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Supported organometallic complexes Part 34: synthesis and structures of an array of diamine(ether–phosphine)ruthenium(II) complexes and their application in the catalytic hydrogenation of *trans*-4-phenyl-3-butene-2-one☆

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Dedicated to Professor Pierre Braunstein.

Abstract

The novel diamine–bis(ether–phosphine)ruthenium(II) complexes $Cl_2Ru(\eta^1\text{-}Ph_2PCH_2\text{–}CH_2OCH_3)_2(diamine)_2$(**3L$_1$**–**3L$_{11}$**) have been obtained by reaction of equimolar amounts of $Cl_2Ru(P\cap O)_2$ (**2**) with the respective diamines **L$_1$**–**L$_{11}$** in good yields. X-ray structural investigations of **3L$_2$** and **3L$_8$** show monoclinic unit cells with the space group $P2_1/c$. The octahedrally coordinated ruthenium atoms have each two *trans*-chlorides and *cis*-phosphines which is in agreement with NMR studies in solution. With the exception of **3L$_4$** all mentioned ruthenium complexes are highly catalytically active in the hydrogenation of the α,β-unsaturated ketone *trans*-4-phenyl-3-butene-2-one. In most cases the conversions and selectivities toward the formation of the unsaturated alcohol *trans*-4-phenyl-3-butene-2-ol were 100% with high turnover frequencies under mild conditions.

Keywords: Ruthenium(II) complexes; Crystal structures; Ether–phosphines; Hemilabile ligands; Catalytic hydrogenation

1. Introduction

Combinatorial chemistry and parallel syntheses become increasingly important in several areas of chemistry [2,3]. Recently this technique has been transferred to heterogeneous and homogeneous catalysis [1,2,4]. A prospective objective of our group is the combination of parallel syntheses and interphase chemistry and its transfer to catalysis. Interphase catalysts demonstrate a great importance since they are able to combine the advantages of homogeneous and heterogeneous catalysis with a marked reduction of notorious drawbacks like leaching and reduced catalytic activity of the reactive centers [5–11]. In a recent paper [12], we reported on a synthetic route to a set of neutral and cationic diamine–bis(ether–phosphine)ruthenium(II) complexes and their complete structural characterization. Compounds of this type can easily be supported in polysiloxane matrices and are potential candidates for the application of parallel methods. Due to the hemilabile character the oxygen donor is regarded as an intramolecular solvent impeding decomposition of the complex by protection of vacant coordination sites [12–17]. The weak ruthenium–oxygen bonds in bis(chelate)ruthenium(II) complexes of the type $Cl_2Ru(P\cap O)_2$ are easily cleaved during the reaction with diamines. Diaminediphosphineruthenium(II) complexes with classical phosphine ligands were already successfully employed in the catalytic hydrogenation of unsaturated ketones with high diastereo- and enantioselectivity [18–25]. By the employment of ether–phosphines the introduction of diamines is kinetically controlled and the formation of by-products is avoided [12].

☆ For Part 33 see Ref. [1].

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Here we wish to report on the preparation and characterization of a variety of novel diamine–bis(ether–phosphine)ruthenium(II) complexes using aliphatic diamines with different substituents in the backbone as well as chiral cycloaliphatic and aromatic, and substituted aromatic diamines. Complexes of this type proved to be efficient catalysts in the hydrogenation of a conjugated ketone. In a future step these complexes will be simultaneously tested in a specially designed parallel autoclave.

2. Experimental

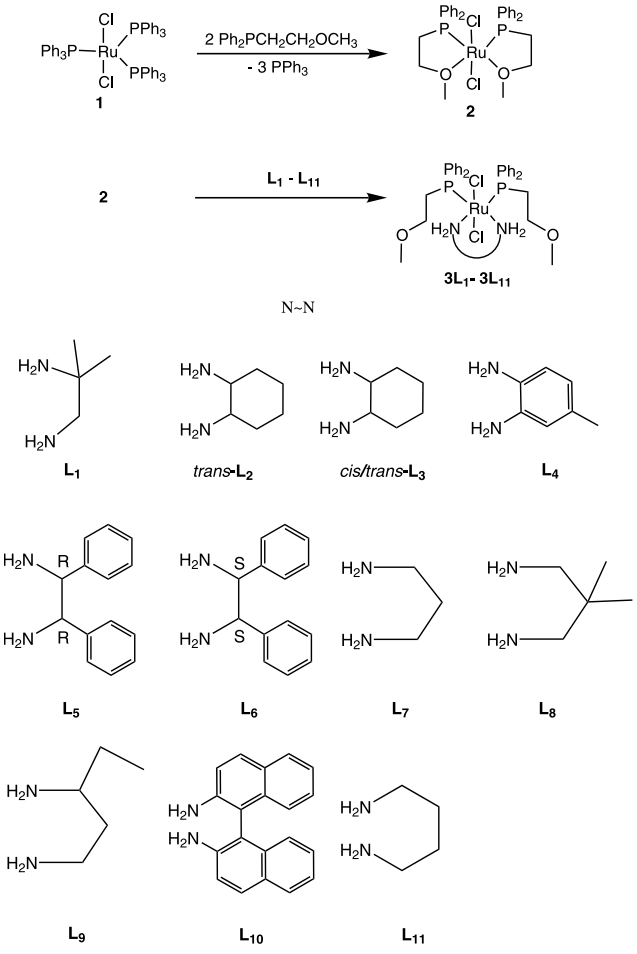
2.1. General remarks, materials, and instrumentations

All reactions were carried out in an inert atmosphere (argon) by using standard high vacuum and Schlenk-line techniques unless otherwise noted. Prior to use CH_2Cl_2, n-hexane, and Et_2O were distilled from CaH_2, $LiAlH_4$, and from sodium/benzophenone, respectively.

The ether–phosphine ligand $Ph_2PCH_2CH_2OCH_3$ was prepared according to literature methods [26]. The *trans*-4-phenyl-3-butene-2-one and the diamines were purchased from Acros, Fluka, and Merck and had to be purified. Ph_3P and $RuCl_3 \cdot 3H_2O$ were available from Merck and Chempur, respectively, and were used without further purification. Elemental analyses were carried out on an Elementar Vario EL analyzer. High-resolution ^1H, $^{13}C\{^1H\}$, DEPT 135, and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker DRX 250 spectrometer at 298 K. Frequencies are as follows: ^1H NMR 250.12 MHz, $^{13}C\{^1H\}$ NMR 62.9 MHz, and $^{31}P\{^1H\}$ NMR 101.25 MHz. Chemical shifts in the ^1H and $^{13}C\{^1H\}$ NMR spectra were measured relative to partially deuterated solvent peaks which are reported relative to TMS. ^{31}P chemical shifts were measured relative to 85% H_3PO_4 ($\delta = 0$). IR data were obtained on a Bruker IFS 48 FT IR spectrometer. Mass spectra: EI MS; Finnigan TSQ70 (200 °C). FAB MS; Finnigan 711 A (8 kV), modified by AMD and reported as mass/charge (m/z). The analyses of the hydrogenation experiments were performed on a GC 6000 Vega Gas 2 (Carlo Erba Instrument) with a FID and capillary column PS 255 [10 m, carrier gas, He (40 kPa), integrator 3390 A (Hewlett Packard)].

2.2. General procedure for the preparation of the complexes $3L_1$–$3L_{11}$ (see Scheme 1)

The corresponding diamine ligand (10% excess of $\mathbf{L_1}$–$\mathbf{L_{11}}$) was dissolved in 25 ml of dichloromethane and the solution was added dropwise to a stirred solution of **2** in 25 ml of dichloromethane. After the reaction mixture was stirred approximately for 45 min at room temperature (r.t.), the color changed from red to yellow. After removal of any turbidity by filtration (P4), the volume of the solution was concentrated to about 5 ml under reduced pressure. Addition of 40 ml of diethyl ether caused the precipitation of a solid which was filtered (P4), then dissolved again in 40 ml of dichloromethane and concentrated under vacuum to a volume of 5 ml. Addition of 80 ml of n-hexane caused the precipitation of a solid which was filtered (P4) and washed three times with 25 ml of n-hexane each and dried under vacuum.



Scheme 1.

2.2.1. $3L_1$

Complex **2** (300 mg, 0.454 mmol) was treated with $\mathbf{L_1}$ (0.05 ml, 0.50 mmol) to give $\mathbf{3L_1}$. Yield 299 mg (88%) of a yellow powder, m.p 227 °C, dec. 250 °C. ^1H NMR ($CDCl_3$): δ (ppm) 1.1 (s, 6H, CH_3), 2.5 (m, 4H, PCH_2), 2.8 (m, 4H, CH_2O), 2.8–3.0 (m, 6H, NH_2CH_2), 2.94, 2.96 (s, 6H, OCH_3), 7.17–7.60 (m, 20H, C_6H_5). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ (ppm) 38.3, 39.0 (AB pattern, $^2J_{PP} =$ 36.29 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ (ppm) 25.5 (m, PCH_2), 29.1 (s, CH_3), 54.7 (s, NCH_2), 55.7 (s, $NC(CH_3)_2$), 58.2 (s, OCH_3), 69.22, 69.29 (2s, CH_2O), 128.3 (m 27a, $N = 14.14$ Hz, m-C_6H_5), 129.3 (s, p-C_6H_5), 133.1 (m 27b, $N = 8.08$ Hz, o-C_6H_5), 134.17,

134.67 (2m 27c, $N = 8.08$ Hz, i-C_6H_5). FAB MS: (m/z) 748.2 (M^+). *Anal*. Calc. for $C_{34}H_{46}Cl_2N_2O_2P_2Ru$: C, 54.55; H, 6.19; Cl, 9.47; N, 3.74. Found: C, 54.38; H, 6.47; Cl, 9.35; N, 3.64%.

2.2.2. *3L₂ (with trans-L₂)*

Complex **2** (300 mg, 0.454 mmol) was treated with $\mathbf{L_2}$ (0.061 ml, 0.50 mmol) to give **3L₂**. Yield 337 mg (96%) of a yellow–brown powder, m.p. 221 °C, dec. 224 °C. ^{1}H NMR ($CDCl_3$): δ (ppm) 1.0–3.4 (m, 22H, CH_2CH_2, PCH_2, NCH, NH_2, OCH_2), 2.9 (s, 6H, OCH_3), 7.2–7.7 (m, 20H, C_6H_5). ^{31}P{^{1}H} NMR ($CDCl_3$): δ (ppm) 38.8 (s). ^{13}C{^{1}H} NMR ($CDCl_3$): δ (ppm) 24.9 (s, CH_2), 25.4 (m, PCH_2), 36.2 (s, CH_2), 57.7 (s, NCH), 58.2 (s, OCH_3), 69.3 (s, CH_2O), 128.3 (m 27a, $N = 8.08$ Hz, m-C_6H_5), 129.2, 129.4 (2s, p-C_6H_5), 132.6, 133.4 (2 m 27b, $N =$ 8.08, o-C_6H_5), 134.4, 134.7 (2 m 27c, $N = 69.72$, i-C_6H_5). FAB MS: (m/z) 774.2 (M^+). *Anal.* Calc. for $C_{36}H_{48}Cl_2N_2O_2P_2Ru$: C, 55.55; H, 6.19; Cl, 9.47; N, 3.74. Found: C, 55.33; H, 6.43; Cl, 9.35; N, 3.42%.

2.2.3. *3L₃ (mixture of cis/trans-L₃)*

Complex **2** (300 mg, 0.454 mmol) was treated with $\mathbf{L_3}$ (0.060 ml, 0.50 mmol) to give **3L₃**. Yield 337 mg (96%) of a yellow–brown powder, m.p. 218 °C, dec. 221 °C. ^{1}H NMR ($CDCl_3$): δ (ppm) 1.0–3.4 (m, 22H, CH_2CH_2, PCH_2, NCH, NH_2, OCH_2). 2.9 (s, 6H, OCH_3), 7.1–7.8 (m, 20H, C_6H_5). ^{31}P{^{1}H} NMR ($CDCl_3$): δ (ppm) 38.6, 38.9 (2s). ^{13}C{^{1}H} NMR ($CDCl_3$): δ (ppm) 22.2, 24.9 (2s, CH_2), 25.4 (m, PCH_2), 29.0, 36.2 (2s, CH_2), 54.1 (s, NCH), 57.7 (s, NCH), 58.2 (s, OCH_3), 69.3 (s, CH_2O), 128.3 (m 27a, $N = 8.08$ Hz, m-C_6H_5), 129.2, 129.3, 129.4 (3s, p-C_6H_5), 132.6, 132.9, 133.3 (3m 27b, $N = 8.08$, o-C_6H_5), 134.4, 134.7 (2m 27c, $N = 69.72$, i-C_6H_5). FAB MS: (m/z) 774.2 (M^+). *Anal*. Calc. for $C_{36}H_{48}Cl_2N_2O_2P_2Ru$: C, 55.55; H, 6.19; Cl, 9.47; N, 3.74. Found: C, 55.45; H, 6.33; Cl, 9.28; N, 3.56%.

2.2.4. *3L₄*

Complex **2** (300 mg, 0.454 mmol) was treated with $\mathbf{L_4}$ (0.061 g, 0.50 mmol) to give **3L₄**. Yield 337 mg (95%) of a light orange powder, m.p. 220 °C, dec. 224 °C. ^{1}H NMR ($CDCl_3$): δ (ppm) 2.1 (s, 3H, CH_3), 2.4 (m, 4H, PCH_2), 2.9 (s, 6H, OCH_3,) 3.0 (m, 4H, OCH_2), 4.4 (br, 4H, NH_2), 6.5–7.8 (m, 23H, C_6H_5, C_6H_3). ^{31}P{^{1}H} NMR ($CDCl_3$): δ (ppm) 40.6 (s). ^{13}C{^{1}H} NMR ($CDCl_3$): δ (ppm) 21.0 (s, CH_3), 25.4 (m, PCH_2), 58.2 (s, OCH_3), 69.2 (s, CH_2O), 127.5, 128.2, 128.3 (3s, C_6H_3), 128.5 (m 27a, $N = 8.76$ Hz, m-C_6H_5), 129.6 (s, p-C_6H_5), 133.0 (m 27b, $N = 8.76$ Hz, o-C_6H_5), 134.4 (m 27c, $N = 36.38$ Hz, i-C_6H_5), 137.5, 139.9 (s, br, C_6H_3). FAB MS: (m/z) 872.2 (M^+). *Anal.* Calc. for $C_{37}H_{44}Cl_2N_2O_2P_2Ru$: C, 56.78; H, 5.67; Cl, 9.06; N, 3.58. Found: C, 56.39; H, 6.00; Cl, 9.16; N, 3.79%.

2.2.5. *3L₅*

Complex **2** (300 mg, 0.454 mmol) was treated with $\mathbf{L_5}$ (0.105 g, 0.50 mmol) to give **3L₅**. Yield 356 mg (90%) of a yellow powder, m.p. 232 °C, dec. 239 °C. ^{1}H NMR ($CDCl_3$): δ (ppm) 2.2–4.2 (m, 14H, PCH_2, OCH_2, NH_2CH), 2.93 (s, 6H, OCH_3), 6.7–7.7 (m, 30H, C_6H_5). ^{31}P{^{1}H} NMR ($CDCl_3$): δ (ppm) 39.0 (s). ^{13}C{^{1}H} NMR ($CDCl_3$): δ (ppm) 25.8 (m, PCH_2), 58.2 (s, OCH_3), 63.9 (s, NCH), 69.3 (s, OCH_2), 127.2 (s, o-C_6H_5), 128.2 (s, p-C_6H_5), 128.3 (m 27a, $N = 8.08$ Hz, m-C_6H_5), 128.9 (s, m-C_6H_5), 129.3, 129.5 (2s, p-C_6H_5), 132.6, 133.3 (2m 27b, $N = 8.08$ Hz, o-C_6H_5) 134.4 (2m, i-C_6H_5), 140.2 (s, i-C_6H_5). FAB MS: (m/z) 872.2 (M^+). *Anal*. Calc. for $C_{44}H_{50}Cl_2N_2O_2P_2Ru$: C, 60.55; H, 5.77; Cl, 8.12; N, 3.21. Found: C, 60.28, H, 5.48; Cl, 7.98; N, 3.03%.

2.2.6. *3L₆*

Complex **2** (300 mg, 0.454 mmol) was treated with $\mathbf{L_6}$ (0.105 g, 0.50 mmol) to give **3L₆**. Yield 348 mg (88%) of a yellow powder, m.p. 220 °C, dec. 224 °C. ^{1}H NMR ($CDCl_3$): δ (ppm) 2.2–4.2 (m, 14H, PCH_2, OCH_2, NH_2CH), 2.93 (s, 6H, OCH_3), 6.7–7.7 (m, 30H, C_6H_5). ^{31}P{^{1}H} NMR ($CDCl_3$): δ (ppm) 39.0 (s). ^{13}C{^{1}H} NMR ($CDCl_3$): δ (ppm) 24.5 (m, PCH_2), 56.8 (s, OCH_3), 62.5 (s, NCH), 67.9 (s, CH_2O), 125.8 (s, o-C_6H_5), 126.8 (s, p-C_6H_5), 126.9 (m 27a, $N = 8.79$ Hz, m-C_6H_5), 127.6 (s, m-C_6H_5), 127.9, 128.1 (2s, p-C_6H_5), 131.1, 131.9 (2m 27b, $N = 8.08$ Hz, o-C_6H_5), 133.2 (2m, i-C_6H_5), 138.8 (s, i-C_6H_5). FAB MS: (m/z) 872.2 (M^+). *Anal*. Calc. for $C_{44}H_{50}Cl_2N_2O_2P_2Ru$: C, 60.55; H, 5.77; Cl, 8.12; N, 3.21. Found: C, 60.31, H, 5.50; Cl, 7.97; N, 2.90%.

2.2.7. *3L₇*

See Ref. [12].

2.2.8. *3L₈*

Complex **2** (300 mg, 0.454 mmol) was treated with $\mathbf{L_8}$ (0.059 ml, 0.49 mmol) to give **3L₈**. Yield 310 mg (90%) of a yellow powder, m.p. 206 °C, dec. 213 °C. ^{1}H NMR (CD_2Cl_2): δ (ppm) 0.8 (s, 6H, $C(CH_3)_2$), 2.2 (m, 4H, NCH_2), 2.6 (m, 2H, PCH_2), 2.8 (br, s, 10H, NH_2, OCH_3), 2.9 (s, 4H, CH_2O), 7.2–7.7 (m, 20H, C_6H_5). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ (ppm) 40.69 (s). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ (ppm) 25.4 (s, $C(CH_3)_2$), 26.2 (m, PCH_2), 34.5 (s, $C(CH_3)_2$), 50.0 (s, CH_2N), 58.1 (s, OCH_3), 69.5 (s, CH_2O), 128.2 (m 27a, $N = 8.77$ Hz, m-C_6H_5), 129.2 (s, p-C_6H_5), 132.7 (m 27c, $N = 33.68$ Hz, i-C_6H_5) 133.2 (m 27b, $N = 7.42$ Hz, o-C_6H_5). FAB MS: (m/z) 734.2 (M^+). *Anal*. Calc. for $C_{35}H_{48}Cl_2N_2O_2P_2Ru$: C, 55.12; H, 6.34; Cl, 9.30; N, 3.67. Found: C, 54.94; H, 5.92; Cl, 9.20; N, 3.59%.

2.2.9. $3L_9$

Complex **2** (300 mg, 0.454 mmol) was treated with $\mathbf{L_9}$ (0.059 ml, 0.49 mmol) to give $\mathbf{3L_9}$. Yield 308 mg (88%) of a yellow powder, m.p. 197 °C, dec. 199 °C. ^{1}H NMR ($CDCl_3$): δ (ppm) 0.9 (t, $^3J_{HH} = 7.38$ Hz, CH_3), 1.1–2.6 (m, 19H, $CH_2CHCH_2CH_2$, NH_2, PCH_2, CH_2O), 2.6 (s, 6H, OCH_3), 7.2–7.7 (m, 20H, C_6H_5). ^{31}P{^{1}H} NMR ($CDCl_3$): δ (ppm) 40.2, 40.7 (AB pattern, $^2J_{PP} = 35.35$ Hz). ^{13}C{^{1}H} NMR ($CDCl_3$): δ (ppm) 9.2 (s, CH_3), 25.5 (m, PCH_2), 32.8 (s, CH_2CH_3), 34.3 (s, CH_2CH_2N), 39.6 (s, CH_2N), 51.3 (s, CHN), 57.6 (s, OCH_3), 68.9 (s, CH_2O), 127.8–128.2 (m, *m*-C_6H_5), 129.5–129.6 (m, *p*-C_6H_5), 132.5 (m, *i*-C_6H_5) 133.2–133.7 (m, *o*-C_6H_5). FAB MS: (*m*/*z*) 762.2 (M^+). *Anal.* Calc. for $C_{35}H_{48}Cl_2N_2O_2P_2Ru$: C, 55.12; H, 6.34; Cl, 9.30; N, 3.67. Found: C, 54.89. H, 5.96; Cl, 9.29; N, 3.69%.

2.2.10. $3L_{10}$

Complex **2** (300 mg, 0.454 mmol) was treated with $\mathbf{L_{10}}$ (0.141 g, 0.50 mmol) to give $\mathbf{3L_{10}}$. Yield 368 mg (86%) of a light brown powder, m.p. 210 °C, dec. 215.1 °C. ^{1}H NMR ($CDCl_3$): δ (ppm) 1.7 (m, 4H, PH_2), 2.9 (s, 6H, OCH_3), 3.0 (m, 4H, CH_2O), 4.3 (d, $^2J_{HH} = 8.55$ Hz, 2H, NH_2), 5.0 (d, $^2J_{HH} = 8.55$ Hz, 2H, NH_2), 64–7.9 (m, 32H, C_6H_5, $C_{20}H_{12}$). ^{31}P{^{1}H} NMR ($CDCl_3$): δ (ppm) 43.4 (s). ^{13}C{^{1}H} NMR ($CDCl_3$): δ (ppm) 24.6 (m, PCH_2), 58.2 (s, OCH_3), 69.4 (s, CH_2O), 128.3–129.2 (m, *m*-C_6H_5), 129.7, 130.1 (2s, *p*-C_6H_5), 132.4, 134.3 (2m, *o*-C_6H_5) 133.3 (m, *i*-C_6H_5), 119.9, 123.4, 124.8, 125.8, 126.7, 131.3, 133.8, 134.0, 134.1, 140.6 (10s, $C_{20}H_{12}$). FAB MS: (*m*/*z*) 774.2 (M^+). *Anal*. Calc. for $C_{36}H_{48}Cl_2N_2O_2P_2Ru$: C, 63.56; H, 5.33; Cl, 7.50; N, 2.96. Found: C, 63.17; H, 5.6; Cl, 7.43; N, 2.82%.

2.2.11. $3L_{11}$

Complex **2** (300 mg, 0.454 mmol) was treated with $\mathbf{L_{11}}$ (0.043 ml, 0.494 mmol) to give $\mathbf{3L_{11}}$. Yield 152.7 mg (45%) of a yellow powder, m.p. 132 °C, dec. 141 °C. ^{1}H NMR ($CDCl_3$): δ (ppm) 1.6 (br, 8H, $2CH_2CH_2$), 2.3 (m, 4H, PCH_2), 2.62–3.1 (br, 8H, NH_2, CH_2O), 2.9 (s, 6H, OCH_3), 7.1–7.6 (m, 20H, C_6H_5). ^{31}P{^{1}H} NMR ($CDCl_3$): δ (ppm) 40.2 (s). ^{13}C{^{1}H} NMR ($CDCl_3$): δ (ppm) 27.7 (m, PCH_2), 40.3 (s, CH_2), 56.6 (s, NCH_2), 57.5 (s, OCH_3), 68.5 (s, CH_2O), 128.3 (m 27a, $N = 8.78$ Hz, *m*-C_6H_5), 129.4 (s, *p*-C_6H_5), 133.6 (m 27c, $N = 33.68$ Hz, *i*-C_6H_5) 133.7 (m 27b, $N = 7.42$ Hz, *o*-C_6H_5). FAB MS: (*m*/*z*) 747.87 (M^+). *Anal.* Calc. for $C_{34}H_{46}Cl_2N_2O_2P_2Ru$: C, 54.55; H, 6.19; Cl, 9.47; N, 3.74. Found: C, 54.28; H, 6.40; Cl, 9.34, N, 3.73%.

2.3. General procedure for the catalytic studies

The respective diamine–bis(ether–phosphine)ruthenium(II) complex (0.026 mmol) was placed in a 150 ml Schlenk tube and solid KOH (0.26 mmol) was added as a cocatalyst. The solid mixture was stirred and warmed during the evacuation process to remove oxygen and water. Subsequently the Schlenk tube was filled with argon and 20 ml of 2-propanol was added. The mixture was vigorously stirred, degassed by two freeze–thaw cycles, and then sonicated for 20–40 min (this is important to complete the dissolving of the catalyst and cocatalyst). A solution of *trans*-4-phenyl-3-butene-2-one (26 mmol) in 60 ml of 2-propanol was subjected to a freeze–thaw cycle in a different 150 ml Schlenk tube and was added to the catalyst solution. Finally the reaction mixture was transferred to a pressure Schlenk tube which was pressurized with dihydrogen of 1–4 bar. The reaction mixture was vigorously stirred at 35 °C for 1 h. During the hydrogenation process samples were taken from the reaction mixture to control the conversion and turnover frequency. 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.

2.4. X-ray structural analyses for complexes $3L_2$ and $3L_8$

Crystals of $\mathbf{3L_2}$ and $\mathbf{3L_8}$ were grown by slow diffusion of diethyl ether into a solution of the complex in dichloromethane. Data were collected at 173(2) K on a Siemens P4 diffractometer operating in the ω scan mode, using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Details of crystal data, data collection, and structure refinement are given in Table 1. The structures were solved by direct methods using the Bruker SHELXS-97 program [28a] and refined by full-matrix least-squares on F^2 using the Bruker SHELXL-97 program [28b]. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were constrained to idealized positions using a riding model (with free rotation for methyl groups). The difference electron density map and thermal ellipsoids of $\mathbf{3L_2}$ indicated a disorder of the cyclohexane ring of the diamine; this disorder was treated by introducing split positions corresponding to the opposite enantiomeric form of the ligand; the occupation number was allowed to refine, giving a ratio of 0.708:0.292.

3. Results and discussion

3.1. Synthesis of the diamine–bis(ether–phosphine)ruthenium(II) complexes ($3L_1$–$3L_{11}$)

If the bis(ether–phosphine)ruthenium(II) complex **2** [12,14] is treated with the different diamines $\mathbf{L_1}$–$\mathbf{L_{11}}$ in dichloromethane the yellow, somewhat air-sensitive mixed diamine–bis(ether–phosphine)ruthenium(II) complexes $\mathbf{3L_1}$–$\mathbf{3L_{11}}$ are formed in good to excellent yields (Scheme 1). They are soluble in chlorinated organic solvents and insoluble in ethers and aliphatic

Table 1
Crystal data and structure refinement for **3L$_2$** and **3L$_8$**

	3L$_2$	**3L$_8$**
Crystal habit	block	plate
Crystal color	orange	orange
Crystal size (mm)	0.6 × 0.6 × 0.6	0.5 × 0.3 × 0.08
Empirical formula	$C_{36}H_{48}Cl_2N_2O_2P_2Ru$	$C_{35}H_{48}Cl_2N_2O_2P_2Ru$
Formula weight	774.67	762.66
a (Å)	15.645(2)	11.4223(14)
b (Å)	9.5424(15)	28.394(4)
c (Å)	24.828(7)	12.2829(13)
α (°)	90	90
β (°)	92.640(15)	117.654(11)
γ (°)	90	90
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
Z	4	4
Reflections collected/unique	18 307/8506	9684/8091
R_{int}	0.0319	0.0391
Limiting indices	$-20 \le h \le 1$, $-12 \le k \le 12$, $-32 \le l \le 32$	$-1 \le h \le 14$, $-1 \le k \le 36$, $-15 \le l \le 14$
θ Range for data collection (°)	2.29–27.50	2.00–27.51
Completeness to θ (%)	99.8	99.9
Absorption coefficient (mm^{-1})	0.688	0.720
Absorption correction	none	none
Data/restraints/parameters	8506/0/464	8091/0/402
Goodness-of-fit on F^2	1.060	1.033
Final R indices $[I > 2\sigma(I)]$, R_1/wR_2	0.0240/0.0605	0.0568/0.1885
R indices (all data), R_1/wR_2	0.0271/0.0619	0.0812/0.2261
Extinction coefficient	0.00301(16)	0.0001(5)
Largest difference peak/hole (e $Å^{-3}$)	0.353/−0.641	1.770/−1.708

hydrocarbons. Their molecular composition was corroborated by FAB MS. The yield of the complexes **3L$_1$**–**3L$_{11}$** strongly depends on electronic and steric factors of the diamine ligands. If one or both hydrogen atoms at the nitrogen donors are replaced by alkyl or aryl groups no reaction takes place. This is clearly a steric effect. On the other hand if in 1,2-phenylenediamine **L$_4$** a methyl group is introduced in the *para*-position of a NH_2 function the yield increases from 59 [12] to 95%, an observation which is in agreement with an electronic effect. Electron withdrawing substituents like NO_2 groups instead of a methyl function give rise to an inverse effect, the yield drops to about 13% [25].

3.2. NMR and IR spectroscopic investigations

In the ^{1}H NMR spectra of the diamine–bis(ether–phosphine)ruthenium(II) complexes (**3L$_1$**–**3L$_{11}$**) characteristic sets of signals are observed, which are attributed to the phosphine as well as to the diamine ligands. Their assignment was supported by two-dimensional H,H COSY experiments which establish the connectivity between NH_2 and CH_2 functions in the diamine ligand, and between CH_2O and CH_2P groups in the phosphine fragment. The integration of the ^{1}H resonances confirm that the phosphine to diamine ratios are in agreement with the compositions of **3L$_1$**–**3L$_{11}$**. Furthermore, the chemical shifts of the singlets due to the protons of the methoxy groups are consistent with the η^1-P∼O unit [12]. In the $^{31}P\{^1H\}$ NMR spectra of **3L$_2$**, **3L$_3$**, **3L$_5$**–**3L$_8$**, **3L$_{10}$**, and **3L$_{11}$**, the singlets indicate that the phosphine groups are chemically equivalent in solution which is compatible with the C_{2v} symmetry of the $RuCl_2$(ether–phosphine)$_2$diamine complexes. While in the cases of **3L$_1$** and **3L$_9$** the asymmetric diamines cause loss of the C_2 axis resulting in a splitting of the ^{31}P resonances into AB patterns, in **3L$_4$**, the asymmetry is too remote to generate an observable splitting of the $^{31}P\{^1H\}$ NMR signal. The phosphorus chemical shifts and the ^{31}P–^{31}P coupling constants suggest that the ether–phosphines are η^1-P–O coordinated [12–17] and are positioned *cis* to each other. Thus, if a diamine chelate is present, both chlorines have to be in mutual *trans*-arrangements. The $^{13}C\{^1H\}$ NMR spectra also corroborate the structures given in Scheme 1. Characteristic ^{13}C signals are due to the η^1-P∼O binding mode as well as due to the aliphatic and aromatic diamines.

The IR spectra of the complexes **3L$_1$**–**3L$_{11}$** in particular show four sets of characteristic absorptions in the ranges 3386–3300, 3272–3205, 3178–3165, and 280–260 cm^{-1}, which can be assigned to NH_2, amine–CH, phosphine–CH and RuCl stretching vibrations, respectively.

3.3. X-ray structural determination of trans-3L$_2$ and 3L$_8$

To get a better insight into structural parameters complexes **3L$_2$** and **3L$_8$** have been selected for X-ray structural investigations. Crystal structures of **3L$_2$** and **3L$_8$** are shown in Fig. 1, relevant bond distances, angles and torsion angles are collected in Table 2. Both compounds crystallize as *trans*-chloro-*cis*-phosphine isomers with approximate C_2 symmetry. Ruthenium is at the center of a mostly regular octahedron, where Ru(1), P(1), P(2), N(1), and N(2) deviate by less than 0.1 Å from the equatorial least-squares plane, while the chlorine ligands are bent away from their axial positions toward the diamine ligand, forming Cl–Ru–Cl angles of 164.89° (**3L$_2$**) and 166.72° (**3L$_8$**). The different sizes of the diamine chelate rings result in distinctly different N–Ru–N angles of 77.85° (**3L$_2$**) in the five-membered ring versus 84.54° (**3L$_8$**) in the six-membered chelate, but the bite angles of both diamine ligands are obviously sufficiently small to leave the opposing P–Ru–P angles unaffected, 92.39° (**3L$_2$**) and 91.72° (**3L$_8$**).

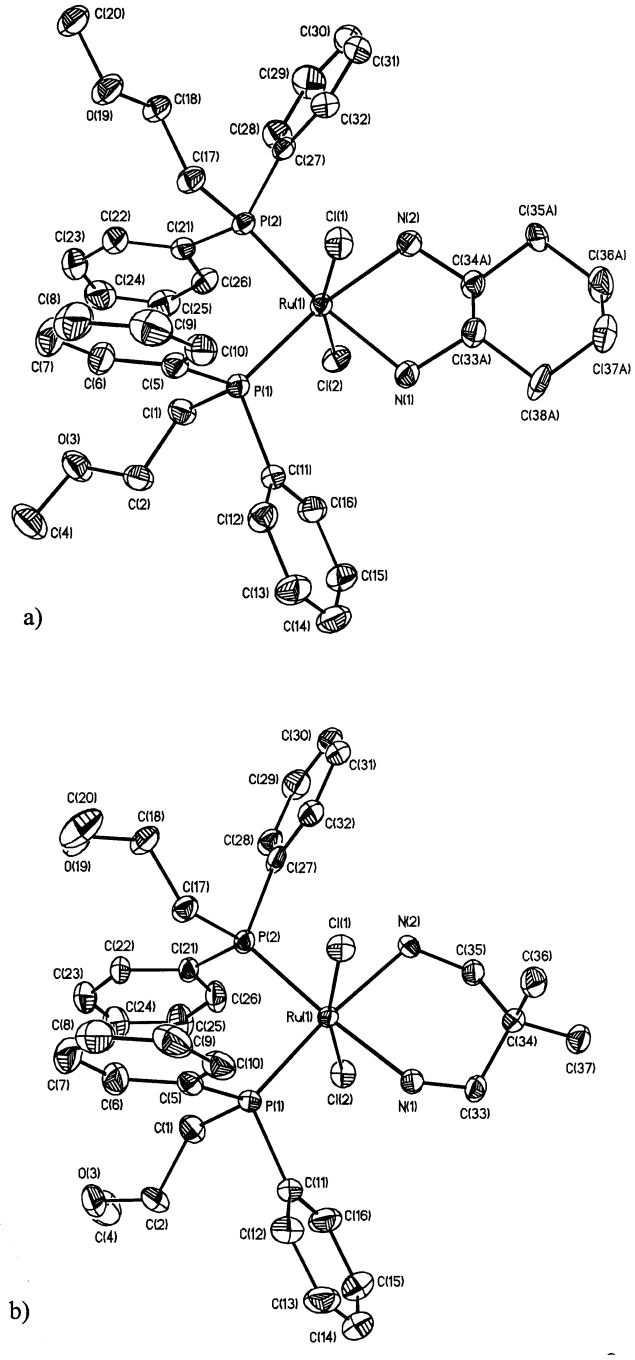


Fig. 1. ORTEP plots of (a) $3L_2$ and (b) $3L_8$ with atom labeling scheme. Thermal ellipsoids are drawn at the 50% probability level, hydrogens are omitted for clarity.

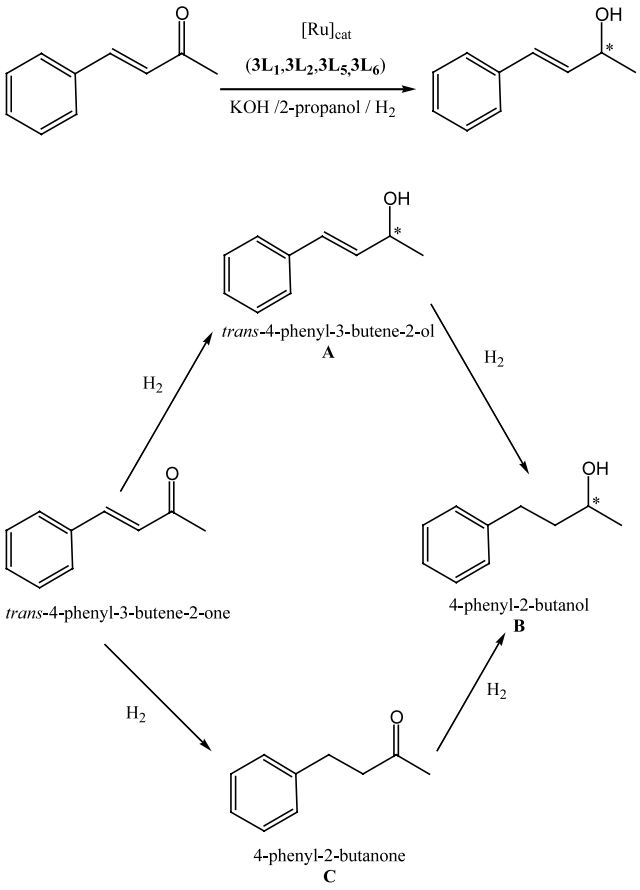
In $3L_2$, the *trans*-diaminocyclohexane ligand forms a typical five-membered chelate with twist conformation, similar to the complex with 1,2-diaminoethane [12]. This allows the cyclohexane ring to adopt a chair conformation. In $3L_8$, the six-membered diamine chelate also has a chair structure, but is flattened about the position of the metal; e.g. the dihedral angle between the planes N(1)–Ru(1)–N(2) and N(1)–C(33)–N(2)–C(35) is 31.09° compared with 56.98° between N(1)–C(33)–N(2)–C(35) and C(33)–C(34)–C(35). This is in contrast to six-membered cobalt(III) diamine rings that tend to form more regular chair conformations [29]. The Ru–N distances of 2.170(4) and 2.209(4) Å in $3L_8$, where nitrogen is *trans* to phosphorus, are shorter than those in a complex of *trans*-diaminocyclohexane where nitrogen is *trans* to hydrogen atoms, with Ru–N distances of 2.225(5) and 2.284(5) Å [20].

Table 2
Selected bond lengths (Å) and bond and torsion angles (°) for $3L_2$ and $3L_8$

	$3L_2$	$3L_8$
Bond lengths		
Ru(1)–Cl(1)	2.4141(6)	2.4178(13)
Ru(1)–Cl(2)	2.4050(5)	2.4303(14)
Ru(1)–P(1)	2.2737(7)	2.2807(14)
Ru(1)–P(2)	2.2881(5)	2.3037(14)
Ru(1)–N(1)	2.1790(13)	2.170(4)
Ru(1)–N(2)	2.1797(14)	2.209(4)
Bond angles		
Cl(1)–Ru(1)–Cl(2)	164.894(15)	166.72(5)
P(1)–Ru(1)–P(2)	92.38(2)	91.72(5)
N(1)–Ru(1)–N(2)	77.76(5)	84.54(16)
N(1)–Ru(1)–Cl(1)	84.74(4)	83.66(14)
N(2)–Ru(1)–Cl(1)	83.62(4)	82.73(12)
N(1)–Ru(1)–Cl(2)	84.15(4)	88.16(14)
N(2)–Ru(1)–Cl(2)	84.04(4)	86.10(12)
P(1)–Ru(1)–Cl(1)	98.985(15)	99.53(5)
P(2)–Ru(1)–Cl(1)	91.787(15)	89.47(5)
P(1)–Ru(1)–Cl(2)	92.027(16)	90.93(5)
P(2)–Ru(1)–Cl(2)	98.090(15)	98.42(5)
Torsion angles		
N(2)–Ru(1)–N(1)–C(33,33A)	17.5(2)	−38.8(4)
N(1)–Ru(1)–N(2)–C(35)		35.2(4)
N(1)–Ru(1)–N(2)–C(34A)	12.2(2)	
Ru(1)–N(1)–C(33,33A)–C(34,34A)	−43.3(4)	62.6(6)
N(1)–C(33)–C(34)–C(35)		−68.5(6)
N(1)–C(33A)–C(34A)–N(2)	53.1(4)	
Ru(1)–N(2)–C(35)–C(34)		−53.9(6)
Ru(1)–N(2)–C(34A)–C(33A)	−38.6(4)	
C(33)–C(34)–C(35)–N(2)		64.1(6)

3.4. Catalytic activity of the ruthenium(II) complexes $3L_1$, $3L_2$, and $3L_4$–$3L_9$ in the selective hydrogenation of an α,β-unsaturated ketone

To study the catalytic activity of the ruthenium(II) complexes *trans*-4-phenyl-3-butene-2-one was selected as a model substrate, because three different possibilities of hydrogenation are to be expected (Scheme 2). The selective hydrogenation of the carbonyl group affords the corresponding unsaturated alcohol *trans*-4-phenyl-3-butene-2-ol (**A**), which is the most desired product. In that case the conjugation is interrupted and this effect is observable in the UV spectrum. Unwanted and hence of minor interest is the hydrogenation of the C=C double bond, leading to the saturated ketone (**C**). Also not in the focus of our interest is the hydrogenation of both the



Scheme 2.

C=O and C=C bonds resulting in the formation of the saturated alcohol (**B**). 2-Propanol served as a solvent reagent, but the catalysts were only active in the presence of excess hydrogen and a cocatalyst (KOH) [20–23,30,31]. Aprotic and chlorinated solvents resulted only in moderate to low yields. All hydrogenations were carried out under mild conditions between 1 and 4 bar hydrogen pressure. Results are listed in Table 3.

The hydrogen pressure has not affected the regioselectivity, but strongly influences the turnover frequencies (Table 3, runs 6–9). When the reaction was carried out in 2-propanol using catalyst $\mathbf{3L_6}$ at 35 °C with a molar substrate : catalyst (S/C) ratio of 1000:1, the turnover frequency was 200 h^{-1} at 0.4 bar of hydrogen pressure. By increasing the H_2 pressure to 1, 2, and 4 bar the turnover frequencies were enhanced from 1204 via 1688 to 2439 h^{-1}.

The excellent selectivity in the hydrogenation of only the carbonyl group is reminiscent of a stoichiometric reduction using $NaBH_4$. However, only those complexes were successful which were provided with 1,2-diamines. If 1,3-diamines were employed as coligands the selectivity decreases in favor of the hydrogenation of the C=C bond (Table 3, runs 10–13, and Scheme 2, **C**). Only in the case of catalyst $\mathbf{3L_4}$ a completely selective hydrogenation of the C=C function was observed with a low turnover frequency (Table 3, run 4, and Scheme 2, **C**). In no case the complete hydrogenation to give **B** has been observed (Table 3).

4. Conclusion

In this work a set of 11 novel (ether–phosphine)-ruthenium(II) complexes were made available which were provided with different aliphatic and cycloaliphatic diamines. The most valuable catalyst were those with aliphatic and cycloaliphatic amines, they have been proved to be highly active hydrogen catalysts with excellent conversions and turnover frequencies even

Table 3
Hydrogenation of *trans*-4-phenyl-3-butene-2-one [a]

Run	Catalyst	Conversion (%)[b]	H_2 (bar)	TOF [c]	Selectivity (%) [b]		
					A	**B**	**C**
1	**2**	32	3	126	0	0	100
2	$\mathbf{3L_1}$	67	2	673	100	0	0
3	$\mathbf{3L_2}$	100	3	1587	100	0	0
4	$\mathbf{3L_4}$	17	4	15	0	0	100
5	$\mathbf{3L_5}$	100	4	1240	100	0	0
6	$\mathbf{3L_6}$	40	0.4	200	100	0	0
7	$\mathbf{3L_6}$	100	1	1204	100	0	0
8	$\mathbf{3L_6}$	100	2	1688	100	0	0
9	$\mathbf{3L_6}$	100	4	2439	100	0	0
10	$\mathbf{3L_7}$	100	1	1500	79.5	0	20.6
11	$\mathbf{3L_8}$	61	1	610	76.4	0	23.6
12	$\mathbf{3L_8}$	97	4	1429	82.4	0	17.6
13	$\mathbf{3L_9}$	100	4	1000	71.6	0	23.4

[a] Reaction was conducted at 35 °C using 3–5 g of substrate (S/C = 1000) in 80 ml of 2-propanol [Ru:KOH:Substrate][1:10:1000].
[b] Yields and selectivities were determined by GC.
[c] TOF, turnover frequency ($mol_{sub}\ mol_{cat}^{-1}\ h^{-1}$).

under mild conditions. Also they show a 100% selectivity toward the hydrogenation of the carbonyl function of the conjugated ketone *trans*-PhCH=CHC(O)Me. Only complex **3L$_4$** was able to hydrogenate the C=C bond of the ketone, exclusively, however, with a low conversion and turnover frequency.

5. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 179993 (**3L$_2$**), and 179994 (**3L$_8$**). Copies may be obtained free of charge from the Director CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44-1223-336 033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/conts/retrieving.html).

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