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Carbonyl complexes of ruthenium(II) with unsymmetrical phosphine–phosphinesulfide ligands of the type $Ph_2P(CH_2)_nP(S)Ph_2$, $n = 1–4$

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Abstract

Reaction of $[Ru(CO)_2Cl_2]_n$ with ligands $Ph_2P(CH_2)_nP(S)Ph_2$ ($n = 1$(**a**), 2(**b**), 3(**c**), 4(**d**)) in 1:1 molar ratio produces complex *cis*-$[Ru(CO)_2Cl_2(P\cap S)]$(**1a**) ($P\cap S = \eta^2$-(P, S) coordinated) and *cis*-$[Ru(CO)_2Cl_2(P–S)]$(**1b**–**d**) ($P–S = \eta^1$-(P) coordinated), while 1:2 molar ratio yields complex of the type *cis*-$[Ru(CO)_2Cl_2(P–S)_2]$(**2a**–**d**). The complex **2a** undergoes partial decarbonylation reaction in CH_2Cl_2–hexane solution to give a new chelated complex $[Ru(CO)Cl(P\cap S)_2]Cl$(**2a′**). Abstraction of halide with $AgClO_4$ from the non-chelated complexes **1b**–**d** and **2a**–**d** afford corresponding chelated complexes $[Ru(CO)_2Cl(P\cap S)](ClO_4)$(**3b**–**d**) and $[Ru(CO)_2(P\cap S)_2](ClO_4)_2$(**4a**–**d**). The molecular structure of the complex **2a′** has been determined by single crystal X-ray diffraction. The ruthenium atom is at the centre of slightly distorted octahedral structure having the two phosphorus atoms of the two chelated P, S coordinated ligands at *trans* to each other, one CO group and Cl atom completing the coordination sphere. Other complexes have been characterized by elemental analysis, IR, ^{1}H and ^{31}P {H} NMR spectroscopy.

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1. Introduction

The coordination chemistry of unsymmetrical chelating phosphine–phosphineoxide (P, O) ligands has got considerable interest because of their structural novelty and catalytic applicability [1–5]. Due to the presence of two different types of donor sites in the ligands they are capable of coordinating either as a monodentate (η^1-(P) coordinated) or bidentate chelating (η^2-(P, O) coordinated) fashion depending upon the central metal atom and its environment [3,6]. One more advantage of such ligands is that they contain two non-equivalent phosphorus atoms possessing *cis* coordination donor sites [7,8]. Hence, the complexes of such ligands allow for the direct measurement of phosphorus–phosphorus coupling constant ($^2J_{P–P}$) which is very much important in respect of geometry investigation of the complexes. Literature survey reveals that, phosphine–phosphinesulfide (P, S) ligands have got less attention, despite the chemistry of such ligands is as potentially interesting as that of P, O donors ligands. Though a few platinum metal complexes of such P, S ligands have appeared in literature [3,5,6,9–11] but to the best of our knowledge, only one ruthenium complex, $[(\eta^6\text{-}C_6Me_6)RuCl_2\{\eta^1\text{-}PPh_2CH_2P(S)Ph_2\}]$ has so far been reported [9].

In this paper we report synthesis, spectroscopic characterization including one X-ray crystal structure of a complex and reactivity of some ruthenium(II)

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carbonyl complexes of phosphine–phosphinesulfide ligands with an ultimate aim to use them as catalyst precursor for organic synthesis.

2. Experimental

All the solvents used were distilled under nitrogen prior to use. Carbon and hydrogen analyses were done on a Perkin–Elmer 2400 elemental analyzer. Chloride analyses were performed by standard analytical method [12]. FT-IR spectra of range 4000–400 cm^{-1} and 400–200 cm^{-1} were recorded using Perkin–Elmer 2000 and Perkin–Elmer 883 spectrophotometer, respectively, in KBr disc. NMR data were recorded on a Bruker DPX 300 MHz spectrometer and the ^{1}H and ^{31}P NMR chemical shifts were quoted relative to $SiMe_4$ and 85% H_3PO_4 as internal and external standard, respectively, using $CDCl_3$ and d_6-acetone as solvent. Melting points were determined with a BUCHI B-540 apparatus. $RuCl_3 \cdot 3H_2O$ was purchased from M/S Arrora Matthey Ltd, Kolkata, India. Analytically pure $Ph_2P(CH_2)_nPPh_2$ ($n = 1$–4) and elemental sulfur were purchased from M/S Aldrich, USA and used without further purification. The ligands, $Ph_2P(CH_2)_nP(S)Ph_2$ were prepared by refluxing a solution of $Ph_2P(CH_2)_nPPh_2$ in benzene with one molar equivalent of elemental sulfur for 3 h under nitrogen and purified by chromatographic techniques. The starting complex $[Ru(CO)_2Cl_2]_n$ was prepared by following literature method [13–16].

2.1. Synthesis of metal complexes

2.1.1. $[Ru(CO)_2Cl_2(P\cap S)]$(**1a**) and $[Ru(CO)_2Cl_2(P–S)]$(**1b–d**)

0.0877 mmol of $[Ru(CO)_2Cl_2]_n$ was dissolved in 10 cm^3 methanol and to this 0.0877 mmol of corresponding ligand **a**–**d** in 10 cm^3 dichloromethane was added. The reaction mixture was stirred at room temperature for about 2 h and the solvent was evaporated under vacuum to produce a yellow compound. The compound so obtained was washed with diethyl ether and recrystallized from dichloromethane solution.

2.1.2. $[Ru(CO)_2Cl_2(P–S)_2]$ (**2a–d**)

0.031 mmol of complex **1a**–**d** was dissolved in 10 cm^3 dichloromethane and to this 0.031 mmol of corresponding ligand **a**–**d** in 10 cm^3 dichloromethane was added. A yellow compound was obtained following the same reaction condition used for the complex **1a**–**d**. After washing with diethyl ether the complexes were recrystallized from dichloromethane solution. The complex **2a**–**d** could be synthesized directly by treating 0.0439 mmol of $[Ru(CO)_2Cl_2]_n$ in 10 cm^3 MeOH solution with 0.0877 mmol of ligands **a**–**d** in 10 cm^3 dichloromethane solution.

2.1.3. $[Ru(CO)_2Cl(P\cap S)]ClO_4$ (**3b–d**) and $[Ru(CO)_2(P\cap S)_2](ClO_4)_2$ (**4a–d**)

0.0228 mmol of **1b**–**d** and 0.0114 mmol of **2a**–**d** were dissolved in 10 cm^3 dichloromethane and to each of these 10 cm^3 methanol solution of 0.0228 mmol $AgClO_4$ was added. The reaction mixtures were refluxed under nitrogen for 3 h. The dirty white precipitate of silver chloride (AgCl) was filtered off and the light yellow filtrate was evaporated to dryness under vacuum to get a light yellow solid. The solid compounds were washed with methanol followed by diethyl ether. The complexes were recrystallized from acetone.

Analytical data and physical properties of complexes are shown in Table 1.

2.2. X-ray crystallography

A suitable crystal of the complex **2a′** for X-ray diffraction study was developed from a CH_2Cl_2–hexane solution. The crystal data and structure refinement for the complex are given in Table 2.

3. Results and discussion

Reaction of $[Ru(CO)_2Cl_2]_n$ with equimolar quantity of the ligand **a** gives octahedral six-coordinated complex *cis*-$[Ru(CO)_2Cl_2(P\cap S)]$(**1a**) (Scheme 1). In the complex **1a**, the two terminal carbonyl groups are *cis* to each other as they show two almost equally intense ν(CO) bands at 1994 and 2066 cm^{-1} (Table 3) [17–19]. The ν(PS) band occurs at 576 cm^{-1} which is about 30 cm^{-1} lower than that of the free ligand ($\nu(PS) = 606$ cm^{-1}) indicating chelation via metal sulfur bond formation [3,9]. The presence of only one ν(RuCl) band at ca. 351 cm^{-1} in **1a** indicates two chlorides are mutually *trans* to each other [20,21]. The ^{1}H NMR spectra (Table 3) of **1a** show two multiplet resonances in the range δ 7.12–7.40 and δ 7.62–8.13 ppm attributed to two non-equivalent phenylic protons and a doublet of doublet signal at δ 3.79 ppm for methylene protons. The chelate formation in **1a** is further corroborated by a 0.44 ppm down field shift of the methylene protons compared to the free ligand. The ^{31}P {H} NMR spectra (Table 3) exhibit two distinct doublet resonances at δ 40.9 and 57.8 ppm for tertiary phosphorus (P_1) and pentavalent phosphorus (P_2), respectively [5]. As compared to the free ligand, the P_1 and P_2 atoms show a down field shift of δ 63.6 and 12.6 ppm, respectively, which is in good agreement with the chelate formation in complex **1a** [6,22]. The observed low $^{2}J_{P–P}$ value of 76.3 Hz indicates that phosphorus and sulfur atoms of the ligand coordinated to the metal atom in the complex **1a** are *cis* to one another [20,23]. Thus on the basis of IR and NMR data the most probable structure of **1a** is shown in Figure A.

Table 1
Analytical data and physical properties of complexes

Complex	Yield (%)	Melting point (°C)	Elemental analysis found (Calc.) in %		
			C	H	Cl
1a	93	85 (dec.)	50.21 (50.27)	3.44 (3.41)	10.94 (11.02)
1b	97	206	51.01 (51.03)	3.60 (3.64)	10.76 (10.78)
1c	96	217	51.80 (51.74)	3.84 (3.87)	10.51 (10.56)
1d	96	229	52.50 (52.44)	4.02 (4.08)	10.39 (10.34)
2a	98	90 (dec.)	58.86 (58.82)	4.12 (4.15)	6.65 (6.69)
2b	97	248	59.46 (59.51)	4.38 (4.41)	6.49 (6.52)
2c	97	257	60.13 (60.16)	4.68 (4.66)	6.33 (6.36)
2d	98	248	60.73 (60.78)	4.83 (4.89)	6.24 (6.20)
3b	86	160	46.47 (46.51)	3.29 (3.32)	4.88 (4.91)
3c	89	178	47.28 (47.25)	3.50 (3.53)	4.80 (4.82)
3d	90	181	47.91 (47.96)	3.70 (3.73)	4.71 (4.73)
4a	90	148	52.56 (52.49)	3.68 (3.70)	–
4b	89	153	53.31 (53.25)	3.92 (3.94)	–
4c	86	183	53.94 (53.98)	4.15 (4.18)	–
4d	86	100	54.73 (54.67)	4.36 (4.40)	–

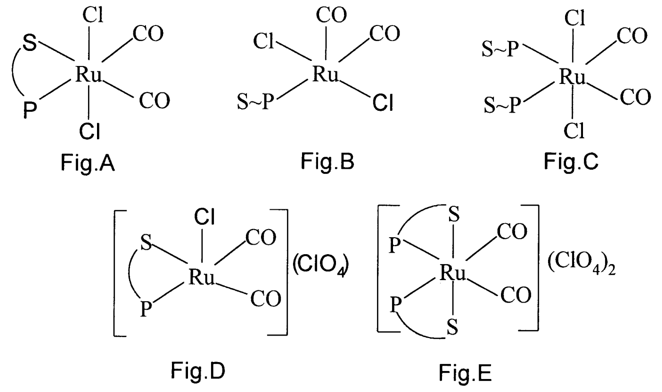


Fig.A Fig.B Fig.C

Fig.D Fig.E

Chart 1.

In contrast to the ligand **a**, the reaction of the ligand **b**–**d** with $[Ru(CO)_2Cl_2]_n$ in one molar equivalent ratio produces 16 election five-coordinated non-chelated complex *cis*-$[Ru(CO)_2Cl_2(P\text{–}S)]$ (**1b**–**d**). Similar type of five-coordinated complexes were also reported earlier [24]. In case of complex **1b**–**d**, η^1-(P) coordination is favoured over η^2-(P, S) coordination mode though the latter could lead to a more favourable 18 electron complex. It may be attributed to the fact that the η^2-(P, S) coordination would lead to six, seven and eight member rings which are unfavourable due to high ring strain [25]. Similar to complex **1a**, two equally intense terminal ν(CO) bands of the complex **1b**–**d** appear in the range 1993–2071 cm^{-1} due to two *cis* carbonyl groups. The ν(PS) band occurs almost in the same position as that of corresponding free ligand **b**–**d** suggesting η^1-(P) coordination mode of the ligand. The observed single ν(RuCl) band in the range 345–352 cm^{-1} is consistent with mutually *trans* disposition of the chlorides. The ^{1}H NMR spectra of this complex show characteristics resonance (Table 3) for phenylic and methylene protons.

Table 2
Crystal data and structure refinement for the complex **2a′**

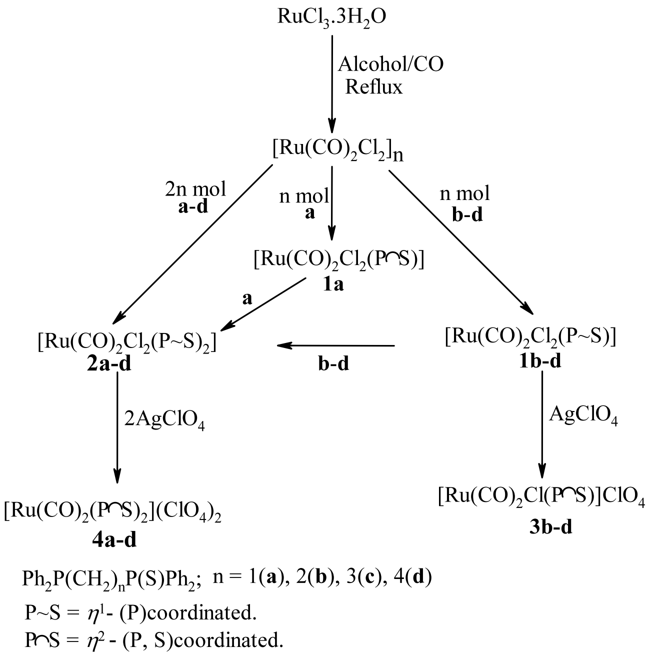
Empirical formula	$C_{51.50}H_{45}Cl_3OP_4RuS_2$
Formula weight	1075.29
Temperature (K)	125(2)
Wavelength (Å)	0.71073
Crystal system	monoclinic
Space group	$P2_1/n$
a (Å)	13.062(6)
b (Å)	20.739(10)
c (Å)	19.689(10)
α (°)	90
β (°)	107.259(8)
γ (°)	90
V (Å^3)	5093(4)
Z	4
D_{calc} (Mg m^{-3})	1.402
Absorption coefficient (mm^{-1})	0.709
$F(0\,0\,0)$	2196
Crystal size (mm)	12 × 1 × 01
θ Range for data collection	2.21–25.08
Index ranges	$-11 \leq h \leq 15$, $-22 \leq k \leq 24$, $-23 \leq l \leq 16$
Reflections collected	21019
Independent reflections	8469 [$R_{int} = 0.1931$]
Completeness to $\theta = 25.08°$	93.6%
Absorption correction	multiscan
Max. and min. transmission	1.00000 and 0.521595
Refinement method	full-matrix least-squares on F^2
Data/restraints/parameters	8469/0/572
Goodness-of-fit on F^2	0.936
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.1111$, $wR_2 = 0.1860$
R indices (all data)	$R_1 = 0.3072$, $wR_2 = 0.2599$
Largest difference peak and hole (e Å^{-3})	0.743 and −0.522

Similar to the complex **1a**, the ^{31}P {H} NMR spectra of **1b**–**d** also show two doublet resonances, one relatively high field at around δ 23–34 ppm for the P$_1$ atom and

Table 3
IR, ^{31}P {H} and ^{1}H values (δ in ppm; $^{2}J_{P-P}$ in Hz) of the complexes

Complex	IR (cm^{-1})			^{31}P {H} NMR			^{1}H NMR	
	ν(CO)	ν(PS)	ν(RuCl)	δ_P	$\delta_{P=S}$	$^{2}J_{P-P}$	C_6H_5	$-(CH_2)_n-$
1a	1994, 2066	576	351	40.9d	57.8d	76.3	7.12–7.40m, 7.62–8.13m	3.79dd
1b	1995, 2066	614	352	23.0d	46.4d	65.6	7.05–7.46m, 7.77–8.47m	2.72m, 3.12m
1c	1993, 2071	612	348	33.8d	49.9d	66.9	7.26–7.47m, 7.73–7.83m	2.65m, 1.65m
1d	1995, 2067	613	345	33.5d	43.3d	44.8	7.34–7.52m, 7.72–7.86m	2.48m, 2.05m
2a	1990, 2067	607	347	24.4d	41.2d	71.9	7.20–7.44m, 7.65–8.03m	3.62dd
2b	1995, 2066	613	360	26.6d	46.5d	67.4	7.06–7.46m, 7.67–8.29m	2.74m, 3.43m
2c	1993, 2070	611	340	37.7d	47.2d	41.3	7.26–7.47m, 7.74–8.04m	2.56m, 1.63m
2d	1993, 2071	614	345	19.9d	43.2d	77.5	7.24–7.46m, 7.72–7.89m	2.45m, 2.03m
3b	1996, 2067	574	346	45.0d	55.7d	41.9	7.49–7.62m, 7.70–7.94m	3.21m, 4.01m
3c	1997, 2065	580	352	44.0d	54.8d	45.7	7.54–7.72m, 7.81–8.10m	3.26m, 2.89m
3d	1992, 2069	580	359	48.7d	57.9d	49.8	7.48–7.59m, 7.73–8.00m	3.19m, 2.99m
4a	1994, 2062	577	–	37.7d	64.5d	46.2	7.27–7.62m, 7.71–8.12m	3.80dd
4b	1992, 2066	575	–	41.6d	52.2d	58.1	7.53–7.66m, 7.68–8.01m	3.30m, 3.96m
4c	1999, 2068	579	–	44.1d	56.2d	54.2	7.45–7.66m, 7.81–7.98m	3.14m, 2.85m
4d	1991, 2063	582	–	47.1d	46.3d	57.2	7.40–7.70m, 7.82–7.95m	3.12m, 2.96m

Free ligand (**a**–**d**): IR: ν(PS): 606(**a**), 614(**b**), 612(**c**), 614(**d**); ^{31}P NMR: δ_P and $\delta_{P=S}$: −22.7, 45.2d (**a**); −16.8, 42.6d(**b**); −13.2, 47.1d(**c**); −15.5, 43.1d(**d**); ^{1}H NMR: $-(CH_2)_n-$: 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.



Scheme 1.

other low field at around δ 43–50 ppm for the P_2 atom. The large down field shift of about 39–49 ppm compared to the free ligand for the P_1 atom is consistent with the monodentate nature of the ligand. Theoretically, the five-coordinated complex **1b**–**d** could have two geometrical arrangements, either a square pyramidal or trigonal bipyramidal structure. Thus, on the basis of spectroscopic evidences (IR and NMR) only, the possibility of the two structures can not be distinguished. However, on steric point of view, the square pyramidal arrangement (Figure B) seems to be better possibility than the trigonal bipyramidal structure [24].

Reaction of **1a**–**d** with one molar equivalent of corresponding ligand **a**–**d** yields six-coordinated octahedral complex $[Ru(CO)_2Cl_2(P{-}S)_2]$(**2a**–**d**) (Scheme 1). The complex **2a**–**d** can also be prepared directly by treating $[Ru(CO)_2Cl_2]_n$ with ligand **a**–**d** in 1:2 molar ratio. The complex **2a**–**d** exhibit ν(PS) band almost in the same position as that of corresponding free ligand (Table 3) suggesting phosphine–phosphinesulfide ligand is coordinated to the metal through the tertiary phosphorus atom only. The position and nature of ν(CO) and ν(RuCl) bands in the IR spectrum (Table 3) is well agreed with the mutual *cis* disposition of the terminal CO groups and *trans* disposition of the chlorides. The ^{1}H NMR spectra of **2a**–**d** show two characteristics multiplet resonances for phenylic protons at around δ 7.06–7.47 and δ 7.65–8.29 ppm in addition to methylene protons resonances. Similar to the complex **1a**–**d**, the ^{31}P {H} NMR spectra of **2a**–**d** show two doublet resonances at around δ 19–38 and δ 41–48 ppm due to P_1 and P_2 atom, respectively. The low $^{2}J_{P-P}$ values (Table 3) suggest that the two tertiary phosphorus atoms of the two ligands are mutually *cis* to one another [20,23]. Thus, Figure C is the most probable structure of complex **2a**–**d**.

Abstraction of halide from non-chelated complex **1b**–**d** and **2a**–**d** by one and two molar equivalents of $AgClO_4$, respectively, lead to chelated complex $[Ru(CO)_2Cl(P\cap S)]ClO_4$ (**3b**–**d**) and $[Ru(CO)_2(P\cap S)_2](ClO_4)_2$ (**4a**–**d**) (Scheme 1). In the complex **3b**–**d** and **4a**–**d**, the ν(PS) band appears in the range 574–582 cm^{-1} which is 29–40 cm^{-1} lower compared to the corresponding non-chelated complex **1b**–**d** and **2a**–**d** indicating η^2-(P, S) coordination mode of the ligand. Similar to other complex, the IR spectra show characteristics bands for *cis* carbonyl groups. In addition, the IR spectra also show two new bands in the range 1087–1099 cm^{-1} and 620–628 cm^{-1} for uncoordinated ClO_4^- anion [9,26,27]. The chelate formation in **3b**–**d** and **4a**–**d** can also be substantiated from the ^{31}P {H} NMR spectra (Table 3) where a large down field shift is observed for both the tertiary and pentavalent phosphorus atoms. The $^2J_{P-P}$ values are consistent with mutual *cis* arrangement of the phosphorus and sulfur atoms in **3b**–**d** and two phosphorus atoms in **4a**–**d**, respectively. The ^1H NMR spectra of the complexes show characteristics resonance for phenylic and methylene protons. Similar to the five-coordinated complex **1b**–**d**, the complex **3b**–**d** would also be expected to have a square pyramidal geometry and the most probable structure is shown in Figure D. Again, similar to the other six coordinated octahedral complexes **1a**, **2a**–**d**, the most probable structure of complex **4a**–**d** is shown in Figure E.

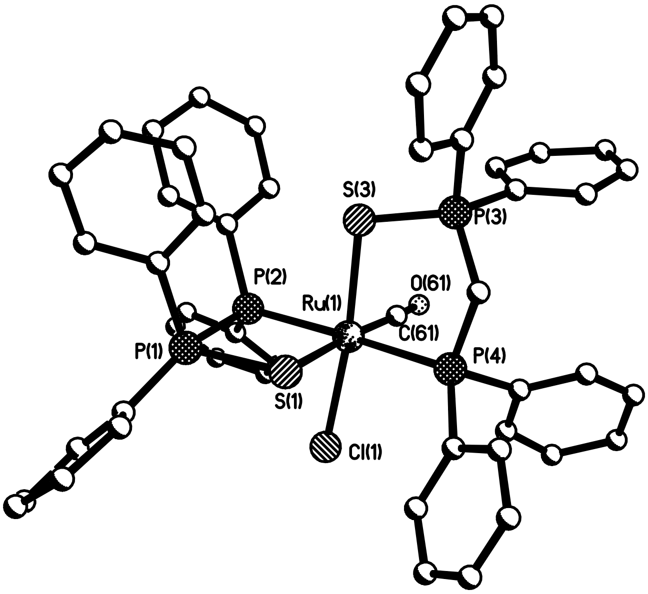
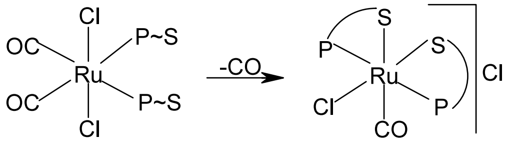


Fig. 1. Crystal structure of $[Ru(CO)Cl\{Ph_2PCH_2P(S)Ph_2\}_2]Cl$(**2a′**).

Table 4
Selected bond lengths (Å) and bond angles (°) of the complex **2a′**

Bond lengths	
Ru(1)–C(61)	1.859(17)
Ru(1)–P(2)	2.341(4)
Ru(1)–P(4)	2.353(4)
Ru(1)–S(3)	2.386(4)
Ru(1)–S(1)	2.451(4)
Ru(1)–Cl(1)	2.403(4)
Bond angles	
C(61)–Ru(1)–P(2)	93.1(5)
C(61)–Ru(1)–P(4)	91.3(5)
P(2)–Ru(1)–P(4)	175.54(16)
C(61)–Ru(1)–S(3)	89.7(6)
P(2)–Ru(1)–S(3)	89.35(14)
P(4)–Ru(1)–S(3)	90.96(14)
C(61)–Ru(1)–Cl(1)	92.6(5)
P(2)–Ru(1)–Cl(1)	85.08(14)
P(4)–Ru(1)–Cl(1)	94.43(14)
S(3)–Ru(1)–Cl(1)	174.06(14)
C(61)–Ru(1)–S(1)	175.9(6)
P(2)–Ru(1)–S(1)	90.68(13)
P(4)–Ru(1)–S(1)	84.86(14)
S(3)–Ru(1)–S(1)	91.73(15)
Cl(1)–Ru(1)–S(1)	86.29(15)

It is interesting that the dicarbonyl complex **2a** on storing in CH_2Cl_2–hexane solution for about 15 days undergoes a partial decarbonylation reaction resulting a monocarbonyl chelated complex $[Ru(CO)Cl(P\cap S)_2]Cl$ (**2a′**) (Scheme 2) as indicated by a single terminal ν(CO) band at 1969 cm^{-1}. Such decarbonylation reaction was also observed in rhodium α-(2-furyl)-*N*-phenylnitrone complex [28]. The two dangling P, S coordinated ligands undergo chelation which is corroborated by the shifting of free ν(PS) band at 606 to 577 cm^{-1}. In order to obtain an unambiguous characterization of the complex **2a′**, an X-ray diffraction study was undertaken. The arrangement of the atoms in the crystal are shown in the Fig. 1 and some important bond angles and bond lengths are listed in Table 4. In the molecule, Ru(II) is situated at the centre of a slightly distorted octahedral coordination environment with two chelated P, S coordinated ligands, one CO group and one Cl atom. Due to the strong *trans* effect, both the phosphorus atoms are mutually *trans* to each other and hence the complex is apparently preferred. The Ru–Cl and Ru–P distances are within the range of values typical for Ru(II) complexes [29,30]. The Ru–S(1) distance is slightly larger than Ru–S(3) and the weakening of the bond in the former results from the stronger *trans* influence of the CO group compared to Cl atom. The bond angles for S(3)–Ru–Cl, P(2)–Ru–P(4) and C(61)–Ru–S(1) are 174.06°, 175.54° and 175.90°, respectively, and are therefore slightly deviated from 180°. This deviation is probably due to steric effect of the bulky phenyl rings. In the five member chelate rings, the angles P(4)–Ru–S(3) and P(2)–Ru–S(1) are 90.96° and 90.68°, respectively, and the slight deviation from 90° is probably due to strain of five member ring [29].



2a **2a′**

Scheme 2.

4. Supplementary material

Supplementary data are available from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK on request. CCDC deposition number 208116. 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 www: http://www.ccdc.cam.ac.uk).

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