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Bis(methoxyethyldimethylphosphine)ruthenium(II) Complexes as Transfer Hydrogenation Catalysts

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Dedicated to Professor Heinrich Nöth on the Occasion of his 75th Birthday

Abstract. Diamineruthenium(II) complexes containing the hemilabile methoxyethyldimethylphosphine ligand, $[Cl_2Ru(\mathbf{L_n})(\eta^1\text{-}Me_2PCH_2CH_2OMe)_2]$ ($\mathbf{2L_n}$) (n = 1-12, Scheme 1), have been synthesized from the starting materials $Me_2PCH_2CH_2OMe$, $[Ru(COD)Cl_2]_n$, and the respective diamines $\mathbf{L_1}$-$\mathbf{L_{12}}$. The structure of complex $\mathbf{2L_5}$ reveals that two chlorides are in *trans* position, while in complex $\mathbf{2L_{11}}$ the two chlorides favor a *cis* configuration. Most of the complexes are highly catalytic active in the hydrogen transfer reduction of acetophenone. The experimental study indicates that the replacement of phenyl groups for methyl functions in the ether-phosphine ruthenium(II) complexes resulted in a switch of the hydrogenation mechanism from direct hydrogenation to transfer hydrogenation. The reason is attributed to the better donor ability of methyl groups compared to phenyl substitutents. Thus the metal center becomes more electron-rich and inhibits the binding of dihydrogen to the ruthenium(II) complex fragment.

Keywords: Ruthenium(II) complexes; Ether-phosphines; Diamine ligands; Crystal structures; Transfer hydrogenation; Catalysis

Bis(methoxyethyldimethylphosphin)ruthenium(II)-Komplexe als Transfer-Hydrier-Katalysatoren

Inhaltsübersicht. Die Diaminruthenium(II)-Komplexe, die den hemilabilen Methoxyethyldimethylphosphin-Liganden $[Cl_2Ru(\mathbf{L_n})(\eta^1\text{-}Me_2PCH_2CH_2OMe)_2]$ ($\mathbf{2L_n}$) enthalten (n = 1-12, Schema 1), erhält man durch Umsetzung von $Me_2PCH_2CH_2OMe$ mit $[Ru(COD)Cl_2]_n$ und den jeweiligen Diaminen $\mathbf{L_1}$-$\mathbf{L_{12}}$. In der Struktur von $\mathbf{2L_5}$ befinden die beiden Chlorliganden in *trans*-Position, während sie in Komplex $\mathbf{2L_{11}}$ *cis*-Konfiguration bevorzugen. Die meisten dieser Komplexe erweisen sich katalytisch als hochaktiv in der Wasserstofftransfer-Hydrierung von Acetophenon. Die experimentelle Studie zeigt, daß der Ersatz von Phenylgruppen gegen Methylfunktionen in den (Ether-phosphin)ruthenium(II)-Komplexen einen Wechsel des Mechanismus von der direkten Hydrierung zu einer Transferhydrierung herbeiführt. Der Grund liegt in der besseren Elektronendonorfähigkeit der Methylgruppen im Vergleich zu den Phenylsubstituenten. Das Metallzentrum wird somit elektronenreicher und hemmt die Anlagerung von Diwasserstoff an das Rutheniumkomplex-Fragment.

Introduction

Novel or improved catalytic reactivities can be achieved with coordination and organometallic complexes with well-designed structural, electronic, and stereochemical features. One major way to control and adjust their catalytic performances is the modification of the structure or nature of the surrounding ligands. Small differences in the coordination sphere of transition metals commonly lead to dramatic changes in the selectivity and activity of catalytic reactions [2, 3]. Therefore the study of the relationship between the structure of the ligands and the physicochemical properties of the corresponding metal complexes has been the subject of many investigations in order to understand the reactivity in catalysis [4−7].

Due to their remarkable performance in the asymmetric hydrogenation of unsaturated carbonyl compounds [8, 9], mixed diamine(phosphine)ruthenium(II) complexes have received much attention in recent years [10, 11]. In 2-propanol two competitive mechanisms are discussed. Transfer hydrogenation with 2-propanol as hydrogen source and the direct hydrogenation with molecular hydrogen. In the latter case a metal-ligand bifunctional mechanism has been proposed in which at least one NH and RuH unit is intimately involved in the hydride transfer process [12]. Further theoretical and experimental work suggested that the intra-

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molecular heterolytic splitting of dihydrogen across the polar Ru=N bond of the resulting amido complexes is the turnover limiting step [13, 14]. It is assumed that electron-deficient ruthenium(II) complexes favor the heterolysis of the coordinated dihydrogen and results in a direct hydrogenation. In contrast to this, if the metal center is electron rich, the coordination of dihydrogen is hampered and the hydrogenation with molecular hydrogen is inhibited. Thus the electronic properties of the coordination center will play an important role in the catalytic performance. Furthermore, among many combinations of different diamines and phosphines, in particular aryl phosphines have been employed, e.g. 1,1′-binaphthalene-2,2′-diylbis(diphenylphosphine) (binap) [12, 15−18], however, ruthenium(II) complexes with alkylphosphines hitherto have not been considered.

Recently we reported on a series of diaminebis(ether-diphenylphosphine)ruthenium(II) complexes which are catalytically active in the selective hydrogenation of α,β-unsaturated ketones [19, 20]. To adjust the properties of the phosphine ligands and to extend the library of diaminediphosphineruthenium(II) complexes, we incorporated the dialkylether-phosphine ligand $Me_2PCH_2CH_2OMe$ into our investigations. Actually, metal complexes provided with the ether-phosphine ligand $Me_2PCH_2CH_2OMe$ are very rare. To our knowledge, only two complexes were described in the literature [21, 22]. The replacement of both phenyl groups for methyl functions at the phosphorus atom will not only affect the steric factor around the metal center, also the electronic properties of the complex will change, resulting in a different catalytic performance. Here we wish to present our results on the successful synthesis, crystal structures, and catalysis of a series of diamine-bis(methoxyethyldimethylphosphine)ruthenium(II) complexes **2L$_1$-2L$_{12}$** (see Scheme 1).

Results and Discussion

Synthesis of Complexes 2L$_2$-2L$_5$ and 2L$_7$-2L$_{12}$

For the syntheses of the mixed diamine-bis(methoxyethyldimethylphosphine)ruthenium(II) complexes **2L$_2$-2L$_5$** and **2L$_7$-2L$_{12}$** according to Scheme 1, advantage of the hemilabile character of ether-phosphine ligands was taken [23, 24]. Complexes **2L$_1$** and **2L$_6$** were already described in the literature [1]. It has been shown that this is a straightforward and efficient way to prepare these pre-catalysts. However, different from $Ph_2PCH_2CH_2OMe$-containing complexes, the precursor $Cl_2Ru(\eta^2\text{-}Me_2PCH_2CH_2OMe)_2$ (**1**) is difficult to obtain in pure state when $Cl_2Ru(PPh_3)_3$ served as a starting compound. Finally $[Cl_2Ru(COD)]_n$ was reacted with $Me_2PCH_2CH_2OMe$ in a ratio of 1 : 2 in 2-propanol 12 hours under reflux to give **1**. Because of its instability in the solid state compound **1** was not isolated, but treated in situ with the diamines **L$_2$-L$_5$** and **L$_7$-L$_{12}$**.

The weak ruthenium-oxygen interaction in complex **1** can easily be cleaved by the stronger nitrogen donors of the bidentate diamine ligands. Mixing the above-mentioned solution of **1** in 2-propanol with a slight excess of the diamines **L$_2$-L$_5$** and **L$_7$-L$_{12}$** in dichloromethane results in the formation of the complexes **2L$_2$-2L$_5$** and **2L$_7$-2L$_{12}$** in satisfying to good yields. They are soluble in most organic solvents except alkanes and diethyl ether and can be stored under argon. Their molecular compositions were corroborated by FAB mass spectra. The yields of **2L$_2$-2L$_5$** and **2L$_7$-2L$_{12}$** largely depend on the yield of the precursor compound **1**, which can be improved by working under an atmosphere of hydrogen, and also on the purity of the diamines used.

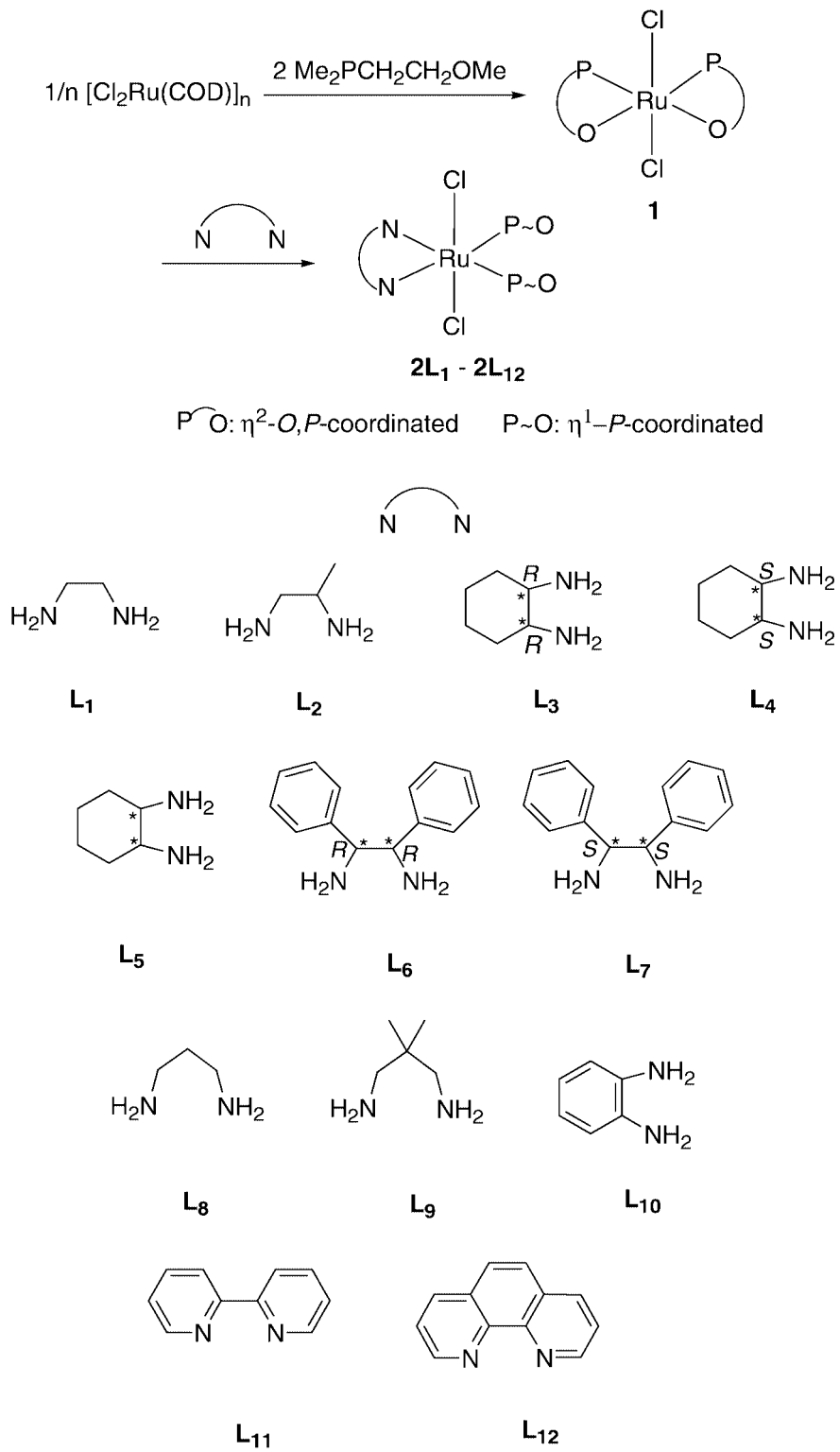
NMR Spectroscopic Investigations

In the ^1H and $^{13}C\{^1H\}$ NMR spectra of **2L$_2$ - 2L$_5$** and **2L$_7$ - 2L$_{12}$** characteristic sets of ^1H and ^{13}C signals are observed which arise from the phosphine and diamine ligands, respectively (see Experimental Section). Their assignment was supported by DEPT and two-dimensional H,H-COSY experiments which establish the connectivity between NH_2 and CH_2 as well as between OCH_2 and CH_2P functions in the diamine and phosphine ligands, respectively. The experiments are also able to distinguish between the carbon atom of the CH_2 moiety and other carbon entities. The integration of the proton resonances indicates that the phosphine to diamine ratio is in agreement with the expected composition of **2L$_2$ - 2L$_5$** and **2L$_7$ - 2L$_{12}$**. Furthermore, the chemical shifts of the ^1H and ^{13}C singlets originating from the methoxy functions are consistent with an η^1-P∼O unit. The occurrence of a singlet each in the $^{31}P\{^1H\}$ NMR spectra of all complexes except **2L$_2$** points to chemically equivalent phosphine groups. For complex **2L$_2$**, the asymmetric diamine accounts for a loss of the C_2 axis resulting in a splitting of the ^{31}P resonance into an AB pattern. Since the diamines favor a chelating arrangement, both phosphorus donors should be in *cis*-position, while two chloride ligands are *trans* to each other. In particular this has been confirmed by an X-ray structural analyses of **2L$_5$**. Compared to the corresponding complexes with diphenylmethoxyethylphosphine ligands [19, 25], the ^{31}P signals in the $^{31}P\{^1H\}$ NMR spectra of **2L$_2$-2L$_5$** and **2L$_7$-2L$_{12}$** are shifted 16−20 ppm to higher field.

X-ray Structural Analyses of 2L$_5$ and 2L$_{11}$

Crystals suitable for X-ray structural analysis have been obtained for complexes **2L$_5$** and **2L$_{11}$**. The molecular structures of complexes **2L$_5$** and **2L$_{11}$** are shown in Figures 1 and 2. Selected bond distances and bond angles of both complexes are listed in Table 1.

In the case of complex **2L$_5$**, two independent molecules, A and B, constitute the asymmetric unit (Fig. 1). Only molecule A has approximate C_2 symmetry. In both molecules, the ruthenium atom is coordinated by two phosphorus and nitrogen atoms each, stemming from two ether-phosphines and one 1,2-diaminocyclohexane, as well as by two chlorine atoms to form an octahedral arrangement. Both Cl ligands



Scheme 1

are bound to the ruthenium center in *trans* position, forming angles of 172.81(2) (molecule A) and 170.78(2)° (molecule B), which are very close to those in complex $\mathbf{2L_6}$ [1], 171.3°, and smaller than those in complex $\mathbf{2L_1}$ [1], 175.1°, but they are still bigger than those in $[Cl_2Ru(NPDA)(\eta^1\text{-}Ph_2PCH_2CH_2OMe)_2]$ (NPDA = 1,8-naphthalenediamine), 167.56(2)° [25]. This finding is attributed to the smaller steric requirements of the methyl groups at the phosphorus

Table 1 Selected Bond Lengths/Å and Bond Angles/° for $\mathbf{2L_5}$ and $\mathbf{2L_{11}}$

	$\mathbf{2L_5}$		
	molecule A	molecule B	$\mathbf{2L_{11}}$
Bond lengths			
Ru(1)-Cl(1)	2.4370(7)	2.4348(7)	2.4823(8)
Ru(1)-Cl(2)	2.4317(7)	2.4354(8)	2.4425(8)
Ru(1)-P(1)	2.2624(7)	2.2614(7)	2.2600(9)
Ru(1)-P(2)	2.2587(7)	2.2620(7)	2.3141(8)
Ru(1)-N(1)	2.190(2)	2.183(2)	2.110(2)
Ru(1)-N(2)	2.196(2)	2.183(2)	2.066(2)
Bond angles			
Cl(1)-Ru(1)-Cl(2)	172.81(2)	170.78(2)	89.92(3)
P(1)-Ru(1)-P(2)	95.68(3)	94.63(3)	94.54(3)
N(1)-Ru(1)-N(2)	78.75(8)	78.64(8)	77.93(9)
N(1)-Ru(1)-Cl(1)	85.54(6)	86.97(6)	81.77(7)
N(2)-Ru(1)-Cl(1)	90.03(6)	84.36(6)	87.81(7)
P(1)-Ru(1)-Cl(1)	93.93(7)	95.47(3)	173.11(3)
P(2)-Ru(1)-Cl(1)	91.62(3)	94.06(3)	91.51(3)
N(1)-Ru(1)-Cl(2)	88.95(6)	88.04(6)	91.56(7)
N(2)-Ru(1)-Cl(2)	84.37(6)	87.06(6)	169.46(7)
P(1)-Ru(1)-Cl(2)	90.93(3)	88.47(3)	86.82(3)
P(2)-Ru(1)-Cl(2)	93.12(3)	93.93(3)	89.90(3)

atoms compared to the phenyl residues in the latter complex. 1,2-Diaminocyclohexane and the two ether-phosphine ligands are located *cis* to each other. Ru, P, and N atoms deviate by less than 0.08 Å from the equatorial RuP_2N_2 least-squares plane in molecule A, and 0.04 Å in molecule B. The bond distances Ru-N, Ru-P, and Ru-Cl are very close to those in complexes $\mathbf{2L_1}$ and $\mathbf{2L_6}$ [1]. The crystal water molecules connect two neighboring molecules of $\mathbf{2L_5}$ through hydrogen bonds, forming an infinite chain (see Fig. 1).

In the crystal structure of $\mathbf{2L_{11}}$, the complex forms the *cis*-chloro isomer during crystallization, although it was shown by spectroscopic methods to be the *trans*-chloro isomer in solution. The coordination arrangement of ruthenium is a fairly regular octahedron, in contrast to the similar complex $[Cl_2Ru(en)(\eta^1\text{-}Ph_2PCH_2CH_2OMe)_2]$ (en = ethylenediamine) [25]. The different *trans* influence of the ligands at ruthenium atom affects the Ru-P distances only marginally, with Ru1-P2 (2.3141(8) Å) (*trans* to nitrogen atom) slightly longer than Ru1-P1 (2.2600(9) Å) (*trans* to the chloride ligand).

Catalytic Transfer Hydrogenation of Acetophenone by Complexes $\mathbf{2L_1}$-$\mathbf{2L_{12}}$

Carbonyl compounds are catalytically transferred to alcohols either with molecular hydrogen or via a hydrogen transfer reaction using 2-propanol as hydrogen source [26−29]. The first mentioned method proceeds at smooth (low temperature and low pressure) conditions which is useful for sensitive substrates. By way of contrast, hydrogen transfer reactions are much simpler but less applicable. To test their catalytic performance, complexes $\mathbf{2L_1}$-$\mathbf{2L_{12}}$ were applied in the direct and transfer hydrogenation. Interestingly, they show no activity in the direct hydrogenation of acetophenone and α,β-unsaturated ketones in contrast to the corresponding bis(ether-diphenylphosphine)(diamine)-ruthenium(II) complexes [19]. Rather, complexes $\mathbf{2L_1}$-$\mathbf{2L_{12}}$ display a very good performance in the transfer hydrogenation of acetophenone to 1-phenylethanol with yields of more than 90 % after 0.5 − 4.0 hours (Scheme 2, Table 3, Fig. 3).

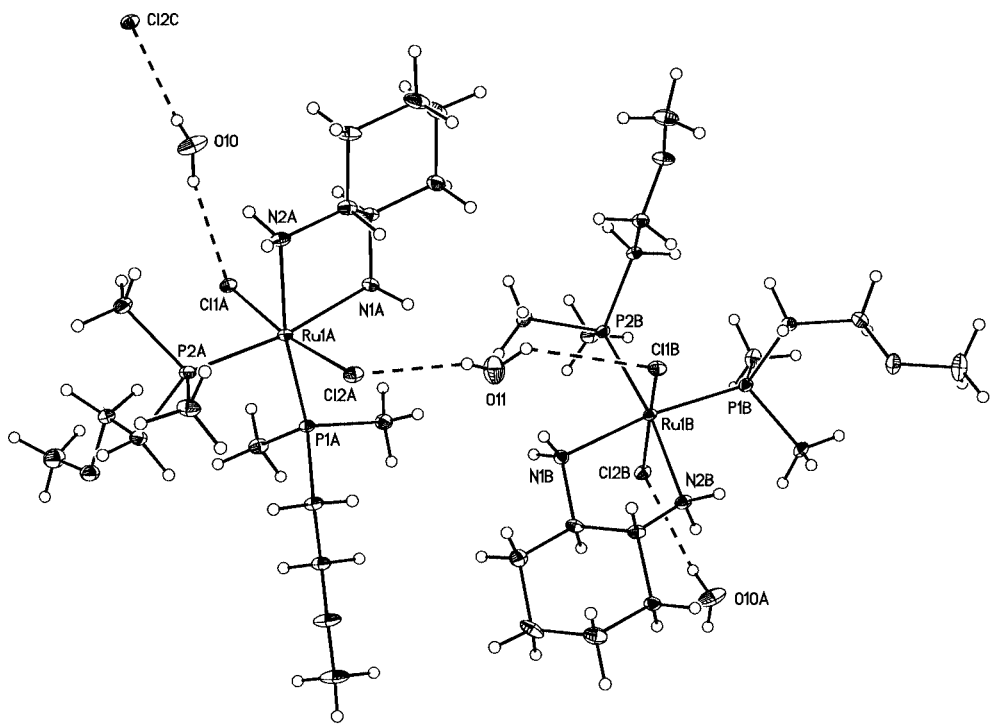


Fig. 1 ORTEP drawing of complex $\mathbf{2L_5}$ showing the H-bonding network. Thermal ellipsoids are drawn at the 20 % probability level.

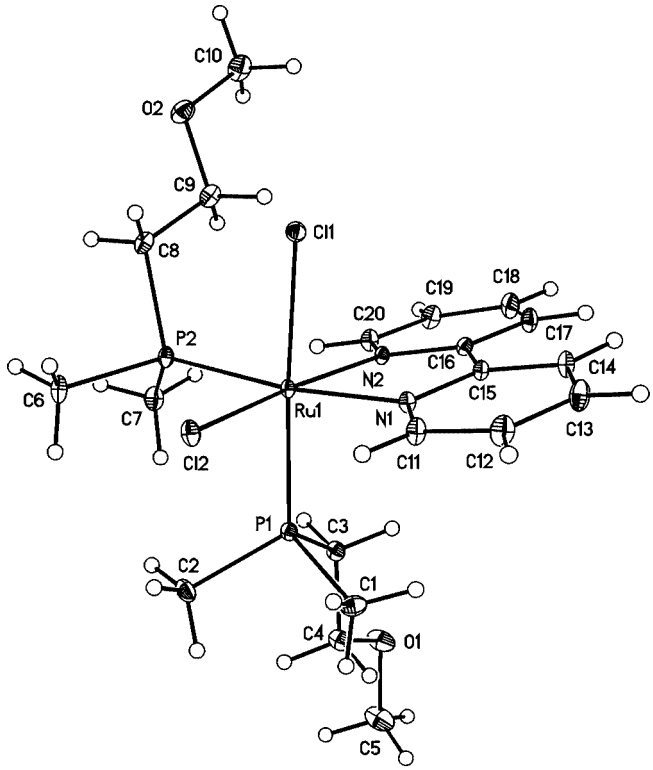
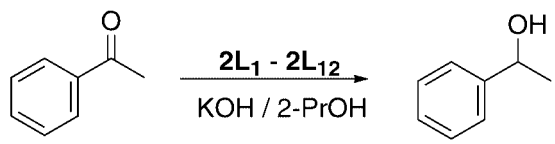


Fig. 2 ORTEP drawing of complex $\mathbf{2L_1}$. Thermal ellipsoids are drawn at the 20 % probability level.



Scheme 2

Evidently complexes $\mathbf{2L_1}$ and $\mathbf{2L_8}$ display the highest activity (yield > 90 % after 30 minutes). Complex $\mathbf{2L_9}$ gives rise to the highest yield (97.6 % after one hour). Ruthenium(II) complexes with alkyldiamine ligands are more productive than that one containing an aromatic diamine ($\mathbf{2L_{10}}$). However, complexes containing diaminocyclohexane ligands need a longer induction period. This is different from the behavior in the direct hydrogenation of ether-diphenylphosphine ruthenium(II) complexes, where the complex with diaminocyclohexane shows the higher activity. Furthermore, bipyridine and phenanthroline ruthenium(II) complexes with ether-diphenylphosphine are not active in the direct hydrogenation, whereas complexes $\mathbf{2L_{11}}$ and $\mathbf{2L_{12}}$ work very well in the transfer hydrogenation, although the reaction rate is slow. The reason might be traced back to a different reaction mechanism (see below) [14,30].

In the case of $\mathbf{2L_6}$, the effects of the reaction conditions were checked in more detail. It was established that the catalyst still performs very well even at a ratio of [sub.] : [KOH] : [cat.] = 2000 : 10 : 1, only the rate is decreased. It should be mentioned that the ratio of [sub.] : [cat.] in the transfer hydrogenation generally is reported to be 200 : 1, even 50 : 1, and reaction times are longer [29−31] . Remarkably all catalysts were only active in the presence of the strong base KOH as a co-catalyst, weak bases like K_2CO_3, did not activiate the catalytic reaction. The temperature plays an important role in the reaction rate and enantioselectivity. At reflux conditions, there is almost no enantioselectivity. At 50 °C, the yield reached 3.3 % at 1 hour and 87.1 % at 8 hours, and the *ee* values (*R*-1-phenylethanol) decreased from 15.4 % at 1 hour to 4.5 % at 8 hours.

Table 2 Transfer Hydrogenation of Acetophenone by Complexes $\mathbf{2L_1}$ - $\mathbf{2L_{12}}$[a)]

Catalysts	Yield (%) [b)]		
	0.5 h	1.0 h	4.0 h
$\mathbf{2L_1}$	93.4	94.3	96.4
$\mathbf{2L_2}$	81.6	94.4	94.6
$\mathbf{2L_3}$	28.9	74.4	93.3
$\mathbf{2L_4}$	34.5	86.6	91.1
$\mathbf{2L_5}$	39.8	66.3	89.6
$\mathbf{2L_6}$	60.0	92.6	93.2
$\mathbf{2L_6}$ [c)]	26.8	69.6	94.8
$\mathbf{2L_6}$ [d)]	25.2	51.5	93.7
$\mathbf{2L_7}$	57.9	88.6	93.8
$\mathbf{2L_8}$	90.0	94.4	94.8
$\mathbf{2L_9}$	73.4	97.6	98.2
$\mathbf{2L_{10}}$	42.8	60.0	89.6
$\mathbf{2L_{11}}$	37.0	59.60	94.6
$\mathbf{2L_{12}}$	69.1	82.0	94.1

[a)] Reaction conditions: 0.75 ml of acetophenone, 15 ml of 2-propanol, [sub.] : [KOH] : [cat.] = 500 : 10 : 1, 82 °C.
[b)] Yields were determined by GC.
[c)] The same reaction conditions except [sub.] : [KOH] : [cat.] = 1000 : 10 : 1.
[d)] The same reaction conditions except [sub.] : [KOH] : [cat.] = 2000 : 10 : 1.

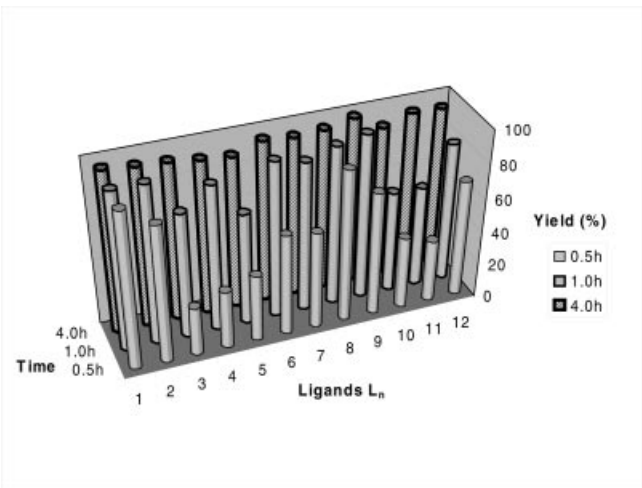


Fig. 3 Transfer hydrogenation of acetophenone by complexes $\mathbf{2L_1}$-$\mathbf{2L_{12}}$.

If the phenyl substituents at the phosphorus atoms of the ligands are replaced for methyl groups as in the complexes $\mathbf{2L_1}$-$\mathbf{2L_{12}}$, no activity is found in the direct hydrogenation.

This finding agrees with the metal-ligand bifunctional mechanism [12]. As pointed out the activity to cleave the dihydrogen bond to give an active ruthenium hydride intermediate is the key step for the direct hydrogention [13, 14]. Dihydrogen coordinated to ruthenium(II) can be strongly activated for heterolysis if the metal center is sufficiently electron-deficient which is the case if diphenylphosphine ligands are used [19]. The metal centers in **2L$_1$-2L$_{12}$** become too electron-rich due to the donating property of the dimethylphosphine entities, resulting in a weak hydrogen binding ability. Consequently, replacing phenyl substituents in ether-phosphine ligands for methyl residues will change the corresponding ruthenium(II) complexes from direct hydrogenation catalysts to transfer hydrogenation catalysts.

Conclusion

In this work a series of bis(2-methoxyethyldimetylphosphine)ruthenium(II) complexes containing different diamines have been made accessible and fully characterized. While in solution all complexes prefer a *trans*-$RuCl_2$ configuration, in solid state *cis* and *trans* isomers are formed. Most of the complexes are highly active in the catalytic transfer reduction of acetophenone. The catalysts still perform very well even at a ratio of [sub.] : [KOH] : [cat.] = 2000 : 10 : 1. The presence of a strong base as a co-catalyst is a basic requirement for the transfer hydrogenation. It has been clearly demonstrated that the exchange of diphenylphosphine groups for dimethylphosphine functions in ruthenium(II) complexes alters the hydrogenation mechanism. Because of the donating properties of methyl groups in complexes **2L$_1$-2L$_{12}$** the transfer hydrogenation reaction is favored.

Experimental

General Comments

All experiments were carried out under an atmosphere of argon by use of standard Schlenk techniques. Solvents were dried with appropriate reagents, distilled, degassed, and stored under argon. $RuCl_3 \cdot 3H_2O$ was purchased from ChemPur. 1,2-Diaminoethane (**L$_1$**), 1,2-diaminopropane (**L$_2$**), *1R,2R*-1,2-diaminocyclohexane (**L$_3$**), *1S,2S*-1,2-diaminocyclohexane (**L$_4$**), *trans*-(±)-1,2-diaminocyclohexane (**L$_5$**), 1*R*,2*R*-1,2-diamino-1,2-diphenylethane (**L$_6$**), 1*S*,2*S*-1,2-diamino-1,2-diphenylethane (**L$_7$**), 1,3-diaminopropane (**L$_8$**), 1,3-diamino-2,2-dimethylpropane (**L$_9$**), 1,2-diaminobenzene (**L$_{10}$**), 2,2′-bipyridine (**L$_{11}$**), and 1,10-phenanthroline (**L$_{12}$**) were obtained from Acros, Fluka, and Merck, respectively. The precursors $[Cl_2Ru(COD)]_n$ [32] and $Me_2P(CH_2)_2OCH_3$ [33] were synthesized according to literature methods. Complexes **1**, **2L$_1$**, and **2L$_6$** were prepared by known procedures [1].

Elemental analyses were performed with an Elementar Vario EL analyzer. FAB mass spectra were taken on a Finnigan MAT 711 A instrument, modified by AMD and reported as mass/charge (*m*/*z*). High-resolution ^{1}H, ^{31}P{^{1}H}, and ^{13}C{^{1}H} NMR spectra were recorded on a Bruker DRX 250 spectrometer at 298 K. Frequencies and standards are as follows: ^{31}P{^{1}H} NMR, 101.25 MHz; ^{13}C{^{1}H} NMR, 62.90 MHz. The ^{1}H and ^{13}C chemical shifts were calibrated to solvent peaks, which are reported relative to TMS. ^{31}P chemical shifts were measured relative to 85 % H_3PO_4 (δ = 0).

General Procedure for the Syntheses of the Complexes 2L$_2$-2L$_5$ and 2L$_7$-2L$_{12}$

The corresponding diamine ligands **L** were dissolved in 10 ml of dichloromethane and added dropwise to a solution of **1** in 2-propanol [1]. After the reaction mixture has been stirred for another 1.5 h, the volume of the solution was concentrated to about 5 ml under reduced pressure. Addition of 60 ml of *n*-hexane caused the precipitation of a solid, which was filtered off (P3), washed three times with 30 ml portions of *n*-hexane and dried under vacuum.

[Cl$_2$Ru(L$_2$)(η^1-Me$_2$PCH$_2$CH$_2$OMe)$_2$] (2L$_2$): A solution of **L$_2$** (0.077 ml, 0.90 mmol) in CH_2Cl_2 was reacted with the above-mentioned solution of **1** in 2-PrOH. Yield: 299 mg (75 %) of a yellow powder, dec. 207 °C.

$C_{13}H_{36}Cl_2N_2O_2P_2Ru$ (483.36): calcd C 32.10, H 7.46, N 5.76 %; found C 32.02, H 7.43, N 5.58 %. MS (FAB): *m*/*z* = 486.0 (M^+).

^{1}H NMR ($CDCl_3$): δ = 1.25 (d, $^3J_{HH}$ = 6.60 Hz, 3H, CCH_3,), 1.37 (m, 12H, PCH_3), 2.07 (m, 4H, PCH_2), 2.66 (m, 1H, CH), 2.87 (br, 2H, NH_2), 3.23 (br, 2H, NH_2), 3.27, 3.28 (s, 6H, OCH_3), 3.60 (m, 6H, OCH_2, NCH_2). **^{31}P{^{1}H} NMR** ($CDCl_3$): δ = 21.6, 21.5 (AB pattern, $^2J_{PP}$ = 4.6 Hz). **^{13}C{^{1}H} NMR** ($CDCl_3$): δ = 16.8 (m, PCH_3), 20.9 (s, CCH_3) 31.4 (m PCH_2), 49.6 (s, NCH_2), 51.1 (s, NCH), 58.9, 58.8 (s, OCH_3), 68.7 (s, OCH_2).

[Cl$_2$Ru(L$_3$)(η^1-Me$_2$PCH$_2$CH$_2$OMe)$_2$] (2L$_3$): A solution of **L$_3$** (0.102 g, 0.90 mmol) in CH_2Cl_2 was reacted with the above-mentioned solution of **1** in 2-PrOH. Yield: 345 mg (80 %) of a yellow powder, dec. 217 °C.

$C_{16}H_{40}Cl_2N_2RuO_2P_2$ (526.42): calcd C 36.51, H 7.66, N 5.32 %; found C 36.93, H 7.58, N, 4.93 %. MS (FAB): *m*/*z* = 526.4 (M^+).

^{1}H NMR ($CDCl_3$): δ = 1.14, 1.64 2.03, 3.69 (m, 10H, C_6H_{10}), 1.34 (br, 12H, PCH_3), 2.03 (m, 4H, PCH_2), 2.57 (br, 2H, NH_2), 2.89 (br, 2H, NH_2), 3.26 (s, 6H, OCH_3), 3.60 (m, 4H, OCH_2). **^{31}P{^{1}H} NMR** ($CDCl_3$): δ = 23.0 (s). **^{13}C{^{1}H} NMR** ($CDCl_3$): δ = 14.0 (m, PCH_3), 24.0 (s, CH_2), 30.0 (m, PCH_2), 35.6 (s, CH_2), 56.4 (s, NCH), 57.7 (s, OCH_3), 67.6 (s, OCH_2).

[Cl$_2$Ru(L$_4$)(η^1-Me$_2$PCH$_2$CH$_2$OMe)$_2$] (2L$_4$): A solution of **L$_4$** (0.102 g, 0.90 mmol) in CH_2Cl_2 was reacted with the above-mentioned solution of **1** in 2-PrOH. Yield: 336 mg (77 %) of a yellow powder, dec. 217 °C.

$C_{16}H_{40}Cl_2N_2RuO_2P_2$ (526.42): calcd C 36.51, H 7.66, N 5.32 %; found C 36.91, H 7.56, N 4.94 %. MS (FAB): *m*/*z* = 526.4 (M^+).

^{1}H NMR ($CDCl_3$): δ = 1.17, 1.65, 2.07, 3.68 (m, 10H, C_6H_{10}), 1.38 (br, 12H,PCH_3), 2.07 (m, 4H, PCH_2), 2.59 (br, 2H, NH_2), 2.86 (br, 2H, NH_2), 3.27 (s, 6H, OCH_3), 3.60 (br, 4H, OCH_2). **^{31}P{^{1}H} NMR** ($CDCl_3$): δ = 23.1 (s). **^{13}C{^{1}H} NMR** ($CDCl_3$): δ = 13.5 (m, PCH_3), 23.2 (s, CH_2), 29.4 (m, PCH_2), 34.8 (s, CH_2), 55.8 (s, NCH), 56.9 (s, OCH_3), 66.9 (s, OCH_2).

[Cl$_2$Ru(L$_5$)(η^1-Me$_2$PCH$_2$CH$_2$OMe)$_2$] (2L$_5$): A solution of **L$_5$** (0.102 g, 0.90 mmol) in CH_2Cl_2 was reacted with the above-mentioned solution of **1** in 2-PrOH. Yield: 345 mg (80 %) of a yellow powder, dec. 217 °C.

$C_{16}H_{40}Cl_2N_2RuO_2P_2$ (526.43): calcd C 36.51, H 7.66, N 5.32 %; found C 36.55, H 7.66, N 5.21 %. MS (FAB): *m*/*z* = 526.1 (M^+).

^{1}H NMR ($CDCl_3$): δ = 1.21, 1.69, 2.11, 3.71 (m, 10H, C_6H_{10}), 1.42 (m, 12H, PCH_3), 2.11 (m, 4H, PCH_2), 2.64 (br, 2H, NH_2), 2.91 (br, 2H, NH_2), 3.32 (s, 6H, OCH_3), 3.64 (m, 4H, OCH_2). **^{31}P{^{1}H} NMR** ($CDCl_3$): δ = 23.1 (s). **^{13}C{^{1}H} NMR** ($CDCl_3$): δ = 15.2 (m, PCH_3), 25.0 (s, CH_2), 31.0 (m, PCH_2), 36.6 (s, CH_2), 57.5 (s, NCH), 58.7 (s, OCH_3), 68.6 (s, OCH_2)

$[Cl_2Ru(L_7)(\eta^1\text{-}Me_2PCH_2CH_2OMe)_2]$ ($2L_7$): A solution of L_7 (0.191 g, 0.90 mmol) in CH_2Cl_2 was reacted with the above-mentioned solution of **1** in 2-PrOH. Yield: 410 mg (80 %) of a yellow powder, dec. 215 °C.
$C_{24}H_{42}Cl_2N_2RuO_2P_2$ (624.53): calcd C 46.16, H 6.78 %, N 4.49; found C 45.91, H 6.74, N 4.38 %. MS (FAB): *m/z* = 624.1 (M^+).

^{1}H NMR ($CDCl_3$): δ = 1.40 (m, 12H, PCH_3), 2.08 (m, 4H, PCH_2), 3.23 (s, 6H, OCH_3), 3.62 (m, 4H, OCH_2), 3.80 (m, 2H, CH), 4.26 (m, 4H, NH_2), 7.06-7.17 (m, 10H, C_6H_5). **$^{31}P\{^1H\}$ NMR** ($CDCl_3$): δ = 23.1 (s). **$^{31}C\{^1H\}$ NMR** ($CDCl_3$): δ = 15.5 (m, PCH_3), 31.4 (m, PCH_2), 58.7 (s, OCH_3), 63.6 (s, NCH), 68.6 (s, OCH_2), 127.5, 128.4, 129.2, 140.8 (C_6H_5).

$[Cl_2Ru(L_8)(\eta^1\text{-}Me_2PCH_2CH_2OMe)_2]$ ($2L_8$): A solution of L_8 (0.075 ml, 0.90 mmol) in CH_2Cl_2 was reacted with the above-mentioned solution of **1** in 2-PrOH. Yield: 259 mg (65 %) of a yellow powder, dec. 209 °C.
$C_{13}H_{36}Cl_2N_2RuO_2P_2$ (486.1): calcd C 32.10, H 7.46, N 5.76 %; found C 32.03, H 6.98, N 5.54 %. MS (FAB): *m/z* = 486.4 (M^+).

^{1}H NMR ($CDCl_3$): δ = 1.40 (m, 12H, PCH_3), 1.80 (m, 2H, CCH_2C), 2.09 (m, 4H, PCH_2), 3.17 (br, 4H, NH_2), 3.31 (s, OCH_3), 3.34 (br, 4H, NCH_2), 3.67 (m, 4H, OCH_2). **$^{31}P\{^1H\}$ NMR** ($CDCl_3$): δ = 22.6 (s). **$^{13}C\{^1H\}$ NMR** ($CDCl_3$): δ = 15.5 (m, PCH_3), 30.0 (s, CH_2) 31.2 (m, PCH_2), 40.9 (s, NCH_2), 59.0 (s, OCH_3), 69.0 (s, OCH_2).

$[Cl_2Ru(L_9)(\eta^1\text{-}Me_2PCH_2CH_2OMe)_2]$ ($2L_9$): A solution of L_9 (0.104 ml, 0.90 mmol) in CH_2Cl_2 was reacted with the above-mentioned solution of **1** in 2-PrOH. Yield: 312 mg (74 %) of a yellow powder, dec. 213 °C.
$C_{15}H_{40}Cl_2N_2RuO_2P_2$ (514.41): calcd C 35.02, H: 7.84, N 5.45 %; found C 34.72, H 8.20, N 5.42 %. MS (FAB): *m/z* = 514.3 (M^+).

^{1}H NMR ($CDCl_3$): δ = 0.92 (s, 6H, $C(CH_3)_2$), 1.36 (m, 12H, PCH_3), 2.05 (m, 4H, PCH_2), 2.83 (br, 4H, NH_2), 3.28 (s, 6H, OCH_3), 3.38 (m, 4H, NCH_2), 3.64 (m, 4H, OCH_2). **$^{31}P\{^1H\}$ NMR** ($CDCl_3$): δ = 22.6 (s). **$^{13}C\{^1H\}$ NMR** ($CDCl_3$): δ = 15.5 (m, PCH_3), 25.2 (s, CCH_3), 31.1 (m, PCH_2), 34.6 (s, CCH_3), 50.9 (s, NCH_2), 58.9 (s, OCH_3), 68.9 (s, OCH_2).

$[Cl_2Ru(L_{10})(\eta^1\text{-}Me_2PCH_2CH_2OMe)_2]$ ($2L_{10}$): A solution of L_{10} (0.098 g, 0.90 mmol) in CH_2Cl_2 was reacted with the above-mentioned solution of **1** in 2-PrOH. Yield: 299 mg (70 %) of a red powder, dec. 197 °C.
$C_{16}H_{34}Cl_2N_2O_2P_2Ru$ (520.38): calcd C 36.93, H 6.59, N 5.38 %; found C 36.85, H 6.60, N, 5.17 %. MS (FAB): *m/z* = 519.0 (M^+).

^{1}H NMR ($CDCl_3$): δ = 1.45 (m, 6H, PCH_3), 2.15 (m, 4H, PCH_2), 3.29 (s, 6H, OCH_3), 3.66 (m, 4H, OCH_2), 5.31 (br, 4H, NH_2), 7.08-7.14, 7.25-7.31 (m, 4H, C_6H_4). **$^{31}P\{^1H\}$ NMR** ($CDCl_3$): δ = 24.8 (s). **$^{13}C\{^1H\}$ NMR** ($CDCl_3$): δ = 13.6 (m, PCH_3), 29.8 (m, PCH_2), 56.8 (s, OCH_3), 66.4 (s, OCH_2), 125.5, 126.0, 138.2 (C_6H_4).

$[Cl_2Ru(L_{11})(\eta^1\text{-}Me_2PCH_2CH_2OMe)_2]$ ($2L_{11}$): A solution of L_{11} (141 mg, 0.90 mmol) in CH_2Cl_2 was reacted with the above-mentioned solution of **1** in 2-PrOH. Yield: 303 mg (60 %) of a red powder, dec. 207 °C.
$C_{20}H_{34}Cl_2N_2O_2P_2Ru$ (568.42): calcd C 42.26, H 6.03, N 4.93 %; found C 42.60, H 6.30, N 5.17 %. MS (FAB): *m/z* = 567.3 (M^+).

^{1}H NMR ($CDCl_3$): δ = 1.70 (m, 12H, PCH_3), 2.40 (m, 4H, PCH_2), 3.35 (s, 6H, OCH_3), 3.81 (m, 4H, OCH_2), 7.70, 7.82, 8.22, 9.57 (m, 8H, $C_{10}H_8N_2$). **$^{31}P\{^1H\}$ NMR** ($CDCl_3$): δ = 22.1 (s). **$^{13}C\{^1H\}$ NMR** ($CDCl_3$): δ = 14.3 (m, PCH_3), 28.9 (m, PCH_2), 58.8 (s, OCH_3), 66.9 (s, OCH_2), 121.8, 134.3, 137.2, 149.6, 154.4 ($C_{10}H_8N_2$).

$[Cl_2Ru(L_{12})(\eta^1\text{-}Me_2PCH_2CH_2OMe)_2]$ ($2L_{12}$): A solution of L_{12} (162 mg, 0.90 mmol) in CH_2Cl_2 was reacted with the above-mentioned solution of **1** in 2-PrOH. Yield: 359 mg (74 %) of a red powder, dec. 213 °C.
$C_{22}H_{34}Cl_2N_2O_2P_2Ru$ (592.45): calcd C 44.60, H 5.78, N 4.73 %; found C 44.16, H 5.57, N 4.59 %. MS (FAB): *m/z* = 591.3.0 (M^+).

^{1}H NMR ($CDCl_3$): δ 1.70 (m, 12H, PCH_3), 2.40 (m, 4H, PCH_2), 3.36 (s, 6H, OCH_3), 3.81 (m, 4H, OCH_2), 7.70, 7.83, 8.22, 9.57 (m, 8H, $C_{12}H_8N_2$). **$^{31}P\{^1H\}$ NMR** ($CDCl_3$): δ = 18.0 (s). **$^{13}C\{^1H\}$ NMR** ($CDCl_3$): δ = 14.4 (m, PCH_3), 28.7 (m, PCH_2), 57.3 (s, OCH_3), 67.7 (s, OCH_2), 122.8, 125.8, 129.0, 133.6, 148.4, 158.4 ($C_{12}H_8N_2$).

X-ray structural analyses for complexes $2L_5$ and $2L_{11}$

Crystals of complex **$2L_5$** were obtained by slow diffusion of *n*-hexane from a Schlenk tube containing some degassed water into a dichloromethane solution of the complex in a smaller tube immersed into the above-mentioned schlenk tube containing water/*n*-hexane. Crystals for complex **$2L_{11}$** were obtained by layer-diffusion of *n*-hexane into dichloromethane solutions of the complex. Selected crystals were mounted on a P4 Siemens diffractometer by using a perfluorinated polyether (Riedel de Haen) as protecting agent. Graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å) was used for the measurement of intensity data in the ω-scan mode. The data were corrected for polarization and Lorentz effects. The structures were solved by Patterson synthesis (**$2L_5$**) or direct methods (**$2L_{11}$**) with SHELXS-86 [34]. Refinement was carried out with full-matrix least-squares methods based on F^2 in SHELXL-97 [35] with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were included at calculated positions using a riding model, except for the hydrogen atoms of the crystal water in **$2L_5$**; they were located from the difference map. For **$2L_5$**, the difference electron density map indicated also a disorder of the cyclohexyl rings of the diamine. This disorder was treated by introducing split positions corresponding to the opposite enantiomeric form of the ligand. The occupation numbers were refined, giving ratios of 0.886 : 0.114 (molecule A) and 0.582 : 0.418 (molecule B). Crystallographic details of the X-ray structure determination of **$2L_5$** and **$2L_{11}$** are summarized in Table 3.
Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 203821 (**$2L_5$**) and 203820 (**$2L_{11}$**). These data can be obtained

Table 3 Crystal Data and Structural Refinement for **$2L_5$** and **$2L_{11}$**

		$2L_5 \cdot H_2O$	**$2L_{11}$**
formula		$C_{16}H_{42}Cl_2N_2O_3P_2Ru$	$C_{20}H_{34}Cl_2N_2O_2P_2Ru$
formula weight/g mol^{-1}		544.43	568.4
crystal system		triclinic	orthorhombic
space group		$P\bar{1}$	Pbca
Z		4	8
cell dimensions (Å/°)	*a*/α	12.540(1) / 61.84(1)	16.785(2)
	b/β	14.897(2) / 83.87(1)	16.344(3)
	c/γ	15.418(2) / 74.09(1)	18.133(3)
V / Å^3		2441.1(5)	4974.7(13)
$\rho_{calc.}$ / gcm^{-3}		1.481	1.518
F(000)		1136	2336
μ / mm^{-1}		1.010	0.992
diffractometer		Siemens P4	Siemens P4
radiation type		Mo Kα (λ = 0.71073 Å)	Mo Kα (λ = 0.71073 Å)
temperature / K		173(2)	173(2)
θ range for data collection (°)		2.01-27.00	2.07-27.49
index range		$-15 \le h \le 7$, $-16 \le k \le 16$ $-19 \le l \le 19$	$-1 \le h \le 21$, $-1 \le k \le 21$ $-23 \le l \le 1$
reflections collected/unique		16132 / 10135	6895 / 5705
refinement method		full-matrix least-squares on F^2	full-matrix least-squares on F^2
data / restraints / parameters		10135 / 28 / 548	5705 / 0 / 269
goodness-of-fit on F^2		1.016	1.036
R_1/wR_2 [I>2σ(I)]		0.0285 / 0.0662	0.0380 / 0.0888
R_1/wR_2 (all data)		0.0377 / 0.0705	0.0517 / 0.0946
largest diff. peak / hole (eÅ^{-3})		0.495 / −0.753	0.833 / −1.019

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General Procedure for the Transfer Hydrogenation Study

The respective complexes $\mathbf{2L_1}$ - $\mathbf{2L_{12}}$ (0.012 mmol) were placed in a 50 ml flask containing 15 ml of 2-propanol as solvent, and 1 ml of a KOH solution in 2-propanol (57 x 10^{-3} mol/l) was added as a co-catalyst. The mixture was then removed from oxygen by three freeze-thaw cycles. Subsequently the flask was filled with argon and 0.70 ml of 2-acetophenone (6.0 mmol) was added. The reaction mixture was vigorously stirred at 82 °C for 4 h. During the transfer hydrogenation samples were taken from the reaction mixture to check the conversion. The samples were inserted by a special glass syringe into a gas chromatograph and the kind of the reaction products was compared with authentic samples. The results of the catalytic reactions are collected in Table 2.

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References

[1] Z. L. Lu, K. Eichele, E. Lindner, H. A. Mayer, *Inorg. Chem. Commun.* **2003**, *6*, 365.
[2] *Applied Homogeneous Catalysis with Organometallic Compounds − A Comprehensive Handbook in Two Volumes*, B. Cornils, W. A. Herrmann, Wiley-VCH, Weinheim, 1996.
[3] O. Kroecher, R. A. Koeppel, M. Froeba, A. Baiker, *J. Catal.* **1998**, *178*, 284.
[4] C. Bolm, *Angew. Chem.* **1991**, *103*, 414; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 542.
[5] H. A. Mayer, W. C. Kaska, *Chem. Rev.* **1994**, *94*, 1239.
[6] J. P. Collman, L. S. Hegedus, J. R. Norton, R. G. Finke, *Principles and Applications of Organotransition Metal Chemistry*, University Science Book, CA, 1987.
[7] P. Braunstein, M. D. Fryzuk, F. Naud, S. J. Rettig, *J. Chem. Soc., Dalton Trans.* **1999**, 589.
[8] K. Abdur-Rashid, A. J. Lough, R. H. Morris, *Organometallics* **2000**, *19*, 2655.
[9] O. M. Akotsi, K. Metera, R. D. Reid, R. McDonald, S. H. Bergens, *Chirality* **2000**, *12*, 514.
[10] T. Ohkuma, H. Doucet, T. Pham, K. Mikami, T. Korenaga, M. Terada, R. Noyori, *J. Am. Chem. Soc.* **1998**, *120*, 1086.
[11] R. Noyori, T. Okhuma, *Angew. Chem.* **2001**, *113*, 40; *Angew. Chem. Int. Ed.* **2001**, *40*, 40.
[12] R. Noyori, M. Yamakawa, S. Hashiguchi, *J. Org. Chem.* **2001**, *66*, 7931.
[13] K. Abdur-Rashid, S. E. Clapham, A. Hadzovic, J. N. Harvey, A. J. Lough, R. H. Morris, *J. Am. Chem. Soc.* **2002**, *124*, 15104.
[14] R. Hartmann, P. Chen, *Angew. Chem.* **2001**, *113*, 3693; *Angew. Chem. Int. Ed.* **2001**, *40*, 3581.
[15] M. J. Burk, W. Hems, D. Herzberg, C. Malan, A. Zanotti-Gerosa, *Org. Lett.* **2000**, *2*, 4173.
[16] K. Abdur-Rashid, M. Faatz, A. J. Lough, R. H. Morris, *J. Am. Chem. Soc.* **2001**, *123*, 7473.
[17] K. Abdur-Rashid, A. J. Lough, R. H. Morris, *Organometallics* **2001**, *20*, 1047.
[18] G. Z. Wang, J. E. Baeckvall, *J. Chem. Soc., Chem. Commun.* **1992**, 980.
[19] E. Lindner, I. Warad, K. Eichele, H. A. Mayer, *Inorg. Chim. Acta* **2003**, in press.
[20] E. Lindner, S. Al Gharabli, I. Warad, H. A. Mayer, S. Steinbrecher, E. Plies, M. Seiler, H. Bertagnolli, *Z. Anorg. Allg. Chem.* **2003**, *629*, 161.
[21] E. Lindner, B. Karle, *Z. Naturforsch.* **1990**, *45b*, 1108.
[22] H. Werner, A. Hampp, B. Windmueller, *J. Organomet. Chem.* **1992**, *435*, 169.
[23] A. Bader, E. Lindner, *Coord. Chem. Rev.* **1991**, *108*, 27.
[24] C. S. Slone, D. A. Weinberger, C. A. Mirkin, *Prog. Inorg. Chem.* **1999**, *48*, 233.
[25] C. Nachtigal, S. Al Gharabli, K. Eichele, E. Lindner, H. A. Mayer, *Organometallics* **2002**, *21*, 105.
[26] R. Noyori, T. Ohkuma, *Pure Appl. Chem.* **1999**, *71*, 1493.
[27] T. Dwars, G. Oehme, *Adv. Synth. Catal.* **2002**, *344*, 239.
[28] E. J. Creyghton, R. S. Downing, *J. Mol. Catal. A: Chem.* **1998**, *134*, 47.
[29] C. Saluzzo, M. Lemaire, *Adv. Synth. Catal.* **2002**, *344*, 915.
[30] G. Zassinovich, G. Mestroni, S. Gladiali, *Chem. Rev.* **1992**, *92*, 1051.
[31] P. Barbaro, C. Bianchini, A. Togni, *Organometallics* **1997**, *16*, 3004.
[32] M. O. Albers, E. Singleton, *Inorg. Synth.* **1989**, *26*, 253.
[33] G. Becker, *Diplomarbeit*, Univ. Tübingen, 1985.
[34] G. M. Sheldrick, *SHELXS-86*, University of Göttingen, Göttingen, Germany, 1986.
[35] G. M. Sheldrick, *SHELXL-97*, University of Göttingen, Göttingen, Germany, 1997.

