

Ruthenium carbonyl clusters of diphosphazanes bearing axially chiral moieties^{*,†}

T. S. Venkatakrishnan, Munirathinam Nethaji and Setharampattu S. Krishnamurthy[‡]

Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560 012, India

Reactions of $\text{Ru}_3(\text{CO})_{12}$ with diphosphazane ligands bearing axially chiral moieties, $\text{X}_2\text{PN}(\text{R})\text{PY}_2$ [$\text{R} = \text{Me}$, $\text{X}_2 = \text{Y}_2 = \text{C}_{20}\text{H}_{12}\text{O}_2$ or $\text{C}_{12}\text{H}_8\text{O}_2$; $\text{R} = \text{CHMe}_2$, $\text{X}_2 = \text{C}_{20}\text{H}_{12}\text{O}_2$, $\text{Y} = \text{OC}_6\text{H}_5$, $\text{OC}_6\text{H}_4\text{Me-4}$, $\text{OC}_6\text{H}_4(\text{OMe-4})$, $\text{OC}_6\text{H}_4\text{Bu}^t\text{-4}$ or C_6H_5 ; $\text{R} = \text{CHMe}_2$, $\text{X}_2 = \text{C}_{12}\text{H}_8\text{O}_2$, $\text{Y} = \text{C}_6\text{H}_5$] in the presence of benzophenone ketyl radical give the ruthenium carbonyl clusters, $\text{Ru}_3(\text{CO})_{10}\{\mu\text{-X}_2\text{PN}(\text{R})\text{PY}_2\}$. IR and NMR data for the complexes are reported. The structures of three complexes have been confirmed by single crystal X-ray crystallographic studies.

TRANSITION metal clusters have received a great deal of attention in fundamental research¹ owing to their interesting chemical and structural properties. They find use as catalysts^{2a}, electrocatalysts^{2b}, precursors for semiconductors^{2b,c} and in other technological fields³. Both homo- and hetero-metallic clusters find wide use in catalysis and the topic has been reviewed recently^{2a}. Though much progress has been made in the area of catalysis by metal clusters^{2a}, cluster degradation remains a major impediment in identifying the actual catalytic species and in understanding the mechanism of such catalysed reactions. Use of anchoring ligands has been the most valuable method to avoid such cluster degradation. In this respect, edge-bridging ligands of the type L-X-L (where L contains a group 14, 15 or 16 donor atom and X (C, N or O))^{2a} are used extensively to form five-membered rings, $\text{M}_2\text{L}_2\text{X}$, to bring the metal atoms in close proximity and also to enhance the stability of metal clusters.

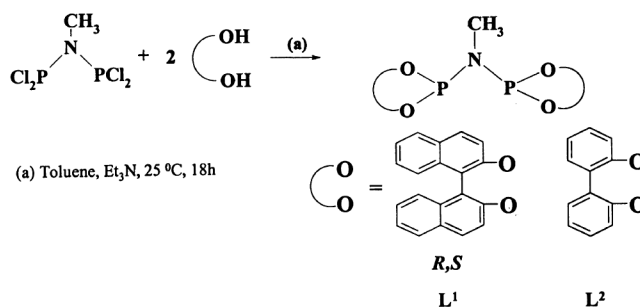
There are several reports on the reactivity of group-8 transition metal carbonyls (Fe, Ru, Os) towards diphosphinoalkanes, $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ ($n = 1$ (dppm)^{4,5a}, $n = 2$ (dppe)⁵) and their dichalcogenides $\text{Ph}_2\text{P}(\text{E})(\text{CH}_2)_n\text{P}(\text{E})\text{Ph}_2$ ($n = 1, 2$)⁶ to give tri or tetranuclear clusters in which the diphosphine adopts a *bridging* mode of coordination. The reactions of $\text{Ru}_3(\text{CO})_{12}$ with achiral P-N-P-type ligands⁷ such as $\text{X}_2\text{PN}(\text{R})\text{PY}_2$ have been investigated extensively by the research groups of Haines^{8a}, and Rosales-Hoz^{8b}. Recently, we reported the reactions of $\text{Ru}_3(\text{CO})_{12}$ with chiral and achiral diphosphazane monosulphides and iso-

lated the sulphur-monocapped clusters, $\text{Ru}_3(\text{CO})_7(\mu_3\text{-S})\{\kappa^2\text{-Ph}_2\text{PN}(\text{R})\text{PPh}_2\}$, in which the diphosphazane adopts a *chelating* mode of coordination⁹. In continuation of our interest in the organometallic chemistry of chiral diphosphazane ligands¹⁰, we report here the results of our studies on the radical-initiated substitution reactions of $\text{Ru}_3(\text{CO})_{12}$ by diphosphazane ligands bearing axially chiral moieties.

Results and discussion

Synthesis of axially chiral diphosphazane ligands

The symmetrically substituted diphosphazanes $\{(R,R)/(S,S)$ and $(R,S)/(S,R)\}-(\text{C}_{20}\text{H}_{12}\text{O}_2)\text{PN}(\text{Me})\text{P}(\text{O}_2\text{C}_{20}\text{H}_{12})$ (L^1) bearing the axially chiral 1,1'-binaphthylene-2,2'-dioxy moiety is prepared by the treatment of bis(dichlorophosphino) methylamine, $\text{Cl}_2\text{PN}(\text{Me})\text{PCl}_2$ with two equivalents of (*racemic*)-1,1'-binaphthyl-2,2'-diol in the presence of triethylamine, as shown in Scheme 1. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the reaction mixture shows two singlets at 143.4 and 144.0 ppm, revealing the presence of a mixture of two diastereomers in the ratio 1 : 2.7. The assignment of the two peaks in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum to the individual diastereomers has been made by synthesizing the optically pure diphosphazane ligand (R,R) -1 or (S,S) -1 by starting from optically pure (*R* or *S*)-1,1'-binaphthyl-2,2'-diol. The addition of the optically pure diphosphazane ligand (R,R) -1 to an NMR sample of the diastereomeric mixture obtained initially, $\{(R,R)/(S,S)$ and $(R,S)/(S,R)\}-(\text{C}_{20}\text{H}_{12}\text{O}_2)\text{PN}(\text{Me})\text{P}(\text{O}_2\text{C}_{20}\text{H}_{12})$ (L^1), enhances the intensity of the singlet at 143.4 ppm indicating that this signal arises from the *racemic*-pair $(R,R)/(S,S)$ -1 and



Scheme 1.

*Dedicated to Prof. S. Ramaseshan on his 80th birthday.

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[‡]For correspondence. (e-mail: sskrish@ipc.iisc.ernet.in)

the other singlet at 144.0 ppm is due to the *meso*-pair, (*R,S*)/(*S,R*)-1. Similarly, the two triplets observed in the ^1H NMR (C_6D_6) spectrum centred at 2.16 and 2.07 ppm for the methyl protons attached to the nitrogen are assigned to the *meso*- and *racemic*-pair respectively. An analogous reaction of 2,2'-bisphenol with bis(dichlorophosphino) methylamine gives L^2 in good yields. The new ligands L^1 and L^2 have been characterized by elemental analysis, melting point, optical rotation (for L^1) and NMR (^1H and ^{31}P) spectroscopy (Tables 1 and 2). The unsymmetrically substituted ligands (L^3 – L^6)¹¹ and (L^7 , L^8)¹² were prepared according to reported procedures.

Reactivity of $\text{Ru}_3(\text{CO})_{12}$ towards diphosphazanes L^1 – L^8

The reaction of $\text{Ru}_3(\text{CO})_{12}$ with diphosphazanes (L^1 – L^8) in THF at 25°C in the presence of benzophenone-ketyl

radical^{5a,8b} (Bruce catalyst) leads to the substitution of two carbon monoxide ligands to give complexes **1**–**8** (Scheme 2) in good yields (Table 1). Complexes **3** and **6** can also be obtained from the reaction of $\text{Ru}_3(\text{CO})_{10}(\text{NCMe})_2$ (ref. 13) with L^3 and L^6 in comparable yields. These complexes have been characterized by elemental analyses, NMR (^1H , ^{31}P) and IR spectroscopic techniques (see Tables 1

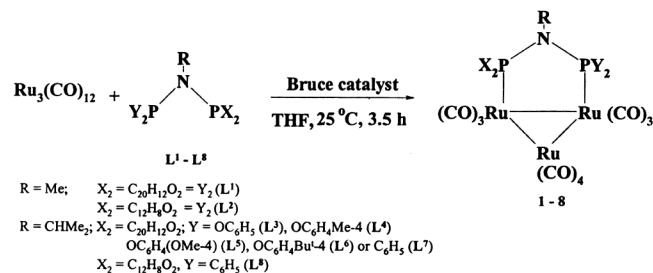


Table 1. Yield, melting point, elemental analysis, ν_{co} (complexes) and optical rotation data for compounds synthesized in the present study

Compound	Yield (%)	Melting point (°C)	Elemental analysis ^a			IR data ^b ν_{co} (cm ⁻¹)	$[\alpha]_{\text{D}}^{25}$ (<i>c</i> = 1, CHCl_3)
			C (%)	H (%)	N (%)		
L ¹	72	195	74.7(74.7)	4.8(4.1)	1.9(2.1)	–	– 95.0 for (<i>R,R</i>) + 200.0 for (<i>S,S</i>)
L ²	70	163	65.2(65.4)	3.8(4.1)	2.5(3.1)	–	–
1	52	201	49.0(49.3)	1.9(2.2)	0.9(1.1)	2089(m), 2030(s), 2008(s), 1988(m)	– 43.0 for (<i>R,R</i>) + 29.0 for (<i>S,S</i>)
2	55	173 (dec.)	39.8(39.6)	1.8(2.0)	0.4(1.3)	2088(m), 2029(vs), 2007(m,sh), 1979(s)	–
3	47	162	45.6(46.1)	2.9(2.5)	0.56(1.2)	2085(vs), 2025(s), 1999(m)	– 114.0 for (<i>R</i>) + 18.0 for (<i>S</i>)
4	48	136 (dec.)	46.8(47.0)	3.1(2.8)	1.1 (1.2)	2088(m), 2025(vs), 2001(vs), 1982(s,sh)	–
5	52	131	44.9(45.8)	2.4(2.7)	0.7(1.1)	2089(m), 2025(vs), 2002(vs), 1985(s,sh)	–
6	56	157 (dec.)	49.8(49.5)	3.8(3.5)	0.7(1.1)	2088(s), 2025(s), 2002(m), 1983(s,sh)	– 92.0 for (<i>R</i>) + 81.0 for (<i>S</i>)
7	40	–	–	–	–	2083(vs), 2047(s), 2007(m), 1998(m)	–
8	40	–	–	–	–	2089(m), 2025(s), 2007(m), 1998(m)	–

^aCalculated values are in paranthesis, ^bm – medium, s – strong, sh – shoulder, vs – very strong.

Table 2. ^1H and ^{31}P NMR data^a for the ligands L^1 and L^2 and ruthenium carbonyl clusters **1**–**8**

Complex	$^{31}\text{P}\{^1\text{H}\}$		$\Delta\delta^b$		CH-CHMe_2	CH_3
	δP_A	δP_X	P_A	P_X		
L ^{1c}	144.0(s) ^d 143.4(s) ^e	–	–	–	–	2.16(t) ^{d,f} 2.07(t) ^{e,g}
L ²	143.6(s)	–	–	–	–	2.40(t)
1	150.0(s)	–	6.6	–	–	1.86(t) ^h
2	149.1(s)	–	5.5	–	–	2.40(t) ^h
3	154.6(d)	146.3(d)	– 1.8	10.1	127.0	1.43, 1.22(d) ^h
4 ⁱ	155.3(d)	147.4(d)	– 3.1	10.2	124.3	1.40, 1.20(d) ^h
5 ^j	155.3(d)	150.0(d)	– 0.4	11.7	124.5	1.40, 1.21(d) ^h
6 ^k	154.7(d)	146.9(d)	– 2.9	9.6	126.7	1.21, 0.88(d) ^h
7	163.5(d)	79.1(d)	15.2	50.8	84.3	1.21(d) ^h
8	161.3(d)	79.7(d)	12.7	51.8	86.5	0.77(d) ^h

^aRecorded in CDCl_3 ; ^b $\Delta\delta = \delta$ (complex) – δ (free ligand); ^c ^1H NMR was recorded in C_6D_6 ; ^d(*R,S/S,R*); ^e(*R,R/S,S*); ^f $^3J_{\text{P-H}} = 3.2$ Hz; ^g $^3J_{\text{P-H}} = 2.9$ Hz; ^h $^3J_{\text{P-H}} = 7.0$ Hz; ⁱ2.43, 2.37 (s, *Me-C}_6\text{H}_4\text{Me-4}*); ^j3.87, 3.82 (s, *Me-C}_6\text{H}_4\text{(OMe-4)}*); ^k1.39, 1.34(s, *Me-CMe}_3*).

and 2). The infrared spectra of these complexes show absorption bands in the region 2089–1979 cm^{-1} , indicating that the carbonyls are bound to the ruthenium centre in a terminal fashion. The solid-state structures of complexes 1–3 have been established by single-crystal X-ray crystallographic studies which confirm that the diphosphazane adopts a bridging mode of coordination, and all the carbonyls are bound in a terminal fashion (see below). Complexes 7 and 8 are not stable in common organic solvents for prolonged periods. Attempts to crystallize them resulted only in decomposed material. Hence, satisfactory elemental analysis could not be obtained for these complexes.

The reaction of $\text{Ru}_3(\text{CO})_{12}$ with the diphosphazane $\text{Ph}_2\text{PN}(\text{CHMe}_2)\text{PPh}_2$ (ref. 14) (in which the phosphorus centres have less π -acceptor character compared to $\text{L}^1\text{--L}^6$) gives a mixture of products [$\delta_{\text{P}} = 85.4$ ($\Delta\delta = +36.6$) and 75.8 ppm ($\Delta\delta = +27.0$)], while an analogous reaction with the chiral diphosphazane $\text{Ph}_2\text{PN}\{(S)\text{--}^*\text{CHMePh}\}\text{PPh}_2$ (ref. 10d) gives a single product [$\delta_{\text{P}} = 78.1$ ppm ($\Delta\delta = +25.9$)]. Attempts to isolate these products in pure form were unsuccessful either by chromatography or by fractional crystallization as the products degraded rapidly. However, it may be noted that the phosphorus chemical shifts are close to those observed for $\text{Ru}_3(\text{CO})_{10}\{\mu\text{--Ph}_2\text{PN}(\text{H})\text{PPh}_2\}$ [$\delta_{\text{P}} = 65.6(\text{s})$ ($\Delta\delta = +22.6$)]^{8b}, $\text{Ru}_3(\text{CO})_{10}\{\mu\text{--Ph}_2\text{PN}(\text{Et})\text{PPh}_2\}$ [$\delta_{\text{P}} = 84.1(\text{s})$ ($\Delta\delta = +22.7$)]^{8a} and $\text{Ru}_4(\mu_4\text{--E})_2(\mu\text{--CO})(\text{CO})_8(\mu\text{--Ph}_2\text{PN}(\text{H})\text{PPh}_2)$ [$E = \text{S}$, $\delta_{\text{P}} = 71.6(\text{s})$ ($\Delta\delta = +28.6$); $E = \text{Se}$, $\delta_{\text{P}} = 67.3(\text{s})$ ($\Delta\delta = +24.3$)]¹⁵ in which the diphosphazane adopts a bridging mode of coordination.

NMR spectroscopic data of complexes 1–8

The NMR data for the complexes 1–8 are listed in Table 2. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of complexes 1 and 2 display a singlet at 150.0 and 149.1 ppm respectively (shifted downfield compared to the free ligand), while complexes 3–8 display an AX pattern. The phosphorus nuclei carrying the aryloxy substituents in complexes 3–6 are downfield shifted by ~ 10 ppm relative to the free ligand, whereas the phosphorus attached to the $(\text{C}_{20}\text{H}_{12}\text{O}_2)$ moiety resonates upfield ($\Delta\delta = -0.4$ to -3.1 ppm) relative to the free ligand. This result indicates a greater degree of metal-to-phosphorus π -back bonding in the $(\text{C}_{20}\text{H}_{12}\text{O}_2)$ -bound phosphorus, resulting in its shielding. In complexes 7 and 8, the two phosphorus atoms are both electronically and sterically different. The PPh_2 phosphorus resonates at ~ 79 ppm, while the phosphorus bound to the electron-withdrawing aryloxy substituent resonates much downfield at ~ 161 ppm. The PPh_2 phosphorus in complexes 7 and 8 is significantly downfield shifted by ~ 50 ppm, while the aryloxy phosphorus is downfield shifted to a relatively smaller extent (12.7–15.2 ppm). These trends in $\Delta\delta$ values are in line with the correlation of $\Delta\delta$ and π -acceptor character of the phosphorus nucleus reported

previously for several transition-metal complexes of P–N–P ligands^{7,16}. The ^1H NMR spectra of complexes 1 and 2 display a triplet at 1.86 and 2.40 ppm, respectively ($^3J_{\text{P--H}} = 7.0$ Hz) for the *N*-methyl protons. The methine proton of the isopropyl group gives rise to a multiplet at ~ 3.75 ppm for complexes 3–6; this signal is observed at ~ 3.45 ppm for complexes 7 and 8. The diastereotopic methyl protons of the isopropyl group give rise to two doublets at 1.43–0.77 ppm ($^3J_{\text{P--H}} = 7.0$ Hz).

Structure of complexes (S,S)-1, 2 and 3

The molecular structures of the three complexes (shown in Figures 1–3) reveal an isosceles triangle of three ruthenium atoms with a bridging diphosphazane in the equatorial plane. The three ruthenium centres are coordinatively saturated and formally conform to 18-electron rule. The coordination geometry around the ruthenium centres can be regarded as distorted octahedral. Selected bond distances and angles are listed in Table 3. Out of the three Ru–Ru–Ru angles, two are close to 60° and the third is slightly smaller ($58.6\text{--}59.0^\circ$). The two ruthenium atoms bridged by the diphosphazane are closer to each other [2.803, 2.818 and 2.793 Å for complexes 1–3, respectively] than to the other ruthenium centres [2.86 Å in 1 and 2, and 2.84 Å in 3]. Such a shortening of the Ru1–Ru2 bond distance is due to the short bite angle of the diphosphazane ligand ($117.7\text{--}119.0^\circ$), which brings the two ruthenium centres close to each other. The Ru–Ru bond distance in the unsymmetrically substituted cluster 3 is shorter (0.02 Å) than the symmetrically substituted clusters 1 and 2. Such a pattern in the Ru–Ru bond distances is observed in similar type of clusters bearing other bidentate phosphorus ligands^{8,17}. The Ru–Ru distances in

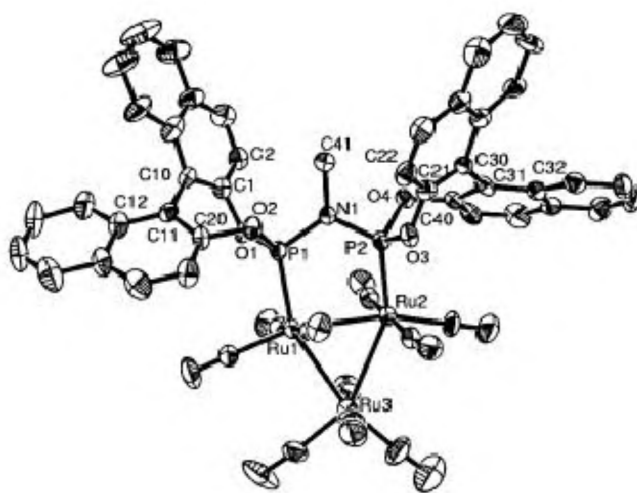


Figure 1. A view (ORTEP, thermal ellipsoids are at 30% probability) of the molecular structure of $[\text{Ru}_3(\text{CO})_{10}\{\mu\text{--}(S,S)\text{--}((\text{C}_{20}\text{H}_{12}\text{O}_2)\text{PN}(\text{Me})\text{P}(\text{O}_2\text{C}_{20}\text{H}_{12}))\}]\text{((S,S)-1)}$ with atomic labelling scheme. Hydrogen atoms have been omitted for clarity.

1–3 are 0.06–0.07 Å longer than in the triruthenium *nido* and tetraruthenium *closo* clusters bearing a bridging diphosphazane and two bridging chalcogenide atoms¹⁵. The average Ru–P bond distances are almost similar in the three complexes (see Table 3), but they are shorter than those observed in *dppa* (~0.06 Å)^{8b}, *dppm*¹⁷ and *dppe*^{5a} analogues (2.30–2.33 Å). These observations also indicate the greater π -accepting nature of the phosphorus centres in the ligands L^1 – L^3 . The torsion angles about the

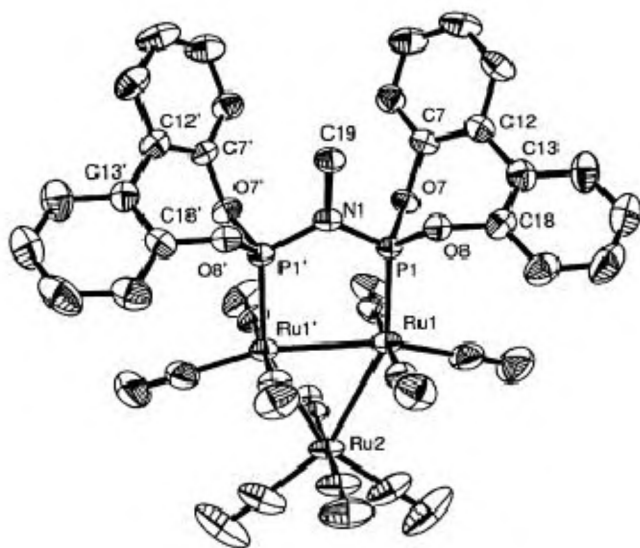


Figure 2. A view (ORTEP, thermal ellipsoids are at 30% probability) of the molecular structure of $[\text{Ru}_3(\text{CO})_{10}\{\mu\text{-}((\text{C}_{12}\text{H}_8\text{O}_2)\text{PN}(\text{Me})\text{P}(\text{O}_2\text{C}_{12}\text{H}_8))\}]$ (**2**) with atomic labelling scheme. Hydrogen atoms and water molecule in the lattice have been omitted for clarity.

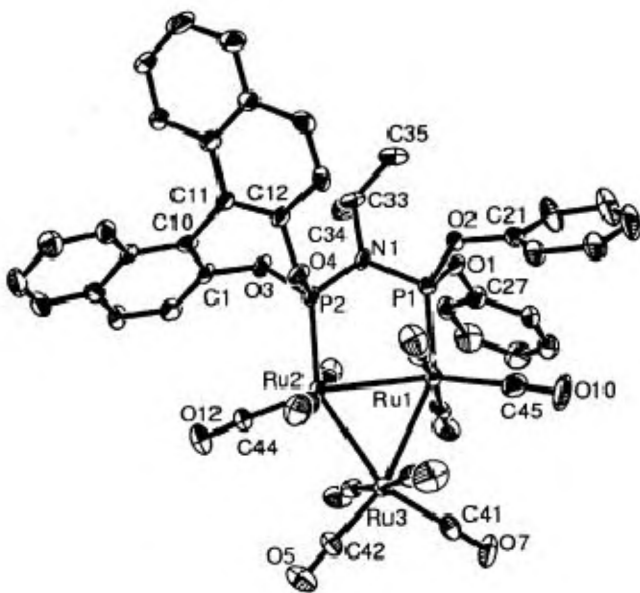


Figure 3. A view (ORTEP, thermal ellipsoids are at 30% probability) of the molecular structure of $[\text{Ru}_3(\text{CO})_{10}\{\mu\text{-}((\text{C}_{20}\text{H}_{12}\text{O}_2)\text{PN}(\text{CHMe}_2)\text{P}(\text{OC}_6\text{H}_5)_2)\}]$ (**3**) with atomic labelling scheme. Hydrogen atoms and hexane (0.5 molecule) in the lattice have been omitted for clarity.

C–C bond in the binaphthyl skeletons in **1** are 50.12 and 50.02° respectively, indicating that both the binaphthyl skeletons are of the *same S-configuration* as in the starting ligand. The packing in the crystal lattice is stabilized by intermolecular hydrogen bonding between the oxygen atoms of the carbonyl group and the hydrogen atoms of the aromatic ring; C–H···O contact distances vary from 3.30 to 3.75 Å, 3.42 to 3.78 Å and 3.22 to 3.71, and the C–H···O angles lie in the range 121.0–154.8°, 120.0–162.8° and 120.6–145.3° for clusters **1**, **2** and **3** respectively (see supplementary information).

Summary

Synthesis and structural characterization of a series of tri-ruthenium clusters of bidentate phosphorus ligands based on the P–N–P skeleton and possessing varying steric and electronic environment at the two phosphorus centres have been realized. Steric encumbrance as well as strong π -acceptor nature of phosphorus governs the stability of the clusters. Chiral ruthenium clusters can be readily prepared by the methodology developed in the present study.

Experimental

General

All reactions and manipulations were carried out under an atmosphere of dry nitrogen using standard Schlenk and vacuum-line techniques. The solvents were purified by standard procedures and distilled under nitrogen prior to use. The NMR spectra were recorded in CDCl_3 at

Table 3. Selected bond distance and angles in (*S,S*)-**1**, **2** and **3**

	Complex 1	Complex 2 ^a	Complex 3
Bond distance (Å)			
Ru1–Ru2	2.803(1)	2.818(1)	2.793(1)
Ru1–Ru3	2.851(1)	2.861(1)	2.851(1)
Ru2–Ru3	2.872(1)	2.861(1)	2.837(1)
Ru–P _{ave}	2.247(2)	2.238(1)	2.257(3)
Ru–C(O) _{axial} (ave)	1.944(12)	1.927(6)	1.942(2)
Ru–C(O) _{eq} (ave)	1.911(10)	1.906(7)	1.914(1)
P–O _{ave}	1.617(6)	1.616(3)	1.607(8)
P1–N1	1.687(7)	1.679(2)	1.692(9)
P2–N1	1.668(7)	1.679(2)	1.654(10)
N–C	1.529(11)	1.491(7)	1.563(15)
Bond angles (°)			
Ru2–Ru1–Ru3	61.06(2)	60.49(1)	60.34(3)
Ru1–Ru2–Ru3	60.29(2)	60.49(1)	60.83(3)
Ru1–Ru3–Ru2	58.65(2)	59.02(2)	58.83(3)
P1–Ru1–Ru2	93.65(6)	90.82(3)	92.17(8)
P2–Ru2–Ru1	87.32(6)	90.82(3)	87.59(8)
P1–N1–P2	119.0(4)	118.3(3)	117.7(6)
P1–N1–C	121.5(6)	120.7(1)	121.3(8)
P2–N1–C	119.1(6)	120.7(1)	120.9(7)

^aBecause of symmetry present in **2**, Ru2 is labelled as Ru(1)' and Ru3 is labelled as Ru2; also P2 is labelled as P1'.

298 K using Bruker AMX-400 MHz and Bruker ACF-200 MHz spectrometers. IR spectra were recorded using a Bruker FT-IR spectrometer as thin film on KBr disk. Elemental analyses were carried out using a Perkin-Elmer 2400 CHN analyser. Melting points were recorded in a Buchi B-540 melting point apparatus and were uncorrected. Optical rotation was measured using a JASCO Digital Polarimeter Model DIP-370. 1,1'-Binaphthylene-2,2'-diol was prepared¹⁸ and resolved¹⁹ according to the reported procedures. Bruce catalyst was prepared by known procedure^{5a}. The ligands (*rac*)-(C₂₀H₁₂O₂)PN(CHMe₂)P(OR)₂ (R = C₆H₅, C₆H₄Me-4, C₆H₄(OMe-4), C₆H₄Bu^t-4) (**L**³-**L**⁶)¹¹, (C₂₀H₁₂O₂)PN(CHMe₂)PPh₂ (**L**⁷)¹², (C₁₂H₈O₂)PN(CHMe₂)PPh₂ (**L**⁸)¹² and Ph₂PN(R)PPh₂ (R = (*S*)-*CHMePh (ref. 10d), CHMe₂ (ref. 14)) were prepared by previously reported procedures. (Cl₂P)₂N(Me) was prepared according to Nixon's procedure²⁰. 2,2'-Bisphenol (Aldrich), C₆D₆ (Aldrich), Ru₃(CO)₁₂ (Strem chemicals) were used as such.

Racemic {(*R,R*)/(*S,S*)} and *meso* {(*R,S*)/(*S,R*)} – (C₂₀H₁₂O₂)PN(Me)P(O₂C₂₀H₁₂), **L**¹

A solution of Cl₂PN(Me)PCl₂ (2.23 g, 0.01 mol) in toluene (60 cm³) was added drop-wise to a toluene (60 cm³) solution of (*racemic* or *R* or *S*)-1,1'-binaphthylene-2,2'-diol (5.72 g, 0.02 mol) and Et₃N (8.4 ml, 0.06 mol) at 0°C over a period of 15 min. The reaction mixture was slowly

warmed to 25°C, stirred for 18 h, filtered to remove Et₃N·HCl and the solvent evaporated to dryness to give a colourless, foamy solid. This solid was loaded over a silica gel column and chromatographed (~ 300 cm³ 1 : 1 (v/v) mixture of benzene/hexane (b.p. 60–80°C) was used as eluant) to obtain **L**¹ as a colourless solid after evaporation of the eluant.

(C₁₂H₈O₂)PN(Me)P(O₂C₁₂H₈), **L**²

This ligand was prepared by following the same procedure as described for **L**¹ (see above) by the reaction of Cl₂PN(Me)PCl₂ (2.23 g, 0.01 mol) with 2,2'-bisphenol (3.724 g, 0.02 mol).

General procedure for the synthesis of the clusters
Ru₃(CO)₁₀{μ-L} (**1–8**)

In a double-necked round-bottom flask fitted with an inlet for nitrogen, Ru₃(CO)₁₂ (0.050 g, 0.078 mmol) was dissolved in THF (6 cm³). To this solution a few drops of benzophenone ketyl solution was syringed in until the solution darkened followed by immediate addition of the ligand. The solution was then stirred at 25°C for 3.5 h. Solvent was removed from the reaction mixture under *vacuo*; the residue was dissolved in CH₂Cl₂ (2 cm³) and subjected to preparative-scale thin-layer chromatography over silica-gel using CH₂Cl₂–hexane (b.p. 60–80°C) (1 : 1 v/v) as eluant to isolate the ruthenium clusters **1–8**,

Table 4. Details of X-ray data collection and refinement for complexes **1–3**

	Complex 1	Complex 2	Complex 3
Empirical formula	C ₅₁ H ₂₇ NO ₁₄ P ₂ Ru ₃	C ₃₅ H ₁₉ NO ₁₄ P ₂ Ru ₃ ·H ₂ O	C ₄₅ H ₂₉ NO ₁₄ P ₂ Ru ₃ ·0.5C ₆ H ₁₄
Formula weight	1242.89	1060.68	1215.93
Temperature, K	293(2)	293(2)	293(2)
Crystal system	Tetragonal	Orthorhombic	Triclinic
Space group	P4 ₃ 2 ₁ 2	Cmca	P-1
Unit-cell dimensions	<i>a</i> = <i>b</i> = 13.709(1) Å, <i>c</i> = 58.056(8) Å	<i>a</i> = 17.987(3) Å <i>b</i> = 6.458(3) Å <i>c</i> = 26.115(4) Å	<i>a</i> = 10.919(3) Å, <i>b</i> = 15.242(3) Å, <i>c</i> = 15.555(3) Å, α = 74.79(4), β = 76.98(4), γ = 82.17(4)
Volume, Å ³	10910.1(2)	7731(2)	2425.6
<i>Z</i>	8	8	2
Density (Calcd), mg/mm ³	1.513	1.823	1.665
Absorption coefficient, mm ⁻¹	0.940	1.310	1.055
Max. and min. transmission	0.6766 and 0.6335		
<i>F</i> (000)	4912	4160	1210
Crystal size, mm	0.31 × 0.26 × 0.24	0.45 × 0.43 × 0.15	0.20 × 0.15 × 0.05
θ range for data collection (°)	1.40–28.02	1.85–28.00	1.38–25.03
Index ranges	– 17 ≤ <i>h</i> ≤ 18, – 17 ≤ <i>k</i> ≤ 16, – 76 ≤ <i>l</i> ≤ 76	– 23 ≤ <i>h</i> ≤ 23, – 21 ≤ <i>k</i> ≤ 20, – 32 ≤ <i>l</i> ≤ 33	0 ≤ <i>h</i> ≤ 12, – 17 ≤ <i>k</i> ≤ 18, – 17 ≤ <i>l</i> ≤ 18
Reflections collected	96196	33043	9039
Independent reflections	13107 [<i>R</i> (int) = 0.0470]	4782 [<i>R</i> (int) = 0.0444]	8505 [<i>R</i> (int) = 0.0635]
Completeness to θ (%)	99.6	99.3	99.5
Refinement method	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	13107/0/640	4782/0/304	8505/0/614
Goodness-of-fit on <i>F</i> ²	1.179	1.052	1.016
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> 1 = 0.0673, <i>wR</i> 2 = 0.1906	<i>R</i> 1 = 0.0410, <i>wR</i> 2 = 0.1054	<i>R</i> 1 = 0.0860, <i>wR</i> 2 = 0.2037
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0823, <i>wR</i> 2 = 0.1970	<i>R</i> 1 = 0.0576, <i>wR</i> 2 = 0.1153	<i>R</i> 1 = 0.1500, <i>wR</i> 2 = 0.2473
Absolute structure parameter	0.05 (5)	–	–
Largest difference peak and hole	1.361 and – 0.504 e.Å ⁻³	1.168 and – 0.621 e.Å ⁻³	1.754 and – 1.868 e.Å ⁻³

($R_f = 0.90$). Single crystals of (*S,S*)-**1**, **2** and *rac*-**3** suitable for single-crystal X-ray diffraction were obtained from *n*-pentane, dichloromethane-methanol and dichloromethane-hexane respectively.

X-ray crystallography

The intensity data for complexes **1** and **2** were obtained at room temperature from a Bruker SMART APEX CCD diffractometer equipped with fine focus 1.75 kW sealed tube Mo-K α X-ray source with increasing ω (width of 0.3 deg per frame) at a scan speed of n s/frame ($n = 5$ for complex **1** and $n = 7$ for complex **2**). The SMART software was used for data acquisition and cell refinement, and the SAINT software for data reduction. Lorentzian and polarization corrections were made on the intensity data. An absorption correction (SADABS) was made for complexes **1** and **2** using SADABS program. The intensity data for **3** was collected on an Enraf-Nonius CAD-4 diffractometer (Mo-K α radiation) using a graphite monochromator at room temperature. Cell constants were obtained by least-squares refinement of the setting angles of 25 reflections in the range $16 < 2\theta < 30^\circ$. The intensity data collection was monitored for any variations by three repeatedly measured control reflections. Lorentzian, polarization and absorption corrections were applied to the intensity data. Pertinent crystallographic data for complexes **1–3** are summarized in Table 4. All the structures were solved by direct methods using SHELXS-97 (ref. 21a); least-square refinements were performed by the full-matrix method with SHELXL-97 (ref. 21b). All non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined isotropically.

Supporting information available

Crystallographic data for complexes (*S,S*)-**1**, **2** and **3** have been deposited with the Cambridge Crystallographic Data Center, CCDC Nos 219538, 219539, 219540 for complexes **1**, **2** and **3** respectively.

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