Di-, tetra- and polynuclear Rh^{I} complexes containing phenylene-1,4diaminotetra(phosphonite), $p-C_{6}H_{4}[N\{P(OC_{6}H_{4}OMe-o)_{2}\}_{2}]_{2}$ and their catalytic investigation towards transfer hydrogenation reactions[†]

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The reactions of phenylene-1,4-diaminotetra(phosphonite), p-C₆H₄[N{P(OC₆H₄OMe-o)₂}₂]₂ (P₂N(Ph)NP₂) (1) with [Rh(COD)Cl]₂ in 1 : 2 and 1 : 1 molar ratio produce tetra- and polymetallic chelate complexes, [Rh₄(COD)₂(μ -Cl)₄(P₂N(Ph)NP₂)] (2) and [Rh₂(μ -Cl)₂(P₂N(Ph)NP₂)]_n (3), respectively. Similar reaction of 1 with [Rh(COD)Cl]₂ in dichloromethane–acetonitrile mixture furnishes a dinuclear complex, [Rh₂Cl₂(CH₃CN)₂(P₂N(Ph)NP₂)] (4). The reaction of 3 or 4 with CO affords a dinuclear carbonyl derivative, [Rh₂Cl₂(CO)₂(P₂N(Ph)NP₂)] (5). Treatment of 4 with 2 equivalents of pyrazine or 4,4'-bipyridine produce one-dimensional Rh¹ coordination polymers, [Rh₂Cl₂(C₄H₄N₂)(P₂N(Ph)NP₂)]_n (6) and [Rh₂Cl₂(C₁₀H₈N₂)(P₂N(Ph)NP₂)]_n (7) in quantitative yields. The catalytic activity of Rh¹ complexes 2–7 have been investigated in transfer hydrogenation reactions.

Introduction

A great deal of interest is currently devoted to the synthesis of multinuclear complexes including coordination polymers using rigid polydentate phosphine ligands.1 Polyphosphines can readily form di-, tetra- and/or polynuclear metal complexes with metals in close proximity to each other, thereby giving rise to strong cooperativity effects in catalytic reactions.² In addition, conformationally rigid polyphosphines with extended conjugation in the framework are potential candidates for designing conducting polymers for effective electronic coupling through ligands.³ Such materials are endowed with novel electronic, magnetic and optical properties and serve as source materials for the production of chemical sensors and electroluminescent devices.⁴ Several systems including carboxylates, aryl-bridged di-isocyanides and alkyne-bridged pyridyl ligands have been used for the preparation of various rhodium polymers which often form porous materials through secondary interactions.⁵ The porous network of $[Rh_2(O_2CPh)_4(pyz)]_n$ (pyz = pyrazine) based on benzoate and pyrazine, prepared by Takamizawa et al., is an efficient system for the inclusion of CO₂ molecules inside the molecular channels in the form of molecular wires.^{5a} However, the polymers reported with these systems have the metal atoms mostly in higher oxidation states (+2 or $+3)^{5a,d.e,6}$ which limits their utility in applications where significant metal-based reactivity is desired. Reports on such polymers with phosphine ligands and also containing Rh^I are scarce and those containing polydentate phosphines with pyridyl linkers are not known in the literature. The only known structurally characterized Rh^{I} coordination polymers are $[RhCl(CO)(dpphex)]_{n}$ [dpphex =

bis(diphenylphosphino)hexane] and $[Rh(dppa)(CO)Cl]_n$ [dppa = 1,2-bis(diphenylphosphino)acetylene].7 Recently, we have utilized a "short-bite" aminobis(phosphine), PhN{ $P(OC_6H_4OMe-o)_2$ }, (I) in combination with various pyridyl ligands to make several multinuclear mixed ligand complexes including coordination polymers.⁸ We have also reported the synthesis of Pd^{II}, Pt^{II} and Cu^I complexes, and catalytic applications of a short-bite tetraphosphonite, $p-C_6H_4[N\{P(OC_6H_4OMe-o)_2\}_2]_2$ (hereafter referred as P₂N(Ph)NP₂).⁹ As a part of our interest in the transition metal chemistry of cyclic and acyclic diphosphazane ligands¹⁰ and their catalytic applications,¹¹ we describe herein the coordinating behavior of phenylene-1,4-diaminotetra(phosphonite), $p-C_6H_4[N{P(OC_6H_4OMe-o)_2}_2]_2$ (1) towards Rh^I derivatives and their utility in transfer hydrogenation reactions. The crystal and molecular structures of a binuclear Rh^I complex and a Rh^I coordination polymer are also described.

Results and discussion

Rh(I) complexes

The ligand p-C₆H₄[N{P(OC₆H₄OMe-o)₂}₂]₂(P₂N(Ph)NP₂) (1) has been prepared by the reaction of p-C₆H₄[N(PCl₂)₂]₂ with four equivalents of 2-(methoxy)phenol in presence of triethylamine.⁹ The reactions of 1 with [Rh(COD)Cl]₂ in 1 : 2 and 1 : 1 molar ratios in dichloromethane lead to the successive replacement of the diene ligands and the formation of chloro-bridged tetra- and polymetallic chelate complexes, [Rh₄(COD)₂(μ -Cl)₄(P₂N(Ph)NP₂)] (2) and [Rh₂(μ -Cl)₂(P₂N(Ph)NP₂)]_n (3), respectively, as shown in Scheme 1. Compound **2** is an orange colored crystalline solid, whereas compound **3** is a pale yellow microcrystalline powder insoluble in most organic solvents. The similar reaction of **1** with [Rh(COD)Cl]₂ in a 1 : 1 ratio in a dichloromethane–acetonitrile mixture (1 : 1) yielded the chelate complex, [Rh₂Cl₂(CH₃CN)₂(P₂N(Ph)NP₂)] (4) in good yield. On refluxing complex **3** in acetonitrile the Rh₂(μ -Cl)₂ bridging units are cleaved to give the binuclear complex **4**.

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Interestingly, compound 4 on heating to $120 \,^{\circ}\text{C}$ under vacuum, produces the polymeric compound 3 in quantitative yield.

The ${}^{31}P{}^{1}H$ NMR spectrum of **2** consists of a doublet centered at 106.9 ppm with a ${}^{1}J_{RhP}$ coupling of 240 Hz, whereas complex 4 shows two doublet of doublets centered at 97.3 and 93.1 ppm with ${}^{1}J_{RhP}$ couplings of 257 and 232 Hz, respectively, with the former corresponding to the phosphorus *trans* to chlorine. The ${}^{2}J_{PP}$ coupling is 88 Hz. The slow bubbling of carbon monoxide gas into a suspension of 3 or 4 in dichloromethane afforded the carbonyl derivative, [Rh₂Cl₂(CO)₂(P₂N(Ph)NP₂)] (5) in quantitative yield. The displacement of coordinated acetonitrile molecules in 4 by pyrazine or 4,4'-bipyridine produce one-dimensional zigzag Rh¹ coordination polymers, $[Rh_2Cl_2(C_4H_4N_2)(P_2N(Ph)NP_2)]_n$ (6) and $[Rh_2Cl_2(C_{10}H_8N_2)(P_2N(Ph)NP_2)]_n$ (7) (Scheme 2). The ³¹P{¹H} NMR spectrum of 5 also shows two doublet of doublets centered at 103.2 and 90.4 ppm with the ${}^{1}J_{RhP}$ couplings of 223 and 192 Hz, respectively, and ${}^{2}J_{PP}$ coupling of 80 Hz. The high frequency resonance is assigned to P-atom trans to Cl.12 The IR spectrum of 5 shows $v_{\rm CO}$ at 2048 and 2006 cm⁻¹.¹³ Because of the poor solubility of complexes 3, 6 and 7, NMR spectroscopic studies could not be

carried out, however, the molecular compositions were confirmed from elemental analysis and mass spectral data. The spectral and analytical data support the proposed formulations of complexes 2–7 and the structures of complexes 4 and 6 were confirmed through single-crystal X-ray diffraction studies. The polymer 6 represents the first structurally characterized Rh¹ polymer having a rigid tetradentate P–N–P system with pyridyl linkers.

The crystal and molecular structures of 4 and 6

Perspective views of compounds **4** and **6** with atom numbering schemes are shown in Fig. 1 and 2, respectively. Crystal data and the details of the structure determinations are given in Table 1, while selected bond lengths and bond angles are given in Table 2. The asymmetric units of **4** and **6** contain half a molecule of the metal complexes while the rhodium adopts an approximate square-planar geometry, with the corners occupied by chlorine, nitrogen and two phosphorus atoms. The core structure of **6** consists of repeating $[(P_2N(Ph)NP_2)(RhCl)_2]$ and pyrazine units arranged in an alternating fashion to form a one-dimensional



Scheme 2



Fig. 1 Molecular structure of 4. All hydrogen atoms have been omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level.



Fig. 2 Molecular structure of 6. All hydrogen atoms and disorder have been omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level.

zigzag coordination polymer. In 4 and 6, the two independent P-N distances differ only slightly [1.699(2), 1.692(2) Å for 4 and 1.694(4), 1.701(4) Å for 6] with a certain degree of double bond character while the P-Rh bond lengths display a larger variation, ranging from 2.141(1) to 2.169(1) Å for 4 and 2.135(1) to 2.179(1) Å for 6. The P-Rh bonds trans to chlorine are shorter than those of trans to nitrogen in both cases. The P-N-P angle shrinks from 115.25(9) to 94.63(9)° (for 4) and 94.74(19)° (for 6) due to the formation of strained four-membered chelate rings. In both complexes the angles around rhodium atom vary over a range of 70–101°, with the smallest being that in the strained, four-membered chelate ring, indicating the distortion in the square planar geometry. In 4 and 6, the bridging phenylene rings are almost parallel to the plane of the P-N-P skeletons with dihedral angles of $1.4(3)^{\circ}$ (P2–N–P1 vs. C30–C31 for 4) and $13.0(7)^{\circ}$ (P1–N1–P2 vs. C15–C16 for 6), respectively.

Transfer hydrogenation reactions

The catalytic transfer hydrogenation of ketones has emerged as a useful and convenient method to prepare secondary alcohols by avoiding the use of molecular hydrogen and pressure apparatus.¹⁴ In a preliminary study, complexes **2–7** have been used for the reduction of acetophenone using 2-propanol as a hydrogen source in the presence of base. The catalytic reactions were carried out with 0.1 g of acetophenone in 5 mL of 2-propanol in the presence of 0.5 mol% of the catalyst and 10 mol% of sodium 2-propoxide as a promoter (substrate : Ru : base = 200 : 1 : 20) under refluxing condition. The progress of the reaction was monitored by gas chromatography and representative catalytic data are given in Table 3. For example, acetophenone is reduced to 1-phenylethanol in the presence of sodium 2-propoxide with >99% conversion in 2-propanol at reflux condition with 0.5 mol% of catalyst **2** within 8 h (Table 3, entry 6). The reactions are slow at room temperature

	4	6
Empirical formula	$C_{66}H_{66}Cl_2N_4O_{16}P_4Rh_2$	$C_{66}H_{64}Cl_2N_4O_{16}P_4Rh_2$
M _r ¹	1571.83	1569.81
Crystal system	Triclinic	Monoclinic
Space group	<i>P</i> 1 (no. 2)	$P2_1/n$ (no. 14)
a/Å	9.2409(5)	16.9519(9)
b/Å	11.0859(6)	11.3413(6)
c/Å	17.0064(9)	18.325(1)
$\alpha/^{\circ}$	84.207(1)	90
$\beta/^{\circ}$	77.819(1)	110.072(1)
$\gamma/^{\circ}$	88.350(1)	90
$V/Å^3$	1694.23(16)	3309.1(3)
Ζ	1	2
$D_{\rm c}/{\rm g~cm^{-3}}$	1.541	1.576
μ (Mo-K α)/mm ⁻¹	0.730	0.748
F(000)	802	1600
Crystal size/mm	$0.07 \times 0.10 \times 0.12$	$0.09 \times 0.12 \times 0.13$
T/K	100	100
2θ Range/°	1.2-28.3	2.0-24.8
Total no. reflns	15149	23110
No. indep. reflns	$7829 (R_{\rm int} = 0.022)$	5711 ($R_{\rm int} = 0.070$)
$\operatorname{GOF}(F^2)$	1.07	1.02
R_1^a	0.0323	0.0467
wR_2^b	0.0810	0.1197
$a R = \sum \ F\ - \ F\ $	$\langle \Sigma F ^{b} R = \{ [\Sigma w (F^{2} -$	$(F^{2})/\sum w(F^{2})^{2} $
$1/[\sigma^2(F^2) + (xP)^2]$	where $P = (F^2 + 2F^2)/3$	· · // _ // (· · · /]] , // =

but proceed at good rates at refluxing conditions. In the absence of base, no conversion was observed and conversion rates were increased with increasing concentration of base.15 Although the reaction conditions were not optimized, all complexes have proven to be active and efficient catalysts leading to nearly quantitative conversion of acetophenone into 1-phenylethanol within 8-18 h. Among them, the tetra-metallic complex 2 appeared to be the most active precursor for the reduction of acetophenone (8 h, TON =199) and further it was used for the reduction of ketones other than acetophenone. The reduction performed with benzophenone yielded 80% of diphenylmethanol after 24 h with complex 2 (Table 3, entry 13). The complex 2 also shows good activity in the transfer hydrogenation of six-membered cyclic ketones (Table 3, entries 14 and 15). Complex 2 catalyzed the transfer hydrogenation of α -tetralone and cyclohexanone very effectively but at different rates (Table 3, entries 14 and 15). The reduction of cyclohexanone yielded less than 1% of the converted product with 10 mol% of base after 24 h under refluxing conditions though a good conversion has been achieved with 20 mol% of base within 24 h. Further, the reduction of 4-bromoacetophenone tends to proceed at significantly lower rate and yield because of the higher mesomeric effect caused by bromide substitution.^{15a,16}

Conclusion

The aminotetra(phosphonite) 1 readily reacts with [Rh(COD)Cl]₂ to give di-, tetra- and polymeric complexes depending upon the reaction conditions and the stoichiometry of the reactants. Displacement of the coordinated solvents from 4 using bridging bipyridyl linkers produces interesting mixed-ligand Rh^I coordination polymers 6 and 7. The Rh^I derivatives are efficient catalysts for the transfer hydrogenation of acetophenone. The polymers produced by rigid polyphosphine of the type 1 have the metals in conjugation with aromatic π -systems through P–N–P skeletons with P-N bonds showing multiple bond character. By choosing appropriate redox-active metals and substituents at the P-centers it is possible to design efficient conducting polymers. Although, we do not see any interlink between the π -conjugation and the catalytic ability of these molecules it is an interesting ligand system which can be explored in both of these avenues. The work in this direction is in progress.

Experimental

General procedures

All manipulations were performed under rigorously anaerobic conditions using Schlenk techniques. All the solvents were purified by conventional procedures and distilled prior to use.¹⁷ The compounds p-C₆H₄[N{P(OC₆H₄OMe-o)₂}₂]₂¹¹ and [Rh(COD)Cl]₂¹⁸ were prepared according to the published procedures. Pyrazine and 4,4'-bipyridine were purchased from Aldrich Chemicals and used as such without further purification. Other chemicals were obtained from commercial sources and purified prior to use.

Instrumentation

The ¹H and ³¹P{¹H} NMR (δ in ppm) spectra were recorded using a Varian VXR 400 spectrometer operating at the appropriate frequencies using TMS and 85% H₃PO₄ as internal and external references, respectively. Infrared spectra were recorded on a Nicolet Impact 400 FTIR instrument as KBr disks. The microanalyses were performed using a Carlo Erba Model 1112

 Table 2
 Selected bond distances (Å) and bond angles (°) for complexes 4 and 6

Complex 4				Complex 6			
P1-N1	1.6989(19)	P1-N1-P2	94.63(9)	P1-N1	1.694(4)	P1-N1-P2	94.74(19)
P2-N1	1.6921(19)	P1-Rh-P2	70.68(2)	P2-N1	1.701(4)	P1-Rh1-P2	70.75(5)
Rh–P1	2.1686(6)	Cl-Rh-P1	101.75(2)	Rh1–P1	2.1791(13)	Cl1-Rh1-P1	102.14(5)
Rh–P2	2.1409(6)	P2-Rh-N2	97.78(6)	Rh1–P2	2.1352(13)	P2-Rh1-N2	98.49(13)
Rh–N2	2.090(2)	P1-Rh-N2	168.02(6)	Rh1–N2	2.165(5)	P1-Rh1-N2	167.94(13)
Rh–Cl	2.3940(6)	Cl-Rh-P2	172.23(2)	Rh1–Cl1	2.3762(13)	Cl1-Rh1-P2	171.22(5)
P1-O1	1.6042(16)	Cl-Rh-N2	89.88(6)	P1O1	1.607(4)	Cl1-Rh1-N2	88.02(13)
P1-O3	1.6110(17)	Rh-P1-O1	126.55(6)	P1–O3	1.616(3)	Rh1–P1–O1	125.20(14)
P2O5	1.6056(17)	Rh–P1–O3	124.55(7)	P2–O5	1.608(4)	Rh1–P1–O3	126.14(14)
P2O7	1.6146(17)	Rh–P2–O5	124.74(7)	P2–O7	1.611(4)	Rh1-P2-O5	121.11(15)
N1-C30	1.431(3)	Rh-P2-O7	126.05(6)	N1-C15	1.440(6)	Rh1-P2-O7	129.58(15)

Table 3 Transfer hydrogenation reactions of acetophenone

$R_{1} \xrightarrow{O} R_{2} + \xrightarrow{OH} \xrightarrow{Catalyst} R_{1} \xrightarrow{OH} R_{2} + \xrightarrow{O}$							
Entry	Ketone	Catalyst	Conditions ^a	Conv. ^{<i>b</i>} (%)	TON ^e		
1	Acetophenone	None	[/] PrONa (10 mol%), reflux, 24 h	1			
2	Acetophenone	None	PrONa (30 mol%), reflux, 20 h	50			
3	Acetophenone	None	PrONa (40 mol%), reflux, 20 h	66			
4	Acetophenone	[Rh(COD)Cl] ₂	0.5 mol%. 'PrONa (10 mol%), reflux, 10 h	48	96		
5	Acetophenone	[Rh(COD)Cl] ₂	0.5 mol%. 'PrONa (10 mol%), reflux, 24 h	61	122		
6	Acetophenone	2	0.5 mol%. 'PrONa (10 mol%), reflux, 8 h	> 99	199		
7	Acetophenone	3	0.5 mol%. 'PrONa (10 mol%), reflux, 7 h	83	166		
8	Acetophenone	4	0.5 mol%. 'PrONa (10 mol%), reflux, 5 h	78	156		
9	Acetophenone	5	0.5 mol%. 'PrONa (10 mol%), reflux, 8 h	92	184		
10	Acetophenone	6	0.5 mol%. 'PrONa (10 mol%), reflux, 18 h	100	200		
11	Acetophenone	7	1 mol%. 'PrONa (10 mol%), reflux, 8 h	98	98		
12	4-Bromoacetophenone	2	0.5 mol%. 'PrONa (10 mol%), reflux, 24 h	34	68		
13	Benzophenone	2	0.5 mol%. 'PrONa (10 mol%), reflux, 24 h	80	160		
14	α-Tetralone	2	0.5 mol%. 'PrONa (10 mol%), reflux, 24 h	70	140		
15	Cyclohexanone	2	0.5 mol%. 'PrONa (20 mol%), reflux, 24 h	100	200		

^{*a*} Acetophenone (0.1 g), 'PrONa (10 mol%), catalyst (0.5 mol%), 'PrOH (5 mL). ^{*b*} Conversion to coupled product determined by GC, based on acetophenone; average of two runs. ^{*c*} Defined as mol product per mol of catalyst.

elemental analyzer. The melting points were observed in capillary tubes and are uncorrected.

Synthesis of [Rh₄(COD)₂(μ-Cl)₄(P₂N(Ph)NP₂)] (2). A solution of **1** (0.037 g, 0.030 mmol) in CH₂Cl₂ (5 mL) was added dropwise to a solution of [RhCl(COD)]₂ (0.030 g, 0.061 mmol) also in CH₂Cl₂ (5 mL) with constant stirring. The reaction mixture was allowed to stir at room temperature for 4 h. The resulting solution was concentrated to 2 mL, layered with 1 mL of petroleum ether, and stored at $-30 \degree$ C for 1 day to give analytically pure yellow–orange crystalline product **2**. Yield: 82% (0.050 g); mp 178–180 °C. Anal. Calc. for C₇₈H₈₄N₂O₁₆P₄Rh₄Cl₄: C, 47.25; H, 4.27; N, 1.41. Found: C, 47.19; H, 4.23; N, 1.46%. ¹H NMR (400 MHz, CDCl₃): δ 7.79–6.75 (m, Ph, 36H), 5.50 (br s, CH, 8H), 3.71 (s, OCH₃, 24H), 2.01 and 1.92 (d, CH₂, 16H). ³¹P{¹H} NMR (162 MHz, CDCl₃): δ 106.9 (d, ¹J_{RhP} = 240 Hz).

Synthesis of $[Rh_2(\mu-Cl)_2(P_2N(Ph)NP_2)]_{\mu}$ (3). A solution of $[RhCl(COD)]_2$ (0.031 g, 0.063 mmol) in CH_2Cl_2 (5 mL) was added dropwise to a solution of 1 (0.077 g, 0.063 mmol) also in CH_2Cl_2 (7 mL) with constant stirring. The reaction mixture was allowed to stir at room temperature for 4 h and the resulting yellow–orange precipitate was collected by filtration and washed with diethyl ether twice (5 mL each). Yield: 88% (0.083 g); mp 198–200 °C (decomp.). Anal. Calc. for $C_{62}H_{60}N_2O_{16}P_4Rh_2Cl_2$: C, 49.99; H, 4.06; N, 1.88. Found: C, 49.93; H, 4.01; N, 1.92%.

Synthesis of $[Rh_2Cl_2(CH_3CN)_2(P_2N(Ph)NP_2)]$ (4). A solution of $[RhCl(COD)]_2$ (0.008 g, 0.017 mmol) in acetonitrile (5 mL) was added dropwise to a solution of 1 (0.021 g, 0.017 mmol) in CH₂Cl₂ (5 mL) with constant stirring. The reaction mixture was allowed to stir at room temperature for 15 min and was then stored at room temperature for 24 h to give analytically pure yellow crystals of 4. Yield: 79% (0.022 g); mp 238–240 °C (decomp.). Anal. Calc. for C₆₆H₆₆N₄O₁₆P₄Rh₂Cl₂: C, 50.43; H, 4.23; N, 3.56. Found: C, 50.50; H, 4.26; N, 3.52%. ¹H NMR (400 MHz, CDCl₃): δ 7.74–6.63 (m, Ph, 36H), 3.52 (s, OCH₃, 24H), 1.95 (s, CH₃CN, 6H). ³¹P{¹H} NMR (162 MHz, CDCl₃): δ 97.3 (dd, ¹ J_{RhP} = 257 Hz), 93.1 (dd, ¹ J_{RhP} = 232 Hz, ² J_{PP} = 88 Hz).

Synthesis of [Rh₂Cl₂(CO)₂(P₂N(Ph)NP₂)] (5). Carbon monoxide gas was bubbled through a suspension of **3** (0.0626 g, 0.042 mmol) (or **4**) in dichloromethane (15 mL) with constant stirring at room temperature until the solution became clear (~15 min). The solution was concentrated under reduced pressure, layered with 2 ml of petroleum ether and stored at $-30 \,^{\circ}$ C for 1 day to afford **5** as a yellow crystalline product. Yield: 93% (0.060 g); mp 218–220 $\,^{\circ}$ C (decomp.). Anal. Calc. for C₆₄H₆₀N₂O₁₈P₄Rh₂Cl₂: C, 49.73; H, 3.91; N, 1.81. Found: C, 49.62; H, 4.01; N, 1.76%. ¹H NMR (400 MHz, CDCl₃): δ 8.00–6.65 (m, Ph, 36H), 3.50 (s, OCH₃, 24H). ³¹P{¹H} NMR (162 MHz, CDCl₃): δ 103.2 (dd, ¹J_{RhP} = 223 Hz), 90.4 (dd, ¹J_{RhP} = 192 Hz, ²J_{PP} = 80 Hz). FT-IR (KBr disc) cm⁻¹: *v*(CO) 2048 (s), 2006 (s).

Synthesis of $[Rh_2Cl_2(C_4H_4N_2)(P_2N(Ph)NP_2)]_n$ (6). A solution of pyrazine (0.001 g, 0.017 mmol) in CH₂Cl₂ (5 mL) was added dropwise to a solution of 4 (0.026 g, 0.017 mmol) in acetonitrile (10 mL) with constant stirring. The reaction mixture was allowed to stir at room temperature for 4 h to give a red precipitate which was collected by filtration. Crystals suitable for X-ray analysis were grown by the slow diffusion of an acetonitrile solution of 4 into a dichloromethane solution of pyrazine. Yield: 95% (0.025 g); mp 192–194 °C (decomp.). Anal. Calc. for C₆₆H₆₄N₄O₁₆P₄Rh₂Cl₂: C, 50.50; H, 4.11; N, 3.57. Found: C, 50.48; H, 4.16; N, 3.51%.

Synthesis of $[Rh_2Cl_2(C_{10}H_8N_2)(P_2N(Ph)NP_2)]_n$ (7). This was synthesized by a procedure similar to that of **6** using two equiv. of 4,4'-bipyridine (0.003 g, 0.020 mmol) and 4 (0.0157 g, 0.010 mmol). Yield: 84% (0.0138 g); mp 240–242 °C (decomp.). Anal. Calc. for $C_{72}H_{68}N_4O_{16}P_4Rh_2Cl_2$: C, 52.54; H, 4.16; N, 3.40. Found: C, 52.43; H, 4.08; N, 3.47%.

General procedure for the transfer hydrogenation reactions

In a dry two-necked round bottom flask under an atmosphere of nitrogen were placed appropriate amount of catalyst (0.5 mol%) in 2-propanol (5 mL) and it was stirred at room temperature for 15 min. The corresponding ketones were added to the mixture and stirred for another 15 min at room temperature. A 2-propanol solution of sodium isopropoxide (10 mol%) (prepared by the dissolution of metallic sodium into the hot 2-propanol) was then added and the resulting mixture was refluxed under an atmosphere of nitrogen and the course of the reaction was monitored by GC analysis. After completion of the reaction, the solvent was removed under reduced pressure. The residual mixture was diluted with H₂O and Et₂O (10 mL each), washed with brine and extracted with $Et_2O(2 \times 6 \text{ mL})$. The combined organic fractions were dried (MgSO₄), stripped of the solvent under vacuum and the residue was redissolved in 5 mL of dichloromethane. An aliquot was taken with a syringe and subjected to GC analysis. Conversions were calculated relative to the ketones as an internal standard.

X-Ray crystallography

A crystal of each of the compounds 4 and 6 suitable for X-ray crystal analysis was mounted in a Cryoloop[™] with a drop of Paratone oil and placed in the cold nitrogen stream of the KryoflexTM attachment of the Bruker APEX CCD diffractometer. Full spheres of data were collected using 606 scans in ω $(0.3^{\circ} \text{ per scan})$ at $\phi = 0$, 120 and 240° under the control of the APEX2 program suite.¹⁹ The raw data were reduced to F² values using the SAINT+ software²⁰ and global refinements of unit cell parameters using 6709 or 7047 reflections chosen from the full data sets were performed. Multiple measurements of equivalent reflections provided the basis for empirical absorption corrections as well as corrections for any crystal deterioration during the data collection (SADABS²¹). Both the structures were solved by direct methods and refined by full-matrix least-squares procedures using the SHELXTL program package.22 Hydrogen atoms were placed in calculated positions and included as riding contributions with isotropic displacement parameters tied to those of the attached non-hydrogen atoms.

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