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Supported organometallic complexes part 39: cationic diamine(ether–phosphine)ruthenium(II) complexes as precursors for the hydrogenation of *trans*-4-phenyl-3-butene-2-one ☆

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Dedicated to Professor Helmut Werner on the occasion of his 70th birthday

Abstract

Treatment of $RuCl_2(\eta^1\text{-}Ph_2PCH_2CH_2OCH_3)_2$(diamine) (**1L$_1$**–**1L$_7$**) with one equivalent of AgX (X = OTf, BF_4) in CH_2Cl_2 results in the formation of the monocationic ruthenium(II) complexes $[RuCl(\eta^1\text{-}Ph_2PCH_2CH_2OCH_3)(\eta^2\text{-}Ph_2PCH_2CH_2OCH_3)(diamine)]^+X^-$ (**2L$_1$**–**2L$_7$**). These complexes were characterized by NMR, and mass spectroscopy as well as by elemental analyses, **2L$_1$** additionally by an X-ray structural analysis. Complex **2L$_1$** crystallizes in the monoclinic space group $C2/c$ with $Z = 8$. The monocationic and neutral complexes were applied as catalysts in the selective hydrogenation of *trans*-4-phenyl-3-butene-2-one. With the exception of **1L$_3$/1L$_7$** and **2L$_3$/2L$_7$** all catalysts showed high activities and selectivities toward the hydrogenation of the carbonyl group under mild conditions. However, the activity of the cationic catalysts is only half of that of their neutral congeners.

Keywords: Ruthenium(II) complexes; Crystal structure; Hemilabile ligands; Catalytic hydrogenation

1. Introduction

Recently, Noyori and co-workers [2–4] published several papers in which they described the catalytic activity of 1,2-diamine(diphosphine)ruthenium(II) complexes in the selective hydrogenation of conjugated ketones. 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 [3,4]. Further theoretical and experimental work suggested that the intramolecular heterolytic splitting of dihydrogen across the polar Ru=N bond of the resulting amido complex is the turnover limiting step [5–8]. 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) [2–7].

The introduction of hemilabile ether–phosphine ligands enables a facile incorporation of different types of diamines leading to a series of diamine(ether–phosphine)ruthenium(II) complexes [9–14], which proved to be highly active catalysts in the hydrogenation of functionalized carbonyl compounds [9,15–22]. Complexes of this type are easily obtained by reaction of $RuCl_2(P^\frown O)_2$ ($P^\frown O = \eta^2$-O,P-coordinated ether–phosphine ligand, $Ph_2PCH_2CH_2OCH_3$) with aliphatic or aromatic, chiral

☆ For Part 38, see [1].

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or achiral as well as protic or aprotic 1,2- or 1,3-diamines [1,9,12,14].

In continuation of our investigations in this paper the synthesis and characterization of novel monocationic diamine(ether–phosphine)ruthenium(II) complexes are reported and their catalytic behavior is compared with their neutral precursors [9,16]. The abstraction of a chloride from the corresponding neutral ruthenium(II) complexes leaves a vacant coordination site which subsequently is occupied by an ether–oxygen donor. By incoming substrates this very weak bond is easily ruptured [9,14,15,23].

2. Experimental

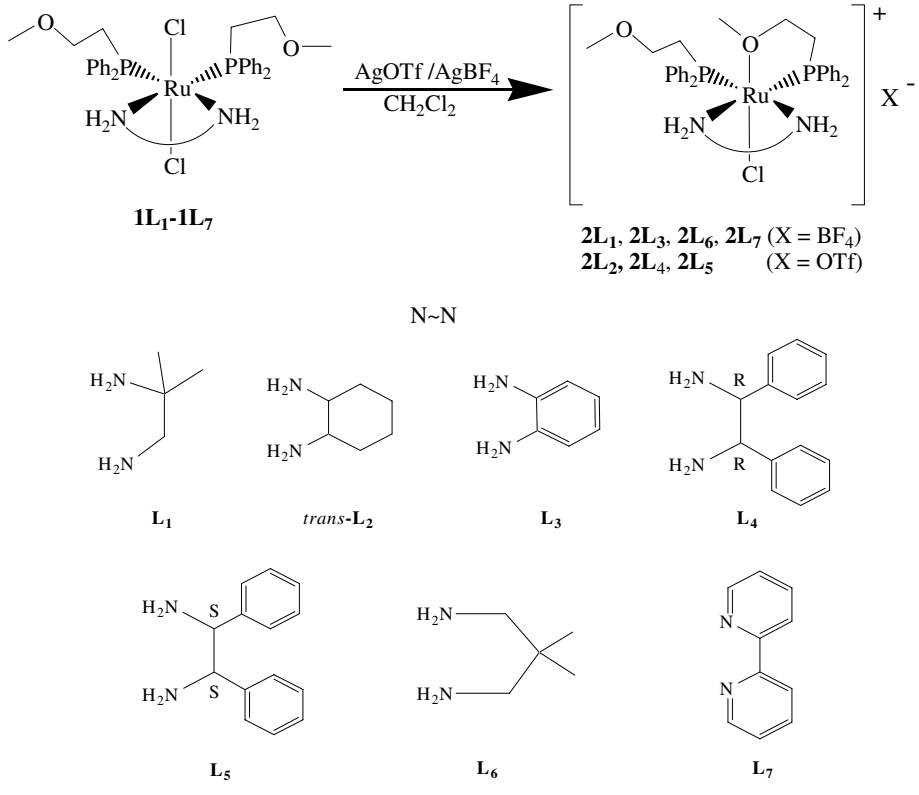
2.1. General remarks, materials, and instrumentations

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 dichloromethane, *n*-hexane, and diethyl ether 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 the literature methods [18]. The diamines were purchased from Acros, Fluka, and Merck and were purified. Ph_3P, BuLi, $CH_3OCH_2CH_2Cl$, AgOTf, $AgBF_4$, 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, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra, as well as the DEPT 135 experiment 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. In those cases where different stereoisomers are observed the integration refers to the main isomer. ^{31}P chemical shifts were measured relative to 85% H_3PO_4. Mass spectra: EI-MS; Finnigan TSQ70 (200 °C). FAB-MS; Finnigan 711A (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 monocationic complexes *2L₁–2L₇ (see Scheme 1)*

(a) Excess (2%) of AgOTf was added to the neutral complexes **1L₂**, **1L₄**, and **1L₅** [9] in a 100-ml Schlenk



Scheme 1.

tube. The solid mixture was stirred and warmed for 5 min, then 20 ml of dichloromethane was added and the solution was stirred for 5 min. After filtration through silica the solution was concentrated to about 2 ml under reduced pressure. The corresponding cationic complex was precipitated by addition of 30 ml of diethyl ether, filtered off (P3), washed three times with 25 ml portions of diethyl ether, and dried under vacuum.

(b) A solution of $AgBF_4$ (5% excess) in 25 ml of dichloromethane was added to a solution of the neutral complexes **1L$_1$**, **1L$_3$**, **1L$_6$**, and **1L$_7$** [9] in 25 ml of dichloromethane and the solution was stirred for 4 h. After filtration through silica the solution was concentrated to a small volume (2 ml). The addition of 100 ml of diethyl ether caused the precipitation of a solid, which was filtered off (P3), washed three times with 25 ml portions of diethyl ether, and dried under vacuum.

2.2.1. *2L$_1$*

Complex **1L$_1$** (300 mg, 0.401 mmol) was treated with $AgBF_4$ (79 mg, 0.406 mmol) to give **2L$_1$**. Yield 244 mg (77%) of a yellow powder. ^{1}H NMR (CD_2Cl_2): 2.0–4.0 (m, 14H, CH_2P, $H_2NCH_2CNH_2$, CH_2O), 0.99, 1.10, 1.18, 1.24 (4s, 6H, $C(CH_3)_2$), 2.98, 3.06, 3.71, 3.79 (4s, 6H, OCH_3), 6.42–8.21 (m, 20H, C_6H_5). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): isomer a (67%), δ (ppm) 56.6 (d, $^2J_{PP} = 38.14$ Hz), 48.7 (d, $^2J_{PP} = 38.14$ Hz); isomer b (33%), 55.6 (d, $^2J_{PP} = 37.23$ Hz), 47.0 (d, $^2J_{PP} = 37.23$ Hz). FAB-MS: (m/z) 713.2 ($M^+ - BF_4$). *Anal.* Calc. for $C_{34}H_{46}BClF_4N_2O_2P_2Ru$: C, 51.05; H, 5.79; Cl, 4.43; N, 3.50. Found: C, 51.11; H, 5.71; Cl, 4.34; N, 3.50%.

2.2.2. *2L$_2$*

Complex **1L$_2$** (300 mg, 0.387 mmol) was treated with AgOTf (100 mg, 0.389 mmol) to give **2L$_2$**. Yield 313 mg (91%) of a yellow powder. ^{1}H NMR (CD_2Cl_2): 0.8–4.0 (m, 22H, CH_2P, $H_2NCHCH_2CH_2$, CH_2O), 2.89, 3.10, 3.64, 3.70 (4s, 6H, OCH_3), 6.4–8.1 (m, 20H, C_6H_5). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): isomer a (80%), δ (ppm) 58.7 (d, $^2J_{PP} = 37.23$ Hz), 48.3 (d, $^2J_{PP} = 37.23$ Hz); isomer b (20%), 56.8 (d, $^2J_{PP} = 37.23$ Hz), 49.4 (d, $^2J_{PP} = 37.23$ Hz). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 24.2–36.3 (8s, $NH_2CHCH_2CH_2$), 30.1–36.0 (m, PCH_2), 56.9–61.7 (8s, NCH, OCH_3), 68.29, 68.85, 73.79, 74.25 (4d, $^3J_{PC} = 4.88$ Hz, CH_2O), 128.2–131.4 (C_6H_5). FAB-MS: (m/z) 739.2 ($M^+ - OTf$). *Anal.* Calc. for $C_{37}H_{48}ClF_3N_2O_5SP_2Ru$: C, 50.03; H, 5.45; Cl, 3.99; N, 3.15; S, 3.61. Found: C, 50.17; H, 5.35; Cl, 4.20; N, 3.07; S, 3.48%.

2.2.3. *2L$_3$ and 2L$_7$*

See [7].

2.2.4. *2L$_4$*

Complex **1L$_4$** (300 mg, 0.344 mmol) was treated with AgOTf (89 mg, 0.346 mmol) to give **2L$_4$**. Yield 319 mg (95%) of a yellow powder. ^{1}H NMR (CD_2Cl_2): 0.7–4.3 (m, 14H, CH_2P, OCH_2, H_2NCH), 2.86, 2.94, 4.1, 4.3 (4s, 6H, OCH_3), 6.3–7.7 (m, 30H, C_6H_5). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): isomer a (80%), δ (ppm) 58.4 (d, $^2J_{PP} = 37.23$ Hz), 47.5 (d, $^2J_{PP} = 37.23$ Hz); isomer b (20%), 54.4 (d, $^2J_{PP} = 37.23$ Hz), 47.4 (d, $^2J_{PP} = 37.23$ Hz). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 23.1–32.4 (m, PCH_2), 58.3–69.3 (8s, H_2NCH, OCH_3), 68.61, 69.25, 74.21, 74.63 (4d, $^3J_{PC} = 4.52$ Hz, CH_2O), 126.6–130.1 (C_6H_5). FAB-MS: (m/z) 837.2 ($M^+ - OTf$). *Anal.* Calc. for $C_{45}H_{50}ClF_3N_2O_5SP_2Ru$: C, 54.79; H, 5.11; Cl, 3.59; N, 2.84; S, 3.25. Found: C, 54.74; H, 5.37; Cl, 3.47; N, 2.97; S, 3.59%.

2.2.5. *2L$_5$*

Complex **1L$_5$** (300 mg, 0.344 mmol) was treated with AgOTf (89 mg, 0.346 mmol) to give **2L$_5$**. Yield 320 mg (96%) of a yellow powder. ^{1}H NMR (CD_2Cl_2): 0.7–4.6 (m, 14H, CH_2P, OCH_2, H_2NCH), 2.88, 2.97, 4.2, 4.4 (4s, 6H, OCH_3), 6.5–7.8 (m, 30H, C_6H_5). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): isomer a (80%), δ (ppm) 58.5 (d, $^2J_{PP} = 37.23$ Hz), 47.7 (d, $^2J_{PP} = 37.23$ Hz); isomer b (20%), 54.8 (d, $^2J_{PP} = 37.23$ Hz), 47.6 (d, $^2J_{PP} = 37.23$ Hz). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 24.2–32.8 (m, PCH_2), 58.7–69.2 (8s, H_2NCH, OCH_3), 68.62, 69.26, 74.30, 74.58 (4d, $^3J_{PC} = 4.52$ Hz, CH_2O), 127.6–131.4 (C_6H_5). FAB-MS: (m/z) 837.2 ($M^+ - OTf$). *Anal.* Calc. for $C_{45}H_{50}ClF_3N_2O_5SP_2Ru$: C, 54.79; H, 5.11; Cl, 3.59; N, 2.84; S, 3.25. Found: C, 54.70; H, 5.30; Cl, 3.67; N, 2.98; S, 3.60%.

2.2.6. *2L$_6$*

Complex **1L$_6$** (300 mg, 0.394 mmol) was treated with $AgBF_4$ (78 mg, 0.401 mmol) to give **2L$_6$**. Yield 224 mg (70%) of a yellow powder. ^{1}H NMR (CD_2Cl_2): δ (ppm) 0.42, 0.83 (2s, 6H, CH_3), 1.2–3.7 (m, 16H, CH_2P, H_2NCH_2, CH_2O), 3.00, 3.66 (2s, 6H, OCH_3), 6.4–8.1 (m, 20H, C_6H_5). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ (ppm) 51.4 (d, $^2J_{PP} = 37.21$ Hz), 43.0 (d, $^2J_{PP} = 37.21$ Hz). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 18.41, 25.37 (2s, $2CH_3$), 23.88, 29.54 (2d, $^1J_{PC} = 4.4$ Hz, PCH_2), 47.16, 50.75 (2s, NCH_2), 56.81, 58.75 (2s, OCH_3), 66.54, 71.55 (2d, $^3J_{PC} = 4.50$ Hz, CH_2O), 126.4-135.4 (C_6H_5). FAB-MS: (m/z) 727.2 ($M^+ - BF_4$). *Anal.* Calc. for $C_{35}H_{48}BClF_4N_2O_2P_2Ru$: C, 51.64; H, 5.94; Cl, 4.36; N, 3.44. Found: C, 51.20; H, 5.60; Cl, 4.28; N, 3.05%.

2.3. General procedure for the catalytic studies

The amount (0.026 mmol) of the respective diamine(ether–phosphine)ruthenium(II) complex **1L$_1$**–**1L$_7$** [5] was placed in a 50-ml Schlenk tube and solid AgOTf or $AgBF_4$ (0.026 mmol) was added. The Schlenk tube was evacuated several times and filled with argon. After that 5 ml of CH_2Cl_2 was added and the mixture was stirred (2 min in case of AgOTf and 2 h in case of $AgBF_4$). Subsequently, AgCl was filtered off (P3) and the solution was transferred to a 200-ml Schlenk tube. Then CH_2Cl_2 was completely removed in vacuum. Afterwards

KOH or *t*BuOK (0.26 mmol) as a co-catalyst and *trans*-4-phenyl-3-butene-2-one (26.0 mmol) were mixed together. The solid mixture was stirred and warmed during the evacuation process to remove oxygen. Subsequently, the Schlenk tube was filled with argon and 80 ml of 2-propanol. The mixture was vigorously stirred, degassed by two freeze–thaw cycles, and then sonicated for 30 min (this is important to complete the dissolution of the catalyst and cocatalyst). Finally, the reaction mixture was transferred to a pressure Schlenk tube (250 ml) which was pressurized with H_2 of 3 bar after flushing with H_2 three times. The reaction mixture was vigorously stirred at 35 °C for 1–3 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 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 complex $2L_1$

Complex $\mathbf{2L_1}$ $(C_{34}H_{46}ClN_2O_2P_2Ru)(BF_4)\cdot H_2O$ ($M = 818.01$) crystallizes in the monoclinic, space group $C2/c$, $a = 38.284(7)$, $b = 9.6965(17)$, $c = 20.547(13)$ Å, $\beta = 102.32(3)°$, $V = 7452(5)$ Å^3, $Z = 8$, $D_c = 1.458$ g cm^{-3}, μ(Mo Kα) = 0.634 mm^{-1}. Crystal size $0.6\times0.3\times0.2$ mm^3. Siemens P4 four-circle diffractometer, Mo Kα radiation ($\lambda = 0.71073$ Å), $T = 173(2)$ K. θ range for data collection 2.03–27.51°, limiting indices $-1\leqslant h\leqslant 49$, $-12\leqslant k\leqslant 1$, $-26\leqslant l\leqslant 26$. 10 020 reflections collected, with 8573 unique reflections [$R_{int} = 0.0294$]. Direct methods, full-matrix least-squares on F^2 [24], heavy atoms refined anisotropically, hydrogen atoms in calculated positions (riding model), except for the protons of water (located in difference map, refined isotropically). The tetrafluoroborate anion is rotationally disordered about the B(1)–F(2) bond and was treated by introducing split positions. GOF = 1.025, $R_1[I > 2\sigma(I)] = 0.0408$, wR_2 (all data) = 0.0925.

3. Results and discussion

3.1. Synthesis and characterization of the monocationic complexes $2L_1$–$2L_7$

If the *trans*-dichloro(diamine)(ether–phosphine)ruthenium(II) complexes $\mathbf{1L_1}$–$\mathbf{1L_7}$ [9,12] are treated with one equivalent of $AgBF_4$ ($\mathbf{1L_1}$, $\mathbf{1L_3}$, $\mathbf{1L_6}$, $\mathbf{1L_7}$) or AgOTf ($\mathbf{1L_2}$, $\mathbf{1L_4}$, $\mathbf{1L_5}$) in dichloromethane only one chloride is abstracted. The vacant coordination site in each complex is occupied by an ether–oxygen atom resulting in the formation of the cationic complexes $\mathbf{2L_1}$–$\mathbf{2L_7}$ (see Scheme 1).

In contrast to the reaction with $AgBF_4$, which needs several hours, that with AgOTf proceeds within a few seconds. The brown cationic complexes are sensitive to aerial oxygen, dissolve readily in chlorinated organic solvents, and are insoluble in ethers and aliphatic hydrocarbons. Their molecular composition was corroborated by FAB mass spectra.

3.2. NMR and IR spectroscopic investigations complexes $2L_1$–$2L_7$

In the ^{1}H and ^{13}C{^{1}H} NMR spectra of $\mathbf{2L_1}$–$\mathbf{2L_7}$ characteristic sets of ^{1}H and ^{13}C signals are observed which arise from the phosphine and diamine ligands, respectively. The integration of the proton resonances indicates that the phosphine to diamine ratio is in agreement with the expected composition of $\mathbf{2L_1}$–$\mathbf{2L_7}$. The chemical shifts, the number of resonances, and the coupling patterns confirm the formation of only one η^2-P⌒O chelate ring, which is in agreement that one chloride has been abstracted.

In the ^{31}P{^{1}H} NMR spectra, the doublet of doublets which are observed for $\mathbf{2L_1}$–$\mathbf{2L_7}$ with typical coupling constants between 36.2 and 38.7 Hz agree with the *cis* arrangement of the phosphine ligands. The number of the signals due to the methoxy protons in the ^{1}H NMR spectra is consistent with the isomers which are detected by ^{31}P{^{1}H} NMR spectroscopy. Characteristic features in the ^{13}C{^{1}H} NMR spectra are the singlets of the methoxy carbon atoms of the η^2-P⌒O function, which are shifted downfield (2–5 ppm) compared to those of the η^1-P∼O ligands. For those diamine ligands with reduced symmetry, chiral centers are generated in the complexes which lead to diasteroisomers, and thus to additional resonances in the NMR spectra (see Section 2). As in neutral diamine(ether–phosphine)ruthenium(II) complexes, isomers with phosphine ligands located *trans* to the diamines are formed in solution [9].

3.3. X-ray structural determination of complex $2L_1$

Crystals suitable for an X-ray structural analysis have been obtained for $\mathbf{2L_1}\cdot H_2O$. The molecular structure is shown in Fig. 1, and selected bond distances and angles are given in the figure caption.

There are two ether–phosphine ligands in this cationic complex that differ in their hapticity. The ether chain of the η^1-P-coordinated phosphine ligand adopts an all-*trans* conformation, with torsional angles in the range 168.4–175.1°, while the ether chain of the η^2-O,P-coordinated phosphine forms part of a chelate ring in the twist conformation, with C(13) and C(14) displaced by 0.61 and −0.18 Å above and below the P(1)–Ru(1)–O(1) plane. A similar conformation is found for the chelate ring formed by the diamine ligand, with C(31) and C(32) displaced by −0.48 and 0.17 Å from the N(1)–Ru(1)–N(2) plane. The solvent water forms hydrogen bonds with two neighboring tetrafluoroborate anions,

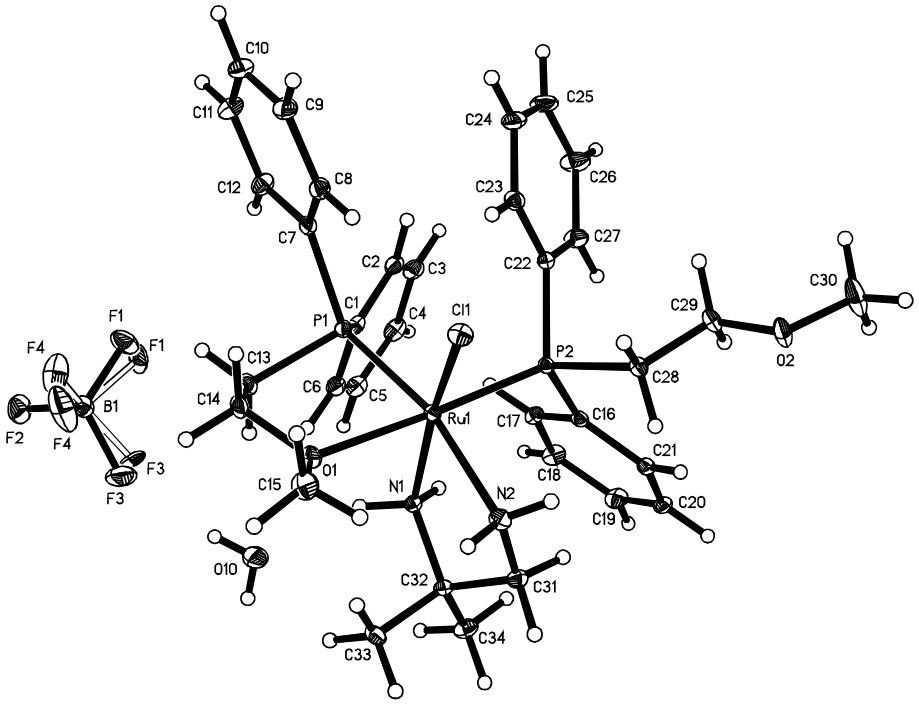


Fig. 1. Molecular structure of $\mathbf{2L_1} \cdot H_2O$. Thermal ellipsoids are drawn at the 20% probability level. Selected distances (in Å) and angles (in °): Ru(1)–N(1), 2.135(2); Ru(1)–N(2), 2.184(3); Ru(1)–P(2), 2.2264(15); Ru(1)–O(1), 2.244(2); Ru(1)–P(1), 2.3040(9); Ru(1)–Cl(1), 2.4159(8); N(1)–Ru(1)–N(2), 79.20(9); P(2)–Ru(1)–P(1), 98.17(3); O(1)–Ru(1)–P(1), 80.98(6).

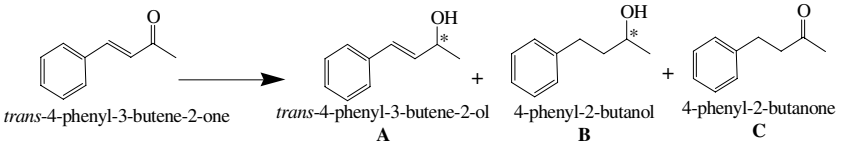
O(19)–H(10A)···F(2) 2.11 Å, O(10)–H(10B)···F(3) 1.94–2.13 Å, resulting in a helical arrangement of alternating water and BF_4^- groups. The cation of $\mathbf{2L_1}$ is "docked" to this helix via weaker hydrogen bonds involving the protons of the amines: N(1)–H(1A)···O(10) 2.34 Å, N(2)–H(2A)···F(1) 2.22 Å.

3.4. Catalytic activity of the cationic ruthenium(II) complexes $2L_1$–$2L_7$ in the selective hydrogenation of trans-4-phenyl-3-butene-2-one

The catalytic activity of several neutral diamine(ether–phosphine)ruthenium(II) complexes in the hydrogenation of unsaturated ketones has already been repeatedly examined [9,14]. To compare the catalytic performance of neutral and the corresponding cationic representatives, the related complexes $\mathbf{1L_1}$–$\mathbf{1L_7}$ and $\mathbf{2L_1}$–$\mathbf{2L_7}$ were tested in the hydrogenation of *trans*-4-phenyl-3-butene-2-one under the same conditions. This unsaturated ketone is a suitable model substrate, because three different reaction products **A**–**C** are to be expected (see Scheme 2). 2-Propanol served as a solvent. The catalysts were only effective in the presence of excess hydrogen and a co-catalyst (KOH, Table 1, runs 1–7 or *t*BuOK runs 8 and 9).

With the exception of $\mathbf{2L_3}$ and $\mathbf{2L_7}$, which are provided with aromatic and aprotic diamine co-ligands, respectively, all monocationic complexes are highly active under mild conditions and except $\mathbf{2L_6}$ they give rise to a 100% selective hydrogenation toward the C=O group in the presence of a C=C function (Table 1). The same is true for the neutral complexes $\mathbf{1L_1}$–$\mathbf{1L_7}$, however, their activity is approximately twice as high as that of their monocationic counterparts (Fig. 2). From the inactivity of the neutral and cationic complexes $\mathbf{1L_3}$, $\mathbf{1L_7}$, and $\mathbf{2L_3}$, $\mathbf{2L_7}$, respectively, it can be concluded that for the cationic complexes the same mechanism as for the neutral counterparts is operative, which requires at least one hydrogen bound to the nitrogen ligands.

The hydrogenation of *trans*-4-phenyl-3-butene-2-one with catalysts $\mathbf{2L_4}$ and $\mathbf{2L_5}$ provided with the (*R*,*R*)- and (*S*,*S*)-diamines $\mathbf{L_4}$ and $\mathbf{L_5}$ afforded the alcohols (*S*)-**A**



Scheme 2.

Table 1
Hydrogenation of *trans*-4-phenyl-3-butene-2-one[a]

Run	Catalyst	Conversion (%)[c]	TOF[b]	Selectivity (%)[c]	Catalyst	Conversion (%)[c]	TOF[b]	Selectivity (%)[c]
1	**1L$_1$**	60	600	100 (**A**)	**2L$_1$**	100	350	100 (**A**)
2	**1L$_2$**	100	1350	100 (**A**)	**2L$_2$**	100	571	100 (**A**)
3	**1L$_3$**[d]	10	9	100 (**C**)	**2L$_3$**[d]	3	2	100 (**C**)
4	**1L$_4$**	100	1030	100 (**A**)	**2L$_4$**	100	480	100 (**A**)
5	**1L$_5$**	100	1280	100 (**A**)	**2L$_5$**	100	610	100 (**A**)
6	**1L$_6$**	93	930	82 (**A**), 18 (**C**)	**2L$_6$**	100	500	73 (**A**), 27 (**C**)
7	**1L$_7$**	0	0	0	**2L$_7$**	0	0	0
8	**1L$_4$**[e]	100	1190	100 (**A**)	**2L$_4$**	100	590	100 (**A**)
9	**1L$_5$**[e]	100	1100	100 (**A**)	**2L$_5$**	100	490	100 (**A**)

[a] Reaction was conducted at 35 C° and 3 bar H_2 in 80 ml of 2-propanol, the ratio of Ru:KOH:substrate was 1:10:1000. The results were collected within 1 and 2 h using catalysts **1L$_1$**–**1L$_7$** and **2L$_1$**–**2L$_7$**, respectively.
[b] TOF, turnover frequency (mol_{sub} mol_{cat}^{-1} h^{-1}).
[c] Yields and selectivities were determined by GC.
[d] Reaction time 15 h.
[e] The reaction was conducted by using 10 equiv. *t*BuOK.

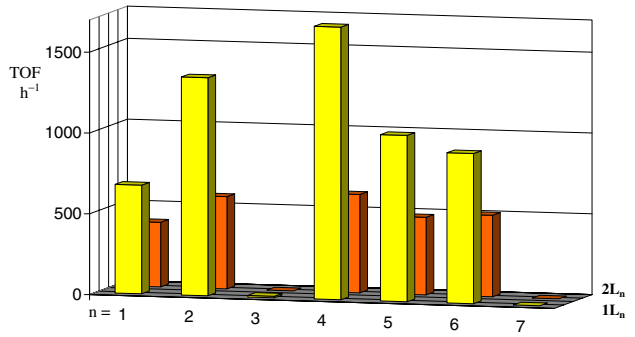


Fig. 2. Hydrogenation of *trans*-4-phenyl-3-butene-2-one by the neutral and monocationic ruthenium(II) complexes **1L**$_n$ and **2L**$_n$, respectively. Reaction conditions: 2-propanol as solvent, KOH as co-catalyst, $T = 35$ °C, pH_2 3 bar.

and (*R*)-**A**, respectively, with ee values of 45% ee $[\alpha]_D^{20} = -6.0^0/+6.0$ (Table 1). A similar result was obtained, when the corresponding neutral complexes **1L$_4$** and **1L$_5$** have been used [12].

4. Conclusion

In this paper, a series of monocationic diamine(ether–phosphine)ruthenium(II) complexes **2L$_1$**–**2L$_7$** were made accessible and structurally characterized. The intention was to compare their catalytic performance with that of their neutral parent compounds **1L$_1$**–**1L$_7$** in the selective hydrogenation of *trans*-4-phenyl-3-butene-2-one. Because of the hemilabile character of the ether–phosphine ligands in **2L$_1$**–**2L$_7$**, a *pseudo*-vacant coordination site is available, which could enhance the formation of a mono- or dihydride intermediate in the mechanism of the hydrogenation of α, β-unsaturated ketones. However, the cationic species showed only half of the catalytic activity compared to their neutral counterparts.

In general when a η^2-H_2 is bound to cationic electrophilic metal centers as in complexes discussed in this manuscript heterolytic cleavage of the hydrogen molecule should be facilitated as well as the transfer of a proton internally to an ancillary ligand. This should lead to an increase of the turnover frequency of the hydrogenation [6,7]. As the opposite is observed the activation of the hydrogen is reduced most likely by a competitive coordination with the hemilabile ligand.

5. Supplementary material

Crystallographic data for the structure have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 209190. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: int. code+(1223)336-033; e-mail: deposit@ccdc.cam.ac.uk).

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References

[1] Z. Lu, K. Eichele, I. Warad, H.A. Mayer, E. Lindner, Z. Jiang, V. Schurig, Z. Anorg. Allg. Chem. 629 (2003) 1308.
[2] T. Ohkuma, H. Ooka, S. Hashiguchi, T. Ikariya, R. Noyori, J. Am. Chem. Soc. 117 (1995) 2675, and references therein.
[3] R. Noyori, M. Yamakawa, S. Hashiguchi, J. Org. Chem. 66 (2001) 7931.

[4] R. Noyori, T. Ohkuma, Angew. Chem., Int. Ed. 40 (2001) 7931, and references therein.
[5] T. Ohkuma, M. Koizumi, K. Muniz, G. Hilt, C. Kabuto, R. Noyori, J. Am. Chem. Soc. 124 (2002) 6508.
[6] K.R. Hartmann, P. Chen, Angew. Chem., Int. Ed. 40 (2001) 3581.
[7] K. Abdur-Rashid, S.E. Clapham, A. Hadzovic, J.N. Harvey, A.J. Lough, R.H. Morris, J. Am. Chem. Soc. 124 (2002) 15104.
[8] K. Minkami, T. Korenaga, Y. Yusa, M. Yamanaka, Adv. Synth. Catal. 2 (2003) 345.
[9] E. Lindner, I. Warad, K. Eichele, H.A. Mayer, Inorg. Chim. Acta 350 (2003) 49.
[10] E. Lindner, M. Schmid, P. Wegner, C. Nachtigal, M. Steimann, R. Fawzi, Inorg. Chim. Acta 296 (1999) 103.
[11] E. Lindner, S. Pautz, R. Fawzi, M. Steimann, Organometallics 17 (1998) 3006.
[12] C. Nachtigal, S. Al-Gharabli, K. Eichele, E. Lindner, H.A. Mayer, Organometallics 21 (2002) 105.
[13] E. Lindner, S. Al-Gharabli, H.A. Mayer, Inorg. Chim. Acta 334 (2002) 113.
[14] A. Bader, E. Lindner, Coord. Chem. Rev. 27 (1991) 108.
[15] E. Lindner, S. Al-Gharabli, I. Warad, H.A. Mayer, S. Steinbrecher, E. Plies, M. Seiler, H. Bertagnolli, Z. Anorg. Allg. Chem. 629 (2003) 161.
[16] E. Lindner, A. Ghanem, I. Warad, K. Eichele, H.A. Mayer, V. Schurig, Tetrahredron: Asymmetry 14 (2003) 1045.
[17] E. Lindner, I. Warad, K. Eichele, H.A. Mayer, unpublished results.
[18] E. Lindner, S. Meyer, P. Wegner, B. Karle, A. Sickinger, B. Steger, J. Organomet. Chem. 335 (1987) 59.
[19] J.G. Handique, A. Purkayashtha, J.B. Baruah, J. Organomet. Chem. 620 (2001) 90.
[20] O. Pämies, J.E. Bäckvall, Chem. Eur. J. 7 (2001) 5052.
[21] M.J. Burk, W. Hems, D. Herzberg, C. Malan, A. Zanotti-Gerosa, Org. Lett. 2 (2000) 4173.
[22] O.M. Akotsi, K. Metera, R.D. Reid, R. McDonald, S.H. Bergens, Chirality 12 (2000) 522.
[23] I. Warad, Ph. D. Thesis, University of Tübingen, Germany, 2003.
[24] SHELXTL NT 5.10, Bruker AXS, Madison, WI, USA, 1998.