

# A new series of iodocarbonyl ruthenium (II) complexes with unsymmetrical phosphine–phosphine sulfide ligands of the type $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{P}(\text{S})\text{Ph}_2$ , $n = 1\text{--}4$ : Isolation and structural investigation

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Received 6 April 2005; received in revised form 21 June 2005; accepted 28 June 2005

Available online 8 August 2005

Ruthenium and Osmium Chemistry Topical Issue

## Abstract

Hexa-coordinated chelate complex  $\text{cis}[\text{Ru}(\text{CO})_2\text{I}_2(\text{P}\cap\text{S})]$  (**1a**) { $\text{P}\cap\text{S} = \eta^2\text{-(P,S)}$ -coordinated} and penta-coordinated non-chelate complexes  $\text{cis}[\text{Ru}(\text{CO})_2\text{I}_2(\text{P}\sim\text{S})]$  (**1b–d**) { $\text{P}\sim\text{S} = \eta^1\text{-(P)}$ -coordinated} are produced by the reaction of polymeric  $[\text{Ru}(\text{CO})_2\text{I}_2]_n$  with equimolar quantity of the ligands  $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{P}(\text{S})\text{Ph}_2$  { $n = 1$ (**a**), 2(**b**), 3(**c**), 4(**d**)} in dichloromethane at room temperature. The bidentate nature of the ligand **a** in the complex **1a** leads to the formation of five-membered chelate ring which confers extra stability to the complex. On the other hand, 1:2 (Ru:L) molar ratio reaction affords the hexa-coordinated non-chelate complexes  $\text{cis}, \text{cis}, \text{trans}[\text{Ru}(\text{CO})_2\text{I}_2(\text{P}\sim\text{S})_2]$  (**2a–d**) irrespective of the ligands. All the complexes show two equally intense terminal  $\nu(\text{CO})$  bands in the range 2028–2103  $\text{cm}^{-1}$ . The  $\nu(\text{PS})$  band of complex **1a** occurs 23  $\text{cm}^{-1}$  lower region compared to the corresponding free ligand suggesting chelation via metal–sulfur bond formation. X-ray crystallography reveals that the Ru(II) atom occupies the center of a slightly distorted octahedral geometry. The complexes have also been characterized by elemental analysis,  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{31}\text{P}$  NMR spectroscopy. © 2005 Elsevier B.V. All rights reserved.

**Keywords:** Ruthenium (II) carbonyl complexes; Unsymmetrical phosphine–phosphine sulfide; Single crystal X-ray structure; Distorted octahedral geometry; Steric effect; IR and NMR spectroscopy

## 1. Introduction

There is currently much interest in the synthesis, characterization and structural investigation of transition metal complexes containing different types of phosphine based mono- and di-chalcogenide ligands like  $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{P}(\text{X})\text{Ph}_2$ ,  $\text{Ph}_2\text{As}(\text{CH}_2)_n\text{P}(\text{X})\text{Ph}_2$ ,  $\text{Ph}_2\text{PNHP}(\text{X})\text{Ph}_2$  and  $\text{Ph}_2\text{As}(\text{X})(\text{CH}_2)_n\text{P}(\text{X})\text{Ph}_2$  [1–12]. Work has

been mainly concentrated on the complexes with  $\text{X} = \text{O}, \text{S}, \text{Se}$  and  $n = 1\text{--}2$ . Rhodium and ruthenium metal carbonyl complexes of *bis*-diphenylphosphino monochalcogenides,  $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{P}(\text{X})\text{Ph}_2$ ;  $\text{X} = \text{O}, \text{S}, \text{Se}$ ;  $n = 1\text{--}2$  are of special interest because of their versatile application in homogeneous catalysis [1–3]. These type of ligands have become of increasing interest because of their dual nature in coordination with the metal center. They exhibit [P]-bonded unidentate coordination or [P,X]-bonded chelating coordination mode, depending on the metal center and its environments. They have the potential for strong bonding between the soft

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phosphorus atom and a soft metal atom and weaker bonding between the metal and the chalcogen atom and chelate formation gives the extra stability to the metal complex. The relatively labile metal–chalcogen bond can be cleaved reversibly to generate a free coordination site for incoming stronger binding ligands or substrates [13] which facilitates catalytic activity of the catalyst. As for example, the P,O chelate complex,  $[\text{RhCl}(\text{CO})\{\text{Ph}_2\text{PCH}_2\text{CH}_2\text{P}(\text{O})\text{Ph}_2\}]$ , catalyses carbonylation of methanol [1]. The mechanism for this catalytic process may involve opening–closing system. Recently, there have been a few reports on some ruthenium chloro-carbonyl complexes derived from  $[\text{Ru}(\text{CO})_2\text{Cl}_2]_n$  and  $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{P}(\text{S})\text{Ph}_2$ ,  $n = 1\text{--}4$  [14–16], but to the best of our knowledge, no ruthenium iodo-carbonyl complex has so far been reported with these types of unsymmetrical phosphine–phosphine monochalcogenide ligands despite the chemistry of such complexes being as potentially important and interesting as that of chloro-complexes.

In this paper, we present the synthetic details, characterization data and structural investigation of some new ruthenium (II) iodo-carbonyl complexes containing the ligands  $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{P}(\text{S})\text{Ph}_2$ ,  $n = 1\text{--}4$ . The molecular structure of one of the synthesized complexes  $[\text{Ru}(\text{CO})_2\text{I}_2(\text{P}\cap\text{S})]$  ( $\text{P}\cap\text{S} = \eta^2\text{-P,S-coordinated Ph}_2\text{PCH}_2\text{P}(\text{S})\text{Ph}_2$ ) established by single crystal X-ray diffraction study is also reported.

## 2. Experimental

### 2.1. Materials

All the solvents used were distilled under nitrogen prior to use. Iodides were analyzed by standard analytical method [17].  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  was purchased from M/s Arrora Matthey Ltd., Kolkata, India. Analytically pure  $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$  ( $n = 1\text{--}4$ ) and elemental sulfur were purchased from M/s Aldrich, USA and used without further purification. The ligands,  $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{P}(\text{S})\text{Ph}_2$  were prepared by refluxing a solution of  $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$  in benzene with one molar equivalent of elemental sulfur for 3 h under nitrogen and purified by chromatographic techniques [15]. The starting complex  $[\text{Ru}(\text{CO})_2\text{I}_2]_n$  was prepared by the literature methods [18,19].

### 2.2. Instrumentation

FT-IR spectra of range 4000–400 and 400–200  $\text{cm}^{-1}$  were recorded using Perkin–Elmer 2000 and Perkin–Elmer 883 spectrophotometer, respectively, in KBr disc. Carbon and hydrogen analyses were done on a Perkin–Elmer 2400 elemental analyzer. NMR data were recorded on a Bruker DPX 300 MHz spectrometer and the  $^1\text{H}$  and  $^{31}\text{P}$  NMR chemical shifts were quoted rela-

tive to  $\text{SiMe}_4$  and 85%  $\text{H}_3\text{PO}_4$  as internal and external standard, respectively, using  $\text{CDCl}_3$  and  $d_6$ -acetone as solvent.

### 2.3. Synthesis of complexes $[\text{Ru}(\text{CO})_2\text{I}_2(\text{P}\cap\text{S})]$ (**1a**) and $[\text{Ru}(\text{CO})_2\text{I}_2(\text{P}\sim\text{S})]$ (**1b–d**)

0.024 mmol of  $[\text{Ru}(\text{CO})_2\text{I}_2]_n$  was dissolved in 10  $\text{cm}^3$  dichloromethane and to this 0.024 mmol of corresponding ligands **a–d** in 10  $\text{cm}^3$  dichloromethane was added. The reaction mixture was stirred at room temperature for about 3 h and the solvent was evaporated under vacuum to produce a yellow compound. The compound was washed with diethyl ether and recrystallized from dichloromethane solution.

### 2.4. Synthesis of complexes $[\text{Ru}(\text{CO})_2\text{I}_2(\text{P}\sim\text{S})_2]$ (**2a–d**)

To a 10  $\text{cm}^3$  dichloromethane solution of  $[\text{Ru}(\text{CO})_2\text{I}_2]_n$  (0.024 mmol), 0.049 mmol of corresponding ligands **a–d** in 10  $\text{cm}^3$  dichloromethane was added. A yellow compound was obtained following the same reaction condition used for the complexes **1a–d**. After washing with diethyl ether the complexes were recrystallized from dichloromethane solution.

### 2.5. Single crystal X-ray crystallographic data collection and refinements of the structure

A crystal of the complex **1a** suitable for X-ray crystallographic analysis was developed from a  $\text{CH}_2\text{Cl}_2$ –hexane solution. Data collection was performed using a Bruker SMART diffractometer, full sphere of data with  $0.3^\circ$  slices, room temperature, Mo  $\text{K}\alpha$  radiation and empirical absorption corrections. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms being refined in idealized geometries. The structure refinements were done by full matrix least square on  $F^2$  using SHELXTL 97 computer program [20]. The crystal data and structure refinement for the complex are listed in Table 1.

## 3. Results and discussion

The polymeric complex  $[\text{Ru}(\text{CO})_2\text{I}_2]_n$  reacts with equimolar quantity of the ligand **a** by cleavage of the iodo bridge to afford a hexa-coordinated  $\eta^2\text{-P,S}$  bonded complex  $[\text{Ru}(\text{CO})_2\text{I}_2(\text{P}\cap\text{S})]$  (**1a**) (Scheme 1). This molecular composition of the complex is well supported by the elemental analysis data (Table 2). The complex was isolated as stable crystalline solid. The solid-state IR spectra of the complex **1a** in KBr plates show two equally intense  $\nu(\text{CO})$  bands at 2098 and 2030  $\text{cm}^{-1}$  attributing the two terminal carbonyl groups are *cis* to one another

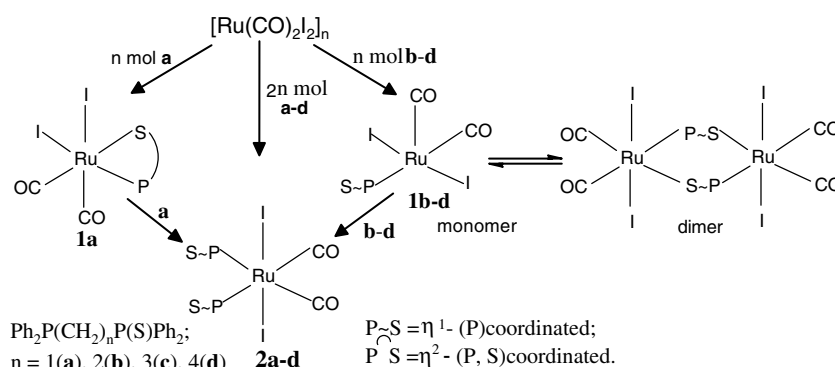
Table 1  
Crystal data and structure refinement of the complex **1a**

Empirical formula	C <sub>27</sub> H <sub>22</sub> I <sub>2</sub> O <sub>2</sub> P <sub>2</sub> RuS
Formula weight	827.32
Temperature (K)	125(2)
Wave length (Å)	0.71073
Crystal system	monoclinic
Space group	P2(1)/n
a (Å)	10.9589(14)
b (Å)	14.0386(18)
c (Å)	18.711(2)
α (°)	90
β (°)	100.953(2)
γ (°)	90
Volume (Å <sup>3</sup> )	2826.2(6)
Z	4
D <sub>calc</sub> (Mg/m <sup>3</sup> )	1.944
Absorption coefficient (mm <sup>-1</sup> )	2.950
F(000)	1584
Crystal size (mm <sup>3</sup> )	0.13 × 0.1 × 0.1
θ range for data collection (°)	1.83–25.44
Index ranges	−12 ≤ h ≤ 13, −16 ≤ k ≤ 16, −22 ≤ l ≤ 17
Reflections collected	17849
Independent reflections	5125 (R <sub>int</sub> = 0.0506)
Completeness to θ = 25.44°	98.0%
Absorption correction	multiscan
Maximum and minimum transmission	1.00000 and 0.854096
Refinement method	full-matrix least-squares on F <sup>2</sup>
Data/restraints/parameters	5125/0/3175
Goodness-of-fit on F <sup>2</sup>	0.626
Final R indices [I > 2σ(I)]	RI = 0.0321, wR <sub>2</sub> = 0.0608
R indices (all data)	RI = 0.0570, wR <sub>2</sub> = 0.0664
Extinction coefficient	0.00049 (8)
Largest difference peak and hole (e/Å <sup>3</sup> )	0.679 and −0.914S

[21,22]. The ν(PS) band at 583 cm<sup>-1</sup> (Table 3) is about 23 cm<sup>-1</sup> lower than that of the free ligand [ν(PS) = 606 cm<sup>-1</sup>] suggesting chelate formation via metal–sulfur bonding [9]. The <sup>1</sup>H NMR spectra (Table 3) of **1a** show two multiplet resonances in the ranges δ 7.18–7.59 and δ 7.67–8.13 ppm which is attributable to the two non-equivalent phenylic protons. The two methylene protons in the chelate ligand do not seem to be

equivalent because in the five-membered chelate ring methylene protons are expected to be above and below the plane containing the metal ion and the two phosphorus atoms [23]. Each of the methylene protons appear separately as doublet of doublet (ddd) centered at 3.89 and 4.77 ppm due to coupling with two phosphorus atoms and the other H which are matching well with the related complexes of the same ligand reported by Gonsalvi et al. [24]. The <sup>31</sup>P NMR spectra (Table 3) exhibit two distinct doublet resonances corresponding to the two different phosphorus atoms. The pentavalent phosphorus atom (P<sub>B</sub>) bonded to the sulfur resonates at high field (δ 53.6 ppm) than the tertiary phosphorus (P<sub>A</sub>) bonded to the metal (δ 61.6 ppm) [25]. As compared to the free ligand, the P<sub>A</sub> and P<sub>B</sub> atom show a down field shift of 84.3 and 8.4 ppm, respectively, which further corroborates the chelation in complex **1a**. In the <sup>13</sup>C spectra, only one signal for the two inequivalent carbonyl carbons is appeared as broad singlet at δ 186 ppm (Table 4), which indicates that the other CO peak is merged and therefore does not appear separately. One doublet of doublet peak is observed at δ 34.0 ppm for the methylene carbon due to coupling with the two non-equivalent phosphorus atoms. The phenyl carbons are found in the range δ 128.61–135.25 ppm.

Unlike to the ligand **a**, the reaction of the ligands **b–d** with [Ru(CO)<sub>2</sub>I<sub>2</sub>]<sub>n</sub> in one molar equivalent ratio gives five-coordinate η<sup>1</sup>-P bonded complexes of the type [Ru(CO)<sub>2</sub>I<sub>2</sub>(P~S)] (**1b–d**) (Scheme 1). The non-chelating mode of the ligands **b–d** in these complexes is favoured over chelating mode because chelation leads to formation of six, seven and eight member ring which are unfavourable due to high ring strain. Similar to the complex **1a**, the ν(CO) bands for the two *cis* terminal carbonyl groups are observed in the range 2033–2103 cm<sup>-1</sup> (Table 3). The ν(PS) band occurs almost in the same position as that of corresponding free ligands which is good agreement with the η<sup>1</sup>-P coordination nature of the ligands. The <sup>1</sup>H NMR spectra of the complexes **1b–d** show the characteristic resonances for the methylene and phenylic protons. As the complex **1a**,



Scheme 1.

Table 2  
Analytical data of the complexes

Complex	Yield (%)	Elemental analysis found (calc.) in %		
		C	H	I
<b>1a</b>	95	39.20 (39.17)	2.64 (2.66)	30.65 (30.68)
<b>1b</b>	98	39.91 (39.94)	2.83 (2.85)	30.20 (30.17)
<b>1c</b>	93	40.70 (40.69)	3.07 (3.04)	29.64 (29.68)
<b>1d</b>	92	41.39 (41.41)	3.20 (3.22)	29.20 (29.19)
<b>2a</b>	96	50.19 (50.17)	3.52 (3.54)	20.39 (20.41)
<b>2b</b>	94	50.93 (50.95)	3.77 (3.78)	19.93 (19.96)
<b>2c</b>	91	51.68 (51.70)	4.03 (4.00)	19.50 (19.53)
<b>2d</b>	95	52.40 (52.42)	4.24 (4.22)	19.09 (19.11)

Table 3  
IR,  $^{31}\text{P}\{-\text{H}\}$  and  $^1\text{H}$  values ( $\delta$  in ppm;  $J_{\text{P-P}}$  in Hz) of the complexes

Complex	IR ( $\text{cm}^{-1}$ )		$^{31}\text{P}\{-\text{H}\}$ NMR			$^1\text{H}$ NMR	
	$\nu(\text{CO})$	$\nu(\text{PS})$	$\delta_{\text{P}}$	$\delta_{\text{P=S}}$	$J_{\text{P-P}}$	$\text{C}_6\text{H}_5$	$-(\text{CH}_2)_n-$
<b>1a</b>	2098	583	61.60d	53.63d	77.4	7.18–7.59m	3.89ddd
	2030					7.67–8.13m	4.77ddd
<b>1b</b>	2036	610	54.93d	45.14d	68.6	7.28–7.56m	2.65m
	2103					7.64–7.96m	3.08m
<b>1c</b>	2033	610	56.62d	52.33d	65.8	7.29–7.56m	2.05m
	2101					7.63–7.81m	2.58m
<b>1d</b>	2033	609	52.34d	43.81d	50.2	7.37–7.53m	2.45m
	2102					7.71–7.88m	2.10m
<b>2a</b>	2028	599	61.52d	49.22d	70.9	7.10–7.56m	3.63dd
	2096					7.67–7.88m	
<b>2b</b>	2034	609	54.31d	45.13d	65.3	7.32–7.54m	2.65m
	2102					7.62–7.77m	3.08m
<b>2c</b>	2032	610	56.44d	52.34d	51.2	7.29–7.43m	1.93m
	2100					7.58–7.84m	2.58m
<b>2d</b>	2033	610	52.53d	44.0d	78.1	7.24–7.44m	2.56m
	2100					7.58–7.87m	2.20m

Free ligands (**a–d**). IR:  $\nu(\text{PS})$ : 606(**a**), 614(**b**), 612(**c**), 614(**d**);  $^{31}\text{P}$  NMR:  $\delta_{\text{P}}$  and  $\delta_{\text{P=S}}$ :  $-22.7$ ,  $45.2\text{d}$  ( $^2J_{\text{P-P}} = 90$  Hz)(**a**);  $-16.8$ ,  $42.6\text{d}$  ( $^3J_{\text{P-P}} = 17$  Hz)(**b**);  $-13.2$ ,  $47.1\text{d}$  ( $^4J_{\text{P-P}} = 167$  Hz)(**c**);  $-15.5$ ,  $43.1\text{d}$  ( $^5J_{\text{P-P}} = 25$  Hz)(**d**);  $^1\text{H}$  NMR:  $-(\text{CH}_2)_n-$ : 3.35dd(**a**); 2.62m, 2.90m(**b**); 2.52m, 1.35m(**c**); 2.40m, 2.00m(**d**).

d, doublet; m, multiplet; dd, doublet of doublet; ddd, doublet of double doublet.

the  $^{31}\text{P}$  NMR spectra of **1b–d** also exhibit two doublet resonances, one relatively low field at  $\delta$  52.34–56.62 ppm for the  $\text{P}_A$  atom and other high field at  $\delta$  43.81–52.33 ppm for the  $\text{P}_B$  atom. The observed large down field shift of about 67–72 ppm compared to the free ligands for the  $\text{P}_A$  phosphorus atom supports the monodentate nature of the ligands. The  $^{13}\text{C}$  NMR spectra of the complexes **1b–d** consist of all characteristic signals for carbonyl carbons, methylene carbons and phenylic carbons (Table 4). The complexes **1b–d** have equivalent CO ligands, which is corroborated by the appearance of a single peak for the two carbonyl carbons.

Further reaction of **1a–d** with one molar equivalent of the ligands **a–d** produces hexa-coordinated  $\eta^1\text{-P}$  bonded complexes  $[\text{Ru}(\text{CO})_2\text{I}_2(\text{P}\sim\text{S})_2]$  (**2a–d**) (Scheme 1). The same complexes can also be synthesized by treat-

Table 4  
 $^{13}\text{C}$  NMR data of the complexes ( $\delta$  in ppm)

Complex	CO	$-(\text{CH}_2)_n-$	$\text{C}_6\text{H}_5$
<b>1a</b>	185.9	34.0dd	128.61–135.25m
<b>1b</b>	186.6	24.34m	128.10–134.0m
<b>1c</b>	186.7	33.23m	128.94–132.23m
<b>1d</b>	186.4	32.72m	128.61–131.14m
<b>2a</b>	186.7	34.51dd	128.63–133.15m
<b>2b</b>	186.6	26.40m	129.0–132.22m
<b>2c</b>	186.4	33.35m	128.91–133.42m
<b>2d</b>	186.7	33.11m	128.64–133.83m

ing  $[\text{Ru}(\text{CO})_2\text{I}_2]_n$  directly with two molar equivalent of the ligands **a–d**. The  $\nu(\text{PS})$  band of the complexes **2a–d** appears almost in the same position as that of the corresponding free ligands suggesting the coordination with the metal center through the tertiary phosphorus atom. As for the complexes **1a–d**, the position and nature of

the  $\nu(\text{CO})$  bands (Table 3) are consistent with the *cis* disposition of the two terminal carbonyl groups. The  $^1\text{H}$  NMR spectra of **2a–d** consist of two characteristics multiplet resonances for phenyl ring protons in the ranges  $\delta$  7.10–7.56 and  $\delta$  7.58–7.88 ppm along with usual signals for methylene protons. The  $^{31}\text{P}$  NMR data of the complexes are in accord with the  $\eta^1\text{-P}$  coordination mode of the ligands. Two distinct doublet resonances are observed at  $\delta$  52.53–61.52 and  $\delta$  44.0–52.34 ppm for tertiary phosphorus and pentavalent phosphorus atom, respectively, which are consistent with equivalent P atoms in the complexes. The low  $J_{\text{P-P}}$  values indicate that the two coordinating phosphorus atoms ( $\text{P}_\text{A}$  and  $\text{P}_\text{B}$ ) are mutually *cis* to one another. The  $^{13}\text{C}$  spectra show only one singlet at around  $\delta$  186 ppm for the two carbonyl carbons, which accounts for the equivalency of the CO groups in the complexes. The characteristics signals for methylene and phenylic carbons are also identified in the complexes. Thus, on the basis of IR and NMR data, the structures of the complexes **2a–d** are proposed to be *cis, cis, trans* with iodide ligands *trans*. In *trans* disposition to each other, the iodide ligands can form strong bond to Ru because of their electronegative and relatively poor  $\sigma$ -donor characters [26].

Careful spectroscopic investigations reveal that the complexes **1b–d** exhibit one additional broad (weak) IR bands at around  $590\text{ cm}^{-1}$  which are about  $25\text{ cm}^{-1}$  lower than the corresponding free  $\nu(\text{PS})$  ligand bands suggesting the formation of metal–sulfur bonds. Therefore, possible equilibrium may exist between mono and bimetallic complexes (PS bridging) as shown in the Scheme 1. In case of complexes **2a–d**, no spectroscopic evidence is found for the formation of such bimetallic complexes.

In order to obtain unambiguous characterization of the complexes **1a–d** and **2a–d**, an X-ray diffraction study was undertaken. Fortunately, a good crystal suitable for X-ray analysis was developed for the complex **1a**,  $[\text{Ru}(\text{CO})_2\text{I}_2(\text{P}\eta\text{S})]$ . The IR and NMR data are well agreed with this molecular structure of the complex. Table 5 lists the relevant bond lengths and bond angles. Fig. 1 shows the arrangements and numbering of atoms in the crystal. The crystal contains a metal occupying the center of a slightly distorted octahedron with two *cis* carbonyl, two *cis* iodides and one *bis* phosphine sulfide ligand bonding via P and S atom to the metal completing the coordination sphere. This atomic arrangements is sterically less hindered and energetically most favoured because the carbon monoxide is a very strongly double bonding ligand and prefers not to be in a *trans* position to another carbon monoxide [27]. The CO is a strong  $\pi$ -acceptor and hence any *trans* ligand competing for electron density from the metal center will weaken the M–CO bond. The *trans* influence of the ligands falls in the sequence  $\text{CO} > \text{P} > \text{I}$ . Thus, the complex containing iodide ligand *trans* to CO group will

Table 5  
Selected bond lengths (Å) and bond angles ( $^\circ$ ) of the complex **1a**

Bond lengths	
Ru–C(27)	1.880(6)
Ru–C(26)	1.903(6)
Ru–P(2)	2.3212(12)
Ru–S(1)	2.4615(13)
Ru–I(2)	2.7451(6)
Ru–I(1)	2.7626(6)
S(1)–P(1)	2.0103(17)
P(1)–C(25)	1.811(4)
P(2)–C(25)	1.835(5)
C(26)–O(26)	1.112(6)
C(27)–O(27)	1.129(6)
Bond angles	
C(27)–Ru–C(26)	93.2(2)
C(27)–Ru–P(2)	96.49(15)
C(26)–Ru–P(2)	93.54(13)
C(27)–Ru–S(1)	86.89(16)
C(26)–Ru–S(1)	175.83(13)
P(2)–Ru–S(1)	90.60(4)
C(27)–Ru–I(2)	175.32(15)
C(26)–Ru–I(2)	90.15(15)
P(2)–Ru–I(2)	86.60(3)
S(1)–Ru–I(2)	89.57(3)
C(27)–Ru–I(1)	86.23(14)
C(26)–Ru–I(1)	90.69(13)
P(2)–Ru–I(1)	174.83(4)
S(1)–Ru–I(1)	85.14(3)
I(2)–Ru–I(1)	90.427(15)
P(1)–Ru–S(1)	105.01(6)
C(25)–Ru(1)–P(2)	107.55(14)

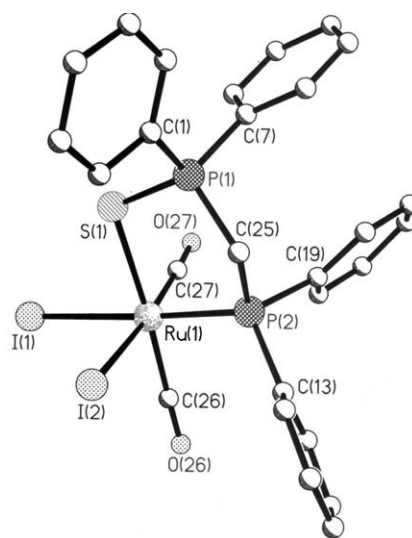


Fig. 1. The structure of  $[\text{Ru}(\text{CO})_2\text{I}_2(\text{Ph}_2\text{PCH}_2\text{P}(\text{S})\text{Ph}_2)]$  (**1a**). Hydrogen atoms are omitted for clarity.

be most stable than isomers with either a P or a CO *trans* to a carbonyl group [28]. The Ru–P bond length is somewhat shorter than the reported complex  $[\text{Ru}(\text{CO})\text{Cl}(\text{P}\eta\text{S})_2]$  [14]. This shortening of the Ru–P bond length is due to the strong  $\pi$ -acceptor property of the two carbonyl groups as a result of which a strong

$d\pi$ – $\pi$  bonding is formed between the Ru and the P atom. The Ru–CO and Ru–S bond lengths are not significantly different from those observed for similar complexes  $[\text{Ru}(\text{CO})_2(\text{BzIPPh}_2)\text{Cl}_2]$  and  $[\eta^6\text{-MeC}_6\text{H}_4\text{-Pr}^i\text{Ru}\{\eta^3\text{-(SPPPh}_2)_2\text{CMe-C,S,S'}\}]\text{PF}_6$  [29,30]. The observed deviation from usual bond angles ( $180^\circ$  and  $90^\circ$ ) of a regular octahedral geometry is probably due to steric requirement to get a most stable structure, where the uncoordinated phenyl rings are oriented away from the plane containing the all bonding groups and atoms to the metal [31]. The deviations of bond angles resemble with the deviations of related complexes involving the same ligands [3,24]. Although, we successfully grew crystals for  $[\text{Ru}(\text{CO})_2\text{I}_2(\text{P}\eta\text{S})]$  (**1a**), no crystal was developed for the same type of complex  $[\text{Ru}(\text{CO})_2\text{Cl}_2(\text{P}\eta\text{S})]$  [14]. The soft Ru metal will prefer to bind with the softest I atom rather than Cl. Moreover, in the absence of the other interaction between the halide and the metal, iodide would be expected to form the strongest bond due to the  $\sigma$ -interaction with the metal. Conversely, we can explain the decarbonylation reaction taking place in the complex  $[\text{Ru}(\text{CO})_2\text{Cl}_2(\text{P}\sim\text{S})_2](\text{P}\sim\text{S} = \eta^1\text{-P-coordinated Ph}_2\text{PCH}_2\text{P(S)Ph}_2)$  to give a new chelate complex  $[\text{Ru}(\text{CO})_2\text{Cl}(\text{P}\eta\text{S})_2]\text{Cl}$ . The molecular structure of this new complex was established by a single crystal X-ray study [14] but, no such decarbonylation was observed in our present complex  $[\text{Ru}(\text{CO})_2\text{I}_2(\text{P}\sim\text{S})_2]$  (**2a**). We have reacted the complex **1a** under vigorous reaction condition with various  $\sigma$ -donor ligands such as  $\text{Ph}_3\text{P}$ ,  $\text{Ph}_3\text{As}$ ,  $\text{Ph}_3\text{Sb}$  and  $\text{Ph}_3\text{PX}$ ; X = O, S, Se in order to investigate the lability of the Ru–S bond in the molecule. Interestingly, these ligands were not able to break the relatively labile metal–sulfur bond as expected.

#### 4. Supplementary material

Supplementary data are available from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK on request. CCDC deposition no. 265528. 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>).

#### Acknowledgments

The authors are grateful to Dr. P.G. Rao, Director, Regional Research Laboratory (CSIR), Jorhat, India, for his kind permission to publish the work. The authors thank Dr. P.C. Borthakur, Head, Material Science Division, RRI, Jorhat, for his encouragement and support.

The Department of Science and Technology (DST), New Delhi is acknowledged for the partial financial grant. The author PC thanks CSIR, New Delhi, for the award of Senior Research Fellowship (SRF).

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