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Ruthenium hydride complexes of chiral and achiral diphosphazane ligands and asymmetric transfer hydrogenation reactions ☆

Thengarai S. Venkatakrishnan, Swadhin K. Mandal, Raghuraman Kannan, Setharampattu S. Krishnamurthy *, Munirathinam Nethaji

Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560012, India

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Dedicated to our colleague M. Raja (Late), whose sudden demise had snatched away from our midst a promising young researcher.

Abstract

The half-sandwhich ruthenium chloro complexes bearing chelated diphosphazane ligands, $[(\eta^5\text{-Cp})RuCl\{\kappa^2\text{-P,P-}(RO)_2PN(Me)\text{-}P(OR)_2\}]$ [R = $C_6H_3Me_2$-2,6] (**1**) and $[(\eta^5\text{-Cp}^*)RuCl\{\kappa^2\text{-P,P-}X_2PN(R)PYY'\}]$ [R = Me, X = Y = Y′ = OC_6H_5 (**2**); R = $CHMe_2$, $X_2 = C_{20}H_{12}O_2$, Y = Y′ = OC_6H_5 (**3**) or $OC_6H_4{}^tBu$-4 (**4**)] have been prepared by the reaction of $CpRu(PPh_3)_2Cl$ with $(RO)_2PN(Me)\text{-}P(OR)_2$ [R = $C_6H_3Me_2$-2,6 (**L**^{1})] or by the reaction of $[Cp^*RuCl_2]_n$ with $X_2PN(R)PYY'$ in the presence of zinc dust. Among the four diastereomers (two enantiomeric pairs) possible for the "chiral at metal" complexes **3** and **4**, only two diastereomers (one enantiomeric pair) are formed in these reactions. The complexes **1**, **2**, **4** and $[(\eta^5\text{-Cp})RuCl\{\kappa^2\text{-P,P-Ph}_2PN((S)\text{-}^*CHMePh)PPhY\}]$ [Y = Ph (**5**) or $N_2C_3HMe_2$-3,5 ($S_CS_PR_{Ru}$)-(**6**)] react with NaOMe to give the corresponding hydride complexes $[(\eta^5\text{-Cp})RuH\{\kappa^2\text{-P,P-}(RO)_2PN(Me)\text{-}P(OR)_2\}]$ (**7**), $[(\eta^5\text{-Cp}^*)RuH\{\kappa^2\text{-P,P′-}X_2PN(R)PY_2\}]$ [R = Me, X = Y = OC_6H_5 (**8**); R = $CHMe_2$, $X_2 = C_{20}H_{12}O_2$, Y = $OC_6H_4{}^tBu$-4 (**9**)] and $[(\eta^5\text{-Cp})RuH\{\kappa^2\text{-P,P-Ph}_2PN((S)\text{-}^*CHMePh)PPhY\}]$[Y = Ph (**10**) or $N_2C_3HMe_2$-3,5 ($S_CS_PR_{Ru}$)-(**11a**) and ($S_CS_PS_{Ru}$)-(**11b**)]. *Only one enantiomeric pair* of the hydride **9** is obtained from the chloro precursor **4** that bears sterically bulky substituents at the phosphorus centers. On the other hand, the optically pure trichiral complex **6** that bears sterically less bulky substituents at the phosphorus gives a mixture of *two diastereomers* (**11a** and **11b**). Protonation of complex **7** using different acids (HX) gives a mixture of $[(\eta^5\text{-Cp})Ru(\eta^2\text{-H}_2)\{\kappa^2\text{-P,P-}(RO)_2PN(Me)P(OR)_2\}]X$ (**12a**) and $[(\eta^5\text{-Cp})Ru(H)_2\{\kappa^2\text{-P,P-}(RO)_2PN(Me)P(OR)_2\}]X$ (**12b**) of which **12a** is the major product independent of the acid used; the dihydrogen nature of **12a** is established by T_1 measurements and also by synthesizing the deuteride analogue **7-D** followed by protonation to obtain the **D–H** isotopomer. Preliminary investigations on asymmetric transfer hydrogenation of 2-acetonaphthone in the presence of a series of chiral diphosphazane ligands show that diphosphazanes in which the phosphorus centers are strong π-acceptor in character and bear sterically bulky substituents impart moderate levels of enantioselectivity. Attempts to identify the hydride intermediate involved in the asymmetric transfer hydrogenation by a model reaction suggests that a complex of the type, $[Ru(H)(Cl)\{\kappa^2\text{-P,P-}X_2PN(R)PY_2\}(solvent)_2]$ could be the active species in this transformation.

Keywords: Diphosphazanes; Half-sandwich complexes; Ruthenium; Hydride complexes; Asymmetric transfer hydrogenation; Catalysis

1. Introduction

The characterization and isolation of coordinatively and electronically unsaturated, highly reactive and therefore short-lived transition metal complexes is an area of considerable interest owing to their importance as key intermediates in various homogeneous catalytic processes such as hydrogenation, hydrosilylation, hydroformylation and

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* Corresponding author. Tel.: +91 80 22932401. Fax: +91 80 23600683/23601552.
E-mail address: sskrish@ipc.iisc.ernet.in (S.S. Krishnamurthy).

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transfer-hydrogenation reactions [1,2]. Among the various catalytic transformations, ruthenium catalyzed asymmetric transfer hydrogenation has evoked considerable interest [2]. Experimental and theoretical studies reveal that the reaction proceeds *via* the formation of a catalytically active metal–hydride species [3–5]. Several research groups have been working on the design of novel ligands for the ruthenium catalyzed transfer hydrogenation of ketones and the chiral variations thereof to achieve high levels of enantioselectivity. A range of transition metal complexes bearing homo- and hetero-donor P–P [6], N–N [6a,7], P–N [8], N–O [9] ligands, terdentate ligands [10] and mixed homo-donor ligands [11] have been reported and their efficiency in transfer hydrogenation investigated. Since the active catalyst or pre-catalyst involves a ruthenium hydride species, the continuing interest could be attributed to the quest to characterize and isolate the hydride intermediates involved in these reactions by fine-tuning the steric and electronic properties of the ancillary ligands. The catalytic species is usually generated *in situ* in the reaction medium from a stable Ru(II) species such as $[RuCl_2(PPh_3)_3]$ or $[RuCl_2(DMSO)_4]$ and the chiral auxiliary.

Recently we reported the synthesis of cyclopentadienyl ruthenium complexes of chiral and achiral diphosphazane ligands [12a]. In continuation of our interest [12a–d] in the organometallic chemistry of diphosphazane ligands [13], we report herein the ruthenium(II) hydride complexes of chiral and achiral diphosphazanes and preliminary investigations on ruthenium catalyzed asymmetric transfer hydrogenation of 2-acetonaphthone in the presence of chiral diphosphazanes.

2. Experimental

2.1. 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 (^1H and $^{31}P\{^1H\}$) were recorded in $CDCl_3$ at 298 K using Bruker ACF-200, Bruker AMX-400 or Bruker Avance-400 spectrometers. 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.

The diphosphazane ligands $X_2PN(R)PY_2$ [R = Me, X = Y = OC_6H_5 (**L**^{2}) [14a]; R = $CHMe_2$, $X_2 = C_{20}H_{12}O_2$, Y = OC_6H_5 (**L**^{3}) or $OC_6H_4{}^tBu$-4 (**L**^{4}) [12b]; X = Y = Ph, R = (*S*)-*CHMePh(**L**^{5}) [14b] or $CHMe_2$ (**L**^{6}) [14c]; R = Me, $X_2 = Y_2$ = (*R*) or (*S*)-$C_{20}H_{12}O_2$ (**L**^{7}) [14d] and R = $CHMe_2$, X_2 = (*R*) or (*S*)-$C_{20}H_{12}O_2$, Y = C_6H_5 (**L**^{8}) [14e]; (S_CR_P)-Ph_2PN((*S*)-*CHMePh)P(Ph)($N_2C_3HMe_2$-3,5) (**L**^{9}) [14b], the complexes $[(\eta^5\text{-Cp})RuCl\{\kappa^2\text{-P,P-}X_2PN((S)\text{-}^*CHMePh)PYY'\}]$ [X = Y = Ph, Y′ = Ph (**5**) or $N_2C_3HMe_2$-3,5 ($S_CS_PR_{Ru}$)-(**6**)] [12a] and the starting materials $[(\eta^5\text{-Cp})Ru(PPh_3)_2Cl]$ [15a] (Cp = cyclopentadienyl), $[RuCl_2(PPh_3)_3]$ [15b] and $[RuCl_2(COD)]_n$ [15c] were prepared according to literature methods. $MeN(PCl_2)_2$ was prepared according to Nixon's procedure [16]. $[Cp^*RuCl_2]_n$ (Cp^* = pentamethyl cyclopentadienyl), CF_3SO_3H, $HBF_4 \cdot Et_2O$, CD_3OD, 2,2′-bipyridine, CF_3SO_3Ag, $P(OPh)_3$ (Aldrich), 2,6-dimethyl phenol (Merck) and $P(OMe)_3$ (local source) were used as received.

Table 1
Yields, melting points and CHN analysis for the compounds synthesized in the present study

Compound	Yield	MP	Elemental analysis[a]		
			C (%)	H (%)	N (%)
L^1	61	152 (d)	69.6 (68.8)	7.2 (6.8)	3.2 (2.4)
1	25	182 (d)	58.4 (58.7)	5.9 (5.7)	2.4 (1.8)
2	30	178 (d)	57.1 (57.2)	5.2 (5.2)	2.1 (1.9)
3	30	180 (d)	62.8 (62.7)	5.0 (5.1)	1.8 (1.6)
4	35	182 (d)	65.5 (65.6)	6.3 (6.3)	1.4 (1.3)
7	45	175 (d)	61.2 (61.4)	6.0 (6.1)	2.1 (1.9)
10	70	–	67.8 (67.7)	5.3 (5.4)	2.2 (2.1)
14	60	130 (d)	68.6 (68.8)	5.2 (5.3)	2.4 (2.5)
18	<10%	190 (d)	57.0 (57.1)	5.2 (5.2)	4.5 (4.7)
19	80	180 (d)	59.6 (59.9)	4.9 (5.0)	1.7 (2.1)
20	80	184 (d)	64.2 (64.3)	4.3 (4.4)	1.5 (1.8)

[a] Calculated values are in parentheses.

The yields, melting points and elemental analyses for the compounds synthesized in the present study are listed in Table 1. The spectroscopic data for the compounds and the results of HPLC studies are presented in Tables 2–4.

2.2. Synthesis of $(RO)_2PN(Me)P(OR)_2$ [R = $C_6H_3Me_2$-2,6] (**L**^{1}) [17]

A benzene (60 cm^3) solution of $Cl_2PN(Me)PCl_2$ (2.33 g, 0.01 mol) was added dropwise to a benzene (60 cm^3) solution of 2,6-dimethylphenol (4.88 g, 0.04 mol) and triethylamine (8.4 cm^3, 0.06 mol) at 0 °C over a period of 15 min. The reaction mixture was stirred at 25 °C for 24 h and heated under reflux for 8 h. The precipitate of $Et_3N \cdot HCl$ was filtered and solvent evaporated from the filtrate in *vacuo* to obtain a light yellow oily residue which was purified by column chromatography using benzene/petrol (1:1 v/v). Evaporation of the eluant yielded the title compound as a colorless oil. The oil was dissolved in dichloromethane–petrol and the solution cooled to 0 °C to obtain a colorless solid. Traces of unreacted phenol adhering to the solid could be removed by triturating the product with petrol. Single crystals of the compound suitable for X-ray diffraction were obtained by slow evaporation of a toluene solution of the compound.

2.3. Synthesis of $[(\eta^5\text{-Cp})RuCl\{\kappa^2\text{-P,P-}(RO)_2PN(Me)P(OR)_2\}]$ [R = $C_6H_3Me_2$-2,6] (**1**)

A 100 cm^3 double necked flask was charged with a mixture of $(\eta^5\text{-Cp})Ru(PPh_3)_2Cl$ (0.200 g, 0.203 mmol) and the ligand **L**^{1} (0.117 g, 0.203 mmol) under nitrogen atmosphere. The mixture was dissolved in benzene (50 cm^3) and the solu-

Table 2
NMR[a] (^{1}H and ^{31}P) data for ligand $\mathbf{L}^1$ and half-sandwich ruthenium complexes **1**–**13**

	$^{31}P\{^1H\}$				^1H		
	δ[b]		$\Delta\delta$[c]		δ		
	P_A	P_X	P_A	P_X	Cp/Cp*	CH_3	Ru–H[d]
$\mathbf{L}^1$	135.1 (s)	–	–	–	–	3.51 (t)[e] 2.13 (s)[f]	–
1	108.8 (s)	–	−26.3	–	4.25	3.39 (t)[e], 2.34, 2.17 (s)[f]	–
2	99.1 (s)	–	−36.4	–	1.78	2.44 (t)[e]	–
3	123.8 (d 60.8)	107.7 (d)	−32.6	−28.5	2.11	1.28, 0.93 (d)[g]	–
4	124.8 (d 60.8)	106.8 (d)	−33.4	−30.0	1.36	1.18, 0.80 (d)[g], 1.35, 1.33 (s)[h]	–
7	120.6 (s)	–	−14.5	–	4.13	3.13 (t)[e], 2.20, 2.17 (s)[f]	−13.06 (t 34)
7-D	120.7 (t $J_{D-P} = 5.0$)	–	−14.4	–	4.13	3.13 (t)[e], 2.20, 2.17 (s)[f]	–
8[i]	114.1 (s)	–	−21.4	–	3.37	2.68 (t)[e]	−11.99 (t 34)
9	122.5 (d 64.8)	118.3 (d)	−35.1	−19.0	2.64	1.48, 0.90 (d)[g], 1.32, 1.28 (s)[h]	−11.39 (t 35)
10[j]	100.4 (d 107.0)	100.9 (br)	+48.2	+48.7	4.57	0.90 (d)[g]	−10.70 (t 30)
11a,b[i,j]	147.2 (d 107.0)[k] 137.4 (d 99.0)[k]	111.9 (d)[l] 101.9 (d)[l]			4.69	1.92 (d)[g], 3.00, 2.57 (s)[m]	−11.06 (dd 34, 26), −11.86 (dd 34, 29)
12a	115.5 (s)	–	−19.6	–	4.65	3.35 (t)[e],	−7.93 (br),
12b	107.8 (s)		−27.3		4.71	2.20, 2.16 (s)[f]	−6.14 (t 27.4)
13a	115.6 (t $J_{D-P} = 13.8$)	–	−19.5	–	4.65	3.35 (t)[e]	−8.00 (t $J_{D-H} = 24.5$),
13b	108.8 (br)		−27.1		4.71	2.20, 2.16 (s)[f]	−6.20 (tt 26.4, $J_{D-H} = 4.0$)

[a] Recorded in $CDCl_3$ in a 200 MHz or 400 MHz spectrometer.
[b] ^2J(P,P) values in parentheses.
[c] δ(complex) − δ(free ligand).
[d] ^2J(P,H) coupling constants in parentheses.
[e] CH_3, N(CH_3), ^3J(P,H) = 7.0 − 12.0 Hz.
[f] CH_3, $OC_6H_3Me_2$-2,6.
[g] CH_3 protons of (*S*)-*CHMePh or $CHMe_2$ group are doublets with ^3J(H,H) = 7.0 Hz.
[h] ^{t}Bu, $OC_6H_4{}^t$Bu-4.
[i] ^{1}H NMR recorded in C_6D_6 and ^{31}P NMR in benzene (200 MHz).
[j] AB spin system.
[k] PPh($N_2C_3HMe_2$-3,5) phosphorus.
[l] PPh_2 phosphorus.
[m] 3,5-Dimethyl pyrazole group protons.

Table 3
Results of catalytic asymmetric transfer hydrogenation of 2-acetonaphthone[a]

Ligand	% Yield	% ee	Enantiomer
(*S*)-$\mathbf{L}^3$	87.7	rac	–
(*R*)-$\mathbf{L}^4$	16.3	35	*R*
(*S*)-$\mathbf{L}^4$	13.0	34	*S*
$\mathbf{L}^5$	85.9	rac	–
(*R*,*R*)-$\mathbf{L}^7$	68.5	10	*R*
(*S*,*S*)-$\mathbf{L}^7$	69.2	12	*S*
(*R*)-$\mathbf{L}^8$	85.2	rac	
(*S*)-$\mathbf{L}^8$	85.0	rac	–
$\mathbf{L}^9$	88.5	rac	–
(*R*,*R*)-$\mathbf{L}^{7,b}$	>99	30	*R*

[a] 200:1:2 ratio of ketone:Ru:ligand.
[b] 100:1:2 ratio of ketone:Ru:ligand.

tion heated under reflux for 60 h. The reaction mixture was concentrated to 5–10 cm^3 and kept at ambient temperature during which a black mass separated out. The solution was filtered and the solvent evaporated to dryness to obtain a residue. The residue was dissolved in ethanol (8–10 cm^3) and kept at ambient temperature for 5 days. The title compound precipitated as a bright yellow-orange solid.

2.4. Synthesis of [(η^5-Cp)RuCl{κ^2-P,P-X_2PN(R)PYY′}] [R = Me, X = Y = Y′ = OC_6H_5 (**2**); R = $CHMe_2$, X_2 = $C_{20}H_{12}O_2$, Y = Y′ = OC_6H_5 (**3**) or $OC_6H_4{}^t$Bu-4 (**4**)]*

A 50 cm^3 double necked flask was charged with a mixture of [(η^5-Cp*)$RuCl_2$]$_n$ (0.050 g, 0.163 mmol), the corresponding diphosphazane (0.179 mmol) and zinc dust (0.053 g, 0.815 mmol) under nitrogen atmosphere. Toluene (30 cm^3) was added and the reaction mixture stirred for 24 h during which the dark brown solution turned bright yellow orange. The ^{31}P NMR spectrum of the reaction mixture displayed resonances corresponding to unreacted diphosphazane in addition to those arising from the product. Heating the reaction mixture under reflux did not improve the yield of the product. The solution was filtered and the solvent evaporated to dryness. The residue was dissolved in ethanol

Table 4
NMR[a] (^{1}H and ^{31}P) data for ruthenium hydride complexes **14**–**20**

	$^{31}P\{^1H\}$[b]				^1H		
	δ		$\Delta\delta$[c]		δ		
	P_A	P_X	P_A	P_X	CH[d]	CH_3[e]	Ru–H[f]
14[g]	91.9	84.9	+39.1	+32.1	4.66	1.08 (d)	−15.27 (q 20)
15	87.5 (s)	–	+38.7	–	4.01	0.60 (d)	−15.17 (q 20)
16	114.3 (s)	–	−20.8	–	–	3.23 (t)[h], 2.13 (s)[i]	−14.88 (t 33.3)
17[j]	108.9(d 36.7)	107.7 (d)	−26.2	−27.4	–	3.32 (t)[h], 2.11 (s)[i]	−13.39 (dd 44.0, 33.3)
18[j]	97.6 (d 9.7)	91.8 (d)	−37.5	−43.3	–	3.74 (t)[h], 2.51, 2.65 (s)[i]	–
19	129.4 (q 31.9)	89.5 (m)	–	+37.3	4.40	2.17 (d)[k], 0.18 (d)	−6.10 (dq 120, 20)
20	118.1 (q 32.4)	88.7(d)	–	+36.5	4.45	0.24 (d)	−6.25 (dq 140, 20)

[a] Recorded in $CDCl_3$ in a 200 MHz or 400 MHz spectrometer except for complex **16** (recorded in CD_3CN).
[b] ^2J(P,P) coupling constants are given in parentheses.
[c] $\Delta\delta = \delta$(complex) − δ(free ligand).
[d] CH proton of (*S*)-*CHMePh or $CHMe_2$ group are multiplets.
[e] CH_3 protons of (*S*)-*CHMePh or $CHMe_2$ group are doublets with ^3J(H,H) = 7.0 Hz.
[f] Numbers within parenthesis are ^2J(P,H) coupling constants.
[g] AA′XX′ spin system.
[h] CH_3 protons of N(CH_3) group, ^3J(P,H) = 7.0 − 11.0 Hz.
[i] CH_3, $OC_6H_3Me_2$-2,6.
[j] ^{31}P NMR spectrum is an AB spin system.
[k] Me, $P(OMe)_3$, ^3J(P,H) = 10.0 Hz.

(8–10 cm^3) and subjected to column chromatography over silica gel using the same solvent. Evaporation of the eluant afforded the title compounds as bright orange solids. Single crystals of complex **4** suitable for X-ray diffraction were obtained from an ethanolic solution.

2.5. Synthesis of [(η^5-Cp)RuH{κ^2-P,P-($RO)_2$PN(Me)P($OR)_2$}] [OR = $OC_6H_3Me_2$-2,6 (**7**)]

The complex [(η^5-Cp)RuCl{κ^2-P,P-X_2PN(R)PX_2}] (0.009 g, 0.011 mmol) [X = $OC_6H_3Me_2$-2,6 (**1**)] was added to a solution of CH_3ONa/CH_3OH [prepared *in situ* by the addition of Na (0.005 g, 0.220 mmol) to CH_3OH (3 cm^3)] under a stream of nitrogen gas. The mixture was heated under reflux for 20 h; methanol was added periodically to maintain the volume. The reaction mixture was cooled to ambient temperature. Solvent was evaporated to dryness to obtain a pale yellow residue of [(η^5-Cp)RuH{κ^2-P,P-$(RO)_2$PN(R)P$(OR)_2$}] (**7**). Single crystals of the title compound were obtained by layering a toluene solution of the compound with petrol.

2.6. Synthesis of [(η^5-Cp*)RuH{κ^2-P,P-X_2PN(R)PYY′}] [R = Me, X = Y = Y′ = OC_6H_5 (**8**); R = $CHMe_2$, X_2 = $C_{20}H_{12}O_2$, Y = Y′ = $OC_6H_4{}^tBu$-4 (**9**)]

A solid sample of the complex [(η^5-Cp*)RuCl{κ^2-P,P-X_2PN(R)PYY′}] (0.011 mmol) [R = Me, X = Y = Y′ = OC_6H_5 (**2**), R = $CHMe_2$, X_2 = $C_{20}H_{12}O_2$, Y = Y′ = $OC_6H_4{}^tBu$-4 (**4**)] was added to a solution of CH_3ONa/CH_3OH [prepared *in situ* by the addition of Na (0.005 g, 0.220 mmol) to CH_3OH (3 cm^3)] under a stream of nitrogen gas. The mixture was heated overnight under reflux and the solution cooled. Solvent was evaporated to dryness to obtain a pale yellow residue. Attempts to obtain a pure sample from the residue were unsuccessful. Both complexes **8** and **9** were characterized only by NMR spectroscopy.

2.7. Synthesis of [(η^5-Cp)RuH{κ^2-P,P-Ph_2PN((*S*)-*CHMePh)PPhY}] [Y = Ph (**10**) or $N_2C_3HMe_2$-3,5 (**11a**,**b**)]

A solid sample of the complex [(η^5-Cp)RuCl{κ^2-P,P-X_2PN((*S*)-*CHMePh)PYY′}] (0.05 g, 0.07 mmol) [X = Y = Ph, Y′ = Ph (**5**) or $N_2C_3HMe_2$-3,5 ($S_CS_PR_{Ru}$)-(**6**)] was treated with CH_3ONa/CH_3OH as described in Section 2.6. The mixture was heated under reflux for 3 h for **5** or 6 h for **6** and the solution cooled. A yellow solid precipitated, which was filtered off and washed with pentane. Complex **10** could be isolated in a pure form. Complex **11** was found to be a diastereomeric mixture of **11a** and **11b**. Complex **11a** could be isolated in low yield (<10%) by dissolution of the yellow solid in deoxygenated pentane followed by cooling the solution to 0 °C for 2 h. The other diastereomer **11b** could not be separated in a pure form. Both **11a** and **11b** were characterized only by NMR spectroscopy.

2.8. Protonation of [(η^5-Cp)RuH{κ^2-P,P-($RO)_2$PN(Me)P($OR)_2$}] (**7**) using different acids, HX (X = CF_3SO_3, BF_4 or CF_3COO)

The protonation experiments were carried out in a NMR tube sealed with a rubber septum. In a typical experiment, complex **7** (0.005 g, 0.007 mmol) was dissolved in

$CDCl_3$ (0.4 cm^3) and HX (0.140 mmol) added; the mixture was shaken well and subjected to NMR measurements. Use of a stoichiometric quantity of the acid did not result in protonation (no dihydride/dihydrogen resonances were observed).

2.9. Transfer hydrogenation of 2-acetonaphthone

A 20 cm^3 double necked flask fitted with a reflux condenser and an inlet for nitrogen was charged with $[RuCl_2(PPh_3)_3]$ (0.014 g, 0.015 mmol) and chiral diphosphazane (0.030 mmol). Freshly distilled and degassed (two freeze–pump–thaw cycles) 2-propanol (6 cm^3) was added and the mixture heated to 80 °C for 30 min. The mixture was cooled to 25 °C and 2-acetonaphthone (0.511 g, 3.000 mmol) and finely crushed KOH (0.002 g, 0.030 mmol) were added. The mixture was then heated to 80 °C for 16 h. Solvent was evaporated from the reaction mixture to obtain a dark brown residue. The yield of the product was calculated from the relative integrated intensities of the starting material and the product as observed by the ^1H NMR spectrum of the reaction mixture. The dark residue was dissolved in ethyl acetate-petrol (1:9 v/v) (~5–6 cm^3) and loaded on top of a silica gel column (20 cm × 1.5 cm) and eluted with the same solvent (~250–300 cm^3) during which the starting material (2-acetonaphthone) was eluted. Further elution gave the desired 2-(2-naphthyl)-ethanol, which was obtained as a solid after evaporation of the eluant. The enantiomeric excess (% ee) of the product was determined by HPLC analysis (see below).

2.10. Synthesis of trans-[Ru(H)Cl{κ^2-P,P-$Ph_2PN(R)PPh_2$}$_2$] [R = (S)-*CHMePh (**14**) or $CHMe_2$ (**15**)]

A mixture of $[RuCl_2(cod)]_n$ (0.050 g, 0.177 mmol), diphosphazane (0.173 g for R = (*S*)-*CHMePh, 0.151 g for R = $CHMe_2$, 0.353 mmol) and Et_3N (1 cm^3) were suspended in ethanol (30 cm^3). The reaction mixture was heated under reflux for 5 h and cooled to room temperature. The title compounds precipitated as bright yellow solids. The mother liquor was decanted; the solid was washed with cold *n*-pentane (3 × 5 cm^3) and dried *in vacuo*. Complex **15** could not be isolated in pure form owing to its high sensitivity to air and moisture. Both the complexes decomposed upon standing in halogenated solvents.

2.11. Synthesis of trans-[Ru(H)(Cl)(κ^2-P,P-L^1)(S)$_2$] [(S = CD_3CN) (**16-d_3**)]

Freshly distilled Et_3N (1 cm^3) was added to a mixture of $[RuCl_2(COD)]_n$ (0.050 g, 0.177 mmol) and $\mathbf{L}^1$ (0.102 g, 0.177 mmol). To the suspension, dry ethanol (30 cm^3) was added and the mixture heated under reflux for 5 h. A bright yellow precipitate formed during the course of the reaction. The reaction mixture was cooled to ambient temperature and the alcohol layer was removed using a syringe to obtain a creamy yellow precipitate. The precipitate was found to be stable in acetonitrile and sensitive towards halogenated solvents. The NMR spectrum of the precipitate was recorded in CD_3CN to obtain the spectroscopic data for complex **16-d_3**. The complex could not be isolated in pure form owing to its high sensitivity and was characterized only by spectroscopic data.

2.12. Synthesis of cis-[Ru(H)(Cl)(κ^2-P,P-L^1)(κ^2-N,N-2,2′-bipyridine)] (**17**)

The creamy yellow precipitate obtained from the reaction mixture as described above was dissolved in a mixture of acetonitrile (15 cm^3) and THF (6 cm^3) to obtain the complex *trans*-[RuH(Cl){κ^2-P,P-$(RO)_2PN(Me)P(OR)_2$}-$(CH_3CN)_2$] (**16**). To this solution 2,2′-bipyridine (0.028 g, 0.177 mmol) was added. The solution turned dark immediately. The solution was stirred at ambient temperature for 75 min. Solvent was evaporated from the reaction mixture to obtain complex **17** as a dark brown solid. Attempts to obtain a pure sample of complex **17** were unsuccessful. Crystallization from dichloromethane–petrol afforded the dichloro complex *cis*-[$RuCl_2${κ^2-P,P-$(RO)_2PN(Me)$-$P(OR)_2$}(κ^2-N,N-2,2′-bpy)] (**18**) as a bright yellow solid.

2.13. Synthesis of trans-[Ru(H){P(OR)$_3$}{κ^2-P,P-Ph_2PN((S)-*CHMePh)PPh_2}$_2$] [R = Me (**19**) or Ph (**20**)]

$P(OR)_3$ (0.072 mmol) and AgOTf (0.018 g, 0.072 mmol) were added to a THF (10 cm^3) solution of complex **14** (0.080 g, 0.072 mmol), under nitrogen atmosphere and the reaction mixture was stirred under dark at ambient temperature for 1.5 h. The reaction mixture was filtered, solvent evaporated under *vacuo*, washed with petrol and dried to obtain a residue. The residue was crystallized from dichloromethane solution layered with petrol to obtain the title compounds as colorless solids.

2.14. HPLC studies

A Merck-Hitachi HPLC system fitted with a binary high pressure pump, Chiralcel-OD column, 20 μl injection loop and UV detector was used to determine the enantiomeric excess obtained in catalytic reactions. A mixture of *n*-hexane and 2-propanol (95:5 v/v) at a flow rate of 0.5 cm^3/min was used as the eluant; the absorbance was monitored at 254 nm. The absolute configuration of the product was determined by comparison of the retention time in HPLC profiles and also from optical rotation values reported in the literature [9b].

2.15. X-ray crystallography

The crystals were mounted on a glass fiber and the intensity data for all the compounds were obtained at room temperature from a Bruker SMART APEX CCD

diffractometer equipped with fine focus 1.75 kW sealed tube Mo-Kα X-ray source with increasing ω (width of 0.3° per frame) at an exposure time of n s/frame ($n = 4$ for $\mathbf{L}^1$, $n = 8$ for **4** and $n = 25$ for **18**). The SMART [18a] software was used for cell-refinement and data acquisition and the SAINT [18b] software was used for data reduction. Lorentz and polarization corrections were made on the intensity data. An absorption correction was made on the intensity data using the SADABS [18c] program. The structures were solved using SHELXTL [18d] and the WinGX graphical user interface [19]. Least-square refinements were performed by the full-matrix method with SHELXL-97 [20]. Pertinent crystallographic data are summarized in Table 5. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined by allowing them to ride with the respective non-H atoms. The solvent molecule (ethanol) and the carbon atoms of the ^{t}Bu groups [C(28), C(29), C(30), C(38), C(39) and C(40)] in **4** showed high thermal parameters and were refined isotropically with shared occupancy factors.

3. Results and discussion

3.1. Synthesis of a sterically bulky diphosphazane, $\boldsymbol{L^1}$

The sterically bulky diphosphazane $(RO)_2PN(Me)P(OR)_2$ ($R = C_6H_3Me_2$-2,6) ($\mathbf{L}^1$) was prepared previously in our laboratory [17]. The experimental details, spectroscopic data and crystal structure are reported here. The reaction of $Cl_2PN(Me)PCl_2$ [16] with four equivalents of 2,6-dimethyl phenol in the presence of triethyl amine as base affords the diphosphazane $(RO)_2PN(Me)P(OR)_2$ ($R = C_6H_3Me_2$-2,6) ($\mathbf{L}^1$). The ^{31}P NMR spectrum of the compound displays a singlet at 135.1 ppm for the magnetically equivalent phosphorus nuclei. A triplet is observed for the methyl protons bound to the nitrogen; a singlet is observed for the methyl group protons present at the ortho positions of the phenoxy rings.

The conformational behavior of "P–N–P" type ligands is well known in the literature [14c,21]. It has been found that the preferred conformation (see Chart 1) depends on

Table 5
Summary of X-ray diffraction data for ligand $\mathbf{L}^1$ and the complexes **4**, **7** and **18**

	$\mathbf{L}^1$	**4** · CH_3CH_2OH	**7**	**18**
Empirical formula	$C_{33}H_{39}NO_4P_2$	$C_{55}H_{66}NO_5P_2ClRu$	$C_{38}H_{45}NO_4P_2Ru$	$C_{43}H_{49}N_3O_4P_2Cl_2Ru \cdot H_2O$
Formula weight	575.59	1019.55	742.76921.76	
Crystal system, space group	Monoclinic, $P2/n$	Triclinic, $P\bar{1}$	Monoclinic, $C2/c$	Orthorhombic, $P2_1cn$
Unit cell dimensions	$a = 12.045(7)$ Å $b = 10.263(6)$ Å $c = 12.478(7)$ Å $\beta = 99.117(9)°$	$a = 11.642(2)$ Å $b = 14.017(3)$ Å c = 16.710(3) Å $\alpha = 77.173(4)°$ $\beta = 84.107(3)°$ $\gamma = 86.093(4)°$	$a = 43.0433(14)$ Å $b = 9.5072(3)$ Å $c = 19.0176(7)$ Å $\beta = 111.414(2)°$	$a = 11.050(5)$ Å $b = 13.017(7)$ Å $c = 31.657(15)$ Å
Volume (Å^3)	1523.0(14)	2641.8(9)	7245.2(4)	4554(4)
Z	2	2	8	4
Density (calcd), Mg/mm^3	1.255	1.282	1.362	1.344
Absorption coefficient (mm^{-1})	0.180	0.454	0.560	0.576
Max. and min. transmission	0.958 and 0.8581	0.9772 and 0.8049	–	–
$F(000)$	612	1068	3088	1904
Crystal size (mm)	$0.875 \times 0.641 \times 0.240$	$0.500 \times 0.240 \times 0.050$	$0.200 \times 0.150 \times 0.100$	$0.195 \times 0.049 \times 0.019$
θ Range for data collection	1.98–27.0°	1.73–27.5°	1.02–23.25°	1.69–28.24°
Index ranges	$-15 \leqslant h \leqslant 15$, $-13 \leqslant k \leqslant 13$, $-15 \leqslant l \leqslant 15$	$-15 \leqslant h \leqslant 15$, $-18 \leqslant k \leqslant 18$, $-21 \leqslant l \leqslant 21$	$-47 \leqslant h \leqslant 47$, $-9 \leqslant k \leqslant 10$, $-21 \leqslant l \leqslant 19$	$-14 \leqslant h \leqslant 13$, $-17 \leqslant k \leqslant 17$, $-41 \leqslant l \leqslant 40$
Reflections collected	15,227	31,013	14,453	38,288
Independent reflections	3332 [R(int) = 0.0745]	12,200 [R(int) = 0.0439]	5209 [R(int) = 0.0645]	10,279 [R(int) = 0.1433]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	3332/0/186	12,200/0/590	5209/0/419	10,279/1/500
Goodness-of-fit on F^2	1.249	1.069	0.999	0.950
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.048$, $wR_2 = 0.1263$	$R_1 = 0.0710$, $wR_2 = 0.1666$	$R_1 = 0.0469$, $wR_2 = 0.0902$	$R1 = 0.0970$, $wR_2 = 0.1805$
R indices all data	$R_1 = 0.0613$, $wR_2 = 0.1329$	$R_1 = 0.1056$, $wR_2 = 0.1829$	$R_1 = 0.0895$, $wR_2 = 0.1048$	$R_1 = 0.2540$, $wR_2 = 0.3027$
Absolute structure parameter				0.02(9)
Largest diff peak and hole (e Å^{-3})	0.473 and −0.291	0.738 and −0.375	0.408 and −0.436	1.946 and −0.658

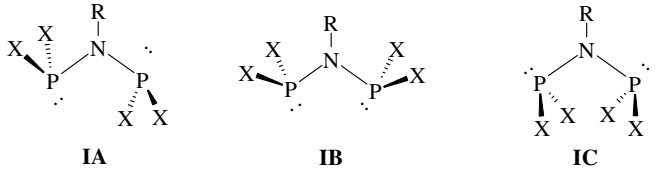


Chart 1. Conformations of diphosphazanes.

the substituents present on the nitrogen and the phosphorus centers. In general, when the substituents R and X are relatively small, a conformation of type **1B** is preferred. But, when the substituents R and/or X are large, a conformation of type **1A** is preferred [21b]. An X-ray crystallographic study (see below) reveals that $\mathbf{L}^1$ adopts a conformation of type **1B** (C_2 conformer) in the solid state as observed recently for the sterically bulky diphosphazanes, $EtN\{P(OR)_2\}_2$ (R = $C_6H_3{}^iPr_2$-2,6 or $C_6H_3Me_2$-2,6) [21d]. A variable temperature NMR spectrum of the ligand $\mathbf{L}^1$ in the range −40 to +55 °C ($CDCl_3$) does not show any change in the spectral pattern indicating that in this temperature range, only one conformer is present in solution owing to the increased rigidity of the ligand.

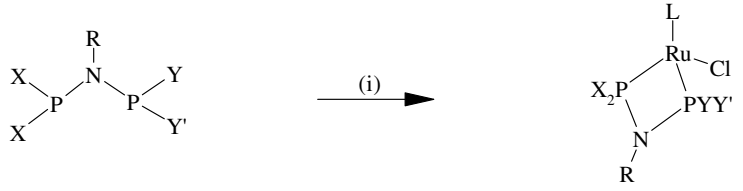
3.2. Synthesis of half-sandwich (Cp and Cp*) ruthenium chloro complexes of diphosphazanes

The synthesis of half-sandwich optically active "*chiral-at-metal*" ruthenium complexes has received considerable interest in recent years because they can be used as probes to follow the stereochemical course of reactions of organometallic complexes and they have also been investigated as promising catalysts for a variety of organic transformations [22]. Active use of chirality at a metal center in enantioselective catalysis is a challenging area [22c,23]. Several ruthenium complexes with a stereogenic metal center have been synthesized using Schiff-base ligands, chiral bidentate ligands with mixed donor sites or chiral diphosphanes that bear chirality at the back-bone of the ligand [24]. There are only two reports on the synthesis of half-sandwich ruthenium complexes of chiral diphosphazane ligands based on the P–N–P motif [12a,25].

The reaction of $[CpRu(PPh_3)_2Cl]$ with one equivalent of $\mathbf{L}^1$ in boiling benzene affords the diphosphazane substituted complex $[(\eta^5\text{-Cp})RuCl\{\kappa^2\text{-P,P-}(RO)_2PN(Me)\text{-}P(OR)_2\}]$ (**1**) (Scheme 1). Complexes **2**–**4** are obtained by the reduction of $[Cp^*RuCl_2]_n$ using zinc dust in the presence of diphosphazanes $\mathbf{L}^2$–$\mathbf{L}^4$. When such a reduction is carried out in the presence of the unsymmetrically substituted diphosphazanes (*rac*)-$(C_{20}H_{12}O_2)PN(CHMe_2)\text{-}P(OR)_2$ [R = C_6H_5 ($\mathbf{L}^3$) or $C_6H_4{}^t$Bu-4 ($\mathbf{L}^4$)], the product would possess a stereogenic metal center. Since the binaphthyl moiety is *racemic* and one sterogenic center is created during the course of the reaction, there exists the possibility of the formation of four diastereomers [(R_aR_{Ru}), (S_aS_{Ru}), (R_aS_{Ru}) and (S_aR_{Ru})] (two enantiomeric pairs). Hence one would expect the ^{31}P NMR spectrum to display two AX spin systems (four doublets) for the two enantiomeric pairs. The ^{31}P NMR spectrum of the reaction mixture displays only two doublets at 124.2 and 107.3 ppm [$^2J(P,P) = 61.2$ Hz] for the $P(O_2C_{20}H_{12})$ and $P(OR)_2$ phosphorus nuclei respectively, in addition to the resonances corresponding to those of the starting diphosphazane indicating stereoselective formation of *only one enantiomeric pair*. Faller and Parr have observed a similar diasteroselectivity in the formation of (arene)ruthenium complexes of 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl monoxide [24n]. Complexes **1**–**4** have been characterized by NMR spectroscopic techniques and the data are listed in Table 2. The ^{31}P chemical shifts of complexes **1**–**4** are *upfield* shifted from that of the free ligand ($\Delta\delta = -26.3$ to -36.4). The structure of complex **4** has been established by single crystal X-ray crystallography. The solid-state structure (see later) reveals the formation of only one enantiomeric pair [(R_aR_{Ru}) and (S_aS_{Ru})].

3.3. Synthesis of half-sandwich (Cp and Cp*) ruthenium hydride complexes of diphosphazanes

Transition metal hydride complexes and their dihydrogen analogues are of great importance in view of the



R = Me, X = Y = Y' = $OC_6H_3Me_2$-2,6 ($\mathbf{L^1}$)
R = Me, X = Y = Y' = OC_6H_5 ($\mathbf{L^2}$)
R = $CHMe_2$, $X_2 = O_2C_{20}H_{12}$, Y = Y' = OC_6H_5 ($\mathbf{L^3}$)
R = $CHMe_2$, $X_2 = O_2C_{20}H_{12}$, Y = Y' = $OC_6H_4{}^t$Bu-4 ($\mathbf{L^4}$)

L = Cp, R = Me, X = Y = Y' = $OC_6H_3Me_2$-2,6 (**1**)
L = Cp*, R = Me, X = Y = Y' = OC_6H_5 (**2**)
L = Cp*, R = $CHMe_2$, $X_2 = O_2C_{20}H_{12}$, Y = Y' = OC_6H_5 (**3**)
L = Cp*, R = $CHMe_2$, $X_2 = O_2C_{20}H_{12}$, Y = Y' = $OC_6H_4{}^t$Bu-4 (**4**)

(i) $CpRu(PPh_3)_2Cl$, benzene, 80 °C, 60h (for **1**)
$[Cp^*RuCl_2]_n$, toluene, zinc dust, 25 °C, 24h (for **2-4**)

Scheme 1. Synthesis of half-sandwich (Cp and Cp*) ruthenium chloro complexes of diphosphazanes.

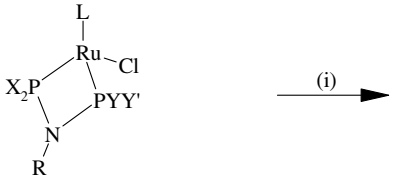
presence of such species as intermediates in several catalytic reactions. There are numerous reports on transition metal (Fe, Ru, Os, W) hydride complexes bearing mono- and diphosphines [26–28] but similar studies using diphosphazanes as ancillary ligands are very much limited [25,29].

The cyclopentadienyl ruthenium chloro complexes [CpRuCl{κ^2-P,P-Ph_2PN((*S*)-*CHMePh)PPh(Y′)}] [Y′ = Ph (**5**), $N_2C_3HMe_2$-3,5 (**6**)] were prepared from the reaction between [(η^5-Cp)$Ru(PPh_3)_2Cl$] and Ph_2PN(R)P-Ph(Y′) [Y′ = Ph (**L**^{5}), $N_2C_3HMe_2$-3,5 (**L**^{9})] as reported earlier [12a]. The reactions of the half-sandwich ruthenium chloro complexes (**1**, **2**, **4**–**6**) with NaOMe in methanolic solutions result in the formation of the ruthenium hydride complexes [CpRuH{κ^2-P,P-X_2PN(R)PY(Y′)}] (**7**–**11**) in good yields (Scheme 2). These complexes have been characterized mainly by NMR spectroscopic technique (Table 2). The ^{31}P NMR spectrum of complex **7** displays a singlet at 120.6 ppm that is *upfield* shifted from that of the free ligand ($\Delta\delta = -14.5$). A similar upfield shift in the ^{31}P resonance is observed for complex **8** ($\Delta\delta = -21.4$). The ^{1}H NMR spectrum of **7** shows a triplet at −13.06 ppm for the ruthenium bound hydride hydrogen. For complex **8**, the Ru–*H* resonance is observed at −11.99 ppm. While complex **7** was isolated in pure form and its solid-state structure established by single crystal X-ray crystallography, complexes **8**, **9** and **10** could not be isolated in pure form owing to their high sensitivity to air and chlorinated solvents. Gamasa and co-workers [25] have reported the synthesis and structural characterization of the indenyl analogue of complex **10**, [(η^5-C_9H_7) Ru(H){κ^2-P,P-Ph_2PN((*S*)-*CHMePh)-PPh_2}] from the corresponding chloro complex.

The reaction involving the trichiral half-sandwich complex [CpRuCl{κ^2-P,P-Ph_2PN((*S*)-CHMePh)PPh(N_2C_3H-Me_2-3,5)}] ($S_CS_PR_{Ru}$)-**6** results in the formation of a diastereomeric mixture of hydride complexes (**11a** and **11 b)** as revealed by NMR spectroscopy. The ^{31}P NMR spectrum shows two AX patterns corresponding to **11a** and **11b**. The ^{1}H NMR spectrum displays two doublet-of-doublets at −11.06 (major) and −11.86 ppm (minor) for the hydride hydrogen corresponding to the two diastereomers. We tentatively assign the configurations ($S_CS_PR_{Ru}$) and ($S_CS_PS_{rRu}$) for the two diastereomers assuming that the phosphorus chirality is unaffected during the reaction. Recrystallization of the mixture from deoxygenated *n*-pentane yields the major diastereomer as a pale yellow solid. The NMR data for these complexes are listed in Table 2.

3.4. Protonation of the ruthenium hydride complex, [CpRuH{κ^2-P,P-$(RO)_2PN(Me)P(OR)_2$}] ($R = C_6H_3Me_2$-2,6) (7)

Though there are several reports on the protonation of half-sandwich ruthenium hydride complexes bearing mono- and diphosphines [26,27], there are no reports on the protonation of ruthenium hydride complexes bearing "P–N–P" type ligands. Protonation of CpRu(P–P)H complexes (P–P = dppm, dppe or dppp) yield exclusively dihydrogen [for dppm] or dihydride complexes [for dppp] or a mixture of both [for dppe] [27a]. It is reported that protonation of Cp*RuH(L_2) [L_2 = dppm, dppp, $(PPh_3)_2$, $(PMe_2Ph)_2$, $(PMePh_2)_2$, $(PMe_3)_2$] with $HBF_4 \cdot Et_2O$ gives a mixture of dihydrogen and dihydride species, the composition of which depends on the nature of the phosphine bound to ruthenium. With the exception of dppm, the thermodynamic product was found to be the dihydride complex. In the case of dppm, the final protonation product was a 2:1 mixture of dihydrogen and dihydride complexes. Such a difference in the Cp and Cp* analogues was attributed to the increase in electron density at ruthenium on going from Cp to Cp* ligand [27d]. The analogous [(η^5-C_9H_7)Ru(H)(P–P)] [27g] complex exhibits a reactivity pattern similar to the [CpRu(H)(P–P)] complex. According to Heinekey and co-workers [27b], the initial kinetic product is always the dihydrogen complex. So far, it has been difficult to determine if the dihydride complex is obtained by direct protonation at the ruthenium or by oxidative addition of the dihydrogen complex. The remarkable stability of the ruthenium hydride complex **7** provided us the opportunity to investigate its reactivity towards different acids (CF_3SO_3H, HBF_4, and CF_3COOH) to ascertain which of the two forms, dihydrogen or dihydride, would be stabi-



L = Cp, R = Me, X = Y = Y' = $OC_6H_3Me_2$-2,6 (**1**)
L = Cp*, R = Me, X = Y = Y' = OC_6H_5 (**2**)
L = Cp*, R = $CHMe_2$, X_2 = $O_2C_{20}H_{12}$, Y = Y' = $OC_6H_4{}^tBu$-4 (**4**)
L = Cp, R = (*S*)-*CHMePh, X = Y = Y' = Ph (**5**)
L = Cp, R = (*S*)-*CHMePh, X = Y = Ph, Y' = $N_2C_3HMe_2$-3,5 (**6**)

(i) CH_3ONa, MeOH, 60 ^{0}C, 20h

L = Cp, R = Me, X = Y = Y' = $OC_6H_3Me_2$-2,6 (**7**)
L = Cp*, R = Me, X = Y = Y' = OC_6H_5 (**8**)
L = Cp*, R = $CHMe_2$, X_2 = $O_2C_{20}H_{12}$, Y = Y' = $OC_6H_4{}^tBu$-4 (**9**)
L = Cp, R = (*S*)-*CHMePh, X = Y = Y' = Ph (**10**)
L = Cp, R = (*S*)-*CHMePh, X = Y = Ph, Y' = $N_2C_3HMe_2$-3,5 (**11**)

Scheme 2. Synthesis of half-sandwich (Cp and Cp*) ruthenium hydrido complexes of diphosphazanes.

lised when a strong π-acceptor ligand is bound to ruthenium. The protonation experiments were carried out in a sealed NMR tube containing a $CDCl_3$ solution of complex **7** at ambient temperature.

Treatment of complex **7** with an excess of HX ($X = CF_3SO_3$, BF_4 or CF_3COO) results in the formation of a mixture of two complexes, $[CpRu(\eta^2\text{-}H_2)\{\kappa^2\text{-}P,P\text{-}(RO)_2PN(Me)P(OR)_2\}][CF_3SO_3]$ (**12a**) and $[CpRu(H)_2\{\kappa^2\text{-}P,P\text{-}(RO)_2PN(Me)P(OR)_2\}][CF_3SO_3]$ (**12b**) (Scheme 3). Depending on the acid used for protonation, the ratio between **12a** and **12b** varies. Nevertheless, the major product in all the cases is the dihydrogen complex **12a** presumably because of the steric bulk of the diphosphazane ligand.

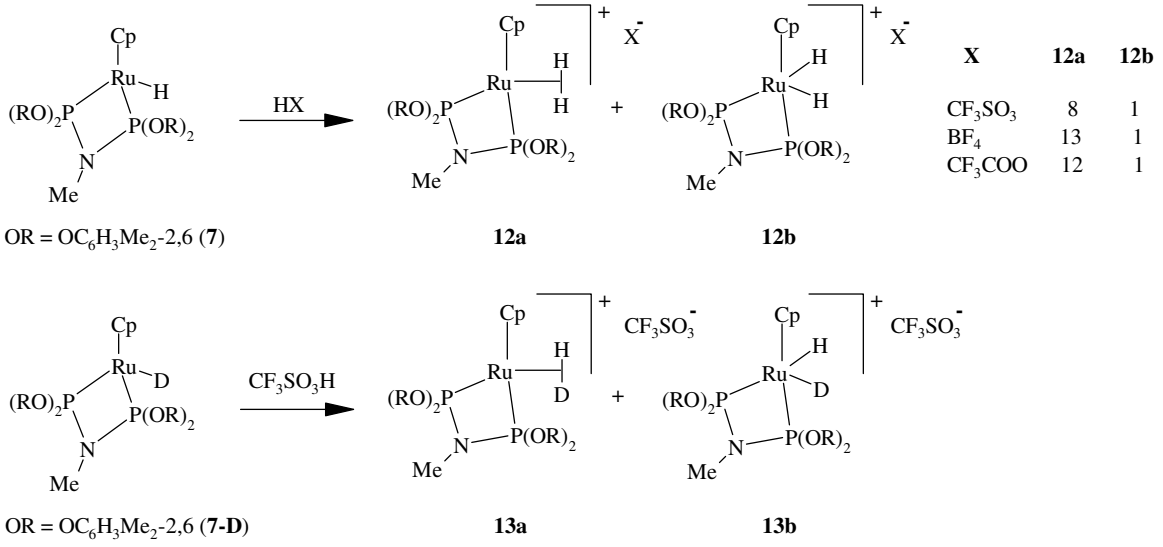
The ^1H NMR spectrum of a $CDCl_3$ solution of **7** upon the addition of HX displays a triplet at −6.20 ppm and a broad resonance at −8.00 ppm. The former resonance is assigned to dihydride hydrogens in the Ru(IV) complex **12b** and the latter to the bound dihydrogen in the Ru(II) complex **12a**. The cyclopentadienyl hydrogens in complexes **12a** and **12b** resonate at 4.65 and 4.71 ppm respectively. No separate resonances were observed for the methyl protons bound to nitrogen and those at the ortho positions of the phenoxy substituents in complexes **12a** and **12b**. The ^{31}P NMR spectrum displays two singlets at 115.5 and 107.8 ppm which are assigned to **12a** and **12b** respectively.

Variable temperature (VT) NMR spectrum (−40 to +50 °C, $CDCl_3$) shows a variation in the ratio of the two species as a function of temperature, but does not show complete coalescence of the resonances in the temperature limit studied. The VT NMR spectrum reveals that complex **12a** is the dominant species throughout the temperature range −40 to +50 °C. The proportion of **12b** increases as the temperature is increased from −40 °C, reaches a maximum at +20 °C (1:8) and then starts dropping again with a further increase in temperature.

Measurement of relaxation time T_1 was carried out at 298 K and 400 MHz to ascertain the nature of the hydride in complexes **12a** and **12b**. The broad resonance at −8.00 ppm has a T_1 value of 10 ms. The triplet at −6.25 ppm has a T_1 value between 150–200 ms. These values indicate the absence of any intramolecular exchange process [27a]. In order to further confirm the dihydrogen nature of the resonance at −8.00 ppm, HD gas (generated from D_2O and NaH) was purged into the reaction mixture to generate the H–D isotopomer of **12a**. No significant quantity of the expected H–D isotopomer was formed (as shown by the absence of a 1:1:1 triplet in the ^1H NMR spectrum).

In order to prepare the H–D isotopomer, we synthesized the deuteride complex **7-D** from CD_3OD (similar to **7** as shown in Scheme 2). The ^{31}P NMR spectrum of **7-D** displays a triplet at 120.7 ppm. Protonation of **7-D** using HOTf affords a mixture of $[CpRu(\eta^2\text{-}HD)\{\kappa^2\text{-}P,P\text{-}(RO)_2PN(Me)P(OR)_2\}][CF_3SO_3]$ (**13a**) and $[CpRu(H)(D)\{\kappa^2\text{-}P,P\text{-}(RO)_2PN(Me)P(OR)_2\}][CF_3SO_3]$ (**13b**). A triplet is observed at −8.01 ppm [$^1J(H,D) = 24.5$ Hz] for the side-on η^2 bound H–D isotopomer in **13a**. A triplet-of-triplets pattern is observed for the hydride proton of **13b** at −6.20 ppm [$^2J(P,H) = 26.4$ Hz, $^2J(H,D) = 4.0$ Hz]. The ^{31}P NMR spectrum displays a triplet at 115.6 ppm [$^2J(P,D) = 13.8$ Hz] and a broad resonance at 108.8 ppm for **13a** and **13b** respectively.

Having synthesized the dihydrogen complex and the corresponding H–D isotopomer, we estimated the H–H distance from the T_1 values [28a,b] and also from the $^1J(H,D)$ values [28c]. The T_1 value of 10 ms corresponds to a H–H distance (r_{H-H}) of 0.788 Å if the H–H rotation is faster on the NMR time scale. If the H–H rotation is slower on the NMR time scale, then the H–H distance is 0.944 Å. The medium value of $^1J(H,D)$ coupling constant for the H–D isotopomer (24.5 Hz) gives a H–H distance of 1.011 Å. This value is close to the value observed for



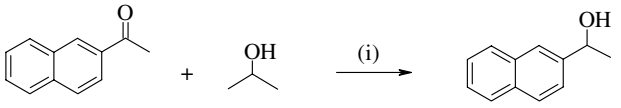
X	12a	12b
CF_3SO_3	8	1
BF_4	13	1
CF_3COO	12	1

Scheme 3. Protonation of complex **7** using different acids.

the complexes [(η^5-C_9H_7)Ru(H_2)(dppm)] [27g] and [CpRu(H_2)(dppm)] [28d]. Thus we conclude that the dihydrogen ligand in our case is in the slow rotating regime with a H–H bond distance of 0.944 Å.

3.5. Catalytic transfer hydrogenation of ketones

The access to a range of symmetrically and unsymmetrically substituted diphosphazanes that differ in steric bulk and π-acceptor capability prompted us to investigate their catalytic activity in asymmetric transfer hydrogenation of ketones. A plethora of ruthenium complexes are known for this transformation [2–11]. No chiral diphosphazane based ruthenium catalysts have been used to-date for this transformation. Asymmetric transfer hydrogenation of 2-acetonaphthone with 2-propanol was used as the model reaction (Scheme 4). In a typical experiment, the catalyst was generated *in situ* from [$RuCl_2(PPh_3)_3$] and two equivalents of chiral diphosphazane and a ketone:ruthenium:ligand ratio of 200:1:2 was used. Chart 2 shows the various chiral diphosphazanes that have been used for transfer hydrogenation and the results are shown in Table 3. It is evident that the ligands (*R*,*R*)-**L**^{7}, (*S*,*S*)-**L**^{7}, (*R*)-**L**^{4} and (*S*)-**L**^{4} induce moderate levels of enantioselectivity in the product while the other ligands do not impart any enantioselectivity. Apparently, axially chiral diphosphazanes that bear sterically encumbered substituent at the phosphorus are more efficient in chiral induction than the other ligands, though the yield of the product is low. Ligands **L**^{5} and **L**^{9} that bear chirality at the carbon are less sterically encumbered at the phosphorus and do not give rise to enantioselectivity. Though ligands **L**^{3} and **L**^{8} bear the axially chiral 1,1′-binaphthylene-2,2′-dioxy moiety, one of the phosphorus centers in these ligands is not sterically crowded; hence these ligands do not impart enantioselectivity. The formation of a diastereomeric mixture of ruthenium hydride complexes **11a** and **11b** from the optically pure trichiral complex **6** and the stereoselective formation of only one enantiomeric pair during the synthesis of complex **4** clearly bring out the importance of steric effect in controlling the enantioselectivity. In an attempt to enhance the enantioselectivity and also to investigate the influence of catalyst ratio on enantioselectivity, the ratio of ketone:ruthenium:ligand was decreased to 100:1:2. The axially chiral ligand (*R*,*R*)-**L**^{7} was used for this study. Upon increasing the mole ratio of the catalyst from 0.5 to 1.0, we found a moderate increase in the enantioselectiviy of the product from 10% to 30% (see Table 3).



(i) $RuCl_2(PPh_3)_3$, 2 equiv. ligand, 3 equiv. KOH, 80 ^{0}C

Scheme 4. Ruthenium catalyzed asymmetric transfer hydrogenation of 2-acetonaphthone.

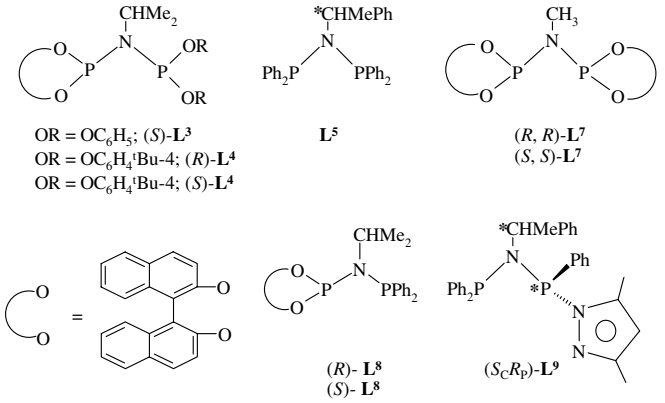


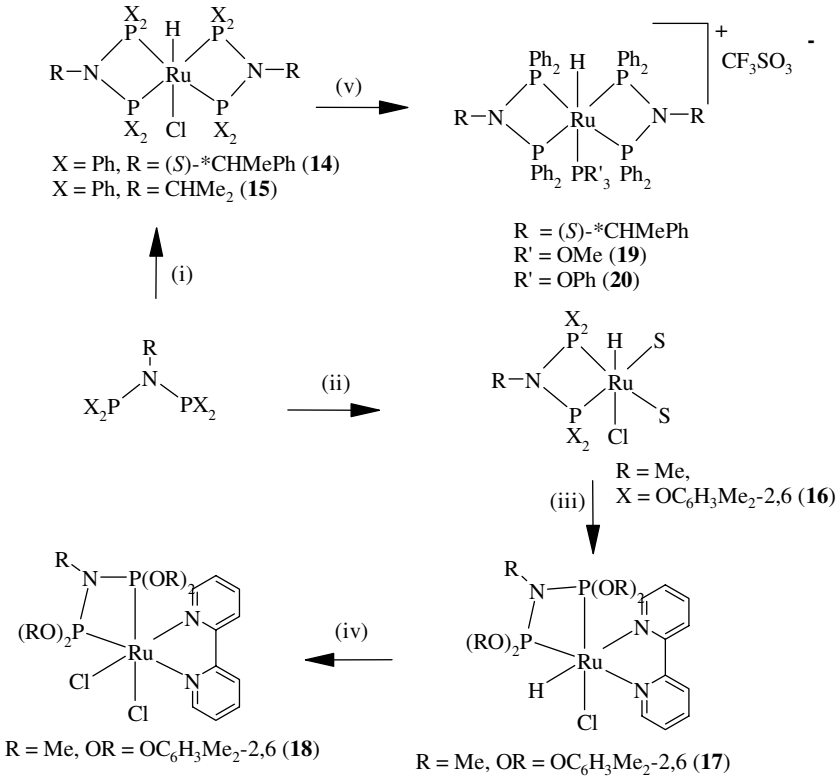
Chart 2. Chiral diphosphazanes employed in asymmetric transfer hydrogenation.

3.6. Synthesis of ruthenium(II) chloro(hydrido) complexes of diphosphazanes

It is well known that ruthenium catalyzed asymmetric transfer hydrogenation proceeds through a hydride intermediate. In order to have an insight into the nature of the hydride species generated under catalytic conditions, we attempted to synthesize chloro and hydrido complexes of ruthenium. Recently, *trans*-dichloro [1i,6b,8d,11b] and *trans*-(chloro)hydrido [1i,6b,11a,30] complexes of ruthenium bearing diphosphines have attracted attention because of their potential usefulness as catalysts in hydrogenation and transfer hydrogenation; some of the complexes have been structurally characterized. The synthesis and structural characterization of *trans*-dichloro ruthenium complexes of diphosphazanes have also been reported [31].

The reaction of [$RuCl_2(COD)$]$_n$ with two molar equivalents of $Ph_2PN(R)PPh_2$ [R = (*S*)-*CHMePh (**L**^{5}) or $CHMe_2$ (**L**^{6})] in the presence of an excess of triethylamine in ethanol give the *trans* chloro hydrido ruthenium complexes *trans*-[Ru(H)Cl{κ^2-P,P-$Ph_2PN(R)PPh_2$}$_2$] [R = (*S*)-*CHMePh (**14**) or $CHMe_2$ (**15**)] (Scheme 5). The ^{31}P NMR spectrum of **14** displays an AA′XX′ pattern for the diastereotopic phosphorus atoms. A singlet is observed at 87.5 ppm for complex **15**. The ^{1}H NMR spectra of complexes **14** and **15** display a quintet pattern at −15.20 ppm for the hydride ligand *trans* to the chloride. The chemical shift, multiplicity and coupling constants reveal that the hydride is located *transoid* to chloride and *cisoid* to two diphosphazane ligands. Based on the observed spectroscopic pattern, we conclude that **14** and **15** are the bis(diphosphazane) chelated Ru(II) derivatives, *trans*-[Ru(H)Cl{κ^2-P,P-$Ph_2PN(R)PPh_2$}$_2$], in which the hydride ligand is located trans to the chloride. The observed hydride chemical shift is close to that reported for other similar type of complexes [30].

In contrast to the reactions of the ligands **L**^{5} and **L**^{6} towards [$RuCl_2(COD)$]$_n$, the reaction of [$RuCl_2(COD)$]$_n$ with either one or two molar equivalents of the sterically bulky diphosphazane $(RO)_2PN(Me)P(OR)_2$ [R = C_6H_3-Me_2-2,6 (**L**^{1})] under similar conditions gives a product,



(i) 0.5 eq. $[RuCl_2(1,5\text{-}COD)]_n$, Et_3N, EtOH, 80 °C, 5 h
(ii) 0.5 or 1 eq. $[RuCl_2(1,5\text{-}COD)]_n$, Et_3N, EtOH, 80 °C, 5 h
(iii) 2,2'-bipyridine, CH_3CN + THF (5:2 v/v), 25 °C, 75 mins
(iv) Crystallization from dichloromethane-petrol
(v) PR'_3, AgOTf, THF, 25 °C, 3h

Scheme 5. Synthesis of ruthenium hydrido and chloro-hydrido complexes of diphosphazanes.

which can be formulated as the hydride complex, *trans*-[RuH(Cl){κ^2-P,P-$(RO)_2PN(Me)P(OR)_2$}$(CD_3CN)_2$] (**16-*d*$_3$**) on the basis of its ^{31}P and ^1H NMR spectral data (Table 4). The phosphorus chemical shift for **16** (114.1 ppm) is shifted *upfield* as compared to that of the parent diphosphazane. The ^1H NMR spectrum displays a triplet at −14.88 ppm; this chemical shift value is close to that observed for complexes **14** and **15** and indicates that the hydride is located *trans* to a strongly basic ligand such as chloride. The multiplicity of the hydride resonance reveals that only one diphosphazane (two phosphorus nuclei) is bound to ruthenium. Complex **16** could not be isolated in a pure form owing to its high sensitivity to air and chlorinated solvents. The formation of only the mono diphosphazane substituted complex **16** even in the presence of two equivalents of the diphosphazane can be attributed to the steric crowding provided by the methyl groups at the two *ortho* positions of the phenoxy substituent, which precludes the coordination of two diphosphazane ligands to ruthenium.

Since complex **16** could not be isolated in pure form, attempts were made to isolate a hydride complex bearing one diphosphazane moiety by substitution of the labile coordinated solvent molecules with a suitable bidentate ligand. Treatment of an acetonitrile–THF solution of complex **16** with one equivalent of 2,2′-bipyridine gives a "dark red complex" (**17**). The ^{31}P NMR spectrum of the "dark red complex" shows an AB spin system at 108.9 and 107.7 ppm [$^2J(A,B) = 36.7$ Hz] indicating the presence of two magnetically non-equivalent phosphorus nuclei. The ^1H NMR spectrum displays a "doublet-of-doublets" at −13.39 ppm [$^2J(P,H) = 44.0$, 33.3 Hz] for the ruthenium bound hydride. Crystallization of the "dark red complex" from dichloromethane–petrol afforded bright yellow-orange crystals. The ^{31}P NMR spectrum of the crystals shows an AB spin system at 97.6 and 91.8 ppm [$^2J(A,B) = 9.7$ Hz]. No hydride resonances were observed in the ^1H NMR spectrum. A single crystal X-ray crystallographic study (see later) was performed on the bright yellow-orange crystals and the compound was found to be *cis*-[$RuCl_2${κ^2-P,P-$(RO)_2PN(Me)P(OR)_2$}(κ^2-N,N-2,2′-bpy)] (bpy = 2,2′-bipyridine) (**18**) (see Fig. 5). Since the complexes **17** and **18** display an AB pattern in their ^{31}P NMR spectra, complex **17** is formulated as *cis*-[Ru(H)Cl-{κ^2-P,P-$(RO)_2PN(Me)P(OR)_2$}(κ^2-N,N-bpy)] (**17**) in which the hydride ligand is located *trans* to a bipyridyl nitrogen atom. Apparently, complex **17** is obtained from complex **16** by *trans–cis* isomerization.

Recently, Albertin and co-workers [32] have synthesized a series of hydride complexes, $[M(H)(N–N)(L)_3]$ (M = Fe [32a], Ru [32b] or Os [32c]; L = monophosphorus ligand, N–N = 2,2′-bipyridine, 1,10-phenanthroline or 5,5′-Me_2-2,2′bipyridine) which display a spectroscopic behavior similar to **17**. These complexes were found to be fluxional in solution and exist as a mixture of *fac*- and *mer*-isomers in solution. The hydride resonance in these *mer*-isomers appears in the range −11.9 to −18.4 ppm depending on the transition metal and the phosphorus ligand *trans* to the hydride ligand. The structure of the *mer*-isomer, *cis*-$[Ru(H)\{P(OEt)_3\}_3(\kappa^2\text{-N,N-bpy})]$ was established by X-ray crystallography [32b].

3.7. Substitution reactions on complex *14*

The reaction of complex **14** with monophosphites $P(OR)_3$ (R = Me or Ph) in the presence of AgOTf afford the phosphite substituted cationic ruthenium complexes **19** and **20**. The ^{1}H NMR spectrum of **19** or **20** displays a doublet-of-quintet pattern at −6.20 ppm for the hydride *trans* to the phosphite ligand. This chemical shift lies downfield from that observed for complexes **14** or **15**. The ^{31}P NMR spectrum displays an AX_4 spin system. The phosphite phosphorus in complexes **19** or **20** appears at ~118–129 ppm as a quintet. The four phosphorus nuclei of the two diphosphazane ligands resonate as a doublet at ~89 ppm. The NMR data for the complexes **14**–**20** are listed in Table 4. The observed NMR spectral pattern for complexes **19** or **20** is similar to that observed for the complexes *trans*-$[RuH\{P(OR_3)\}(dppe)_2]$ (R = Me, Et, ^{i}Pr) [33]. Attempts to synthesize a dihydrogen complex from complex **14** either by (i) protonation using different acids or (ii) abstraction of chloride by AgOTf followed by reaction with H_2 gas were unsuccessful.

3.8. Crystal and molecular structure of $(RO)_2PN(Me)P(OR)_2$ ($\mathbf{L}^1$)

The structure of ligand $\mathbf{L}^1$ is shown in Fig. 1. The compound crystallizes in the space group *P*2/*n* with half a molecule in the asymmetric unit and two molecules in the unit cell. The whole molecule adopts a C_2 conformation in the solid-state. The geometry around the nitrogen is trigonal planar with a P–N–P angle of 115.3(1)°. This value is smaller than that in $Ph_2PN(CHMe_2)PPh_2$ (122.8°) [21b], $Ph_2PN(CHMe_2)PPh(OC_6H_3Me_2\text{-}2,6)$ (122.0°) [34a] ($C_6H_4O_2$)PN(R)PPh_2 (120.7°) [34b] and ^{i}PrN[PhPX][PhPX′] (X, X′ = ^{i}PrNH, EtNHt or PhNH) (119.6–120.7°) [21c] but slightly larger than that observed in $Ph_2PN(R)PPh_2$ [R = C_6H_5, C_6H_4(CN-3), C_6H_4(CN-4)] and $EtN\{P(OR)_2\}_2$ (R = $C_6H_3{}^iPr_2$-2,6 or $C_6H_3Me_2$-2,6) (109.5–114.5°) [21d,34c]. The P–N bond distance in $\mathbf{L}^1$ [1.672(1) Å] is shorter than that in $Ph_2PN(R)PPh_2$ [R = $CHMe_2$ (1.710 Å) [21b], C_6H_5, C_6H_4(CN-3) or C_6H_4(CN-4) (1.723–1.746 Å) [34c], ^{i}Pr[PhPX][PhPX′] (X, X′ = ^{i}PrNH, EtNH or PhNH) (1.705–1.722 Å) [21c], and $Ph_2PN(CHMe_2)PPh(OC_6H_3Me_2\text{-}2,6)$ (1.71 Å) [34a] and close to the values for $EtN\{P(OR)_2\}_2$ (R = $C_6H_3{}^iPr_2$-2,6 or $C_6H_3Me_2$-2,6) (1.674 and 1.693 Å) [21d]. The P–N distances in ($C_6H_4O_2$)PN(R)PPh_2 [34b] that bears two different type of phosphorus atoms shows two different P–N bond lengths. The phosphorus that is *less π-acceptor* in character (“PPh_2” phosphorus) *is farther* from the nitrogen (1.743Å) than the phosphorus that is a *stronger π-acceptor* (1.654 Å). These variations in P–N bond distances can be rationalized on the basis of “negative hyperconjugation” model [35].

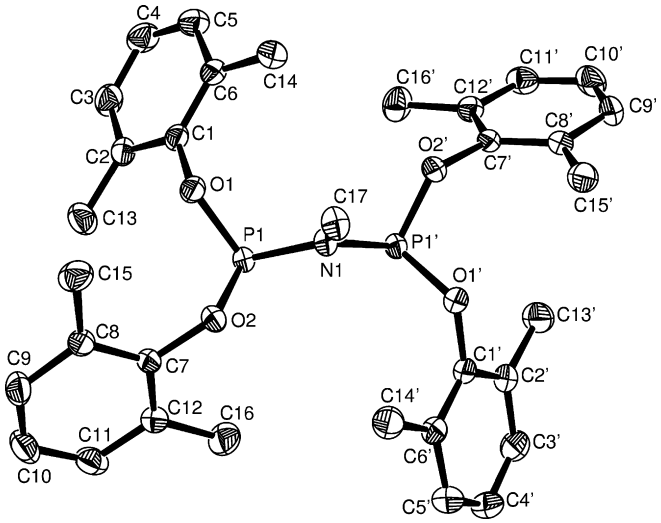


Fig. 1. ORTEP view of the molecular structure of $(RO)_2PN(Me)P(OR)_2$ ($\mathbf{L}^1$). Thermal ellipsoids are drawn at 30% probability level. Hydrogen atoms are omitted for clarity.

3.9. Crystal and molecular structures of the half-sandwich complexes *4* and *7*

The solid-state structures of the complexes **4** and **7** are shown in Figs. 2 and 3 respectively. A comparison of the steric influence of the ligands in complexes **4** and **7** is depicted in Fig. 4. The structures belong to the class of

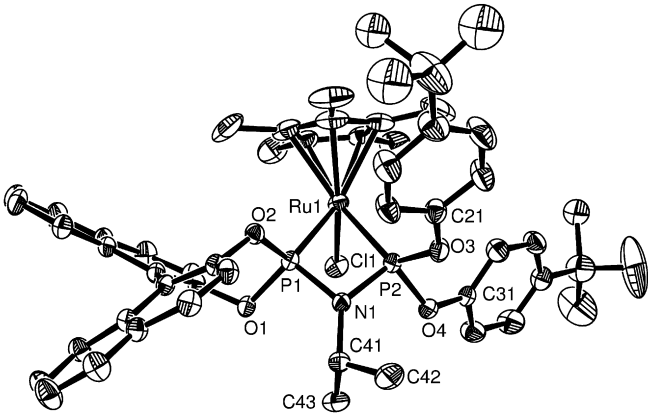


Fig. 2. ORTEP view of the molecular structure of $[(\eta^5\text{-Cp}^*)Ru\{\kappa^2\text{-}P,P\text{-}(C_{20}H_{12}O_2)PN(CHMe_2)P(OC_6H_4{}^tBu\text{-}4)_2\}Cl]$ (**4**). Thermal ellipsoids are drawn at 30% probability level. Hydrogen atoms are omitted for clarity.

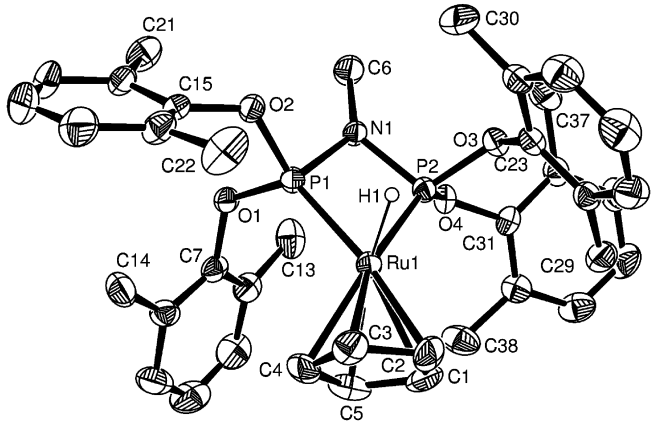


Fig. 3. ORTEP view of the molecular structure of $[(\eta^5\text{-Cp})Ru(H)\{\kappa^2\text{-P,P-}(RO)_2PN(Me)P(OR)_2\}]$ ($R = C_6H_3Me_2$-2,6) (**7**). Thermal ellipsoids are drawn at 30% probability level. Hydrogen atoms (except ruthenium bound hydride) are omitted for clarity.

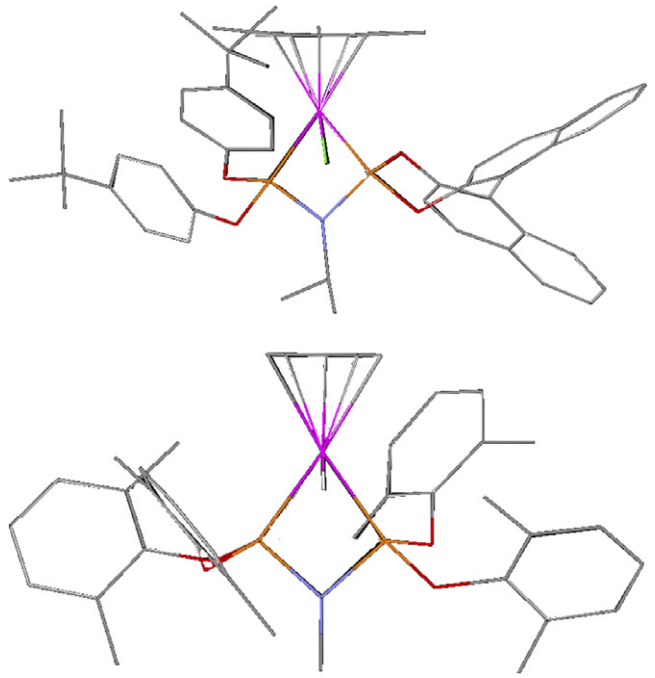


Fig. 4. A view of the molecular structures of the half-sandwich complexes **4** and **7** depicting the steric influence of the ligands.

three-legged piano-stool complexes; the two phosphorus atoms of the diphosphazane and the hydride (or chloride) ligands act as the legs. The coordination geometry around ruthenium can be considered as distorted octahedral. Selected bond distances and angles are listed in Table 6. The bite angle at Ru(1) in complexes **4** and **7** [67.77(4)° and 69.21(5)° respectively] are comparable to each other and similar to that observed in the trichiral cyclopentadienyl ruthenium complex $(S_C S_P R_{Ru})$-$[(\eta^5\text{-}C_5H_5)Ru\{\kappa^2\text{-P,P-}Ph_2PN(R)PPh(N_2C_3HMe_2\text{-}3,5)\}Cl]$ (**6**) [R = (*S*)-*CHMePh] [69.3(1)°] [12a] and the indenyl ruthenium hydride complex $[(\eta^5\text{-}C_9H_7)Ru(H)\{\kappa^2\text{-P,P-}Ph_2PN((S)\text{-}^*CHMePh)PPh_2\}]$ [71.5(1)°] [25]. The P–N–P span angle in complexes **4** and **7** [99.4(2)° and 95.8(2)°] are much smaller than that in complex **6** [119.4(8)°]. This lowering of the span angle of the diphosphazane in these two complexes is due to the increased steric bulk at the phosphorus center. The pentamethyl cyclopentadienyl ring deviates slightly from its ideal planar geometry. In both the complexes, the monodentate ligand (chloride or hydride) is located perpendicular to the diphosphazane. The angles subtended by the centroid of the cyclopentadienyl moiety with the two phosphorus atoms of diphosphazane in complex **7** are almost equal (141.7° and 142.6°); the corresponding values for **4** are 133.5° and 140.1°. Because of the asymmetric nature of the diphosphazane in complex **4**, the pentamethyl cyclopentadienyl ring is tilted slightly towards the binaphthyl phosphorus P(1) [hence a smaller angle, 133.5° for Cp–Ru–P(1)]; the bulky *tert*-butylphenoxy substituents on the phosphorus force the pentamethyl cyclopentadienyl moiety towards the other side of the diphosphazane. A similar tilting of Cp* ring has been observed for the cationic complex, $[(\eta^5\text{-Cp}^*)Ru(\eta^2\text{-}H_2)dppm]\ BF_4$ complex [27d]. The solid-state structure of complex **4** reveals that it consists of the (R_aR_{Ru}) and (S_aS_{Ru}) enantiomeric pair. Such a stereoselective formation of only one enantiomeric pair can be attributed to the steric hinderance offered by the pentamethyl cyclopentadienyl moiety to the bulky substituents at the phosphorus of the diphosphazane ligand.

3.10. Crystal and molecular structure of complex *18*

The structure of the complex *cis*-$[RuCl_2\{\kappa^2\text{-P,P-}(RO)_2PN(Me)P(OR)_2\}\{\kappa^2\text{-}N,N\text{-}2,2'\text{-bipyridine}]$ ($R = C_6H_3Me_2$-2,6)

Table 6
Selected bond lengths (Å) and bond angles (°) in half-sandwich complexes $[Cp^*RuCl\{\kappa^2\text{-}P,P\text{-}(C_{20}H_{12}O_2)PN(CHMe_2)P(OC_6H_4{}^tBu\text{-}4)_2\}]$ (**4**) and $[CpRuH\{\kappa^2\text{-P,P-}(RO)_2PN(Me)P(OR)_2\}]$ [$R = C_6H_3Me_2$-2,6 (**7**)]

Bond distances (Å)			Bond angles (°)		
	4	**7**		**4**	**7**
Ru(1)–P(1)	2.201(2)	2.204(1)	P(1)–N(1)–P(2)	95.8(2)	94.4(2)
Ru(1)–P(2)	2.242(1)	2.197(1)	P(1)–N(1)–C_{alkyl}	131.8(3)	129.9(3)
Ru(2)–Cl(1)	2.425(1)	–	P(2)–N(1)–C_{alkyl}	132.4(3)	133.7(3)
Ru(1)–H(1)	–	1.68(5)	P(1)–Ru(1)–P(2)	69.21(5)	67.77(4)
Ru–$C_{\langle ave\rangle}$	2.223(5)	2.251(6)	P(1)–Ru(1)–Cp[a]	133.5	141.7
P–$N_{\langle ave\rangle}$	1.688(3)	1.685(4)	P(2)–Ru(1)–Cp[a]	140.1	142.6

[a] Centroid of the cyclopentadienyl or pentamethyl cyclopentadienyl moiety.

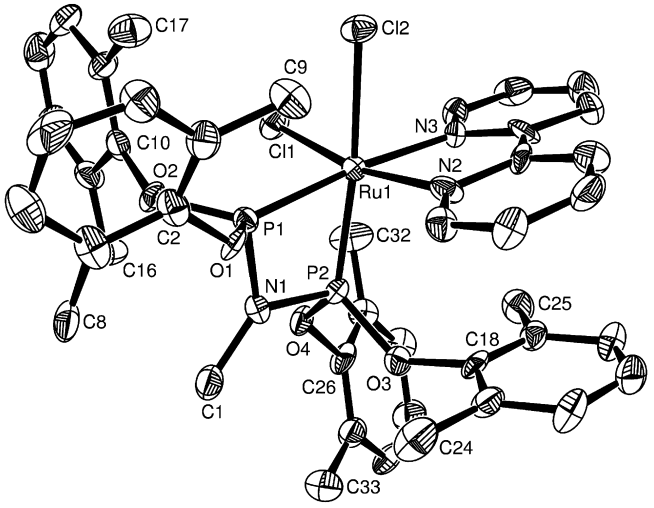


Fig. 5. A view of the molecular structure of *cis*-[$RuCl_2\{\kappa^2$-P,P-$(RO)_2PN(Me)P(OR)_2\}\{\kappa^2$-*N*,*N*-2,2′-bipyridine] (R = $C_6H_3Me_2$-2,6) (**18**). Thermal ellipsoids are drawn at 30% probability level. Hydrogen atoms are omitted for clarity.

(**18**) is shown in Fig. 5. Since complex **18** is a disproportionated product and is obtained during crystallization of complex **17**, the quality of crystals and the diffraction data were not very good. Hence, a detailed discussion of the structural parameters is not attempted here. The complex crystallizes in the chiral space group $P2_1cn$. Selected bond distances and angles are listed in Table 7. The structure reveals an octahedral ruthenium(II) complex in which one of the phosphorus atoms of the diphosphazane ligand is located at the equatorial position and the other is in the axial position. The 2,2′-bipyridine moiety and one chloride ligand occupy the remaining coordination sites in the equatorial plane. The span angle of the diphosphazane [100.6(5)°] is shorter than that of the free ligand. The phosphorus atom *trans* to the chloride ligand is slightly closer to ruthenium [Ru–P(2) = 2.229(3) Å] than the phosphorus that is located *trans* to the nitrogen atom of 2,2′-bipyridine ligand [Ru–P(1) = [2.250(3) Å] (bipyridyl nitrogen is a better π-acceptor than chloride ligand). The chloride ligand *trans* to the phosphorus is farther from ruthenium than the other chloride ligand (phosphorus is a stronger π-acceptor than nitrogen). The nitrogen atom of the bipyridine ligand that is located *trans* to phosphorus is slightly farther from ruthenium [Ru–N(3) = 2.129(9) Å] than the other nitrogen atom of that ligand [Ru–N(2) = 2.09(1) Å] (phosphorus is a better π-acceptor than chloride ligand). The two P–N bond distances are slightly different from each other because the two phosphorus atoms are located at different positions (axial and equatorial).

4. Conclusions

Half-sandwich (Cp and Cp^*) ruthenium chloro complexes of chiral and achiral diphosphazanes and their hydride analogues have been synthesized. The reactions of unsymmetrically substituted diphosphazanes bearing axially chiral 1,1′-binaphthyl-2,2′-dioxy moiety with [(η^5-Cp^*)$RuCl_2$]$_n$ afford "*chiral-at-metal*" half-sandwich ruthenium chloro complexes. The reaction proceeds by a path in which the steric repulsion between the Cp^* moiety and the substituents on the phosphorus favors the formation of only one enantiomeric pair. *The stereochemistry at the ruthenium in these complexes is determined by the configuration of the binaphthyl moiety* as established by X-ray crystal structure of [(η^5-Cp^*)$RuCl\{\kappa^2$-P,P-$X_2PN(R)PYY'\}$] [R = $CHMe_2$, $X_2 = C_{20}H_{12}O_2$, $Y = Y' = OC_6H_4{}^tBu$-4] (**4**). When the diphosphazane bound to ruthenium in the (chloro) cyclopentadienyl complexes is chiral, the reaction with NaOMe/MeOH to form the hydride derivative can proceed *stereoselectively* if the substituents on the phosphorus are sterically bulky as in **4**. Protonation of the ruthenium hydride complex [$CpRuH\{\kappa^2$-P,P-$X_2PN(Me)PX_2\}$] (X = $OC_6H_3Me_2$-2,6) (**7**) affords mainly the dihydrogen complex (**12a**) along with the dihydride complex (**12b**) in smaller amounts owing to the steric crowding of the diphosphazane around ruthenium. Strong π-acceptor character of the phosphorus center(s) and sterically bulky substituents attached to phosphorus appear to promote enantioselectivity in Ru-catalyzed asymmetric transfer hydrogenations using diphosphazanes as chiral auxiliaries. The reaction of the sterically bulky ligand, $X_2PN(Me)PX_2$ (X = $OC_6H_3Me_2$-2,6) (**L**^{1}) with [$RuCl_2$(COD)]$_n$ affords a mono-diphosphazane substituted hydride complex (**16**); such a mono-diphosphazane substituted complex could be the intermediate in asymmetric transfer hydrogenation.

5. Supplementary material

CCDC 628737, 628738, 628739, and 628740 contain the supplementary crystallographic data for (**L**^{1}), (**4**), (**7**), and

Table 7
Selected bond lengths (Å) and bond angles (°) in the complex *cis*-[$RuCl_2\{\kappa^2$-P,P-$(RO)_2PN(Me)P(OR)_2\}\{\kappa^2$-*N*,*N*-2,2′-bipyridine] (R = $C_6H_3Me_2$-2,6) (**18**)

Bond distances (Å)		Bond angles (°)			
Ru(1)–P(1)	2.250(3)	N(2)–Ru(1)–Cl(1)	167.6(3)	P(1)–N(1)–P(2)	100.6(5)
Ru(1)–P(2)	2.229(3)	N(2)–Ru(1)–Cl(2)	83.0(3)	P(1)–Ru(1)–P(2)	70.1(1)
Ru(2)–Cl(1)	2.399(4)	N(3)–Ru(1)–Cl(1)	92.6(4)	P(1)–Ru(1)–Cl(1)	90.2(1)
Ru(1)–Cl(2)	2.479(4)	N(3)–Ru(1)–Cl(2)	83.8(3)	P(1)–Ru(1)–Cl(2)	101.5(1)
Ru(1)–N(2)	2.094(11)	N(2)–Ru(1)–P(1)	100.7(3)	P(2)–Ru(1)–Cl(1)	92.4(1)
Ru(1)–N(3)	2.129(9)	N(2)–Ru(1)–P(2)	96.8(3)	P(2)–Ru(1)–Cl(2)	171.4(2)
P(1)–N(1)	1.651(10)	N(3)–Ru(1)–P(1)	174.1(3)	N(2)–Ru(1)–N(3)	77.2(5)
P(2)–N(1)	1.691(9)	N(3)–Ru(1)–P(2)	104.6(3)	Cl(1)–Ru(1)–Cl(2)	89.1(2)

(**18**). These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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References

[1] (a) B. Cornills, W.A. Herrmann, Applied Homogeneous Catalysis with Organometallic Compounds, Wiley-VCH, Weinheim, 2000;
(b) P.W.N.M. van Leeuwen, Homogeneous Catalysis: Understanding the Art, Kluwer, Academic Publishers, Dordrecht, Netherlands, 2004, pp. 271–229;
(c) W.S. Knowles (Nobel lecture), Angew. Chem., Int. Ed. Engl. 41 (2002) 1998–2007;
(d) J.-P. Genet, Acc. Chem. Res. 36 (2003) 908–918;
(e) B. Breit, Acc. Chem. Res. 36 (2003) 264–275;
(f) I.D. Gridnev, T. Imamoto, Acc. Chem. Res. 37 (2004) 633–644;
(g) J.A. Wiles, C.J.A. Daley, R.J. Hamilton, C.G. Leong, S.H. Bergens, Organometallics 23 (2004) 4564–4568;
(h) C. Daguenet, R. Scopelliti, P.J. Dyson, Organometallics 23 (2004) 4849–4857;
(i) R. Guo, A.J. Lough, R.H. Morris, D. Song, Organometallics 23 (2004) 5524–5529;
(j) K. Rossen, Angew. Chem. Int. Ed. Engl. 40 (2001) 4611–4613.

[2] (a) T. Ohkuma, M. Kitamura, R. Noyori, in: I. Ojima (Ed.), Catalytic Asymmetric Synthesis, second ed., Wiley-VCH, 2000, p. 1;
(b) G.-Q. Lin, Y.-M. Li, A.S.C. Chan, Principles and Application of Asymmetric Synthesis, John Wiley and Sons, 2001;
(c) R. Noyori, T. Okhuma, Angew. Chem. Int. Ed. Engl. 40 (2001) 40–73;
(d) R. Noyori (Nobel lecture), Angew. Chem. Int. Ed. Engl. 41 (2002) 2008–2022.

[3] (a) O. Pàmies, J.-E. Bäckvall, Chem. Eur. J. 7 (2001) 5052–5058;
(b) D.G.I. Petra, J.N.H. Reek, J.-W. Handgraaf, E.J. Meijer, P. Dierkes, P.C.J. Kamer, J. Brussee, H.E. Schoemaker, P.W.N.M. van Leeuwen, Chem. Eur. J. 6 (2000) 2818–2829;
(c) A. Aranyos, G. Csjernyik, K.J. Szabó, J-E. Bäckvall, Chem. Commun. (1999) 351–352;
(d) Y.R. Santosh Laxmi, J.-E. Bäckvall, Chem. Commun. (2000) 611–612;
(e) J.-E. Bäckvall, J. Organomet. Chem. 652 (2002) 105–111.

[4] (a) P.G. Jessop, R.H. Morris, Coord. Chem. Rev. 121 (1992) 155–284;
(b) M. Yamakawa, H. Ito, R. Noyori, J. Am. Chem. Soc. 122 (2000) 1466–1478;
(c) R. Noyori, S. Hashiguchi, Acc. Chem. Res. 30 (1997) 97–102;
(d) C.P. Casey, J. Org. Chem. 68 (2003) 1998–2001.

[5] (a) C.S. Yi, A. He, I.A. Guzei, Organometallics 20 (2001) 3641–3643;
(b) C.J.A. Daley, S.H. Bergens, J. Am. Chem. Soc. 124 (2002) 3680–3691.

[6] (a) P. Dani, T. Karlen, R.A. Gossage, S. Gladiali, G. van Koten, Angew. Chem. Int. Ed. Engl. 39 (2000) 743–745;
(b) V. Cadierno, P. Crochet, J. Díez, S.E. García-garrido, J. Gimeno, Organometallics 23 (2004) 4836–4845;
(c) W. Baratta, P. Da Ros, A. Del Zotto, A. Sechi, E. Aangrando, P. Rigo, Angew. Chem. Int. Ed. Engl. 43 (2004) 3584–3588;
(d) C. Schlünken, M.A. Esteruelas, F. Lahoz, L.A. Oro, H. Werner, Eur. J. Inorg. Chem. (2004) 2477–2487.

[7] (a) K.-J. Haack, S. Hashiguchi, A. Fujii, T. Ikariya, R. Noyori, Angew. Chem. Int. Ed. Engl. 36 (1997) 285–288;
(b) M. Bernard, F. Delbecq, P. Sautet, F. Fache, M. Lemaire, Organometallics 19 (2000) 5715–5722;
(c) M. Ito, M. Hirakawa, K. Murata, T. Ikariya, Organometallics 20 (2001) 379–381;
(d) D.J. Cross, J.A. Kenny, I. Houson, L. Campbell, T. Walsgrove, M. Wills, Tetrahedron: Asymmetry 12 (2001) 1801–1806.

[8] (a) P. Braunstein, F. Naud, S.J. Rettig, New. J. Chem. 25 (2001) 32–39;
(b) A.M. Maj, K.M. Pietrusiewicz, I. Suisse, F. Agbosson, A. Morteux, J. Organomet. Chem. 626 (2001) 157–160;
(c) C. Standfest-Hauser, C. Slugovc, K. Mereiter, R. Schmid, K. Kirchner, L. Xiao, W. Weissensteiner, J. Chem. Soc. Dalton Trans. (2001) 2989–2995;
(d) P. Crochet, J. Gimeno, S. Garcia-Granda, J. Burge, Organometallics 20 (2001) 4369–4377;
(e) C. Saluzzo, J. Breuzard, S. Pellet-Rostaing, M. Vallet, F. Le Guyader, M. Lemaire, J. Organomet. Chem. 643/644 (2002) 98–104.

[9] (a) J. Takehara, S. Hashiguchi, A. Fujii, T. Ikariya, R. Noyori, Chem. Commun. (1996) 233–234;
(b) M. Palmer, T. Walsgrove, M. Wills, J. Org. Chem. 62 (1997) 5226–5228;
(c) K. Everaere, A. Mortreux, M. Bulliard, J. Brussee, A. van der Gen, G. Nowogrocki, J.-F. Carpentier, Eur. J. Org. Chem. (2001) 275–291;
(d) S.J.M. Nordin, P. Roth, T. Tarnai, D.A. Alonso, P. Brandt, P.G. Anderson, Chem. Eur. J. 7 (2001) 1431–1436;
(e) D.J. Cross, I. Houson, A.W. Kawamoto, M. Wills, Tetrahedron Lett. 45 (2004) 843–846;
(f) J. Hannedouche, G.J. Clarkson, M. Wills, J. Am. Chem. Soc. 126 (2004) 986–987;
(g) T. Geldbach, P.J. Dyson, J. Am. Chem. Soc. 126 (2004) 8114–8115.

[10] (a) P. Braunstein, M.D. Fryzuk, F. Naud, S.J. Rettig, J. Chem. Soc. Dalton Trans. (1999) 589–594;
(b) P. Braunstein, F. Naud, A. Pfaltz, S.J. Rettig, Organometallics 19 (2000) 2676–2683.

[11] (a) K. Abdur-Rashid, M. Faatz, A.J. Lough, R.H. Morris, J. Am. Chem. Soc. 123 (2001) 7473–7474;
(b) Y. Xu, N.W. Alcock, G.J. Clarkson, G. Docherty, G. Woodward, M. Wills, Org. Lett. 6 (2004) 4105–4107.

[12] (a) K. Raghuraman, S.S. Krishnamurthy, M. Nethaji, J. Chem. Soc. Dalton Trans. (2002) 4289–4295;
(b) S.K. Mandal, G.A.N. Gowda, S.S. Krishnamurthy, T. Stey, D. Stalke, J. Organomet. Chem. 690 (2005) 742–750;
(c) T.S. Venkatakrishnan, S.S. Krishnamurthy, M. Nethaji, J. Organomet. Chem. 691 (2006) 224–228;
(d) S.K. Mandal, T.S. Venkatakrishnan, A. Sarkar, S.S. Krishnamurthy, J. Organomet. Chem. 691 (2006) 2969–2977.

[13] (a) M.S. Balakrishna, V.S. Reddy, S.S. Krishnamurthy, J.F. Nixon, J.C.T.R. Burckett St. Laurent, Coord. Chem. Rev. 129 (1994) 1–90;
(b) K. Raghuraman, S.K. Mandal, T.S. Venkatakrishnan, S.S. Krishnamurthy, M. Nethaji, Proc. Indian Acad. Sci. (Chem. Sci.) 114 (2002) 233–246;
(c) M. Witt, H.W. Roesky, Chem. Rev. 94 (1994) 1163;
(d) P. Bhattacharyya, J.D. Woollins, Polyhedron 14 (1995) 3367.

[14] (a) M.S. Balakrishna, T.K. Prakasha, S.S. Krishnamurthy, U. Siriwardane, N.S. Hosmane, J. Organomet. Chem. 390 (1990) 203–216;

(b) R.P.K. Babu, S.S. Krishnamurthy, M. Nethaji, Tetrahedron: Asymmetry 6 (1995) 427–438;
(c) R.J. Cross, T.H. Green, R.J. Keat, J. Chem. Soc., Dalton Trans. (1976) 1424–1428;
(d) T.S. Venkatakrishnan, M. Nethaji, S.S. Krishnamurthy, Curr. Sci. 85 (2003) 969–974;
(e) R.P.K. Babu, K. Aparna, S.S. Krishnamurthy, M. Nethaji, Phosphorus, Sulfur, Silicon Relat. Elem. 103 (1995) 39–53.

[15] (a) M.I. Bruce, C. Hameister, A.G. Swincer, R.C. Wallisa, Inorg. Synth. 21 (1982) 78–79;
(b) P.S. Hallman, T.A. Stephenson, G. Wilkinson, Inorg. Synth. 12 (1970) 237–240;
(c) M.A. Bennett, G. Wilkinson, Chem. Ind. (London) (1959) 1516.

[16] J.F. Nixon, J. Chem. Soc. (A) (1968) 2689–2692.

[17] M. Raja, S.S. Krishnamurthy, unpublished results.

[18] (a) Bruker SMART, V. 6.028, Bruker AXS Inc., Madison, WI, USA, 1998;
(b) Bruker SAINT, V. 6.02, Bruker AXS Inc., Madison, WI, USA, 1998;
(c) G.M. Sheldrick, SADABS, University of Göttingen, Germany, 1997;
(d) Bruker SHELXTL, NT V. 5.10, Bruker AXS Inc., Madison, WI, USA, 1998.

[19] L.J. Farrugia, J. Appl. Crystallogr. 32 (1999) 837–838.

[20] G.M. Sheldrick, SHELXL-97, Program for refinement of crystal structures, University of Göttingen, Germany, 1997.

[21] (a) I.J. Colquhoun, W. McFarlane, J. Chem. Soc., Dalton Trans. (1977) 1674–1679;
(b) R. Keat, L.M. Muir, K.W. Muir, D.S. Rycroft, J. Chem. Soc., Dalton Trans. (1981) 2192–2198;
(c) T.R. Prout, T.W. Imiolczyk, F. Berthelemy, S.M. Young, R.C. Haltiwanger, A.D. Norman, Inorg. Chem. 33 (1994) 1783–1790;
(d) G. Prabhusankar, N. Palanisami, R. Murugavel, R.J. Butcher, Dalton Trans. (2006) 2140–2146.

[22] (a) E.P. Kundig, C.M. Saudan, G. Bernardinelli, Angew. Chem. Int. Ed. Engl. 38 (1999) 1219–1223;
(b) W. Baratta, A.D. Zotto, P. Rigo, Organometallics 18 (1999) 5091–5096;
(c) H. Brunner, Angew. Chem. Int. Ed. Engl. 38 (1999) 1194–1208;
(d) H. Brunner, C. Valerio, M. Zabel, New J. Chem. 24 (2000) 275–280;
(e) W. Baratta, W.A. Hermann, R.M. Kratzer, P. Rigo, Organometallics 19 (2000) 3664–3669;
(f) H. Brunner, H.B. Kagan, G. Kreutzer, Tetrahedron: Asymmetry 14 (2003) 2177–2187;
(g) A. Doppiu, A. Salzer, Eur. J. Inorg. Chem. (2004) 2244–2252.

[23] (a) G. Consiglio, F. Morandini, Chem. Rev. 87 (1987) 761–778;
(b) H. Brunner, Adv. Organomet. Chem. 18 (1980) 151–206.

[24] (a) J.W. Faller, K.J. Chase, Organometallics 14 (1995) 1592–1600;
(b) H. Brunner, R. Oeschey, B. Nuber, J. Chem. Soc. Dalton. Trans. (1996) 1499–1508;
(c) H. Brunner, R. Oeschey, B. Nuber, Organometallics 15 (1996) 3616–3624;
(d) H. Brunner, B. Nuber, M. Prommesberger, Tetrahedron: Asymmetry 9 (1998) 3223–3229;
(e) H. Brunner, M. Prommesberger, Tetrahedron: Asymmetry 9 (1998) 3231–3239;
(f) J.W. Faller, B.P. Patel, M.A. Albrizzio, M. Curtis, Organometallics 18 (1999) 3096–3104;
(g) H. Brunner, F. Henning, M. Zabel, Z. Anorg. Allg. Chem. 630 (2004) 91–96;
(h) H. Brunner, F. Henning, Monatsh. Chem. 135 (2004) 885–897;
(i) H. Brunner, M. Weber, M. Zabel, Coord. Chem. Rev. 242 (2003) 3–13;
(j) H. Brunner, C. Zettler, M. Zabel, Monatsh. Chem. 134 (2003) 1253–1269;
(k) H. Brunner, A. Köllnberger, M. Zabel, Polyhedron 22 (2003) 2639–2646;
(l) H. Brunner, T. Zwack, M. Zabel, W. Beck, A. Böhm, Organometallics 22 (2003) 1741–1750;
(m) H. Brunner, T. Zwack, M. Zabel, Polyhedron 22 (2003) 861–865;
(n) J.W. Faller, J. Parr, Organometallics 19 (2000) 1829–1832.

[25] K. Bieger, J. Díez, M.P. Gamasa, J. Gimeno, M. Pavlišta, Y. Rodríguez-Álvarez, S. García-Granda, R. Santiago-García, Eur. J. Inorg. Chem. (2002) 1647–1656.

[26] (a) M. Peruzzini, R. Poli, Recent Advances in Hydride Chemistry, Elsevier, 2001;
(b) G.J. Kubas, Metal Dihydrogen and σ-Bond Complexes, Kluwer Academic, New York, 2001.

[27] (a) F.M. Conroy-Lewis, S.J. Simpson, J. Chem. Soc., Chem. Commun. (1987) 1675–1676;
(b) M.S. Chinn, D.M. Heinekey, J. Am. Chem. Soc. 112 (1990) 5166–5175;
(c) G. Jia, R.H. Morris, J. Am. Chem. Soc. 113 (1991) 875–883;
(d) G. Jia, A.J. Lough, R.H. Morris, Organometallics 11 (1992) 161–171;
(e) W.T. Klooster, T.F. Koetzle, G. Jia, T.P. Fong, R.H. Morris, A. Albinati, J. Am. Chem. Soc. 116 (1994) 7677–7681;
(f) M.G. Basallote, J. Duran, M.J. Fernández-Trujillo, A. Máñez, Organometallics 19 (2000) 695–698;
(g) M.Y. Hung, S.M. Ng, Z. Zhou, C.P. Lau, G. Jia, Organometallics 19 (2000) 3692–3699;
(h) J.K. Law, H. Mellows, D.M. Heinekey, J. Am. Chem. Soc. 124 (2002) 1024–1030;
(i) E. Cayuela, F.A. Jalón, B.R. Manzano, G. Espino, W. Weissensteiner, K. Mereiter, J. Am. Chem. Soc. 126 (2004) 7049–7062.

[28] (a) P.J. Desrosiers, L. Cai, Z. Lin, R. Richards, J. Halpern, J. Am. Chem. Soc. 113 (1991) 4173–4184;
(b) K.A. Earl, G. Jia, P.A. Maltby, R.H. Morris, J. Am. Chem. Soc. 113 (1991) 3027–3039;
(c) P.A. Maltby, M. Schlaf, M. Steinbeck, A.J. Lough, R.H. Morris, W.T. Klooster, T.F. Koetzle, R.C. Srivastava, J. Am. Chem. Soc. 118 (1996) 5396–5407;
(d) S.J. Litster, A.D. Redhouse, S.J. Simpson, in: Proceedings of the conference Chemistry of the Platinum Group Metals, University of Cambridge, Cambridge, England, 1990, pp. C–48, cited in [27d].

[29] (a) J. Ellermann, C. Schelle, F.A. Knoch, M. Moll, D. Pohl, Monatsh 127 (1996) 783–800;
(b) J. Ellermann, C. Schelle, M. Moll, F.A. Knoch, W. Bauer, Z. Anorg. Allg. Chem. 621 (1995) 789–798;
(c) K.J. Edwards, J.S. Field, R.J. Haines, B.D. Homann, M.W. Stewart, J. Sundermeyer, S.F. Woollam, J. Chem. Soc. Dalton Trans. (1996) 4171–4181.

[30] (a) P.A. van der Schaaf, R. Kolly, A. Hafner, Chem. Commun. (2000) 1045–1046;
(b) S.H. Liu, S.-Y. Yang, S.T. Lo, Z. Xu, W.S. Ng, T.B. Wen, Z.Y. Zhou, Z. Lin, C.P. Lau, G. Jia, Organometallics 20 (2001) 4161–4169;
(c) K. Abdur-Rashid, A.J. Lough, R.H. Morris, Organometallics 20 (2001) 1047–1049;
(d) T. Li, R. Churlaud, A.J. Lough, K. Abdur-Rashid, R.H. Morris, Organometallics 23 (2004) 6239–6247.

[31] (a) M.S. Balakrishna, R. Pande, J.T. Mague, Polyhedron 22 (2003) 587–593;
(b) J. Díez, M.P. Gamasa, J. Gimeno, Y. Rodríguez, S. García-Granda, Eur. J. Inorg. Chem. (2004) 2078–2085.

[32] (a) G. Albertin, S. Antoniutti, M. Bortoluzzi, Inorg. Chem. 43 (2004) 1328–1335;
(b) G. Albertin, S. Antoniutti, A. Bacchi, C. D'Este, G. Pelizzi, Inorg. Chem. 43 (2004) 1336–1349;
(c) G. Albertin, S. Antoniutti, S. Pizzol, J. Organomet. Chem. 689 (2004) 1639–1647.

[33] N. Mathew, B.R. Jagirdar, R.S. Gopalan, G.U. Kulkarni, Organometallics 19 (2000) 4506–4517.

[34] (a) H. Krishna, S.S. Krishnamurthy, M. Nethaji, Polyhedron 25 (2006) 3189–3200;
(b) R.P.K. Babu, S.S. Krishnamurthy, M. Nethaji, Heteroat. Chem. 2 (1991) 477–485;
(c) Z. Fei, R. Scopelliti, P.J. Dyson, J. Chem. Soc., Dalton Trans. (2003) 2772–2779.

[35] (a) S.S. Krishnamurthy, Phosphorus, Sulfur, Silicon Relat. Elem. 87 (1994) 101–111;
(b) R. Murugavel, S.S. Kumaravel, S.S. Krishnamurthy, J. Chandrasekar, J. Chem. Soc., Dalton Trans. (1994) 847–852;
(c) A.B. Chaplin, J.A. Harrison, P.J. Dyson, Inorg. Chem. 44 (2005) 8407–8417.