Synthesis, characterisation and thermal studies of ruthenium(II) carbonyl complexes of functionalised tripodal phosphine chalcogen donor ligands, $[CH_3C(CH_2P(X)Ph_2)_3]$, where X = Se, S, O

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A B S T R A C T

The polymeric ruthenium(II) carbonyl complex, $[Ru(CO)_2Cl_2]_n$ reacts with 1,1,1-tris-(diphenyl-phosphinomethyl)ethane trichalcogenide ligands, $[CH_3C(CH_2P(X)Ph_2)_3]$, where X = Se(**a**), S(**b**) and O(**c**) in 1:1 (metal:ligand) molar ratio to afford hexa-coordinated complexes of the type η^2-(X,X)-$[Ru(CO)_2Cl_2P_3X_3]$ (**1a–c**). The complexes **1a–c** exhibit two equally intense ν(CO) bands in the range 1979–2060 cm^{-1} indicating *cis*-disposition of the two terminal carbonyl groups. The values of ν(CO) frequencies containing different ligands, in general, follow the order: $P_3O_3 > P_3S_3 > P_3Se_3$ which may be explained in terms of 'Soft–Hard' (Ru(II)–O) and 'Soft–Soft' (Ru(II)–S/Se) interactions. The complexes have been characterized by elemental analyses, mass, ^{1}H, ^{31}P, ^{77}Se and ^{13}C NMR spectroscopy. The thermal stability of the complexes has also been studied.

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1. Introduction

The chemistry of transition metal complexes with the tripodal tridentate phosphine ligand 1,1,1-tris(diphenylphosphinomethyl)ethane (P_3) has been developed in the last two decades [1]. In particular, complexes containing $[M(P_3)]$ or $[M(CO)_x(P_3)]$ ($x = 1$, 2 or 3) fragment (M = Re, Ru, Rh or Ir) are studied extensively because of their reactivity, structural novelty and catalytic activities [2–6]. However, organophosphorus ligands such as tertiary phosphineoxides, sulphides, or selenides bearing O, S, or Se donor atoms have got much attention due to their coordination chemistry, extractive metallurgy, catalytic properties, and structural chemistry [7,8]. Metal complexes of mono- and di-tertiary phosphine chalcogenides particularly oxides, sulfides and selenides are reported [9–14]; but studies with poly-tertiary phosphine chalcogenides are only a few [15–19]. The multidentate tertiary phosphine chalcogen derivatives provide an interesting set of ligands whose coordination chemistry is rich from the structural aspect, bonding interaction and spectroscopic point of view. But, to our knowledge, there is no report of ruthenium(II) carbonyl complexes containing P_3X_3 as

chalcogen donor ligands. In this paper, we report synthesis, spectroscopic characterization and thermal studies of ruthenium(II) carbonyl complexes of the type $[Ru(CO)_2Cl_2P_3X_3]$ (**1**) [X = Se(**a**), S(**b**) and O(**c**)] with an ultimate aim to use them as catalyst for selective organic transformations. The ν(CO) frequencies of the complexes are discussed in terms of the soft/hard acid/base concept.

2. Experimental

All solvents were distilled under N_2 prior to use. Tetrahydrofuran (THF) was dried using standard literature procedure. $RuCl_3 \cdot xH_2O$ was purchased from M/S Arrora Matthey Ltd., Kolkota, India. $[CH_3C(CH_2PPh_2)_3]$, elemental sulfur and selenium were purchased from M/S Aldrich, USA and used without further purification. H_2O_2 was obtained from Ranbaxy, New Delhi, India and estimated before use.

Elemental analyses were performed on a Perkin-Elmer 2400 elemental analyzer. IR spectra (4000–400 cm^{-1}) were recorded on KBr discs in a Perkin-Elmer system 2000 FT-IR spectrophotometer. The ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded at room temperature in CDCl$_3$ solution on a Bruker DPX-300 Spectrometer and chemical shifts are reported relative to SiMe$_4$ and 85% H$_3$PO$_3$ as internal and external standards respectively. Selenium-77 NMR (51.52 MHz) spectra were recorded in CDCl$_3$ solution on a Jeol Delta 270MHz Spectrometer at room temperature. Mass spectra of the complexes

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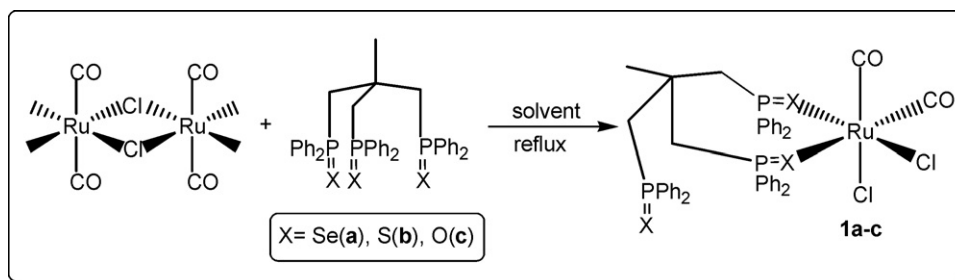
Scheme 1. Syntheses of the complexes **1a–c**.

were recorded on ESQUIRE 3000 Mass Spectrometer. Thermal analyses of the complexes were carried out using a thermal analyzer (TA instrument, Model STD 2960 simultaneous DTA–TGA) under N_2 atmosphere with a heating rate of 10 °C/min.

2.1. Syntheses of the ligands, $[CH_3C(CH_2P(X)Ph_2)_3]$, where (X = Se, S, O)

The ligands $[CH_3C(CH_2P(Se)Ph_2)_3]$(**a**), $[CH_3C(CH_2P(S)Ph_2)_3]$(**b**) and $[CH_3C(CH_2P(O)Ph_2)_3]$(**c**) were synthesized by slightly modifying standard literature methods [16,19–21]. The ligand '**a**' was prepared by refluxing a solution of $[CH_3C(CH_2PPh_2)_3]$ (1 g, 1.6 mmol) in toluene with the appropriate quantity of black selenium (383 mg, 4.85 mmol). After the selenium has dissolved, the solvent was removed under vacuum and the isolated solids were recrystallised from dichloromethane and hexane [21]. The ligand '**b**' was prepared in a similar manner by stirring the solution of $[CH_3C(CH_2PPh_2)_3]$ (1 g, 1.6 mmol) in toluene with a threefold excess elemental sulfur (155 mg, 4.85 mmol) at room temperature [19,20]. The ligand '**c**' was prepared by oxidation of $[CH_3C(CH_2PPh_2)_3]$ (1.5 g, 2.4 mmol) with excess H_2O_2 in acetone [16,19].

2.2. Synthesis of the starting complex, $[Ru(CO)_2Cl_2]_n$

The starting complex $[Ru(CO)_2Cl_2]_n$ was prepared by passing CO through a refluxing solution of $RuCl_3 \cdot 3H_2O$ in ethanol for about 24 h [22–25].

2.3. Synthesis of the complex, $[Ru(CO)_2Cl_2(P_3Se_3)]$ (**1a**)

0.218 mmol (50 mg) of $[Ru(CO)_2Cl_2]_n$ was dissolved in THF (10 cm³), to that 0.218 mmol (188 mg) of ligand **a** in 10 cm³ THF was added dropwise by using a syringe. The reaction mixture was refluxed for 2 h. The solvent was evaporated under reduced pressure to get a solid product which was washed with diethyl ether and finally recrystallised from dichloromethane solution to generate a brown solid compound. Yield: 84%.

2.4. Synthesis of the complex, $[Ru(CO)_2Cl_2(P_3S_3)]$ (**1b**)

$[Ru(CO)_2Cl_2]_n$ (0.439 mmol, 100 mg) was dissolved in methanol (10 cm³) and the ligand '**b**' (0.439 mmol, 317 mg) was dissolved in dichloromethane (10 cm³). Both the solutions were mixed together and refluxed for 3 h. The solvent was removed and the solid residue was washed with diethyl ether. The resulting yellow compound was recrystallised from dichloromethane/hexane to give the complex '**1b**'. Yield: 82%.

2.5. Synthesis of the complex, $[Ru(CO)_2Cl_2(P_3O_3)]$ (**1c**)

The complex '**1c**' was prepared by mixing a solution of 0.218 mmol (50 mg) of $[Ru(CO)_2Cl_2]_n$ in THF (10 cm³) and

0.218 mmol (147 mg) of ligand **c** in dichloromethane. The resulting mixture was refluxed for 5 h and the solvent was removed under reduced pressure to get a solid product, which was washed with diethyl ether and finally recrystallised from dichloromethane solution to generate a greenish yellow solid compound. Yield: 78%.

3. Results and discussion

3.1. Preparative considerations

The polymeric complex $[Ru(CO)_2Cl_2]_n$ reacts with equimolar quantity of the ligands (**a–c**) by cleavage of the chloro bridge to produce hexa-coordinated η^2-X,X bonded complexes $[Ru(CO)_2Cl_2P_3X_3]$ (Scheme 1). All the complexes **1a–c** thus prepared are microcrystalline solids, stable in air and moisture. Elemental analyses of the complexes **1a–c** were determined and the results matched well with the calculated values of molecular composition $[Ru(CO)_2Cl_2P_3X_3]$ (Table 1).

3.2. IR and NMR (^1H, ^{31}P, ^{13}C and ^{77}Se) spectra

The IR spectrum (Table 2) of the complex **1a** shows two equally intense ν(CO) bands in the regions 2044 and 1979 cm⁻¹, indicating the presence of two terminal CO groups *cis* to one another [10,12]. ν(P–Se) bands at around 546, 539 and 533 cm⁻¹ are about 2, 9 and 15 cm⁻¹ lower than that in the corresponding free ligand [ν(P–Se) = 548 cm⁻¹], suggesting two of the three P–Se groups are bonded through chalcogen donors. The $^{31}P\{^1H\}$ NMR spectra of the complex **1a** show two singlets centred at δ = 19.3 and 22.9 ppm (intensity ratio 2:1) for three pentavalent P-atoms respectively, exhibiting an up field shift compared to the free ligand (δ = 23.1). The ^1H NMR spectra (Table 2) of **1a** show three multiplet resonances in the ranges δ 7.07–7.26, δ 7.39–7.64 and δ 7.93–8.2 ppm which is attributable to the three non-equivalent phenylic protons. Each of the methylene protons appear separately as doublet centered at 4.02 and 4.42 ppm due to coupling with one phosphorus atom and the other hydrogen which are matching well with the related complexes of similar type of bidentate ligands reported by Dutta et al.

Table 1
Elemental analyses and mass spectrometric data of ligands and their complexes.

Compounds	Expected molecular weight	Found (cald.) (%)		Mass (m/z)
		C	H	
a	861.69	56.93 (57.10)	4.35 (4.52)	861.5
b	720.69	67.79 (68.26)	5.21 (5.41)	719.8
c	672.69	72.91 (73.13)	5.38 (5.80)	673
1a	1089.69	46.89 (47.35)	3.23 (3.58)	1089.1
1b	948.69	54.12 (54.39)	4.03 (4.11)	949.4
1c	900.69	57.06	4.52	674.1
		(57.29)	(4.33)	695.8

Table 2
Important IR (cm^{-1}), ^{1}H, ^{31}P and ^{77}Se NMR (δ in ppm) values of the ligands and their complexes.

Compounds	IR (cm^{-1})		^{31}P	^{77}Se		^{1}H NMR		
	ν(CO)]	ν(P–X)	P = X	P = Se	J_{P-Se} (Hz)	CH$_3$	CH$_2$	C$_6$H$_5$
a	–	548	23.1(s)	−298(d)	715	0.59(s)	4.02(d)	7.15–7.41(m)
								8.0–8.06 (m)
b	–	625	35.5(s)			0.64(s)	3.8(d)	6.98–7.40(m)
		611						7.97–8.02(m)
c	–	1175	32.3(s)			0.85(s)	3.19(d)	7.27–7.50(m)
								7.65–7.85(m)
1a	1979	546	22.9(s)	−295(d)	710	0.60(s)	4.02(d)	7.07–7.26(m)
	2044	539	19.3(s)	−265(d)	605		4.42(d)	7.39–7.64(m)
		533						7.93–8.2(m)
1b	1984	624	41.3(s)			0.68(s)	3.76(d)	7.03–7.48(m)
	2059	606	35.8(s)				3.92(d)	7.80–7.90(m)
								7.96–8.13(m)
1c	1988	1174	38.2(s)			0.91(s)	3.18(d)	7.15–7.35(m)
	2060	1168	32.7(s)				3.27(d)	7.45–7.61(m)
								7.75–7.86(m)

s = singlet, d = doublet, m = multiplet.

[12] and Gonsalvi et al. [26]. The three methylene protons in the chelate ligand do not seem to be equivalent which may be explained by considering the fact that out of three P–Se donors, two of them have coordinated to the metal center and the remaining one arm is dangling [19]. This fact is well supported by its corresponding IR and ^{31}P{^{1}H} NMR data. In the ^{13}C NMR spectra, only one weak signal for the two carbonyl carbons is appeared as broad singlet at δ 187.1 ppm. The phenyl and other carbons are found in their respective range (Table 3).

Similar to **1a**, the complexes **1b** and **1c** also exhibit two intense ν(CO) bands in the region 2060–1984 cm^{-1} respectively, attributing the presence of two terminal CO groups *cis* to one another. It is observed that the order of appearance of ν(CO) bands in respect of energy is **1a** < **1b** < **1c**, which may be explained in terms of 'Soft–Hard' [Ru(II)(Soft)–O(Hard)] and 'Soft–Soft' [Ru(II)(Soft)–S/Se(Soft)] interactions between the metal atom and the chalcogen donors. 'Se' and 'S' in complexes **1a** and **1b** respectively interact strongly with 'Soft' ruthenium(II) in contrast to 'Hard' oxygen (O) donor in complex **1c**. Because of the 'Soft–Soft' interaction, the electron density increases on the central metal atom which leads to donate more dπ-electrons to the antibonding π^* orbital of the CO [13,27,28] and consequently reduces the CO bond order, which in turn lowers the ν(CO) frequency. The ν(P–X) (X = S, O) bands in the complexes **1b** and **1c** occur at 624, 606 [ν(P–S)] and 1174, 1168 cm^{-1} [ν(P–O)] respectively are lower than their corresponding free ligands [ν(P–S) = 625, 611 cm^{-1} and ν(P–O) = 1175 cm^{-1}]. The appearance of ν(P–X) in **1a–c** at relatively lower stretching values on KBr disk compared to those reported metal complexes [9–13] has prompted us to record the IR spectra in nujol mull for confirmation whether any substitution by bromide (from KBr) has occurred. The results of ν(CO) and ν(P–X) bands

indicated a marginal changes of ±1 cm^{-1} suggesting the halide substitution is very much unlikely. The ^{31}P{^{1}H} NMR spectra of the complexes **1b** and **1c** show two singlets centred at δ = 35.8, 41.3 ppm, and 32.7, 38.2 ppm respectively for three pentavalent P-atoms, which show a downfield shift compared to the free ligands **b** (35.5 ppm) and **c** (32.3 ppm). The intensity ratio of the two singlets from higher value to the lower value is found to be 2:1 in both the complexes (**1b** and **1c**). The occurrence of IR bands at around 546, 624 and 1174 cm^{-1} and their corresponding ^{31}P NMR peak at 22.9, 35.8 and 32.7 ppm in the respective complexes **1a–c** indicate the presence of one dangling P–X (Scheme 1). The ^{1}H NMR spectra (Table 2) of the complexes **1b** and **1c** show the characteristic resonances for the methylene and phenylic protons. Similar to the complex **1a**, the ^{13}C NMR spectra of the complexes **1b** and **1c** also consist of all characteristic signals for carbonyl and other carbons (Table 3).

The ^{77}Se NMR spectra of the complex **1a** exhibit two doublets centered at −295 ppm (J_{P-Se} = 710 Hz) and −265 ppm (J_{P-Se} = 605 Hz) for three P–Se groups which show a downfield shift compared to the free ligand {δ = −298 ppm (d, J_{P-Se} = 715 Hz)}. The significant different chemical shifts as well as the coupling constants of the complex **1a** from that of the free ligand, and the observed peak intensity of **1a** reveal that two of the P–Se groups have undergone chelate formation leaving one arm dangling. Although no such evidence is available for the compounds containing P$_3$S$_3$ and P$_3$O$_3$, the similar ^{31}P {^{1}H} NMR spectra and the infrared spectral evidence [ν(P–X), X = S, O] are sufficient to confirm coordination of S and O in the compounds **1b** and **1c** respectively.

3.3. Electrospray mass spectrometry

The solubility of the complexes **1a–c** was investigated in chloroform and their m/z values were analyzed by considering both positive and negative mode of ion polarity. Poor ionization was apparent for the complex **1c** with [**c**+Na]$^+$ and [**c**+H]$^+$ being the main features in the resulting spectra. Better quality spectra were obtained for the complexes **1a,b** which showed peaks consistent with expected molecular ion peak. A cluster of peaks of low intensity centered at m/z = 1089.1 (**1a**) and 949.4 (**1b**) are assigned to [Ru(CO)$_2$Cl$_2$P$_3$Se$_3$]$^+$ and [Ru(CO)$_2$Cl$_2$P$_3$S$_3$]$^+$ respectively (Table 1).

Table 3
Important ^{13}C NMR data of the ligands and their complexes (δ in ppm).

Compounds	CH$_3$	CH$_2$–P = X	C	C$_6$H$_5$	CO
a	26.1(q)	40.9(dt)	42.9(q)	128.38–132.78(m)	–
b	26.4(q)	41.8(dt)	42.3(q)	128.33–134.23(m)	–
c	29.1(q)	41.1(dt)	39.7(q)	128.57–134.51(m)	–
1a	26.2(q)	41.2(dt)	42.3(q)	128.83–132.30(m)	187.1
1b	25.9(q)	41.9(dt)	41.5(q)	128.92–134.32(m)	186.5
1c	28.7(q)	41.8(dt)	38.8(q)	128.98–134.68(m)	186.2

dt = doublet of triplet, q = quartet.

3.4. Thermal analysis

The thermal behaviour of the new compounds was investigated using simultaneous differential thermoanalysis (DTA) and thermogravimetry (TG) in a nitrogen atmosphere. The complex **1a** decomposes in two steps, the first step observed in the temperature range 210–255 °C with a total mass loss of 5.2% which can be assigned to the removal of two CO groups. Similarly, the complex **1b** also undergoes decomposition by the loss of two CO groups in the temperature range 130–180 °C with a mass loss of 5.8%. These results can be corroborated by a similar type of complexes reported by Soliman et al. [29]. Further decomposition of the complexes **1a** and **1b** proceeds in multiple stages that extend in the temperature ranges at 250–460 °C and 280–520 °C respectively. The observed mass loss notified by TG curve fits in each case perfectly as the loss of the fragmented organic ligand, whereby the corresponding DTA curve shows a strong endothermic effect. The complex **1c**, on the other hand, shows mass loss at the temperature of about 70 °C may be due to the elimination of solvent (THF) molecule from the matrix. On increasing the temperature up to about 300 °C, there is a total mass loss of about 10.0% in the temperature ranges of 100–130 °C and 240–300 °C, which may be due to the removal of moisture and CO groups respectively from the complex moiety. The presence of THF and water molecules in the complex matrix as indicated by TG curve is also partially supported by elemental analysis. On further increasing the temperature, there are at least three stages of mass losses in the range of 300–500 °C corresponding to decomposition of organic ligands from the matrix indicated by three endothermic events in the DTA curve. The observed mass loss may be due to the elimination of molecules like HCl, CO, H_2O, etc. formed from decomposed moieties of the metal complex.

4. Conclusions

The coordination capability and bonding interactions of three functionalized tripodal phosphine chalcogen donors ligands, viz. $[CH_3C(CH_2P(Se)Ph_2)_3]$(**a**), $[CH_3C(CH_2P(S)Ph_2)_3]$(**b**) and $[CH_3C(CH_2P(O)Ph_2)_3]$(**c**) toward $[Ru(CO)_2Cl_2]_n$ were studied. The ligands **a**–**c** favour to generate hexa-coordinated η^2-X,X bonded complexes of the type $[Ru(CO)_2Cl_2(CH_3C(CH_2P-(X)Ph_2)_3)]$ (**1a**–**c**) leaving one arm dangling. 'Soft–Hard' and 'Soft–Soft' interactions between the metal and the chalcogen donors for the complexes **1a**–**c** are found to be operative. Such complexes may find applications as efficient catalysts in organic transformations under considerably higher temperature environment.

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