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Journal of Organometallic Chemistry 690 (2005) 1–13
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Functional phosphines XV. Ruthenium complexes containing $C_5H_8(PR_2)_2$ and $Ph_2PCH_2CR'_2NH_2$ ligands (R = Me, Ph, OPh; R′ = H, Me): synthesis and application to homogeneous >C=O hydrogenation and transfer hydrogenation ☆

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Received 10 May 2004; accepted 19 July 2004

Abstract

Treatment of $[Ru(\eta^4\text{-}C_8H_{12})\{\eta^3\text{-}(CH_2)_2CMe\}_2]$ with C_2 chiral cyclopentane-1,2-diyl-bis(phosphines) *trans*-1,2-$C_5H_8(PR_2)_2$ in hexane afforded the chelate complexes $[Ru\{\eta^3\text{-}(CH_2)_2CMe\}_2\{1,2\text{-}C_5H_8(PR_2)_2\}]$, where R = Me (**2**), Ph (**3**), NC_5H_{10} (**4**), and OPh (**5**). The mixed-ligand compounds $[RuCl_2\{1,2\text{-}C_5H_8(PR_2)_2\}(Ph_2PCH_2CR'_2NH_2)]$ [R′ = H: R = Me (**6**), Ph (**7**), OPh (**8**); R′ = Me: R = Ph (**9**)] were obtained by reactions of the bis(2-methylallyl) precursors **2**, **3**, and **5** with methanolic HCl in acetone, followed by the addition of the required aminophosphine in DMF. The $(P\cap P)_2$- and $(P\cap N)_2$-chelated complexes $[RuCl_2\{1,2\text{-}C_5H_8(PMe_2)_2\}_2]$ (**1**) and $[RuCl_2(Ph_2PCH_2CMe_2NH_2)_2]$ (**10**) resulted from $RuCl_3 \cdot 3H_2O$ and 1,2-$C_5H_8(PMe_2)_2$ or $Ph_2PCH_2CMe_2NH_2$ under reducing conditions. The crystal structures of **1**, **3**, **4**, **6**, **7**, **9**, and **10** were determined by single-crystal X-ray diffraction. Complexes **7**, **9**, and **10**, activated by KOBu-*t*, *i*-PrOH, were used as catalysts for the transfer hydrogenation of acetophenone with *i*-PrOH as the hydrogen source. Base modified complex **10** also turned out to be an active catalyst for the direct hydrogenation of the ketone by H_2 under pressure.

Keywords: Ruthenium; Bis(phosphines); *P,N* ligands; X-ray structure analysis; Hydrogenation

1. Introduction

$(P,N)_2$-coordinated transition metal complexes, in particular Noyori's outstanding ruthenium(II) compounds $[RuX_2\{bis(phosphine)\}(1,2\text{-diamine})]$, have been dominating the field of homogeneous >C=O hydrogenation for several years. In the presence of an excess of strong base, especially potassium alkoxide in isopropanol, these complexes catalyze the reduction of ketones by molecular hydrogen with consistently high enantioselectivities, if appropriate chiral bis(phosphines) and diamines are used as steering ligands [2]. Ru^{II}-catalyzed hydrogenations of ketones are also exceptional with regard to their generally high chemoselectivity for >C=O over >C=C< reduction as well as the very large substrate-to-catalyst ratios (up to 2×10^6) that can be reached. It has been pointed out that this extraordinary activity alone can attract industrial attention, because the catalytic hydrogenation of ketones by the inexpensive, easy to handle, and ideally atom-economic reductant H_2 to afford achiral or racemic alcohols at low

☆ Part XIV: [1a]; simultaneously Part XVII of "Chiral Bis(phosphines)" (Parts XVI and XV: [1b,1c]).

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0022-328X/$ - see front matter © 2004 Published by Elsevier B.V.
doi:10.1016/j.jorganchem.2004.07.062

catalyst loadings could substitute the traditional stoichiometric >C=O reduction by means of conventional hydride transfer reagents such as $NaBH_4$ or $LiAlH_4$ [3]. These are more expensive, more difficult to handle, and produce undesired inorganic hydroxides as compulsory by-products.

In continuation of our work on >C=C< and >C=O hydrogenation catalysts based on Rh^I, Ir^I, and Ir^{III} complexes containing the structurally versatile chiral cyclopentane-1,2-diyl-bis(phosphine) or β-aminophosphine bidentates previously prepared in our group [1], we here describe the synthesis of some *P*,*N*-coordinated Ru^{II} compounds derived from such chelate ligands and give a first account of their properties as catalysts for the reduction of the standard test substrate acetophenone. In two different ways do these complexes contrast with the advanced Noyori systems, where the central metal is always coordinated to the two phosphorus and nitrogen atoms of one bis(phosphine) and one diamine ligand: either their coordination spheres are made up of one chelating bis(phosphine) and one aminophosphine to form *P*∩*P*/*P*∩*N* derivatives as examplified by $[RuCl_2\{1,2\text{-}C_5H_8(PR_2)_2\}(Ph_2PCH_2CR'_2NH_2)]$ (R = Me, Ph, OPh; R′ = H, Me), or their structural motif features the pairwise *P*∩*N* coordination of two aminophosphine ligands such as, e.g., in $[RuCl_2(Ph_2P\text{-}CH_2CMe_2NH_2)_2]$. The proven *P*-modular character of the *trans*-1,2-$C_5H_8(PR_2)_2$ ligands, where the P–C- or P–O-bonded structural components can be interchanged systematically and easily [1c], adds more structural flexibility to the design of Ru^{II} (pre)catalysts than hitherto reported [4]. The benefit of such complexes with great diversity in the structures of their ligands and coordination spheres is that they facilitate the rational tuning of the catalysts by providing insight into the relations which exist between the catalytic performance and the stereoelectronic properties of the active metal–ligand template.

One further aspect of the present investigations was to probe such complexes in cross experiments as (pre)catalysts for *both* direct >C=O hydrogenation with molecular H_2 as reducing agent [2] *and* transfer hydrogenation with isopropanol as the source of H^+ and H^- equivalents [5]. As summarized in a current in-depth paper dealing with this specific topic [3], just a very few comparative studies have been carried out until recently on the catalytic application of one and the same type of complexes in direct as well as transfer hydrogenation. Throughout the exploratory studies described hereafter, racemic 1,2-$C_5H_8(PR_2)_2$ and achiral $Ph_2PCH_2CR'_2NH_2$ chelating ligands rather than optically active 1,2-$C_5H_8(PR_2)_2$ bis(phosphines) [1c] and $R_2PCH(Ph)CH(Me)NHR$ aminophosphines [1d] were employed for the sake of experimental simplicity.

2. Experimental

2.1. General remarks

All manipulations were performed under nitrogen using standard Schlenk techniques. Solvents were distilled from the appropriate drying agents prior to use. IR: Mattson Polaris. NMR: Bruker DPX 300 (300.1 MHz for ^1H, 75.5 MHz for ^{13}C, and 121.5 MHz for ^{31}P) at 20 ± 2 °C with $SiMe_4$ (or the solvent) as internal or H_3PO_4 as external standards (downfield positive; "m": deceptively simple multiplets [6]).Mass spectra: Jeol MS 700. Published procedures were used for the synthesis of the starting materials 1,2-$C_5H_8(PCl_2)_2$ [7], 1,2-C_5H_8 $(PR_2)_2$ (R = Me, Ph [7], NC_5H_{10}, OPh [8]), Ph_2PCH_2- CMe_2NH_2 [1d], $[RuCl_2(PPh_3)_3]$ [9], $[Ru(H)(Cl)(PPh_3)_3]$ [10], $[Ru(\eta^4\text{-}C_8H_{12})Cl_2]_n$ [11,12a], and $[Ru(\eta^4\text{-}C_8H_{12})$ $\{\eta^3\text{-}(CH_2)_2CMe\}_2]$ [12a]. $RuCl_3 \cdot 3H_2O$ (Pressure Chemical Co.), KOBu-*t* (Aldrich), and $Ph_2PCH_2CH_2NH_2$ (Fluka) were obtained commercially.

2.2. Metal complexes

2.2.1. *[RuCl₂{1,2-C₅H₈(PMe₂)₂}₂] (**1**)*

Stirring an ethanol solution (~20 mL) of 151 mg (0.72 mmol) of $RuCl_3 \cdot 3H_2O$ and 289 mg (1.52 mmol) of 1,2-$C_5H_8(PMe_2)_2$ at reflux temperature for 5 h resulted in the deposition of a beige precipitate which was filtered off, washed with ethanol (3 × 3 mL) und dried under vacuum. Recrystallization from CH_2Cl_2/Et_2O at −20 °C gave the product as orange crystals composed of equimolar quantities of the {(*R*,*R*,*R*,*R*)/(*S*,*S*,*S*,*S*)} and (*R*,*R*,*S*,*S*) diastereomers; yield 340 mg (85%). Anal. Found: C, 39.17; H, 7.01. Calc. for $C_{18}H_{40}Cl_2P_4Ru$ (552.35): C, 39.14; H, 7.30%. ^1H NMR ($CDCl_3$): δ = 1.23, 1.34 (both $X_3AA'X'_3$ – s, 12 H each, both PCH_3), 1.48–1.53, 1.67–1.75, 2.10–2.21 (all m, 4H each, all CH_2), 2.32–2.34 (m, 4H, CH). $^{13}C\{^1H\}$NMR ($CDCl_3$): δ = 5.16, 5.88 (both $AA'X$-"qui", $\sum J(P,C)$ = 23.26 Hz each, both PCH_3), 9.60, 9.71 (both $AA'X$-"qui", $\sum J(P,C)$ = 25.45 Hz each, both PCH_3), 21.06, 21.11 (both s, both C^4H_2), 29.78, 30.12 (both $AA'X$-"t", $\sum J(P,C)$ = 6.54 Hz each, both $C^{3,5}H_2$), 47.97 ($AA'X$-"qui", $J(P,C)$ = 27.61 Hz, $C^{1,2}H$). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 9.78, 10.43 (both s of equal intensity; stereoisomers not assigned).

2.2.2. *[Ru{η³-(CH₂)₂CMe}₂{1,2-C₅H₈(PMe₂)₂}] (**2**)*

A solution-suspension of 192 mg (0.60 mmol) of $[Ru(\eta^4\text{-}C_8H_{12})\{\eta^3\text{-}(CH_2)_2CMe\}_2]$ and 155 mg (0.60 mmol) of 1,2-$C_5H_8(PMe_2)_2$ in 10 mL of hexane was heated at reflux temperature for 5 h. The slightly cloudy mixture was filtered and the filtrate was evaporated to dryness. The residue was triturated with 3 mL of

acetone, filtered off, washed with acetone (3 × 1 mL) and dried in vacuo. Recrystallization from hexane at −20 °C afforded the complex as a diastereomeric mixture of the (Λ-*R*,*R*)/(Δ-*S*,*S*) and (Δ-*R*,*R*)/(Λ-*S*,*S*) pairs of enantiomers; yield 159 mg (65%) of pale yellow needles pertinaciously retaining variable amounts of solvent of crystallization. Anal. Found: C, 51.44; H, 10.15. Calc. for $C_{17}H_{36}P_2Ru$ (402.12): C, 50.60; H, 8.99%. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 32.31, 36.22 (both s; relative intensities 1:2; diastereomers not assigned).

The following complexes **3**–**5** were obtained analogously.

2.2.3. [Ru{η³-(CH₂)₂CMe}₂{1,2-C₅H₈(PPh₂)₂}] (3)

From 275 mg (0.86 mmol) of [Ru(η⁴-C_8H_{12}){η³-$(CH_2)_2$CMe}$_2$] and 386 mg (0.88 mmol) of 1,2-$C_5H_8(PPh_2)_2$: 432 mg (77%) of (Δ-*R*,*R*)/(Λ-*S*,*S*)-**3** (X-ray structure analysis) as a greenish yellow powder which contained only marginal amounts of the (Λ-*R*,*R*)/(Δ-*S*,*S*) pair of enantiomers as judged from $^{31}P\{^1H\}$ NMR. Anal. Found: C, 67.79; H, 6.98. Calc. for $C_{37}H_{42}P_2Ru$ (649.72): C, 68.40; H, 6.52%. ^1H NMR ($CDCl_3$): δ = 0.43, 0.48, 1.16, 1.67 (all br, 2H each, all allyl CH_2), 1.73–1.97 (m, 2H, ring CH_2), 1.92 (s, 6H, allyl CH_3), 2.01–2.16, 2.24–2.40 (both m, 2H each, both ring CH_2), 3.45–3.58 (m, 2H, ring CH), 6.68, 7.06, 7.36, 7.82 (all m, 4/6/6/4 H, all C_6H_5). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 24.51 (AA′*X*-"t", $\sum J$(P,C) = 10.90 Hz, $C^{3,5}H_2$), 24.82 (br s, CH_3), 30.59 (t, J(P,C) = 5.45 Hz, C^4H_2), 40.11 (AA′*X*-"t", $\sum J$(P,C) = 18.17 Hz, $C^{1,2}H$), 42.14 (AA′*X*-"t", $\sum J$(P,C) = 9.06 Hz, allyl CH_2 *trans* P), 56.99 (t, J(P,C) = 23.98 Hz, allyl CH_2 *cis* P), 93.99 (s, allyl *C*Me), 126.37, 126.78 131.75, 133.24 (all m, C_6H_5). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 62.65 (s, (Λ-*R*,*R*)/(Δ-*S*,*S*) form; ∼2%), 63.42 (s, (Δ-*R*,*R*)/(Λ-*S*,*S*) form; ∼98%).

2.2.4. [Ru{η³-(CH₂)₂CMe}₂{1,2-C₅H₈[P(NC₅H₁₀)₂]₂}] (4)

From 440 mg (1.37 mmol) of [Ru(η⁴-C_8H_{12}){η³-$(CH_2)_2$CMe}$_2$] and 639 mg (1.38 mmol) of 1,2-$C_5H_8[P(NC_5H_{10})_2]_2$: 402 mg (46%) of grey (Δ-*R*,*R*)/(Λ-*S*,*S*)-**4** (X-ray structure analysis) contaminated by less than 2% of the (Λ-*R*,*R*)/(Δ-*S*,*S*) pair of enantiomers (NMR evidence). Anal. Found: C, 57.70; H, 9.84; N, 7.72. Calc. for $C_{33}H_{62}N_4P_2Ru$ (677.88): C, 58.47; H, 9.22; N, 8.26%. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 23.96 (t, J(P,C) = 5.09 Hz, C^4H_2), 24.74, 25.35, 25.84, 26.56 (all s, allyl CH_3 and piperidino $C^{3\text{-}5}H_2$), 30.39 (AA′*X*-"t", $\sum J$(P,C) = 11.32 Hz, C_5H_8 $C^{3,5}H_2$), 31.51 (br, allyl CH_2 *trans* P), 35.44 (AA′*X*-"t", $\sum J$(P,C) = 10.94 Hz, C_5H_8 $C^{1,2}H$), 48.72 (s, piperidino $C^{2,6}H_2$), 62.26 (t, J(P,C) = 24.34 Hz, allyl CH_2 *cis*-P), 94.68 (s, allyl *C*Me). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 162.91 (s, (Δ-*R*,*R*)/(Λ-*S*,*S*) form; ⩾98%), 164.40 (s, (Λ-*R*,*R*)/(Δ-*S*,*S*) form; ⩽2%).

2.2.5. [Ru{η³-(CH₂)₂CMe}₂{1,2-C₅H₈[P(OPh)₂]₂}] (5)

From 326 mg (1.02 mmol) of [Ru(η⁴-C_8H_{12}){η³-$(CH_2)_2$CMe}$_2$] and 521 mg (1.04 mmol) of 1,2-$C_5H_8[P(OPh)_2]_2$: 472 mg (64%) of isomerically pure **5**. Anal. Found: C, 62.34; H, 5.87. Calc. for $C_{37}H_{42}O_4P_2Ru$ (713.76): C, 62.26; H, 5.93%. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 20.7 (t, J(P,C) = 6.51 Hz, C^4H_2), 25.24 (s, allyl CH_3), 29.14 (br, allyl CH_2 *trans* P), 33.74 (s, $C^{3,5}H_2$), 44.97 (m, $C^{1,2}H$), 56.80 (t, J(P,C) = 28.70 Hz, allyl CH_2 *trans* P), 100.89 (s, allyl *C*Me), 118.72, 118.82, 120.51, 121.72, 128.34, 153.66 (all m, OC_6H_5). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 184.13 (s).

2.2.6. [RuCl₂{1,2-C₅H₈(PMe₂)₂}(Ph₂PCH₂CH₂NH₂)] (6)

A solution of 134 mg (0.33 mmol) of allyl complex **2** in 5 mL of acetone was stirred with 0.38 mL of 2 M aqueous HCl, dissolved in 5 mL of methanol, for 2 h at room temperature. The greenish yellow residue remaining after removal of all volatile material in vacuo was re-dissolved in 2 mL of DMF and treated with 5 mL of a solution of 78 mg (0.34 mmol) of the *P*,*N* ligand in the same solvent. Stirring for 2 h at ambient conditions followed by evaporation to dryness left a yellow semi-solid which was dissolved in 4 mL of acetone. Dilution of the filtered mixture with 10 mL of pentane resulted in the precipitation of the product as a yellow solid which was re-crystallized at −20 °C from a toluene/pentane solvent mixture; yield 74 mg (38%) of orange crystals containing variable amounts of toluene of crystallization. Anal. Found: C, 49.70; H, 6.17; N, 2.08. Calc. for $C_{23}H_{36}Cl_2NP_3Ru$ (591.44): C, 46.71; H, 6.14; N, 2.37; for $C_{30}H_{44}Cl_2NP_3R$, C_7H_8 (683.54): C, 52.71; H, 6.49; N, 2.05%. ^1H NMR ($CDCl_3$): δ = 0.85, 1.13 (both d, J(P,H) = 8.79 Hz each, 3H each, both PCH_3 *trans* N), 1.29, 1.40 (both dd, J(P,H) = 8.79/2.19 Hz each, 3H each, both PCH_3 *trans* P), 1.35–1.54, 1.55–1.79 (both m, 2H each, both C_5H_8 CH_2), 2.04–2.35 (m, 4H, C_5H_8 CH_2 and CH), 2.41–2.63 (m, 2H, CH_2P), 2.85–3.24 (m, 3H, NCH_2 and NH), 3.29 (br, 1H, NH), 7.03–7.80 (m, 10H, C_6H_5). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 4.16, 7.14, 7.26, 12.61 (all d, J(P,C) = 21.80, 26.16, 24.70, 28.34 Hz, all PCH_3), 20.66, 21.31 (both dd, J(P,C) = 16.00/6.49, 17.44/6.57 Hz, both 1 $C_5H_8C^{3,5}$), 28.92 (AB*X*-"t", $\sum J$(P,C) = 13.09 Hz, C_5H_8 C^4H_2), 40.39 (AB*X*-dd $\sum J$(P,C) = 17.37 Hz, PCH_2), 45.89 (d, J(P,C) = 16.61 Hz, NCH_2), 49.62, 50.02 (both AB*X*-"dd", $\sum J$(P,C) = 24.69, 25.14 Hz, both 1 C_5H_8 $C^{1,2}H$), 125.73–134.57 (C_6H_5). $^{31}P\{^1H\}$ NMR ($CDCl_3$): ABX system with $\delta(P_A)$ = 11.50 (PMe_2 *trans* PPh_2), $\delta(P_B)$ = 42.67 (PPh_2), $\delta(P_X)$ = 30.65 (PMe_2 *trans* NH_2), $J(P_A,P_B)$ = 325.92, $J(P_A,P_X)$ = 31.44, and $J(P_B,P_X)$ = 29.59 Hz.

Analogous procedures were used for the preparation of compounds **7**–**9**.

*2.2.7. [$RuCl_2\{1,2\text{-}C_5H_8(PPh_2)_2\}(Ph_2PCH_2CH_2NH_2)$] (**7**)*

From 196 mg (0.39 mmol) of **3** and 70 mg (0.31 mmol) of $Ph_2PCH_2CH_2NH_2$: 151 mg (52%) of **7** as orange-yellow crystals. Anal. Found: C, 60.37; H, 5.71; N, 1.36. Calc. for $C_{43}H_{44}Cl_2NP_3Ru$ (839.67): C, 61.50; H, 5.71; N, 1.67%. ^1H NMR ($CDCl_3$): δ = 1.58–2.16, 2.26–2.64, 2.67–3.18 (all m, 6/3/3 H, CH_2 and CH), 3.54, 4.00 (both br, 1 H each, both 1NH), 6.67–7.68 (m, 30 H, C_6H_5). $^{31}P\{^1H\}$ NMR ($CDCl_3$): ABX system with $\delta(P_A)$ = 35.31, $\delta(P_B)$ = 38.64 (both PPh_2 in mutual *trans* position), $\delta(P_X)$ = 46.29 (PPh_2 *trans* NH_2), $J(P_A,P_B)$ = 315.72, $J(P_A,P_X)$ = 29.59, $J(P_B,P_X)$ = 31.44 Hz.

*2.2.8. [$RuCl_2\{1,2\text{-}C_5H_8[P(OPh)_2]_2\}(Ph_2PCH_2CH_2NH_2)$] (**8**)*

From 362 mg (0.50 mmol) of **5** and 121 mg (0.52 mmol) of $Ph_2PCH_2CH_2NH_2$ after recrystallization of the crude product from CH_2Cl_2/pentane (2:3): 151 mg (52%) of a an ochre solid containing the *mer*,*trans* and *fac*,*cis* isomers of **8** in an approximate 3:2 molar ratio. Anal. Found: C, 57.44; H, 5.67; N, 1.97. Calc. for $C_{43}H_{44}Cl_2NO_4P_3Ru$ (903.09): C, 57.44; H, 4.91; N, 1.55%. $^{31}P\{^1H\}$ NMR ($CDCl_3$); *mer*,*trans*-**8**: ABX system with $\delta(P_A)$ = 35.06 (PPh_2), δ (P_B) = 162.38 ($P(OPh)_2$ *trans* PPh_2), $\delta(P_X)$ = 176.81 ($P(OPh)_2$ *trans* NH_2), $J(P_A,P_B)$ = 439.31, $J(P_A,P_X)$ = 39.77, $J(P_B,P_X)$ = 41.61 Hz. *fac*,*cis*-**8**: ABX system with $\delta(P_A)$ = 174.39, $\delta(P_B)$ = 206.12 (both $P(OPh)_2$), $\delta(P_X)$ = 31.25 (PPh_2), $J(P_A,P_B)$ = 44.81, $J(P_A,P_X)$ = 23.06, $J(P_B,P_X)$ = 18.44 Hz.

*2.2.9. [$RuCl_2\{1,2\text{-}C_5H_8(PPh_2)_2\}(Ph_2PCH_2CMe_2NH_2)$] (**9**)*

From 481 mg (0.74 mmol) of **3** and 190 mg (0.74 mmol) of $Ph_2PCH_2CMe_2NH_2$ at 70 °C: 304 mg (48%) of **9** as a beige solid which was repeatedly reprecipitated from a CH_2Cl_2/hexane and CH_2Cl_2/Et_2O solvent mixtures. The product pertinaciously retained variable amounts of diethyl ether of crystallization. Anal. Found: C, 63.00; H, 7.39; N, 1.33. Calc. for $C_{45}H_{48}Cl_2NP_3Ru$ (867.78): C, 62.28; H, 5.58; N, 1.61; for $C_{45}H_{48}Cl_2NP_3Ru$, $0.50(C_4H_{10}O)$ (904.78); i.e., single crystals grown from Et_2O/toluene/hexane: C, 63.39; H 5.90; N, 1.55; for $C_{45}H_{48}Cl_2NP_3Ru$, $2(C_4H_{10}O)$ (1016.03): C, 62.65; H, 6.75; N, 1.38%. ^1H NMR ($CDCl_3$): δ = 0.72, 1.43 (both 2, 3H each, both CH_3), 1.87–2.20, 2.43–2.46, 2.62–2.86, 2.91–2.94, 3.15–3.22 (all m, 4/1/1/3/1H, CH_2 and CH), 3.92, 4.20 (both br, 1H each, both 1NH), 6.86–7.33 (m, 30H, C_6H_5). $^{31}P\{^1H\}$ NMR ($CDCl_3$): ABX system with $\delta(P_A)$ = 32.50, $\delta(P_B)$ = 37.10 (both PPh_2 in mutual *trans* position), $\delta(P_X)$ = 44.93 (PPh_2 *trans* NH_2), $J(P_A,P_B)$ = 314.73, $J(P_A,P_X)$ = 29.60, $J(P_B,P_X)$ = 31.44 Hz.

*2.2.10. [$RuCl_2(Ph_2PCH_2CMe_2NH_2)_2$] (**10**)*

A mixture of 150 mg (0.72 mmol) of $RuCl_3 \cdot 3H_2O$, 150 mg of zinc dust (~3 equiv.), and 373 mg (1.45 mmol) of the *P*,*N* ligand in 20 mL of THF was heated at reflux temperature for 3 h. The residue obtained after filtration over Al_2O_3, elution with 40 mL of THF, and evaporation of all volatile material was triturated with methanol/diethyl ether (1:1), filtered off, and thoroughly washed with diethyl ether and methanol; yield 182 mg (36%) of an orange powder which retained some MeOH solvent even after prolonged drying under vacuum. Anal. Found: C, 55.87; H, 6.31; N, 3.61. Calc. $C_{32}H_{40}Cl_2N_2P_2Ru$ (686.57): C, 55.98; H, 5.87; N, 4.08; for $C_{32}H_{40}Cl_2N_2P_2Ru$, C_3H_4O (742.673): C, 56.60; H, 5.97; N, 3.77%. ^1H NMR ($CDCl_3$): δ = 1.25 (s, 12 H, CH_3), 2.83 (br, 4H, CH_2), 3.76 (br, 4H, NH_2), 6.85–7.30 (m, 20 H, C_6H_5); (CH_3OH) = 3.38 (d, J(*H*, *H*) = 6.00 Hz). ^{13}C $\{^1H\}$ NMR ($CDCl_3$): δ = 34.00 (s, CH_3), 46.47 (AA′*X*-"t", $\sum J(P,C)$ = 25.40 Hz, CH_2), 59.69 (s, CMe_2), 129.67 (s, phenyl C^4), 131.20 (s, phenyl $C^{3,5}$), 135.75 (s, phenyl $C^{2,6}$), 139.68 (AA′*X*-"t", $\sum J(P,C)$ = 39.24 Hz, phenyl C^1). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 56.54 (s).

2.3. Catalytic hydrogenation of acetophenone

2.3.1. General procedures

Solutions of the precatalysts **7**, **9**, or **10** (typically 2–5×10^{-3} M) were prepared in benzene/isopropanol (1:1; used both for transfer and direct hydrogenation), neat isopropanol, or benzene (solvents employed in direct hydrogenation experiments). KOBu-*t* was dissolved in *i*-PrOH to make up a 0.02 M solution. Aliquots of these solutions were then mixed to generate catalyst-to-base ratios of 1:5 (transfer and direct hydrogenation) or 1:100 (direct hydrogenation only). After stirring the mixtures for 30 min at 50 °C under nitrogen, acetophenone was added in quantities corresponding to substrate-to-catalyst ratios of 200:1 for transfer hydrogenation experiments and 2000:1 or 10000:1 for catalytic runs carried out under the conditions of direct >C=O hydrogenation. The final volumes of the reaction mixtures amounted to ~10–15 mL.

In transfer hydrogenations, stirring under an inert atmosphere was continued at 50 °C. For monitoring the progress of the reactions, small aliquots were removed at intervals, evaporated to dryness, re-dissolved in diethyl ether, and filtered over a short silica gel column. Volatile material was distilled off and the mixtures of products were analyzed by ^1H NMR. Conversions and product compositions were determined on the basis of the integrations of the PhC(O)CH_3 and PhCH(OH)CH_3 signals.

For direct hydrogenation of the substrate by H_2, the initial catalyst/substrate mixtures were transferred in small Schlenk tubes equipped with a magnetic stirring

bar to an autoclave. The autoclave was pressurized and vented several times with H_2 (Messer-Griesheim; 99.999%), and finally pressurized to 20 bar and kept at 60 °C for 3 h. Work-up and determination of conversions and product compositions were done as outlined above for the mixtures of products resulting from transfer hydrogenation.

2.3.2. Results of transfer hydrogenation experiments

Ph(Me)CO/**10**/KOBu-*t* = 200:1:5 in C_6H_6/*i*-PrOH (1:1) at 60 °C for: 0.5 h, ~2%; 1 h, 24%; 2 h, 68%; 3 h, 95% of PhCH(Me)OH (Fig. 8).

Ph(Me)CO/**7**/KOBu-*t* = 200:1:5 in C_6H_6/*i*-PrOH (1:1) at 50 °C for: 1 h, 84%; 3 h, 97%; 4 h, 98% of PhCH(Me)OH (Fig. 9: -■-).

Ph(Me)CO/**9**/KOBu-*t* = 200:1:5 in C_6H_6/*i*-PrOH (1:1) at 50 °C for: 1 h, 29%; 1.5 h, 37%; 2 h, 42%; 2.5 h, 50%; 3 h, 53%; 3.5 h, 56%; 4 h, 58%; 4.5 h, 61%; 5 h, 65% of PhCH(Me)OH (Fig. 9: −□−).

Ph(Me)CO/**7**/KOBu-*t* = 2000:1:5 in C_6H_6/*i*-PrOH (1:1) at 50 °C for: 1 h, 19%; 3 h, 50%; 5 h, 65%; 24 h, 85%; 30 h, 86% of PhCH(Me)OH (Fig. 10).

2.3.3. Results of direct ≻C═O hydrogenations

Ph(Me)CO/**10**/KOBu-*t* = 2000:1:5 in C_6H_6: 19% of PhCH(Me)OH.

Ph(Me)CO/**10**/KOBu-*t* = 2000:1:5 in C_6H_6/Me_2C-DOH: 70% of PhCH(Me)OH (no deuterated product detected).

Ph(Me)CO/**10**/KOBu-*t* = 2000:1:5 in *i*-PrOH: 47% of PhCH(Me)OH.

Ph(Me)CO/**10**/KOBu-*t* = 2000:1:100 in *i*-PrOH: PhCH(Me)OH formed in quantitative yield.

Ph(Me)CO/**10**/KOBu-*t* = 10000:1:100 in *i*-PrOH: 30% of PhCH(Me)OH.

2.4. X-ray structure determinations

Single crystals of **1** (0.40 × 0.30 × 0.28 mm), **3** (0.49 × 0.40 × 0.25 mm), **4** (0.50 × 0.13 × 0.13 mm), **6** · C_7H_8 (0.80 × 0.18 × 0.13 mm), **7** (0.30 × 0.10 × 0.03 mm), **9**·1/2Et_2O (0.35 × 0.23 × 0.08 mm), and **10** (0.38 × 0.30 × 0.25 mm) were obtained from the following solvents and solvent mixtures: $CDCl_3$ (**10**), toluene/pentane (**3**, **6** · C_7H_8), toluene/acetone (**4**), CH_2Cl_2/Et_2O (**7**), $CHCl_3$/Et_2O (**1**), and Et_2O/toluene/hexane (**9** · 1/2Et_2O). Diffraction measurements were made at ambient temperature or at −90 ± 2 °C (**6** · C_7H_8, **9** · 1/2Et_2O) on an Enraf-Nonius CAD-4 MACH 3 diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å): orientation matrices and unit cell parameters from the setting angles of 25 centered medium-angle reflections; collection of the diffraction intensities by ω scans; data either uncorrected for absorption (**3**, **4**) or corrected for absorption using appropriate semi-empirical [13a] (**1**: T_{min} = 0.777, T_{max} = 0.796; **10**: T_{min} = 0.734, T_{max} = 0.809), interpolation [13b] (**6**: T_{min} = 0.844, T_{max} = 0.845), or refined [13c] (**7**: T_{min} = 0.723, T_{max} = 0.751; **9** · 1/2Et_2O: T_{min} = 0.804, T_{max} = 0.899) methods. The structures were solved by direct methods and subsequently refined by full-matrix least-squares procedures on F^2 with allowance for anisotropic thermal motion of all non-hydrogen atoms employing the WINGX package [14a] with the relevant programs (SIR-97 [15], SHELXL-97 [16], ORTEP-3 [14b]) implemented therein. Carbon atom C12 of the envelope-shaped cyclopentane backbone of molecule **4** showed the very common flap-like disorder between two positions with half occupancies of the two sites. **1**: $C_{18}H_{40}Cl_2P_4Ru$ (552.35); monoclinic, $P2_1/n$, a = 8.0109(8), b = 16.903(3), c = 9.154(2) Å, β = 96.23(1)°, V = 1232.2(4) Å^3, Z = 2, d_{calc} = 1.513 g cm^{-3}, μ(Mo Kα) = 1.115 mm^{-1}; 2.41° ⩽ Θ ⩽ 23.16°, 1896 reflections collected ($0 \leqslant h \leqslant +8$, $0 \leqslant k \leqslant +18$, $-10 \leqslant l \leqslant +10$), 1756 unique ($R_{int}$ = 0.0289); wR = 0.1100 for all data and 115 parameters, R = 0.0409 for 1529 structure factors $F_o > 4\sigma(F_o)$. **3**: $C_{37}H_{42}P_2Ru$ (649.72); monoclinic, $C2/c$, a = 17.468(5), b = 13.781(4), c = 13.316(2) Å, β = 92.92(3)°, V = 3201(1) Å^3, Z = 4, d_{calc} = 1.348 g cm^{-3}, μ(Mo Kα) = 0.614 mm^{-1}; 2.33° ⩽ Θ ⩽ 30.07°, 4830 reflections collected ($0 \leqslant h \leqslant +24$, $0 \leqslant k \leqslant +19$, $-18 \leqslant l \leqslant +18$), 4692 unique ($R_{int}$ = 0.0109); wR = 0.1066 for all data and 189 parameters, R = 0.0402 for 3769 structure factors $F_o > 4\sigma(F_o)$. **4**: $C_{33}H_{62}N_4P_2Ru$ (677.88); triclinic, $P\bar{1}$, a = 10.320(3) Å, b = 10.6229(8) Å, c = 16.2594(9) Å, α = 97.175(5)°, β = 94.691(11)°, γ = 101.775(13)°, V = 1720.7(5) Å^3, Z = 2, d_{calc} = 1.308 g cm^{-3}, μ(Mo Kα) = 0.576 mm^{-1}; 2.19° ⩽ Θ ⩽ 28.27°, 8823 reflections collected ($-13 \leqslant h \leqslant +13$, $-14 \leqslant k \leqslant +14$, $0 \leqslant l \leqslant +21$), 8530 unique ($R_{int}$ = 0.0159); wR = 0.0759 for all data and 384 parameters, R = 0.0304 for 7276 structure factors $F_o > 4\sigma(F_o)$. **6** · C_7H_8: $C_{23}H_{36}Cl_2NP_3Ru$, C_7H_8 (683.54); triclinic, $P\bar{1}$, a = 10.594(7) Å, b = 11.336(4) Å, c = 15.718(6) Å, α = 97.09(5)°, β = 104.18(6)°, γ = 114.71(6)°, V = 1607(1) Å^3, Z = 2, d_{calc} = 1.413 g cm^{-3}, μ(Mo Kα) = 0.824 mm^{-1}; 2.16° ⩽ Θ ⩽ 28.17°, 8303 reflections collected ($-14 \leqslant h \leqslant 0$, $-13 \leqslant k \leqslant +15$, $-20 \leqslant l \leqslant +20$), 7884 unique ($R_{int}$ = 0.0344); wR = 0.1841 for all data, 324 parameters, and 4 restraints (C atoms of the toluene molecule of crystallization kept in a common plane), R = 0.0641 for 6426 structure factors $F_o > 4\sigma(F_o)$. **7**: $C_{43}H_{44}Cl_2NP_3Ru$ (839.67); triclinic, $P\bar{1}$, a = 10.226(2) Å, b = 11.743(3) Å, c = 18.637(7) Å, α = 76.81(3)°, β = 80.03(2)°, γ = 66.09(2)°, V = 1984(1) Å^3, Z = 2, d_{calc} = 1.406 g cm^{-3}, μ(Mo Kα) = 0.682 mm^{-1}; 2.19° ⩽ Θ ⩽ 24.07°, 6504 reflections collected ($-11 \leqslant h \leqslant +11$, $-13 \leqslant k \leqslant +13$, $0 \leqslant l \leqslant +21$), 6285 unique ($R_{int}$ = 0.0949); wR = 0.2067 for all data and 451 parameters, R = 0.0950 for 2757 structure factors $F_o > 4\sigma(F_o)$. **9** · 1/2Et_2O: $C_{45}H_{48}Cl_2NP_3Ru$, 0.50 ($C_4H_{10}O$) (904.78); triclinic, $P\bar{1}$, a = 12.005(2) Å, b = 13.644(1) Å,

$c = 15.100(3)$ Å, $\alpha = 78.20(1)°$, $\beta = 83.47(1)°$, $\gamma = 65.635(8)°$, $V = 2204.2(6)$ Å^3, $Z = 2$, $d_{calc} = 1.363$ g cm^{-3}, μ(Mo Kα) = 0.620 mm^{-1}; $1.94° \leqslant \Theta \leqslant 30.06°$, 13 508 reflections collected ($0 \leqslant h \leqslant +16$, $-17 \leqslant k \leqslant +19$, $-21 \leqslant l \leqslant +21$), 12 938 unique ($R_{int} = 0.0365$); $wR = 0.1641$ for all data and 478 parameters, $R = 0.0582$ for 8880 structure factors $F_o > 4\sigma(F_o)$. **10**: $C_{32}H_{40}Cl_2N_2P_2Ru$ (686.57); monoclinic, $P2_1/c$, $a = 9.927(4)$, $b = 27.187(6)$, $c = 11.753(6)$ Å, $\beta = 92.30(4)°$, $V = 3169(2)$ Å^3, $Z = 4$, $d_{calc} = 1.439$ g cm^{-3}, μ(Mo Kα) = 0.789 mm^{-1}; $2.05° \leqslant \Theta \leqslant 25.47°$, 6212 reflections collected ($0 \leqslant h \leqslant +12$, $0 \leqslant k \leqslant +32$, $-14 \leqslant l \leqslant +14$), 5862 unique ($R_{int} = 0.0441$); $wR = 0.1896$ for all data and 352 parameters, $R = 0.0570$ for 4224 structure factors $F_o > 4\sigma(F_o)$.

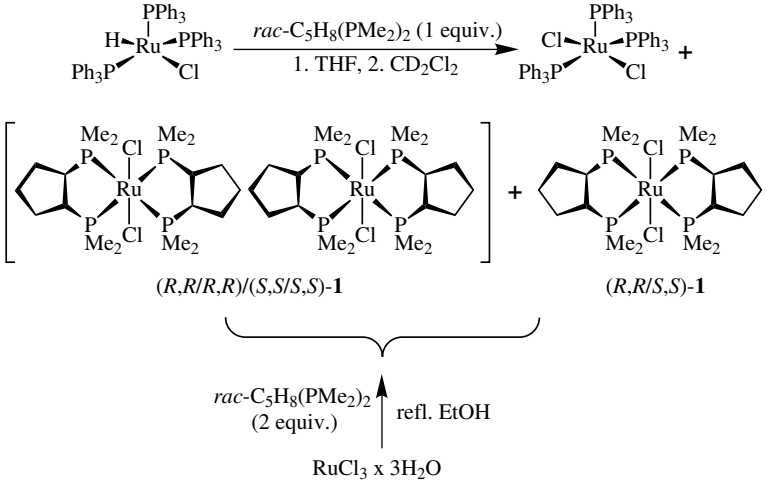
3. Results and discussion

3.1. Synthesis and characterization of the complexes

Morris and coworkers [17] have shown that the ruthenium complexes *trans*-[Ru(H)(Cl){(*R*)-binap} (diamine)] and *trans*-[Ru(H)(Cl){(*R*,*R*)-1,2-C_6H_{10} $(NHPPh_2)_2$} (diamine)], where diamine = $H_2NCMe_2CMe_2NH_2$, (*R*,*R*)-$H_2NCH(Ph)CH(Ph)NH_2$, or (*R*,*R*)-1,2-$C_6H_{10}(NH_2)_2$, can be prepared from [Ru(H)(Cl)$(PPh_3)_3$] by sequential substitution of the required bis(phosphines) and diamines for the monodentate PPh_3 ligands. Attempts to use this protocol for the synthesis of similar *P*∩*P*/*P*∩*N* derivatives, e.g., *trans*-[Ru(H)(Cl){1,2-$C_5H_8(PMe_2)_2$}$(Ph_2PCH_2CH_2NH_2)$], by treating the tris(triphenylphosphine) complex first with racemic 1,2-$C_5H_8(PMe_2)_2$ and then with the *P*,*N* ligand failed: ^{31}P NMR spectra of the product mixtures obtained from reactions of [Ru(H)(Cl)$(PPh_3)_3$] with equimolar quantities of the bis(phosphine) repeatedly showed resonances at $\delta(CD_2Cl_2) = -4.3$ (free PPh_3), 28.4 ($Ph_3P=O$), and 46.7 ([$RuCl_2(PPh_3)_3$]), in addition to two singlets at $\delta = 9.8$ and 10.4. The latter two could be assigned unequivocally to the two {(*R*,*R*/*R*,*R*)/(*S*,*S*/*S*,*S*)} and (*R*,*R*/*S*,*S*) diastereomeric forms of the bis(chelate) complex *trans*-[$RuCl_2${1,2-$C_5H_8(PMe_2)_2$}$_2$] (**1**) by deliberately synthesizing that compound from $RuCl_3 \cdot 3H_2O$ and two equivalents of the *P*,*P* ligand in refluxing ethanol (Scheme 1). Samples of **1** which were recrystallized from $CHCl_3/Et_2O$ likewise contained the {(*R*,*R*/*R*,*R*)/(*S*,*S*/*S*,*S*)} racemate and the (*R*,*R*/*S*,*S*) *meso* form in 1:1 molar ratio, and molecules of the latter were shown to be present in the specimen chosen for the single-crystal structure determination (Fig. 1).

The lack of success in selectively replacing two of the three PPh_3 ligands of [Ru(H)(Cl)$(PPh_3)_3$] by 1,2-$C_5H_8(PMe_2)_2$ is reminiscent of an earlier study of the reaction of [$RuCl_2(PPh_3)_3$] with the *P*,*P* ligands $Ph_2P(CH_2)_n$-PPh_2 (n = 1-4), from which only for $n = 4$ a compound [$RuCl_2${$Ph_2P(CH_2)_nPPh_2$}(PPh_3)] with a seven-membered chelate ring (cf. [Ru(H)(Cl){(*R*)-binap}(PPh_3)] and [Ru(H)(Cl){(*R*,*R*)-1,2-C_6H_{10} $(NHPPh_2)_2$}(PPh_3)] [17]) was isolable [18]. The failure to obtain coordinatively unsaturated complexes for $n < 4$ was attributed to the decrease of the chelate bite angle, which results in sterically less congested coordination spheres, accessible to further substitution with formation of the observed coordinatively saturated derivatives [$RuCl_2${bis(phosphine)}$_2$].

A different approach to Noyori type mixed-ligand complexes utilizes the reaction of diallyl bis(phosphine) complexes [Ru{η^3-$(CH_2)_2CMe$}$_2${bis(phosphine)}] [12] in acetone with methanolic HCl, followed by treatment of the resulting solvated intermediates [$RuCl_2${bis(phosphine)}]$_n$(acetone)$_x$ with one equivalent of a diamine in DMF [19]. Following that procedure, the 1,2-$C_5H_8(PR_2)_2$-substituted diallyl compounds [Ru{η^3-$(CH_2)_2CMe$}$_2${1,2-$C_5H_8(PR_2)_2$}] with R = Me (**2**), Ph



Scheme 1.

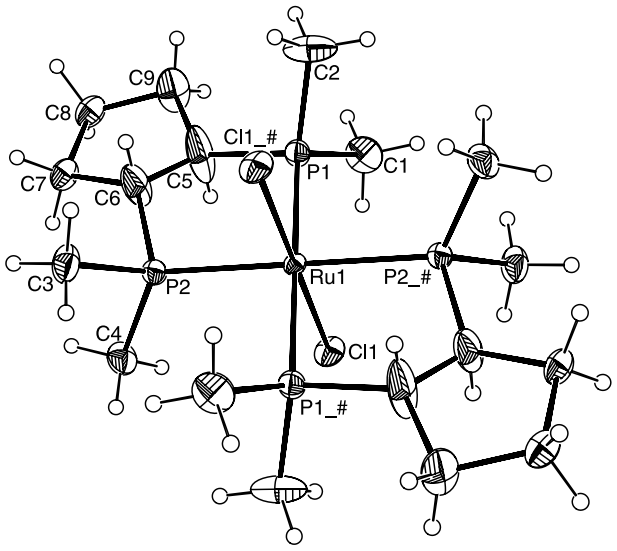
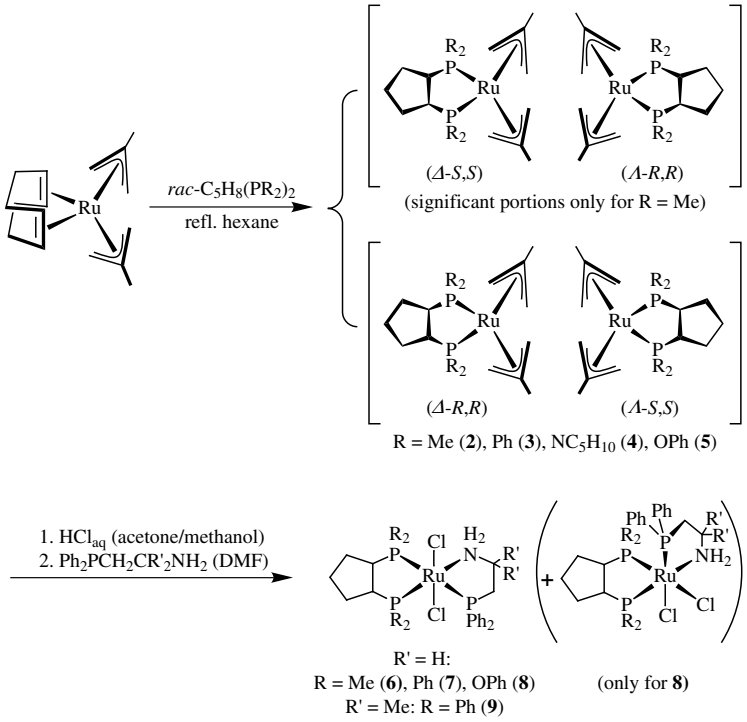


Fig. 1. Perspective view of $[RuCl_2\{1,2\text{-}C_5H_8\ (PMe_2)_2\}_2]$ (1; *meso* form); selected bond lengths [Å] and angles [°]: Ru–Cl1, 2.425(1); Ru1–P1, 2.328(1); Ru1–P2, 2.331(1). Cl1–Ru1–Cl1_#, 180.0, Cl1–Ru1–P1, 90.50(5); Cl1–Ru1–P1_#, 89.50(5); Cl1–Ru1–P2, 90.60(5), Cl1–Ru1–P2_#, 89.40(5); P1–Ru1–P1_#, 180.0; P1–Ru1–P2, 84.80(5); P1–Ru1–P2_#, 95.20; P2–Ru1–P2_#, 180.0. Symmetry transformation used to generate equivalent atoms _#: $-x$, $-y$, $-z$.

(**3**), NC_5H_{10} (**4**), and OPh (**5**), respectively, were prepared by the addition of one equivalent of the chelating bis(phosphine) to $[Ru(\eta^4\text{-}C_8H_{12})\{\eta^3\text{-}(CH_2)_2CMe\}_2]$ in hexane at reflux temperature. Subsequently, the desired *P*∩*P*,*P*∩*N*-coordinated complexes $[RuCl_2\{1,2\text{-}C_5H_8(PR_2)_2\}\ (Ph_2PCH_2CH_2NH_2)]$ [R = Me (**6**), Ph (7), OPh (**8**)] and $[RuCl_2\{1,2\text{-}C_5H_8(PPh_2)_2\}(Ph_2PCH_2CMe_2NH_2)]$ (**9**) were conveniently synthesized by combining **2**, **3**, or **5** first with two equivalents of aqueous HCl in methanol and then with equimolar amounts of the required β-aminophosphine in DMF (Scheme 2). Due to the sensitiveness to acid of the P–N bonds of **4**, the method could not be used for the preparation of a piperidyl-substituted derivative $[RuCl_2\{1,2\text{-}C_5H_8[P(NC_5H_{10})_2]_2\}(Ph_2PCH_2CH_2NH_2)]$.

Because of the racemic nature of the different cyclopentane-based *P*,*P* ligands the diallyl bis(phosphine) complexes **2**–**5** can exist as diastereomeric (Λ-*R*,*R*)/(Δ-*S*,*S*) and (Δ-*R*,*R*)/(Λ-*S*,*S*) pairs of enantiomers. For the PMe_2-substituted derivative **2**, the presence in solution of the two diastereomeric forms was indeed evident from the ^{31}P NMR spectra displaying singlet resonances at $\delta = 32.1$ and 36.2 with relative intensities close to 1:2. In contrast, complexes **3**–**5** having sterically more demanding residues in their $-R_2P$ donor groups were shown by NMR spectroscopy to be formed with diastereoselectivities exceeding 98% (see Section 2). For complexes **3** and **4** the predominating stereoisomers could be assigned as (Δ*R, R*)/(Λ-*S*,*S*) by X-ray structure analysis; Figs. 2 and 3.

Bis(allyl)ruthenium complexes with mondodentate and chelating phosphorus ligands have been the subject of a number of crystallographic studies reported in the past [12a,20,21]. Their coordination geometries have been described as distorted tetrahedral with the two



Scheme 2.

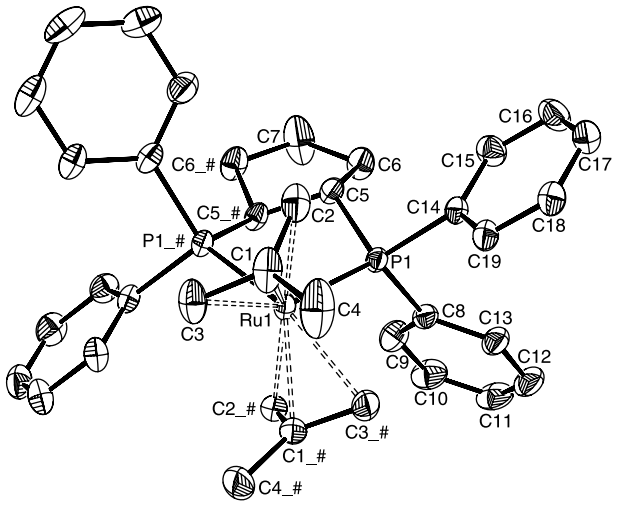


Fig. 2. Perspective view of $[Ru\{\eta^3\text{-}(CH_2)_2CMe\}_2\{1,2\text{-}C_5H_8(PPh_2)_2\}]$(**3**; (Λ-*S*,*S*) form shown); selected bond lengths [Å] and angles [°]: Ru1–P1, 2.3094(7); Ru–C1, 2.175(3); Ru–C2, 2.228(3); Ru–C3, 2.259(3). P1–Ru1–P1_#,86.92(4); P1–Ru1–C1, 123.71(9); P1–Ru1–C2, 91.36(9); P1–Ru1–C3, 155.30(11); P1–Ru1–C1_#,109.61(9); P1–Ru1–C2_#, 91.96(9); P1–Ru1–C3_#, 88.46(9); C1–Ru1–C1_#, 104.3(2); C2–Ru1–C2_#, 175.4(2), C2–Ru1–C3, 64.5(1); C2–Ru1–C3_#, 112.4(1); C3–Ru1–C3_#, 105.2(2). Symmetry transformation used to generate equivalent atoms _#:$-x$, y, $-z + 1/2$.

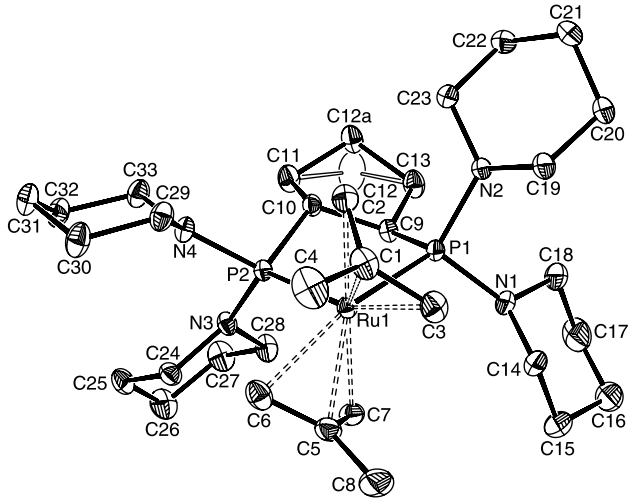


Fig. 3. Perspective view of $[Ru\{\eta^3\text{-}(CH_2)_2CMe\}_2\{1,2\text{-}C_5H_8[P(NC_5H_{10})_2]_2\}]$ (**4**;(Δ-*R*,*R*) form shown); selected bond lengths [Å] and angles [°]: Ru1–P1, 2.3245(5); Ru1–P2, 2.3321(8); Ru1–C1, 2.190(2); Ru1C2, 2.246(2); Ru1–C3, 2.264(2); Ru1–C5, 2.192(2); Ru1–C6, 2.275(2); Ru1–C7, 2.224(2). P1–Ru1P2, 87.42(2); P1–Ru1–C1, 106.11(6); P1–Ru1–C2, 86.95(6); P1–Ru1–C3, 88.30(6); P1–Ru1–C5, 128.03(7); P1–Ru1–C6, 160.88(7); P1–Ru1–C7, 95.97(6); P2–Ru1–C1, 128.74(7); P2–Ru1–C2, 97.23(6); P2–Ru1–C3, 162.34(7); P2–Ru1–C5, 105.57(6); P2–Ru1–C6, 87.56(6); P2–Ru1–C7, 87.51(6); C1–Ru1–C5, 103.61(9); C2–Ru1–C3, 65.42(9), C2–Ru1–C6, 111.99(9); C2–Ru1–C7, 174.55(8); C3–Ru1–C6, 101.69(9); C3–Ru1–C7, 109.98(9); C5–Ru1–C7, 65.38(9).

phosphorus atoms and the two central carbon atoms of the allylic ligands at the corners of the tetrahedron or as pseudo-octahedral with the P donor atoms and the outer allylic carbon atoms defining the coordination polyhedron. Notwithstanding that the distribution of the Ru–C distances in molecules **3** and **4** shows the typical pattern of shorter bonds to the central than to the terminal allyl carbon atoms, we prefer to describe the molecular structures of the two compounds as distorted octahedral in order to emphasize the Δ/Λ helicity of the tris(chelate) complexes and to account for the P–Ru–P bite angles of 86.9° and 87.4°. These are similar to those measured for analogous complexes featuring five-membered chelate rings but are quite different from the virtually ideal tetrahedral P–Ru–P angle of 109.9° displayed by the monophosphine-coordinated complex $[Ru\{\eta^3\text{-}(CH_2)_2CH\}(PPh_3)_2]$ [20a]. The Ru–P distances (Figs. 2 and 3) fall within the range reported for closely related [Ru(allyl){bis(phosphine)}] derivatives [21].

While the reaction sequence outlined by Scheme 2 afforded the bis(phosphine)-aminophosphine complexes **6**, **7**, and **9** as pure *mer*-P_3 stereoisomers, the phenoxy-substituted derivative **8** was produced as an isomeric mixture containing the *fac*- and the *mer*-P_3 forms in close to 3:2 molar ratio. The meridional or facial arrangement of the three $-PR_2$ donor groups in the coordination spheres was easily deduced from the presence or absence of a large (>300 Hz) *trans P*,*P* coupling constant in the characteristic ABX type $^{31}P\{^1H\}$ spectra, but it needed X-ray diffraction analysis to unambiguously assign the *mer* complexes **6**, **7**, and **9** as *trans* rather than *cis* ClRu–Cl isomers (Figs. 4–6).

The molecular structures reveal distorted octahedral coordination geometry around the metal centers as expected. As a consequence of the very different *trans*-bond weakening influences generally exerted by *P* and *N* donor groups, the Ru–P distances opposite the Ru–N bonds are significantly shorter (2.248–2.302 Å) than those in the *trans*-P–Ru–P moieties (2.327–2.366 Å). The Ru–N bond lengths range from 2.150 to 2.194 Å, which is at the lower end of the spread reported for the metal-to-nitrogen separations of previously characterized $[RuCl_2P_3N]$ and $[RuCl_2P_2N_2]$ complexes containing one or two chelated NH_2 or NHR donor functions [22]. The Ru–Cl bond lengths are 2.419 and 2.422 Å in the structure of the $-PMe_2$-coordinated complex **6** and range from 2.415 to 2.442 Å in structures **7** and **9** possessing $-PPh_2$-substituted chelate ligands. Though they appear to be fairly unaffected by the higher steric demand made by $-PPh_2$ than by $-PMe_2$ donors in *cis* positions, increased steric congestion in the coordination spheres of **7** and **9** is manifested by the significant, albeit not uncommon [22], deviation from linearity of the two Cl–Ru–Cl angles (164.0° and 165.6°, set against 170.4° in **6**).

Previous work of the Morris group and ourselves has shown that amine complexes of Ru^{II} and Ir^{I} possessing CH units adjacent to the amino group, in the presence of strong base, tend to undergo degradation of their $H_2N{\cap}NH_2$ or $R_2P{\cap}NH_2$ ligands on C–H bond-breaking

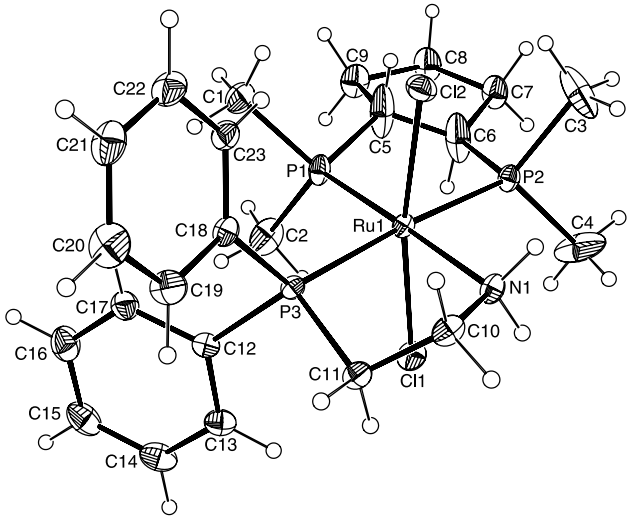


Fig. 4. Perspective view of $[RuCl_2\{1,2\text{-}C_5H_8(PMe_2)_2\}(Ph_2CH_2CH_2NH_2)]$ (**6**); selected bond lengths [Å] and angles [°]: Ru1–Cl1, 2.422(2); Ru1–Cl2, 2.419(2); Ru1–P1, 2.248(2); Ru1–P2, 2.327(3); Ru1–P3, 2.333(3); Ru1–N1, 2.194(4). Cl1–Ru1–Cl2, 170.36(5); Cl1–Ru1–P1, 93.79(7); Cl1–Ru1–P2, 88.16(7); Cl1–Ru1–P3, 88.41(7); Cl1–Ru1–N1, 85.40(12); Cl2–Ru1–P1, 93.45(7); Cl2–Ru1–P2, 86.05(7); Cl2–Ru1–P3, 97.07(7); Cl2–Ru1–N1, 87.46(12); P1–Ru1–P2, 85.63(9); P1–Ru1–P3, 96.62(9); P1–Ru1–N1, 178.74(12); P2–Ru1–P3, 176.02(4); P2–Ru1–N1, 95.30(14); P3–Ru1–N1, 82.40(14).

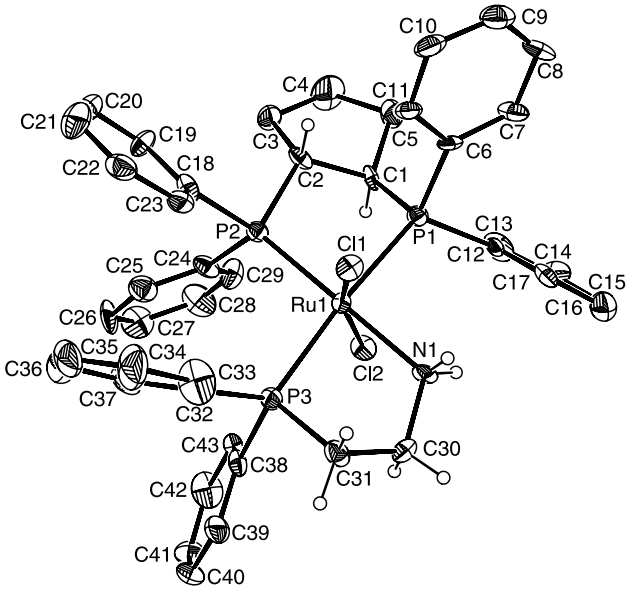


Fig. 5. Perspective view of $[RuCl_2\{1,2\text{-}C_5H_8(PPh_2)_2\}(Ph_2CH_2CH_2NH_2)]$ (**7**); selected bond lengths [Å] and angles [°]: Ru1–Cl1, 2.442(4); Ru1–Cl2, 2.415(4); Ru1P1, 2.366(5); Ru1–P2, 2.288(5); Ru1–P3, 2.348(5); Ru1–N1, 2.150(12). Cl1–Ru1–Cl2, 164.0(1); Cl1–Ru1–P1, 93.89(1); Cl1–Ru1–P2, 102.2(1); Cl1–Ru1–P3, 87.0(1); Cl1–Ru1–N1, 82.4(3); Cl2–Ru1–P1, 82.9(1); Cl2–Ru1–P2, 93.1(1); Cl2–Ru1–P3, 94.8(1); Cl2–Ru1–N1, 82.1(3); P1–Ru1–P2, 85.1(2); P1–Ru1–P3, 175.1(2); P1–Ru1–N1, 93.7(3); P2–Ru1–P3, 99.5(2); P2–Ru1–N1, 175.2(4); P3–Ru1–N1, 81.6(3).

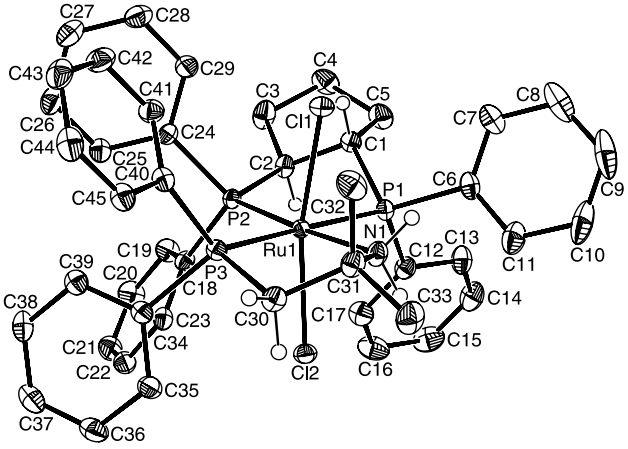
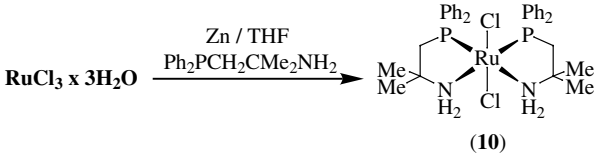


Fig. 6. Perspective view of $[RuCl_2\{1,2\text{-}C_5H_8(PPh_2)_2\}(Ph_2CH_2CMe_2NH_2)]$ (**9**); selected bond lengths [Å] and angles [°]: Ru1–Cl1, 2.427(1); Ru1–Cl2, 2.436(1); Ru1–P1, 2.340(1); Ru1–P2, 2.302(1); Ru1–P3, 2.355(1); Ru1–N1, 2.186(3). Cl1–Ru1–Cl2, 165.58(4); Cl1–Ru1–P1, 84.77(4); Cl1–Ru1–P2, 92.90(4); Cl1–Ru1–P3, 94.13(4); Cl1–Ru1–N1, 84.37(11); Cl2–Ru1–P1, 93.12(4); Cl2–Ru1–P2, 101.02(4); Cl2–Ru1–P3, 86.72(4); Cl2–Ru1–N1, 81.53(11); P1–Ru1–P2, 83.15(4); P1–Ru1–P3, 174.95(4); P1–Ru1–N1, 93.78(10); P2–Ru1–P3, 101.84(4); P2–Ru1–N1, 176.08(10); P3–Ru1–N1, 81.20(10).

pathways formulated as "dehydrogenation of the diamine ligand" [17c] or "β-elimination of imine fragments from initially formed amides" [1d]. In order to circumvent such difficulties ligands that lack hydrogen atoms α to the amino group were used for mechanistic studies, e.g., $H_2NCMe_2CMe_2NH_2$ [17c,17d] and $Ph_2PCH_2CMe_2NH_2$ [1d]. A dichloro ruthenium complex of the latter, $[RuCl_2(Ph_2PCH_2CMe_2NH_2)_2]$ (**10**), was obtained by reacting $RuCl_3 \cdot 3H_2O$ with two equivalents of the aminophosphine in THF in the presence of zinc, similar to the preparation of the *N*,*N*-dimethyl isomer $[RuCl_2(Ph_2PCH_2CH_2NMe_2)_2]$ [24]; Scheme 3.

The coordination geometry of **10** derived from an X-ray structure analysis corresponds to (*OC*-6-13) [23] with the chloro ligands in *trans* positions and the two nitrogen and phosphorus atoms *cis* to each other; Fig. 7. This arrangement is apparently favored over the sterically less crowded geometry in which the diphenylphosphino groups are *trans*, because it puts the strong *trans* influence P donors opposite the weaker *trans* bond influencing amino substituents. Similar geometries were previously reported for the structures of some related complexes, including $[RuCl_2(Ph_2PCH_2CH_2NMe_2)_2]$ [24,25a], $[RuCl_2(Ph_2PCH_2CH_2N$-



Scheme 3.

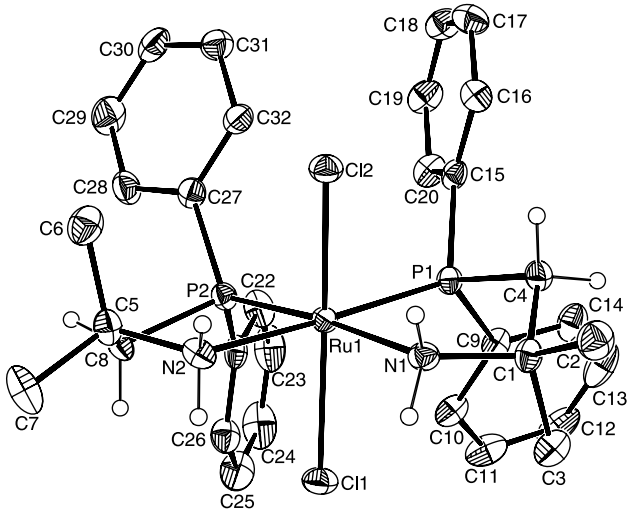


Fig. 7. Perspective view of $[RuCl_2(Ph_2CH_2CMe_2NH_2)_2]$ (**10**); selected bond lengths [Å] and angles [°]: Ru1–Cl1, 2.428(2); Ru1–Cl2, 2.422(2); Ru1–P1, 2.253(2); Ru1–P2, 2.264(2); Ru1–N1, 2.175(6); Ru1–N2, 2.194(6). Cl1–Ru1–Cl2, 161.61(7); Cl1–Ru1–P1, 102.01(8); Cl1–Ru1–P2, 91.19(8); Cl1–Ru1–N1, 94.80(17); Cl1–Ru1–N2, 81.76(17); Cl2–Ru1–P1, 88.63(8); Cl2–Ru1–P2, 101.36(7); Cl2–Ru1–N1, 81.73(16); Cl2–Ru1–N2, 86.49(17); P1–Ru1–P2, 101.86(8); P1–Ru1–N1, 82.51(16); P1–Ru1–N2, 173.83(17); P2–Ru1–N1, 174.63(16); P2–Ru1–N2, 82.83(18); N1–Ru1–N2, 93.0(2).

$HR)_2$] (R = *n*-Pr [22] CH_2Ph [22,25b]), and $[RuCl_2(Ph_2PCH_2CH_2NH_2)_2]$ [25b]. The Ru–N distances, 2.175 Å opposite the longer (2.264 Å) and 2.194 Å opposite the shorter (2.253 Å) Ru–P bond, reflect the expected *trans*-compensatory effects; within experimental error, they appear to be at best slightly elongated if compared to those of $[RuCl_2(Ph_2PCH_2CH_2NH_2)_2]$ (2.164 and 2.180 Å [25b]), which is without bulky methyl substituents adjacent to the amino groups. Similar to the latter, complex **10** features a considerable distortion of the Cl–Ru–Cl axis (161.6°) from linearity.

3.2. Catalytic hydrogenation of acetophenone

Both *P*∩*P*/*P*∩*N*- and $(P\cap N)_2$-coordinated complexes were probed for their behavior as catalysts for ≻C═O reduction under the conditions of direct and transfer hydrogenation.

With acetophenone as the standard test substrate and complexes **7**, **9**, and **10** as hydrogenation catalysts, transfer hydrogenation experiments were carried out at 50–60 °C in isopropanol/benzene (1:1), in the presence of 5 equiv. of KOBu-*t* as activating base. Fig. 8 shows a typical reaction profile obtained with complex **10** at a substrate-to-catalyst ratio (s/c) of 200:1. Transformation of the ketone into the alcohol is seen to follow a sigmoidal curve with parallel consumption of the substrate and formation of the product. The sigmoidal type of the conversion-time curve indicates an inital incubation time during which the catalytically active species is formed from the precatalyst. This period is largely reduced on changing the catalyst complex from **10** to **7**, as shown by the reaction profiles given for the latter in Figs. 9 (s/c 200) and 10 (s/c 2000). Given that the actual catalyst results from the precatalyst complexes $[RuCl_2(Ph_2PCH_2CMe_2NH_2)_2]$ (**10**) and $[RuCl_2\{1,2\text{-}C_5H_8(PPh_2)_2\}(Ph_2PCH_2CH_2NH_2)]$ (**7**) by base-induced abstraction of HCl from the *cis*-ClRu–NH_2-moiety as described for both the base-modified solvent-transfer and direct hydrogenation catalysts [(η^6-arene) RuCl-{$H_2N\cap X$}]/base (X = alkoxide or amide) 3,5b,5c,5d,26 and $[RuX_2\{bis(phosphine)\}(1,2\text{-diamine})]$ [2b,3,5d, 17,17c,17d,27], respectively, the substantial induction period observed for **10** can be ascribed to steric shielding of the amino functions by the adjacent methyl substitu-

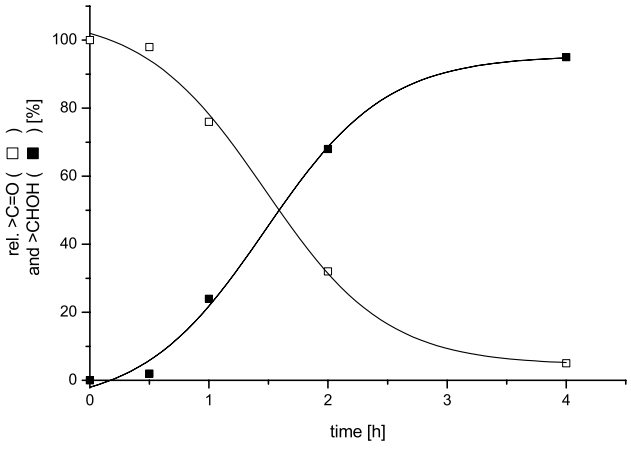


Fig. 8. Conversion-time profile of the transfer hydrogenation of acetophenone catalyzed by **10**-KOBu-*t* (1:5) at s/c 200:1; C_6H_6/*i*-PrOH (1:1), *T* = 60 °C.

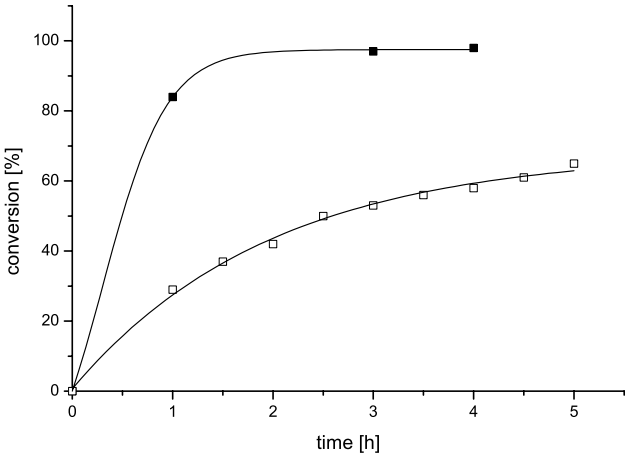


Fig. 9. Conversion-time profiles of the transfer hydrogenation of acetophenone catalyzed by **7**-KOBu-*t* (1:5) (-■-) and **9**-KOBu-*t* (1:5) (–□–) at s/c 200:1; C_6H_6/*i*-PrOH (1:1), *T* = 50 °C.

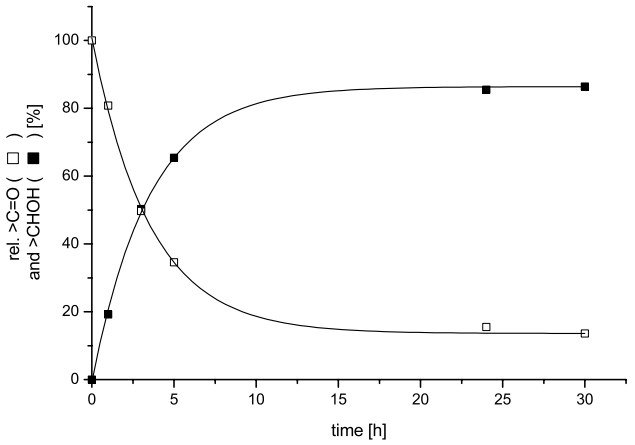


Fig. 10. Conversion-time profile of the transfer hydrogenation of acetophenone catalyzed by **7**-KOBu-*t* (1:5) at s/c 2000:1; C_6H_6/*i*-PrOH (1:1), T = 60 °C.

ents, making NH_2 deprotonation by the base more difficult.

Fig. 9 qualitatively compares the reaction profiles obtained for transfer hydrogenations catalyzed by either $[RuCl_2\{1,2\text{-}C_5H_8(PPh_2)_2\}(Ph_2PCH_2CH_2NH_2)]$ (**7**) or $[RuCl_2\{1,2\text{-}C_5H_8(PPh_2)_2\}(Ph_2PCH_2CMe_2NH_2)]$ (**9**). The clear-cut drop in activity observed for **9** is as expected in that it reflects the hindered accessibility of the reactive Ru–amide and, respectively, RuH–amine bonds [3,5d,26] for the hydrogen donor solvent and the ketone substrate.

Complex **10** was also inspected for its performance as catalyst of the direct hydrogenation of acetophenone. Exploratory reactions, which were run for 3 h at s/c 2000, in the presence of 5 equiv. of added KOBu-*t*, in benzene solution heated at 60 °C under 20 bar of H_2, resulted in 19% substrate conversion, corresponding to a turnover frequency (TOF) of 126 h^{-1}. If a solvent system composed of benzene/Me_2CD OH (1:1) was used under otherwise identical conditions, the yield of the 1-phenylethanol increased to 70% (TOF 467 h^{-1}). No deuterated product was detected, proving that the reaction is a net transfer of hydrogen from the gas and not from the solvent.

The complex, which (as shown above) is a rather active transfer hydrogenation (pre)catalyst giving 95% substrate conversion after 3 h at s/c/KOBu-*t* = 200:1:5 in C_6H_6/*i*-PrOH (1:1) at 60 °C (see Fig. 9 and Section 2), therefore also turns out as an active (pre)catalyst for the direct hydrogenation of the ketone under comparable conditions.

Conversion of the substrate to the alcohol dropped to only 47% (TOF 313 h^{-1}) if the reaction was carried out in neat isopropanol, notwithstanding that this solvent is often used as the medium of choice for Ru-catalyzed ≻C═O hydrogenations [2,27]. The reduced activity of **10** in pure *i*-PrOH compared to C_6H_6/Me_2CHOH (1:1) could be due to catalyst deactivation by Ru-alkoxide formation as a result of an acid–base reaction between a dihydrido intermediate $[Ru(H)_2(Ph_2PCH_2CMe_2NH_2)_2]$, likely to be formed as the catalytically active species under reaction conditions [2,17,27], and either of the alcohols Me_2CHOH and PhCH(Me)OH. The formation of catalytically less active alkoxide complexes has previously been described for ≻C═O hydrogenations catalyzed by $[Ru(H)_2\{(R)\text{-binap}\}(H_2NCMe_2CMe_2NH_2)]$ and attributed to enhanced Brønsted acidity of the alcohols in solvents of higher dielectric constant (<5 for benzene but ~18 for isopropanol) [17d]. Considerably enhanced catalytic activity was therefore expected for less O–H acidic isopropanol solutions of **10**. In full agreement, the addition of base in large excess ([KOBu-*t*]/[**10**] = 100 at s/c 10000) resulted in 30% conversion of acetophenone to 1-phenylethanol after 3 h, corresponding to a turnover frequency of 1000 at $p(H_2)$ = 20 bar and T = 60 °C.

It would be of interest to compare these results with those obtained for the direct hydrogenation of acetophenone catalyzed by $[RuCl_2(Ph_2PCH_2CH_2NH_2)_2]$ and $[RuCl_2(Ph_2PCH_2CH(Me)NH_2)_2]$, which differ only gradually from **10** in the lower degree of methyl substitution at the C_α-NH_2 position. However hydrogenation experiments with the former two compounds, which led to quantitative transformation of Ph(Me)CO and other ketones to the corresponding product alcohols if run for 12 h at s/c 2500 in the presence of 5 equiv. of added KOPr-*i* at 20 °C under ~3.5 bar of H_2, were not conducted in isopropanol but in the neat ketone. Hydrogenations performed in benzene used 2,2-dimethyl-1-phenylpropanone as the substrate at s/c 400 [4]. Hence, it is difficult to draw conclusions on the relative activities of the three catalytic systems.

Further work to exploit $P\cap P/P\cap N$- and $(P\cap N)_2$-coordinated ruthenium complexes with optically active aminophosphine ligands [1d] for catalytic ≻C═O hydrogenation is underway.

4. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition numbers CCDC 237806 (**3**), CCDC 237807 (**6** · C_7H_8), CCDC 237808 (**1**), CCDC 237809 (**4**), CCDC 237810 (**7**), CCDC 237812 (**9** · 1/2Et_2O), and CCDC 237813 (**10**). Copies of the data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (internat.) +44-1223/336-033; e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgements

Support of this work by the *Deutsche Forschungsgemeinschaft* (Bonn, SFB 583) is gratefully acknowledged. We are also indebted to Mrs. S. Hoffmann for her skilful assistance.

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