14)	1.814(7)	Cl(2)–Ru–S(2)	92.56(6)
S(1)–C(15)	1.841(7)	Cl(2)–Ru–P(1)	93.57(6)
S(2)–C(34)	1.803(7)	Cl(2)–Ru–P(2)	92.35(6)
S(2)–C(35)	1.822(6)	S(1)–Ru–S(2)	89.45(6)
P(1)–C(1)	1.834(5)	S(1)–Ru–P(1)	86.00(5)
P(1)–C(7)	1.832(7)	S(1)–Ru–P(2)	171.83(5)
P(1)–C(13)	1.843(7)	S(2)–Ru–P(1)	171.74(6)
P(2)–C(21)	1.820(6)	S(2)–Ru–P(2)	85.52(6)
P(2)–C(27)	1.833(7)	P(1)–Ru–P(2)	99.74(6)
P(2)–C(33)	1.840(6)		

The Ru–P(1) and Ru–P(2) bond lengths are equal within experimental error [2.298(2) and 2.300(2) Å]. Although few structures of Ru complexes with chelating P–S ligands have been reported, these distances are slightly shorter than those observed in *cis,cis,cis*-[$RuCl_2${4-di-*p*-tolylphosphino-(dibenzothiophene)}$_2$], where the Ru–P distance (P *trans* to S) is 2.336(5) Å [22]. Finally, the Ru–S bond lengths of 2.464(2) and 2.451(2) Å are comparable with the mean value of 2.446(3) Å (P *trans* to S), detected in [Ru(dithioformate)$_2$(PPh_3)$_2$] [23].

4. Conclusions

The P,S-ligands employed in this work forms stable six-coordinate [$RuCl_2$(PSR-*P,S*)$_2$] derivatives in which the phosphine-thioether ligands act as bidentate. Only three of the five possible geometrical isomers have been observed, those with mutually P atoms being presumably unstable because of electronic reasons. The kinetic product in the reaction between *cis*-[$RuCl_2(dmso)_4$] and PSR is the all-*cis* derivative **1**, which isomerises in solution into the *cis,cis,trans* one **2**. The latter is the thermodynamic product when R is Me or Et, while complex **2** in turn is slowly transformed into the most stable *trans,cis,cis* isomer **3** when R is Cy. The factors responsible for determining the thermodynamically preferred stereochemistry of the [RuX_2(PSR-*P,S*)$_2$] derivatives are not entirely clear, as in the PSCy-series isomer **2** becomes favoured with respect to **3** on going from X = Cl to X = I. Therefore, the geometry of these species seems to depend also on the size of the halogen atom. It should be noted that in the case of the related [$RuCl_2$(P–O)$_2$] complexes (P–O = P,O-donor ligand) only isomers of the type **3** have been reported, with *trans* Cl atoms and nearly coplanar P–O chelates with *cis* oxygen and phosphorus atoms [3c–e,g,k,4a,c,e,7]. On the other hand also the disulfide derivatives [$RuX_2(RSCH_2CH_2SR)_2$] have been reported to possess a *trans* geometry [10].

The coordination chemistry of the PSR ligands with ruthenium(II) appears significantly different from that of the corresponding POR ligands. A lower tendency to behave as 'hemilabile' ligands emerges for the phosphine-thioethers owing to the stability of the Ru–S bond. As a matter of fact, the cleavage of the Ru–S bond is observed only in the carbonylation of *trans,cis,cis*-[$RuCl_2$(PSCy-*P,S*)$_2$], with formation of the neutral monocarbonyl adduct [$RuCl_2$(CO)(PSCy-*P*)(PSCy-*P,S*)]. In this case the rupture of the Ru–S bond is favoured by the labilising effect of the P atom in *trans* position.

Analogously to **3c**, the related isostructural species *trans,cis,cis*-[$RuCl_2$(POR-*P,O*)$_2$] react with CO to give initially adducts of the type *trans,trans*-[$RuCl_2$(CO)(POR-*P*)(POR-*P,O*)]. However, differently from complexes **6c–8c**, these species react further and reversibly with CO to afford the dicarbonyl derivatives [$RuCl_2$(CO)$_2$(POR-*P*)$_2$] via opening of the second chelate ring [2c,3c–e,g,4a,c,e]. It should be noted that the first step of the reaction leads to the formation of a monocarbonyl of the type **6**, while isomers of the type **7** are not observed. Moreover, the *trans,trans* isomer can be converted into the thermodynamically stable *cis,cis*-[$RuCl_2$(CO)(POR-*P*)(POR-*P,O*)], and such stereochemistry has not been observed in the PSR series. Finally, the cationic complexes [RuCl(CO)(POR-*P,O*)$_2$]$^+$ were not obtained by direct reaction between CO and the dichloro-derivatives, but they can be prepared only by means of chloride abstraction with $AgSbF_6$ on neutral monocarbonyls of the type **6** [4b]. With regard to ruthenium(II) disulfide complexes, it has been reported that *trans*-[RuX_2($PhSCH_2CH_2SPh$)$_2$] ($X = Cl$ or Br) give *trans*-[RuX(CO)($PhSCH_2CH_2SPh$)$_2$] in refluxing 2-methoxyethanol under CO atmosphere. Under the same experimental conditions *trans*-[$RuCl_2$($EtSCH_2CH_2SEt$)$_2$] does not react with carbon monoxide [10].

5. Supplementary material

Additional material available from the author E.Z. comprises calculated H-atom coordinates, thermal parameters, and full lists of bond lengths and angles. The crystallographic tables have been deposited with the Cambridge Crystallographic Data Centre.

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