Ruthenium piano-stool complexes bearing imidazole-based PN ligands

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ABSTRACT

A variety of piano-stool complexes of cyclopentadienyl ruthenium(II) with imidazole-based PN ligands have been synthesized starting from the precursor complexes $[CpRu(C_{10}H_8)]PF_6$, $[CpRu(NCMe)_3]PF_6$ and $[CpRu(PPh_3)_2Cl]$. PN ligands used are imidazol-2-yl, -4-yl and -5-yl phosphines.

Depending on the ligand and precursor different types of coordination modes were observed; in the case of polyimidazolyl PN ligands these were κ^1P-monodentate, κ^2P,N-, κ^2N,N- and κ^3N,N,N-chelating and μ-$\kappa P:\kappa^2N,N$-brigding. The solid-state structures of $[CpRu(\mathbf{1a})_2Cl]\cdot H_2O$ ($\mathbf{5}\cdot H_2O$) and $[\{CpRu(\mu-\kappa^2-N,N-\kappa'^1-P-\mathbf{2b})\}_2](C_6H_5PO_3)_2(C_6H_5PO_3H_2)_2$, a hydrolysis product of the as well determined $[\{CpRu(\mathbf{2b})\}_2](PF_6)_2 2CH_3CN$ ($\mathbf{7b}\cdot 2CH_3CN$) were determined ($\mathbf{1a}$ = imidazol-2-yldiphenyl phosphine, $\mathbf{2b}$ = bis(1-methylimidazol-2-yl)phenyl phosphine, $\mathbf{3a}$ = tris(imidazol-2-yl)phosphine). Furthermore, the complexes $[CpRu(L)_2]PF_6$ (L = imidazol-2-yl or imidazol-4-yl phosphine) have been screened for their catalytic activity in the hydration of 1-octyne.

1. Introduction

The addition of water to alkynes is an important step in the synthesis of carbonyl compounds and has a long history going back as far as 1860, when Berthelot discovered the hydration of acetylene in sulfuric acid [1]. One of the longest known reactions to catalyze the hydration of alkynes is the reaction with mercury(II) salts [2–4]. Even though mercury is extremely hazardous, this reaction is still the favoured process for industrial application because it is reliable and produces good yields [5]. Other metal-based catalysts which catalyze the Markovnikov as well as anti-Markovnikov hydration include $NaAuCl_4$, $RuCl_3$ and $[Ru(III)(EDTA-H)Cl]$, $RhCl_3$, $PtCl_4$ and the Zeise dimer $[\{PtCl_3(CH_2 = CH_2)\}_2]$, just to name a few [6–13]. Besides these homogenous catalysts also heterogenous catalyst systems are used [14–16]

The first ruthenium(II) complex to be known to catalyze the anti-Markovnikov hydration was a phosphine complex described by Tokunaga and Wakatsuki [17,18]. The catalytic activity as well as

the selectivity of ruthenium(II) depends on the nature of the phosphine ligands [19]. Using $PPh_2(C_6F_5)$ and $P(3-C_6H_4SO_3Na)_3$ as ligands leads to selective anti-Markovnikov addition of water and satisfactory yields of the aldehyde. However, these catalytic systems involve a high catalyst/metal loading and yield only moderate turnovers and selectivity. Using cyclopentadienyl ruthenium(II) complexes with monodentate or bidentate phosphine ligands provides an increased catalytic activity as well as selectivity towards the anti-Markovnikov product, e.g. $[CpRu(dppm)Cl]$ (dppm = bis(diphenylphosphino)methane) gives the anti-Markovnikov product in excellent yield while tolerating a wide spectrum of substrates [20].

Nature uses proteins as polyfunctional ligands, which show multiple interactions between the enzyme and either substrate, intermediate(s), or transition state(s) during the catalytic cycle [3]. For example, the tungsteno enzyme acetylene hydratase of *Pelobacter acetylenicus* uses acetylene as the sole carbon source, which is converted to acetaldehyde and then used by the enzyme to build acetic acid and ethanol, important building blocks for the bacteria's metabolism [21–24]. While enzymes are impressive, their structures are complex, and due to their high level of specificity for particular conversions, they are only of minor use for the development of generally efficient catalysts.

More recently, phosphine ligands containing heterocyclic substituents such as pyridinyl or imidazolyl groups were investigated in bifunctional catalysis [25–29]. By modification of the

pyridine ring the reactivity and catalytic activity of the corresponding complexes can be tuned [30]. Grotjahn suggested that the nitrogen heterocycle acts as a bifunctional acid/base catalyst, initiating the protonation of the alkyne and leading to the ruthenium(IV) vinylidene species [31].

In this report we investigated the hydration of terminal alkynes catalyzed by CpRu(II) compounds containing different imidazolyl phosphines as potentially bifunctional PN ligands. The imidazol-2-yl and imidazol-4-yl phosphine ligands employed bear substituents of varying steric demand. Also included were selected bis and tris(imidazolyl)phosphine ligands.

2. Experimental section

2.1. Synthesis

Compounds **1a,b,d** − **3a,b,d** [32,33] and **1h** [34] as well as [CpRu(PPh₃)₂Cl] [35] and [CpRu(C₁₀H₈)]PF₆ [36] were prepared according to literature procedures. All reactions were carried out in Schlenk tubes under an atmosphere of dry nitrogen using anhydrous solvents purified according to standard procedures. All chemicals were purchased from commercial sources and used as received. ¹H and ³¹P NMR spectra were recorded on a Bruker DRX 200 spectrometer. The ^{1}H spectra were calibrated against the residual proton signal of the solvent as an internal reference (CDCl₃: δ_H = 7.30 ppm; methanol-d_4: δ_H = 3.31 ppm; acetone-d_6: δ_H = 2.05 ppm, acetonitrile-d_3: δ_H = 1.94 ppm) while the ³¹P{¹H} NMR spectra were referenced to external 85% H₃PO₄. The ESI mass spectra were recorded on a Finnigan LCQ Deca ion trap API mass spectrometer. The MALDI mass spectra were recorded on a Bruker Ultraflex MALDI-TOF mass spectrometer. The FAB mass spectra were recorded on a Finnigan MAT 8200 mass spectrometer using a nitrobenzylic alcohol (NBA) matrix. Infrared spectra were recorded with a Bruker IFS 66 FT-IR spectrometer. The elemental composition of the compounds was determined with a Perkin Elmer Analysator 2400 at the Institut für Pharmazeutische und Medizinische Chemie, Heinrich-Heine Universität Düsseldorf.

2.1.1. Synthesis of 1-methyl-4,5-diphenylimidazole-2-yl-diphenylphosphine (2-MIP$^{diPh-NMe}$, **1c**)

1-Methyl-4,5-diphenylimidazole (2 g, 8 mmol) is placed in a Schlenk tube equipped with a magnetic stirring bar and dissolved in dry thf (100 mL). At −78 °C n-butyllithium (5.3 mL, 1.6 M in hexane) is added slowly to the solution, which turns deep red. The reaction mixture is stirred at −78 °C for 1 h until the diphenyl-chlorophosphine (1.6 mL, 8.0 mmol) is slowly added to the solution, which turns yellow and is then stirred over night at room temperature. The solvent is removed and the residue is dissolved in with ammonia-saturated dichloromethane. This solution is stirred over night and the white solid is filtered off. The solvent is removed from the filtrate yielding the product as a white-yellow solid, which is dried under vacuum. Yield 2.00 g (60%). ¹H NMR (200 MHz, CDCl₃): δ = 3.57 (s, 3H, CH₃), 7.15−7.74 (m, 20H, Ph). ³¹P{¹H} NMR (200 MHz, CDCl₃): δ = −28.74 (s); ESI (methanol): m/z = 419 [M⁺+H], 341 [M⁺-Ph]; C₂₈H₂₃N₂P·²⁄₃CH₂Cl₂ (475.49): calc. C 72.5, H 5.2, N 5.9; found C 72.6, H 5.3, N 5.5.

2.1.2. Synthesis of 2-tert-butylimidazole-4(5)-yl-diphenylphosphine (4-MIP^{tBu}, **1e**)

1-Methoxymethyl-2-tert-butylimidazole (1.3 g, 8.0 mmol) is placed in a Schlenk tube equipped with a magnetic stirring bar and dissolved in dry thf (100 mL). At −78 °C tert-butyllithium (5.3 mL, 1.6 M in hexane) is added slowly to the solution, which turns deep red. The reaction mixture is stirred at −78 °C for 1 h until the diphenylchlorophosphine (1.6 mL, 8.0 mmol) is slowly added to the

solution, which turns yellow and is then stirred over night at room temperature. The solvent is removed and the residue is dissolved in with ammonia-saturated dichloromethane. This solution is stirred over night and the white solid is filtered off. The solvent is removed from the filtrate and the residue dissolved in acetone/water (10:1) and 2 mL of conc. hydrochloric acid added. The mixture is refluxed for 4 h, all volatiles removed in vacuo and the residue dissolved in a minimum amount of ethanol and sodium hydroxide solution added. The precipitate is filtered off, washed with diethyl ether and dried in vacuo. Yield: 1.06 g (43%). ¹H NMR (200 MHz, CDCl₃): δ = 1.34 (s, 9H, CH₃), 6.91 Hz (s, H$_{im}$), 7.25−7.35 (m, 10H, Ph), 10.80 (very broad, 1H, NH). ³¹P{¹H} NMR (81 MHz, CDCl₃): δ = −31.0. ESI⁺ (methanol): m/z (%) = 309 [M + H]⁺ (100), 249 [M-tBu]⁺ (95). C₁₉H₂₁N₂P·5/3H₂O (308.36): calc. C 67.44, H 7.23, N 8.27; found C 67.49, H 6.90, N 8.14.

2.1.3. Synthesis of 2-phenylimidazole-4(5)-yldiphenylphosphine (4-MIP^{Ph}, **1f**)

1-Methoxymethyl-2-phenylimidazole (1.5 g, 8.0 mmol) is placed in a Schlenk tube equipped with a magnetic stirring bar and dissolved in dry thf (100 mL). At −78 °C tert.-butyllithium (5.3 mL, 1.6 M in hexane) is added slowly to the solution, which turns deep red. The reaction mixture is stirred at −78 °C for 1 h until the diphenylchlorophosphine (1.6 mL, 8.0 mmol) is slowly added to the solution, which turns yellow and is then stirred over night at room temperature. The solvent is removed and the residue is dissolved in with ammonia-saturated dichloromethane. This solution is stirred over night and the white solid is filtered off. The solvent is removed from the filtrate and the residue (which is the protected phosphine, ¹H NMR (200 MHz, CDCl₃): δ = 3.23 (s, 3H, OCH₃), 5.40 (d, J = 1.5 Hz, CH₂), 6.86 Hz (s, H$_{im}$), 7.33−7.85 (m, 15H, Ph). ³¹P{¹H} NMR (81 MHz, CDCl₃): δ = −34.0) dissolved in acetone/water (10:1) and 2 mL of conc. Hydrochloric acid added. The mixture is refluxed for 4 h, all volatiles removed in vacuo and the residue dissolved in a minimum amount of ethanol and sodium hydroxide solution added. The precipitate is filtered off, washed with diethyl ether and dried in vacuo. Yield: 1.39 g (53%). ¹H NMR (200 MHz, CDCl₃): δ = 6.71 Hz (s, 1H, H$_{im}$), 7.15−8.00 (m, 15H, Ph) 8.44 (s, 1H, H$_{im}$), 15.17 (s, broad, 1H, NH). ³¹P{¹H} NMR (81 MHz, CDCl₃): δ = −29.8. ESI MS (methanol): m/z (rel. int.) = 386 (100) [M + NaCl]⁺, 329 (15) [M + H]⁺. C₂₁H₁₇N₂P·C₂H₅OH (374.42): calc. C 73.78, H, 6.19, N 7.48; found C 73.85, H 5.50, N 7.02.

2.1.4. Synthesis of 1-methyl-2-isopropylimidazole-4-yldiphenylphosphine (4-MIP^{iPr,NMe}, **1i**)

1-Methyl-4-iodo-2-isopropylimidazole (1 g, 4 mmol) is dissolved in dichloromethane. One equivalent of ethyl magnesium bromide (3 M in ether) is slowly added to the solution at 0 °C. The clear solution is stirred for 30 min at room temperature before the diphenylchlorophosphine (0.75 mL, 4.0 mmol) is added. The solution is stirred at room temperature over night. The solvent is removed and the soft solid is redissolved in ammonia-saturated dichloromethane and stirred over night. A white solid precipitates which is filtered off. The solvent of the filtrate is removed, yielding a white-yellow solid, which is then stirred in ethanol under addition of 1 mL of hydrochloric acid. The solvent is removed and the solid stirred in ammonia-saturated dichloromethane. The precipitated white solid is removed by filtration and the solvent of the filtrate is removed, resulting in a white powder, which is dried under vacuum. Yield 0.71 g (58%). ¹H NMR (200 MHz, methanol-d_4): δ = 1.34 (d, 6H, CH₃), 3.19 (m, 1H, CH), 3.63 (s, 3H, CH₃), 6.56 (s, 1H, CH), 7.36−7.84 (m, 10H, Ph); ³¹P{¹H} NMR (81 MHz, methanol-d_4): δ = −24.44 (s); EI MS (methanol): m/z = 308 [M⁺]. C₁₉H₂₁N₂P·H₂O (326.15): calc. C 66.50, H 6.70, N 9.83; found C 66.88, H 6.68, N 10.04.

2.1.5. Synthesis of 1-methyl-2-tert-butylimidazole-4-yldiphenylphosphine (4-MIP^{tBu,NMe}, **1j**)

1-Methyl-4-iodo-2-tert-butylimidazole (1.2 g, 45 mmol) is dissolved in dichloromethane. One equivalent of ethyl magnesium bromide (3 M in ether) is slowly added to the solution at 0 °C. The clear solution is stirred for 30 min at 0 °C and another 30 min at room temperature before the diphenylchloro phosphine (0.82 mL, 4.5 mmol) is added. The solution is stirred at room temperature over night. The solvent is removed and the solid is redissolved in ammonia-saturated dichloromethane and stirred over night. A white solid precipitates which is filtered off. The solvent of the filtrate is removed, yielding a white-yellow solid, which is then stirred in ethanol under addition of 1 mL of hydrochloric acid. The solvent is removed and the solid stirred in ammonia-saturated dichloromethane. The precipitated white solid is removed by filtration and the solvent of the filtrate is removed, resulting in a white powder, which is dried under vacuum. The solid is recrystallized from acetone and dried under vacuum. The product was yielded as $MgBr_2$ adduct. Yield 0.88 g (42%). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.67 (s, 9H, CH_3), 3.91 (s, 3H, CH_3), 6.34 (s, 1H, CH), 7.42–8.09 (m, 10H, Ph). ^{31}P$\{^1$H$\}$ NMR (81 MHz, $CDCl_3$): δ = −30.48 (s). MS ESI (methanol): m/z = 527 [LMgBr$_2$ + Na]$^+$ (15). $C_{20}H_{23}N_2PMgBr_2 \cdot NH_3$ (523.53): calc. C 45.88, H 5.01, N 8.03; found C 45.15, H 5.75, N 7.65.

2.1.6. Synthesis of imidazole-2-yl-phenylphosphine (2-BIP^H, **2a**)

A solution of n-butyl lithium in n-hexane (1.6 M, 12 mL, 19 mmol) was added drop-wise to a solution of 3.0 g (18 mmol) of 1-diethoxymethylimidazole in diethyl ether (150 mL) at −78 °C. The reaction mixture was stirred at −40 °C for 1 h and then was cooled to −78 °C and PCl_3 (1.56 g, 8.72 mmol) was added. The reaction mixture was stirred at −78 °C for 1 h and at ambient temperature over night. Concentrated ammonia solution (5 mL) was added, the phases separated, the organic phase was collected and all volatiles were removed in vacuo. The oily residue was dissolved in 100 mL acetone/water (10:1) and stirred at ambient temperature for 72 h. The resulting precipitate was collected by filtration and dried in vacuo. Yield: 1.1 g (52%). ^{1}H NMR (methanol-d_4): δ = 7.27–7.35 (m, 9H). ^{31}P$\{^1$H$\}$ NMR (methanol-d_4): δ = −46 (s). ESI$^+$ (methanol): m/z (%) = 243 [L]$^+$. $C_{12}H_{11}N_4P \cdot CH_3OH$ (274.26): calc. C 56.93, H 5.51, N 20.43; found C 56.4, H 5.6, N 20.7.

2.1.7. Synthesis of [CpRu(κP-**1d**)(PPh$_3$)Cl] (**4**)

[CpRu(PPh$_3$)$_2$Cl] (0.5 g, 0.69 mmol) and **1d** (0.17 g, 0.67 mmol) were heated for 4 h in toluene to reflux. The volatiles were removed in vacuo and the residue treated with n-hexane to give a yellow solid. After filtration the product was chromatographed on silica (CH$_2$Cl$_2$:n-hexane 3:1, followed by CH$_2$Cl$_2$). Yield 52 mg (10%). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.20 (dd, $^3J_{HH}$ = 6.9 Hz, $^3J_{HH}$ = 12.9 Hz, 6H, CH(CH$_3$)$_2$), 2.77 (m, 1H, CH(CH$_3$)$_2$), 4.22 (d, $^3J_{HH}$ = 9.3 Hz, 5H, Cp), 6.72 (s, 1H, Im), 6.98–7.24 (m, 15 H, PPh$_3$), 7.26–7.83 (m, 11H, Ph). ^{31}P$\{^1$H$\}$ NMR (81 MHz, $CDCl_3$): δ = 45.0 (dd, $^2J_{PP}$ = 28.3 Hz, 43.0 Hz), 30.4 (t, $^2J_{PP}$ = 21.3 Hz). MALDI-TOF-MS: m/z (rel. Int.) = 755 [M − 2H]$^+$ (25), 723 [M − Cl]$^+$ (100), 461 [M-PPh$_3$Cl]$^+$ (25). $C_{41}H_{39}ClN_2P_2Ru$ (758.29): calc. C 65.0, H 5.2, N 3.7; found C 65.1, H 4.9, N 3.7.

2.1.8. Synthesis of [CpRu((κP-**1a**)$_2$Cl] (**5**)

[CpRu(PPh$_3$)$_2$Cl] (100 mg, 0.138 mmol) and **1a** (70 mg, 0.28 mmol) were heated to 90 °C for 8 h in toluene (15 mL). The volatiles were removed in vacuo and the residue treated with n-hexane (15 mL). The resulting solid was filtered and dried in vacuo. Yield 61 mg (63%). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 4.38 (s, %H, Cp), 3.44 (br, NH), 6.93 (s, 2H, im), 9.09–7.60 (m, 22H, Ph,im). ^{31}P$\{^1$H$\}$ NMR (81 MHz, $CDCl_3$): δ = 31.7 (s). MALDI-TOF-MS: m/z (rel. Int.) = 671 [M − Cl]$^+$ (100), 460 [M-**1a**-Cl]$^+$ (25). $C_{35}H_{31}N_4P_2ClRu$ (706.13): calc. C 59.5, H 4.4, N 7.9; found C 60.0, H 4.6, N 8.1.

2.1.9. Synthesis of [CpRu(κP-**1d**)$_2$Cl] (**6**)

[CpRu(PPh$_3$)$_2$Cl] (0.51 g, 0.70 mmol) and **1d** (0.38 g, 1.5 mmol) were heated for 20 h in toluene to reflux. The volatiles were removed in vacuo and the residue treated with n-hexane to give a yellow solid. After filtration the product was chromatographed on silica (ethyl acetate). Crystallization from methanol/n-hexane yielded 18 mg (30%) of **6**. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.28 (dd, $^3J_{HH}$ = 6.9 Hz, 14.1 Hz, 12H, CH(CH$_3$)$_2$), 2.85 (sept, 2H, $^3J_{HH}$ = 6.9 Hz, CH(CH$_3$)$_2$), 4.27 (s, 5H, C5H5), 6.75 (s, 2H, ImC5H), 7.06–7.28 (m, 10H, Ph), 7.35–7.80 (m, 10H, Ph), 11.0 (s, 2H, ImNH). ^{31}P$\{^1$H$\}$ NMR (81 MHz, $CDCl_3$): δ = 26.4 (s). MALDI-TOF-MS: m/z (rel. Int.) = 755 [M − Cl]$^+$ (100), 461 [M-**1d**-Cl]$^+$ (25). $C_{41}H_{43}N_4P_2ClRu$ (790.29): calc. C 62.3, H 5.5, N 7.1; found C 62.6, H 5.1, N 7.4.

2.1.10. Synthesis of [{CpRu(μ-κ^2N,N:κ'^1P-**2a**)}$_2$](PF$_6$)$_2$ (**7a**)

50 mg (0.12 mmol) of [CpRu(NCCH$_3$)$_3$]PF$_6$ and **2a** (0.12 mmol, 36 mg) were dissolved in acetonitrile and heated to gentle reflux for 24 h. The volatiles were removed in vacuo, the residue washed with n-hexane and diethyl ether and dried in vacuo. Yield: 69 mg (90%). ^{1}H NMR (500 MHz, acetonitrile-d_3): δ = 3.09 (s, 12H NCH$_3$), 5.23 (s, 5H Cp), 6.79 (s, 2H arom. Im), 6.95 (t, $^3J_{H,H}$ = 8.2 Hz, 1H Ph), 7.13 (s, 2H arom. Im.), 7.40 (t, $^3J_{H,H}$ = 7.6 Hz, 1H Ph), 7.65 (t, $^3J_{H,H}$ = 7.4 Hz, 1H Ph), 7.75 (t, $^3J_{H,H}$ = 7.0 Hz, 1H Ph), 8.23 (t, $^3J_{H,H}$ = 9.6 Hz, 1H Ph) ^{31}P$\{^1$H$\}$ NMR (81 MHz, acetonitrile-d_3): δ = 45.4 (s), −142.7 (sept., $^1J_{PF}$ = 707 Hz). ESI MS (methanol): m/z (rel. int.) = 437 (100) ½ [M + H]$^+$, 355 (15) ½ [M-Im^{NMe}]$^+$. MALDI-TOF-MS (methanol): m/z (rel. int.) = 437 (100) [M]$^+$. $C_{38}H_{40}N_8F_{12}P_4Ru_2$ (1162.81) calc. C 39.3, H 3.5, N 9.6; found C 39.6, H 3.9, N 10.0.

2.1.11. Synthesis of [{CpRu(μ-κ^2N,N:κ'^1P-**2b**)}$_2$](PF$_6$)$_2$ (**7b**)

50 mg (0.12 mmol) of [CpRu(NCCH$_3$)$_3$]PF$_6$ and **2a** (36 mg) were dissolved in acetonitrile and heated to gentle reflux for 24 h. The volatiles were removed in vacuo, the residue washed with n-hexane and diethyl ether and dried in vacuo. Yield 46 mg (67%). ^{1}H NMR (acetonitrile-d_3): δ = 4.91 (s, 5H Cp), 6.95 (s, 2H ImCH), 6.99 (s, 2H ImCH), 7.58–7.80 (m, 5H PPh). ^{31}P$\{^1$H$\}$ NMR (acetonitrile-d_3): δ = 44.4 (s), −143.4 (hept.). MALDI-TOF-MS (CH$_3$CN): m/z (rel. int.) = 816 [M]$^+$ (100), 574 (5), 468 (45), 453 [½ M + NCCD$_3$]$^+$ (30), 409 [½ M]$^+$ (80). $C_{36}H_{35}N_9P_4Ru_2F_{12}$ (1147.75): calc. C 37.7, H 3.1, N 11.0; found C 37.5, H 3.2, N 10.7.

2.1.12. Synthesis of [CpRu(κ^3N,N,N-**3b**)]Cl (**8**)

100 mg (0.138 mmol) of [CpRu(PPh$_3$)$_2$Cl] were dissolved in warm toluene. To the clear orange solution **3a** (38 mg, 0.14 mmol) was added. The solution was warmed to 100 °C and after 30 min a yellow solid precipitated. The reaction mixture was stirred at 100 °C for additional 3 h. After cooling to ambient temperature and filtration the solid was washed with small amounts of toluene and diethyl ether and dried in vacuo. Yield: 51 mg (78%). ^{1}H NMR (200 MHz, methanol-d_4): δ = 4.06 (s, 9H, NCH$_3$), 4.50 (s, 5H, Cp), 7.38 (dd, $^3J_{H,H}$ = 4.0 Hz, $^4J_{H,H}$ = 1.6 Hz, 3H, ImH5), 7.99 (s) (d, $^3J_{H,H}$ = 4.0 Hz, 3H, ImH4). ^{31}P$\{^1$H$\}$ NMR (81 MHz, methanol-d_4): δ = −116.5 (s). MALDI-TOF MS (rel. Int.) = 441 [M − Cl]$^+$ (100). $C_{17}H_{22}N_6ClPRu \cdot H_2O$ (493.90): calc. C 41.4, H 4.5, N 17.0; found C 41.7, H 4.7, N 16.7.

2.1.13. Synthesis of [CpRu(κP-**3a**)(PPh$_3$)Cl] (**9**)

100 mg (0.132 mmol) [CpRu(PPh$_3$)$_2$Cl] were dissolved in 20 mL toluene upon gentle heating. 32 mg (0.13 mmol) of **3a** were added

and the solution was stirred at 70 °C for 6 h. A greenish white solid was separated and the orange solution was subsequently reduced in vacuo. The orange residue was taken up in 2 mL dichloromethane. Column-chromatography on silica gel with dichloromethane and ethyl acetate respectively, gave the product as an orange solid. Yield: 55 mg (57%) ^{1}H NMR (200 MHz, methanol-d_4): δ = 4.54 (s, 5H, Cp), 7.08–7.34 (m, 21H, arom.). ^{31}P{^{1}H} NMR (81 MHz, methanol-d_4): δ = 46 (d, $^2J_{P,P}$ = 45 Hz), 4 (d, $^2J_{P,P}$ = 45 Hz). ESI MS (methanol): m/z (rel. int.) = 399 (100) [M-PPh$_3$Cl]$^+$. MALDI-TOF MS (methanol): m/z (rel. int.) = 399 (60) [M-PPh$_3$Cl]$^+$, 415 (15) [CpRu(2-TIPO^H)]$^+$. C$_{32}$H$_{31}$N$_6$ClP$_2$Ru·2H$_2$O (732.12): calc. C 52.5, H 4.5, N 11.5; found C 52.3, H 4.6, N 11.4.

2.2. General procedure for the catalytic hydration reaction

[RuCp(C$_{10}$H$_8$)]PF$_6$ (22 mg, 0.05 mmol) and the respective ligand (2.2 eq., 0.11 mmol) were dissolved in acetonitrile or dichloromethane, respectively. The solution was stirred at 60 °C over night. Removal of most of the solvent under vacuum and addition of diethyl ether or hexane resulted in the respective ruthenium complex as a fine yellow powder, which is dried under vacuum after filtration. This preformed, but not further purified ruthenium catalyst (0.05 mmol, 5 mol% catalyst loading) was dissolved in acetone (2 mL) and degassed 1-octyne (150 μL) and water (90 μL) were added to the solution. The reaction mixture was stirred at 60 °C in an oil bath. The progress of the reaction was monitored by GC.

2.3. X-ray crystallography

Crystallographic data of [{CpRu(μ-κ^2-N,N-κ'^{1}-P-**2b**)}$_2$](C$_6$H$_5$-PO$_3$H)$_2$(C$_6$H$_5$PO$_3$H$_2$)$_2$, [{CpRu(**2b**)}$_2$](PF$_6$)$_2$2CH$_3$CN (**7b**·2CH$_3$CN), [CpRu(**1a**)$_2$Cl]·H$_2$O (**5**·H$_2$O) and [CpRu(PPh$_3$)$_2$Cl]·CHCl$_3$ were collected at 183(2) K on an Oxford Diffraction Xcalibur system with a Ruby detector using Mo K$_\alpha$ radiation (λ = 0.7107 Å) that was graphite-monochromated. Suitable crystals were covered with oil (Infineum V8512, formerly known as Paratone N), mounted on top of a glass fibre and immediately transferred to the diffractometer. The program suite CrysAlis^{Pro} was used for data collection, multi-scan absorption correction and data reduction [37]. Structures were solved with direct methods using SIR97 [38] and were refined by full-matrix least-squares methods on F^2 with SHELXL-97 [39]. The structures were checked for higher symmetry with help of the program Platon [40]. The crystal of [{CpRu(**2b**)}$_2$](PF$_6$)$_2$2CH$_3$CN (**7b**·2CH$_3$CN) is non-merohedrally twinned. The two twin domains are related by a 180° rotation along uvw (0 0 1). Both domains (ratio 52:48) were integrated with the CrysalisPro software and refined as hklf5. Yellow crystals of **5**·H$_2$O were mounted on a glass fibre with a small amount of inert oil. Data collection was carried out at 100 K using an Oxford Diffraction Xcalibur diffractometer, equipped with

an EOS CCD area detector and a four-circle kappa goniometer using Mo-Kα radiation (λ = 0.71073 Å). Data integration, scaling and empirical absorption correction was carried out using the CrysAlis Pro program package [37]. The structure of was solved using Direct Methods and refined by Full-Matrix-Least-Squares against F^2. All non-hydrogen atoms positions were refined freely and simultaneously using anisotropic displacement parameters. The positional parameters of the hydrogen atoms of the CH groups were refined freely. The positional parameters of the hydrogen atoms of the NH groups were refined with soft N–H distance restraints and individual U$_{iso}$ values. The hydrogen atoms of the water molecule were refine with soft O-H and H-H distance restraints giving these hydrogen atoms a fixed isotropic displacement parameters. All calculations were carried out using the program SHELX97 [39]. Orange crystals of [CpRu(κ^{1}P-**3a**)(PPh$_3$)]Cl·CH$_2$Cl$_2$ (**9**·CH$_2$Cl$_2$) were mounted on a MiTeGen cryoloop with a small amount of inert oil. Data collection was carried out at 150 K using an Oxford Diffraction Gemini E Ultra diffractometer, equipped with an EOS CCD area detector and a four-circle kappa goniometer using Mo-Kα radiation (λ = 0.71073 Å). Data integration, scaling and empirical absorption correction was carried out using the CrysAlis Pro program package [37]. The structure was solved using Direct Methods and refined by Full-Matrix-Least-Squares against F^2. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed at idealised positions and refined using the riding model. All calculations were carried out using the program Olex2 [41]. Important crystallographic data and refinement details are summarised in Table 4. The crystallographic data has been deposited at the CCDC with the ref codes CCDC 820763, 828860, 828861, 837344 and 845941.

3. Results and discussion

3.1. Synthesis of PN ligands

Pyridin-2-ylphosphines are privileged hemilabile PN ligands in transition metal catalysis. Also, imidazole-2-ylphosphines are well-established ligands for transition metal complexes, e.g. Grotjahn et al. recently described the ability of imidazole-2-yldiphenylphosphine to act as a hemilabile PN ligand in Cp*Ir complexes [42] and Caballero et al. observed rearrangement of 1-methylimidazole-2-yldiphenylphosphine (**1b**) in complexes [(arene)Ru(**1b**)Cl$_2$] including P–C bond cleavage in this process

Table 1
Spectroscopic data of the synthesized ligands.

Ligand		δ (^{1}H)/ppm	δ (^{31}P)/ppm
4-MIP^{NMe}	(**1h**)[a]	3.73 (s, 3H, CH$_3$), 6.93 (t, 1H, CH), 7.31–7.42 (m, 10H, Ph), 7.80 (t, 1H, CH)	−22.8 (s)
4-MIP^{iPr,NMe}	(**1i**)[a]	1.34 (d, 6H, CH$_3$), 3.19 (m, 1H, CH), 3.63 (s, 3H, CH$_3$), 6.56 (s, 1H, CH), 7.36–7.84 (m, 10H, Ph)	−24.4 (s)
4-MIP^{tBu,NMe}	(**1j**)[b]	1.67 (s, 9H, CH$_3$), 3.91 (s, 3H, CH$_3$), 6.34 (s, 1H, CH), 7.42–8.09 (m, 10H, Ph)	−30.4 (bs)[c]
2-MIP^{diPh,NMe}	(**1c**)[b]	3.57 (s, 3H, CH$_3$), 7.15–7.74 (m, 20H, Ph)	−28.7 (s)

[a] in methanol-d_4.
[b] in CDCl$_3$.
[c] Mg-salt.

Table 2
^{31}P{^{1}H} NMR shifts of the ligands (δ_L) and the respective ruthenium complexes (δ_C) as well as the coordination shift $\Delta\delta = \delta_C - \delta_L$ (in methanol-d_4).

	δ_L (^{31}P)/ppm	δ_C (^{31}P)/ppm	$\Delta\delta$ (^{31}P)/ppm
CpRu(PPh$_3$)(L)Cl			
2-MIP^H (**1a**)	−23.8	45.0; 29.3	68.8
2-MIP^{NMe} (**1b**)	−29.6	42.5; 27.6	64.3
4-MIP^{iPr} (**1d**)	−24.4	45.0; 30.4	73.0
CpRu(L)$_2$PF$_6$			
2-MIP^H (1a)	−24.8	31.7	56.5
2-MIP^{NMe} (1b)	−30.6	29.3	60.0
4-MIP^{iPr} (1d)	−24.4	31.3	55.7

Table 3
^{31}P{^{1}H} NMR data of [CpRu(PPh$_3$)(**1d**)Cl] (**4**) in different solvents.

Solvent	δ_{PPh_3} (^{31}P)/ppm	$^2J_{PP}$/Hz	δ_{1d} (^{31}P)/ppm	$^2J_{PP}$/Hz
C$_6$D$_6$	45.8	43	25.3	43
CDCl$_3$	44.1	43	26.1	43
(CD$_3$)$_2$CO	44.4	43	23.8	43
CD$_3$OD	52.8	39	−5.1	39

Table 4
Crystallographic data for [CpRu(**1a**)$_2$Cl]·H$_2$O (**5**·H$_2$O), [{CpRu(μ - κ ^{2}-N,N- κ'^{1}-P-**2b**)}$_2$](PF$_6$)$_2$CH$_3$CN (**7b**·CH$_3$CN), [{CpRu(μ - κ ^{2}-N,N- κ'^{1}-P-**2b**)}$_2$](C$_6$H$_5$PO$_3$H)$_2$(C$_6$H$_5$PO$_3$H$_2$)$_2$, [CpRu(κ^{1}P-**3a**)(PPh$_3$)]Cl·CH$_2$Cl$_2$ (**9**·CH$_2$Cl$_2$) and [CpRu(PPh$_3$)$_2$]Cl·CHCl$_3$.

Compound	5·H$_2$O	7b·CH$_3$CN	[{CpRu(2b)}$_2$] (C$_6$H$_5$PO$_3$H)$_2$(C$_6$H$_5$PO$_3$H$_2$)$_2$	9·CH$_2$Cl$_2$	[CpRu(PPh$_3$)$_2$]Cl ·CHCl$_3$
Empirical formula	C$_{35}$H$_{33}$ClN$_4$OP$_2$Ru	C$_{42}$H$_{46}$F$_{12}$N$_{10}$P$_4$Ru$_2$	C$_{62}$H$_{66}$N$_8$O$_{12}$P$_6$Ru$_2$	C$_{33}$H$_{31}$Cl$_3$N$_6$P$_2$Ru	C$_{42}$H$_{36}$Cl$_4$P$_2$Ru
Formula weight	724.11	1244.91	1503.19	781.00	845.52
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic	Triclinic
Space group	P2$_1$/n	P2$_1$/c	P-1	P2$_1$/c	P-1
a [Å]	9.35991(13)	12.1695(4)	11.35775(17)	14.6359(6)	10.0331(3)
b [Å]	19.4751(3)	13.8697(6)	12.3482(2)	8.3887(3)	13.8107(5)
c [Å]	17.2255(3)	13.9362(5)	13.2800(3)	27.1301(12)	14.4657(5)
α [°]	90.00	90.00	117.0250(19)	90.00	100.141(3)
β [°]	93.3452(13)	96.327(3)	104.5021(15)	96.813(4)	106.935(3)
γ [°]	90.00	90.00	91.1715(13)	90.00	99.411(3)
Volume [Å^3]	3134.61(8)	2337.93(15)	1586.69(5)	3307.4(2)	1837.79(11)
Z	4	2	1	4	2
Density (calculated) [Mg/m^3]	1.534	1.768	1.573	1.568	1.528
Absorption coefficient [mm^{-1}]	0.724	0.876	0.696	0.848	0.836
F(000)	1480	1248	768	1584	860
Crystal size [mm^3]	0.47 × 0.11 × 0.10	0.19 × 0.14 × 0.04	0.37 × 0.23 × 0.16	0.14 × 0.07 × 0.05	0.20 × 0.12 × 0.05
Crystal description	Yellow needle	Orange plate	Yellow block	Orange needle	Orange plate
Theta range for data collection [°]	5.15 to 25.00	2.57 to 30.51	2.95 to 36.32	2.95 to 29.5	2.61 to 30.51
Index ranges	−11 ≤ h ≤ 7, −23 ≤ k ≤ 23, −20 ≤ l ≤ 20	−17 ≤ h ≤ 17, −19 ≤ k ≤ 19, −19 ≤ l ≤ 19	−18 ≤ h ≤ 18, −20 ≤ k ≤ 20, −22 ≤ l ≤ 22	−18 ≤ h ≤ 19, −11 ≤ k ≤ 11, −36 ≤ l ≤ 34	−14 ≤ h ≤ 14, −19 ≤ k ≤ 17, −20 ≤ l ≤ 18
Reflections collected	19160	24410[a]	59543	21611	20943
Independent reflections	5465 [R(int) = 0.0407]	24410[a]	15362 [R(int) = 0.0247]	7893 [R(int) = 0.0406]	11219 [R(int) = 0.0328]
Reflections observed	4671	18628	13058	6313	7958
Criterion for observation	>2sigma(I)	>2sigma(I)	>2sigma(I)	>2sigma(I)	>2sigma(I)
Completeness to theta	99,1% to 25.00°	99.9% to 30.51°	99.8% to 36.32°	99.74% to 26.32°	99.9% to 30.51°
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.9554 and 1.0	0.9658 and 0.8980	0.8968 and 0.8362	1.0000 and 0.8779	0.9594 and 0.8045
Data/restraints/parameters	5465/5/499	24410/0/320	15362/0/412	7893/0/406	11219/0/442
Goodness-of-fit on F^2	1.097	1.032	1.116	1.021	0.899
Final R indices [I > 2sigma(I)]	R1 = 0.0307, wR2 = 0.0631	R1 = 0.0454, wR2 = 0.1232	R1 = 0.0271, wR2 = 0.0772	R1 = 0.0376, wR2 = 0.0805	R1 = 0.0360, wR2 = 0.0627
R indices (all data)	R1 = 0.0397, wR2 = 0.0658	R1 = 0.0624, wR2 = 0.1303	R1 = 0.0336, wR2 = 0.0786	R1 = 0.0528, wR2 = 0.0838	R1 = 0.0601, wR2 = 0.0657
Largest diff. peak and hole [e.Å^{-3}]	0.457/−0.484	1.109 and −0.844	0.797 and −0.595	0.714 and −0.649	0.715 and −0.853
CCDC number	845941	837344	828860	820763	828861

[a] Due to the twin integration, there are no independent reflections.

[43]. We synthesised several series of imidazole-based phosphine ligands in the last few years for biomimetic model complexes and metallo-drugs [33,34,44–47]. Here, these ligands as well as some new PN ligands, as depicted in Fig. 1, were used in CpRu-complexes, which should catalyse the hydration of alkynes.

Especially imidazole derivatives with bulky groups such as iso-propyl, phenyl or *tert*-butyl in ortho-position to the imine N atom were chosen since they are known to prevent κ^{2}PN-coordination [30]. Furthermore, ligands without sterically demanding groups

such as 1-methylimidazole-4-yldiphenyl phosphine (**1h**) were synthesized.

The reaction scheme for the synthesis of the new imidazol-4-yl phosphine ligands **1h**–**j** is shown in Scheme 1. The respective imidazole is converted to the 4,5-diiodoimidazole derivative by KI/I$_2$ in basic solution. Reaction of the 4,5-diiodoimidazole derivative with methyl iodide leads to the N-methylated imidazole derivative, which is then converted in two consecutive Grignard reactions to the respective 1-methylimidazol-4-yldiphenyl phosphine.
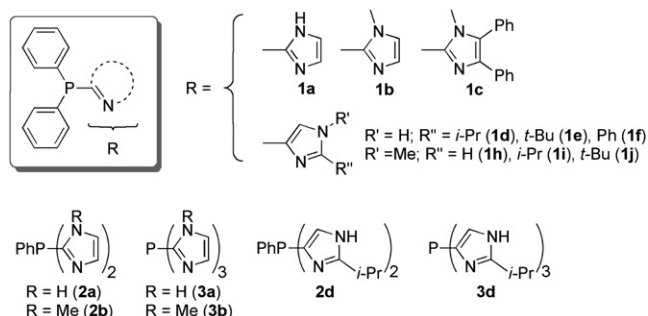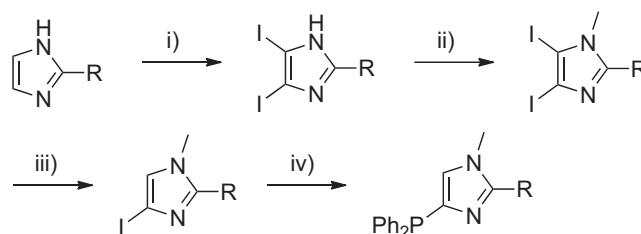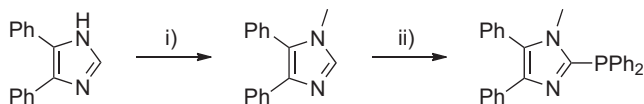

Fig. 1. Imidazol-2-yl- and imidazol-4-yl-phosphine ligands used.

Scheme 1. General route for the synthesis of 1-methylimidazol-4-yldiphenyl-phosphines **1h**–**j** (4-MIP^{NMe}'s), i) I$_2$/KI in aq. NaOH, ii) KOtBu, MeI, thf, iii) EtMgBr, H$_2$O, thf, iv) EtMgBr, Ph$_2$PCl, thf.

Scheme 2. Route for the synthesis of 1-Methyl-4,5-diphenylimidazol-2-yl-diphenyl-phosphine (2-MIP^{diPhNMe}, **1c**): i) KOtBu, MeI, thf, ii) n-BuLi, Ph$_2$PCl, thf.

All steps, including the first Grignard reaction, proceed in good yields, whereas the second Grignard reaction raised some problems. The product was obtained as the magnesium complex, since magnesium coordinates strongly to the imidazole N atom(s). This problem of magnesium adduct formation has already been addressed by Kluwer in the preparation of pyridinylphosphines [48]. Repeated alternating stirring in ethanol, spiked with hydrochloric acid, or ammonia-saturated dichloromethane led to isolation of the ligands 1-methylimidazol-4-yldiphenylphosphine (**1h**) and 1-methy-2-isopropylimidazole-4-yldiphenylphosphine (**1i**). In the case of 1-methyl-2-tert-butylimidazole-4-yldiphenylphosphine (**1j**), even after repeated crystallisation from ethanol, the MgBr$_2$ adduct was obtained.

In addition to the three 1-methylimidazol-4-yl phosphine ligands **1h**–**j**, 1-methyl-4,5-diphenylimidazol-2-yl-diphenylphosphine (**1c**) was synthesized as a new imidazole-2-yl ligand bearing bulky phenyl substituents (Scheme 2). The methylation of 4,5-diphenylimidazol is carried out using methyl iodide. Subsequent lithiation with n-butyllithium and addition of diphenylchlorophosphine leads to the 1-methyl-4,5-diphenylimidazol-2-yl-diphenylphosphine ligand in very good yields. Since lithium does not coordinate as strongly to the imidazole nitrogen atoms as magnesium, the separation of the lithium salts from the ligand is easily accomplished by stirring the crude product with ammonia-saturated dichloromethane followed by filtration.

Spectroscopic data of the four new ligands **1c,h**–**j** is summarized in Table 1. The chemical shifts observed in the ^{31}P NMR spectra are in the typical regime for monoimidazolyldiphenyl phosphines (MIPs) [45,49].

3.2. Synthesis of CpRu-complexes with PN ligands

We exemplarily investigated the basic coordination chemistry of some of the presented imidazole-based PN ligands towards CpRu(II). As ruthenium(II) precursor compounds we used [CpRu(C$_{10}$H$_8$)]PF$_6$, [CpRu(NCMe)$_3$]PF$_6$ and [CpRu(PPh$_3$)$_2$Cl] (Scheme 3).When [CpRu(PPh$_3$)$_2$Cl] was reacted with **1b** at room temperature for three weeks, only one PPh$_3$ ligand was replaced by **1b** yielding [CpRu(PPh$_3$)(**1b**)Cl], as is indicated by two doublets in the ^{31}P NMR spectrum (Table 2). These appeared only in small quantities in addition to signals of the starting materials and free triphenylphosphine. However, reaction of **1b** with the more labile complex [CpRu(NCCH$_3$)$_3$]PF$_6$ in dichloromethane yielded the complex [CpRu(**1b**)$_2$(solvent)]PF$_6$ which exhibits a single singlet in the ^{31}P NMR spectrum at 38 ppm. Both ^{1}H NMR and MALDI mass
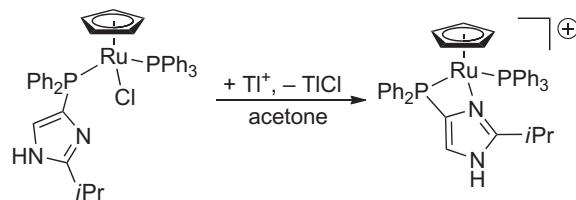

**Scheme 4.** Reaction of [CpRu(PPh$_3$)(**1d**)Cl] (**4**) with TlNO$_3$ in acetone gives a PN chelate.

spectra are also in accordance with the proposed formula. The reaction of two equivalents of **1a** with [CpRu(PPh$_3$)$_2$Cl] below 70 °C in toluene gives [CpRu(**1a**)$_2$Cl] (**5**) by substitution of both PPh$_3$ ligands (singlet, δ (^{31}P) = 31.7 ppm). Minor contamination of the mono-substituted complex (doublet, δ (^{31}P) = 45.0, 29.3 ppm, J = 44 Hz) ligands were transformed into [CpRu(**1a**)$_2$Cl] (**5**) by addition of a slight excess of **1a**. When the reaction mixtures of [CpRu(PPh$_3$)$_2$Cl] and the NH-ligand **1a** were heated above 90 °C, doublets at 120 and 50 ppm in the ^{31}P{^{1}H} NMR spectra were observed. The reaction with one or two equivalents of **1d** gives [CpRu(PPh$_3$)(**1d**)Cl] (**4**) and [CpRu(**1d**)$_2$Cl] (**6**), respectively. For the latter we were not able to obtain a sufficient CHN analysis, although ^{1}H and ^{31}P{^{1}H} NMR and MALDI-TOF mass spectrometry clearly demonstrate the existence of [CpRu(**1d**)$_2$Cl] (**6**). The compound [CpRu(PPh$_3$)(**1d**)Cl] (**4**) shows, as expected, two signals in the ^{31}P NMR spectrum. In non-coordinating or weakly coordination solvents the resonances are found at 45 and 25 ppm with a $^2J_{PP}$ coupling constant of 43 Hz. In the more strongly coordination solvent methanol, which is a good solvent for the solvation of chloride, the resonances are shifted to 53 and −5 ppm with a coupling constant of 39 Hz (Table 3). Especially the high-field shift of the resonance of the P-atom of the ligand **1d** from about 25 to −5 ppm is typical for the change in the coordination mode of the ligand from κP to $\kappa^2 PN$ [50]. This can also be forced in acetone by abstraction of the chloride ligand upon addition of TlNO$_3$ (Scheme 4 and ESI).

The reaction of **2a** with [CpRu(PPh$_3$)$_2$Cl] or [CpRu(NCCH$_3$)$_3$]PF$_6$ gave a single product with a singlet at 45 ppm in the ^{31}P{^{1}H} NMR spectrum and one set of the protons of the methyl groups (singlet at 3.09 ppm), the Cp protons (singlet at 5.23 ppm) and the imidazolyl protons (two doublets at 6.79 and 7.13 ppm) in the ^{1}H NMR, respectively. The most intense signal in the MALDI spectrum is found at m/z = 437 and shows an isotopic pattern characteristic for a compound with two ruthenium atoms and thus a charge of +2. Additionally, a peak with small intensity is found at 874. This is in accordance with a dimeric structure (Scheme 5), which was confirmed by single crystal analysis (see below).

The tripodal tetradentate ligands **3a** and **3b** react with [CpRu(PPh$_3$)$_2$Cl] at elevated temperatures and prolonged reaction times to complexes in which the CpRu-moiety is facially bound by the tripodal ligands in a $\kappa^3 N,N,N$ coordination mode (Scheme 6). The coordination mode can be deduced by the typical high-field
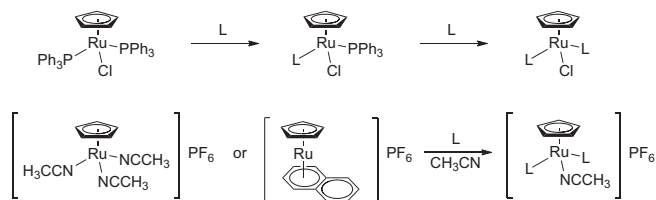
Scheme 3. Reaction of ligands (L) **1a**, **1b** and **1d** with [CpRu(PPh$_3$)$_2$Cl] and [CpRu(NCCH$_3$)$_3$]PF$_6$ or [CpRu(C$_{10}$H$_8$)]PF$_6$.
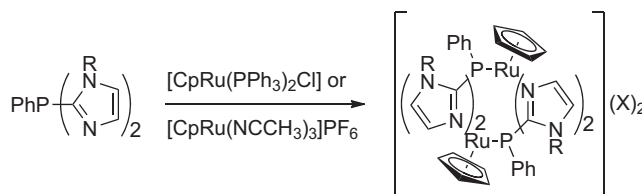
Scheme 5. Reaction of [CpRu(PPh$_3$)$_2$Cl] or [CpRu(NCCH$_3$)$_3$]PF$_6$ with 2-BIP^{NH} (**2a**) and 2-BIP^{NMe} (**2b**) to complexes **7a/b** (X = PF$_6$).
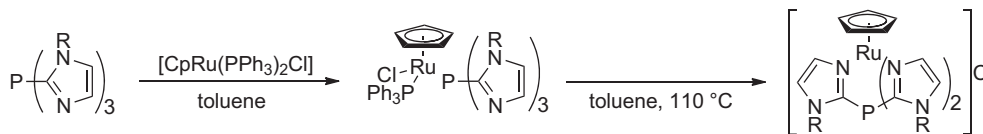
Scheme 6. Reaction of [CpRu(PPh₃)₂Cl] with 2-TIP^{NH} (R = H, **3a**) and 2-TIP^{NMe} (R = Me, **3b**).

shift of the phosphorus resonance of 40–60 ppm to about −110 ppm in κ³N,N,N complexes of these ligands.

At 70 °C and in the non-protic solvent toluene the reaction of **3a** with [CpRu(PPh₃)₂Cl] leads to substitution of only one PPh₃ ligand, which can easily be observed in the ³¹P NMR spectra of the reaction mixture. Two doublets occur for the new species [CpRu(PPh₃)(**3a**) Cl] (**9**) with $^2J_{P,P}$ values of ~50 Hz. This product is also obtained from a reaction of the starting material with 2 equivalents of ligand **3a**. Recrystallisation from chloroform yielded a crystal suitable for single crystal analysis (see below).

3.3. Solid-state structures

Crystals of [CpRu(**1a**)₂Cl]·H₂O (**5**·H₂O) suitable for single crystal structure determination were obtained by slow evaporation of a chloroform solution at air. The CpRu center is coordinated octa-hedral by the η⁵-Cp ligand, a chlorido ligand and two κP-coordi-nated ligands **1a**. Both ligands **1a** form NH⋯Cl hydrogen bonds towards the coordinated chlorido ligand and one is also involved in hydrogen bonding to the co-crystallised water molecule (Fig. 2). The structural motif in [CpRu(**1a**)₂Cl]·H₂O (**5**·H₂O) resembles the one found in [CpRu(L)₂(H₂O)]CF₃SO₃ (L = 1-methyl-3-*tert*.butyldi-phenyl phosphine) [28].

Crystals of [{CpRu(μ-κ²N,N:κ¹P-**2b**)}₂](PF₆)₂CH₃CN (**7b**·CH₃CN) suitable for single crystal structure determination were obtained by slow diffusion of *n*-hexane into a solution of **7b** in acetonitrile. Here ligand **2b** acts as bridging ligand between two CpRu centers (Fig. 3). Such a bridging μ-κ²N,N:κ¹P-coordination mode has tentatively been assigned to the phenylbis(pyridin-2-yl)phosphine ligand (PhPpy₂) in the compound [Mo(CO)₃(PhPpy₂)], which is thought to be a coordination polymer and not a cyclic dimer [51]. In the [{CpRu(μ-κ²N,N:κ¹P-**2b**)}₂]²⁺ cation the coordination geometry of the Ru(II) atoms in the {CpRu(**2b**)} unit is distorted octahedral with a facially bound η⁵-Cp ligand and the P atom of the **2b** ligand as well as two N atoms of the **2b** ligand of the other unit of the {CpRu(**2b**)}₂ dimer. In one crystallisation experiment under non

inert conditions from the reaction solution of [CpRu(PPh₃)₂Cl] together with **2b**, we found yellow crystals of [{CpRu(μ - κ ²-N,N-κ'¹-P-**2b**)}₂](C₆H₅PO₃H)₂(C₆H₅PO₃H₂)₂ which crystallized in the triclinic space group *P*-1 (see ESI). Additionally, we found red crystals of a chloroform solvate of [CpRu(PPh₃)₂Cl] which crystal-lises in the triclinic space group *P*-1 (see ESI). Obviously, **2b** partially hydrolysed under P-C bond cleavage and oxidized to give the phenylhydrogenphosphonate counter ion and the phenyl-dihydrogenphosphonate respectively. Both structures have essen-tially an identical cationic part. Only the cyclopentienyl and the phenyl ring are conformational slightly twisted along the ruthe-nium - cyclopentadienyl centroid and the ispo - para atoms of the phenyl ring respectively.

Red crystals of [CpRu(κ¹P-**3a**)(PPh₃)]Cl·CH₂Cl₂ (**9**·CH₂Cl₂) were obtained by crystallisation from chloroform. The compound crys-tallizes in the monoclinic space group *P*2₁/c. Two of the three H atoms of the NH-functionalities of the ligand **3a** form intra-molecular hydrogen bonds towards Cl1. Another intramolecular hydrogen bond N-H$_{\ddot{A}}$·N$_{1AA}$ results in the formation of a nearly coplanar six-membered ring (Fig. 4). The metric parameters are within the range found in phosphine complexes of the type [CpRu(L)₂Cl] [52–55].

3.4. Catalytic trials with CpRu-based complexes of PN ligands

Grotjahn et al. described the catalytic activity of the complex [CpRu(L)₂(NCCH₃)]PF₆ with the PN ligand 2-diphenylphosphino-6-tert-butylpyridine (L) in the hydration of several terminal alkynes to give up to 99.9% yield within 3 h with a catalyst loading of just 2 mol-% [27].

We used a protocol established for the catalytic hydration of ruthenium(II) pyridinyl phosphine complexes and [CpRu(NCCH₃)₃] PF₆ as well as [CpRu(C₁₀H₈)]PF₆ for the preparation of compounds
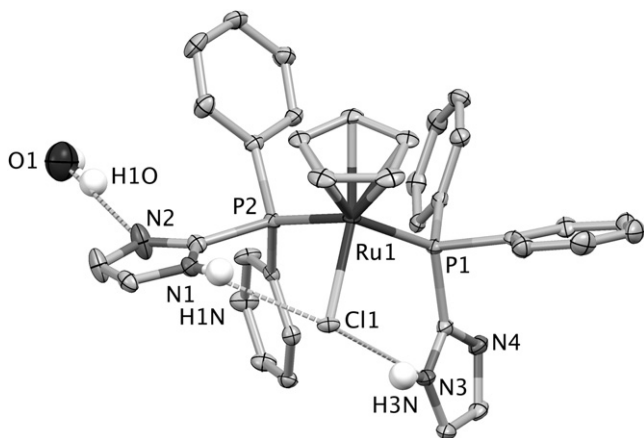
Fig. 2. Solid-state structure of [CpRu(**1a**)₂Cl]·H₂O (**5**·H₂O). Displacement ellipsoids are drawn at 50% level. Hydrogen atoms are drawn at arbitrary radius and non-acidic hydrogen atoms are omitted for clarity.
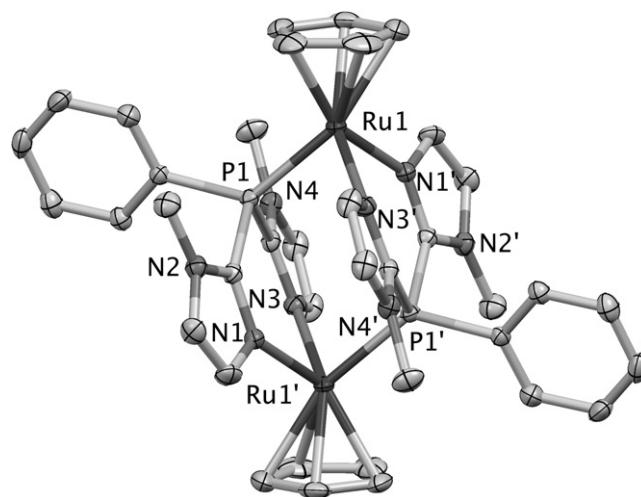

Fig. 3. Solid-state structure of the cation [{CpRu(μ-κ²-N,N-κ'¹-P-**2b**)}₂]²⁺ in [{CpRu(μ - κ ²-N,N- κ'¹-P-**2b**)}₂](PF₆)₂CH₃CN (**7b**·CH₃CN). Displacement ellipsoids are drawn at 50% level. The counter ions, cocrystallized solvent molecules and hydrogen atoms are omitted for clarity.
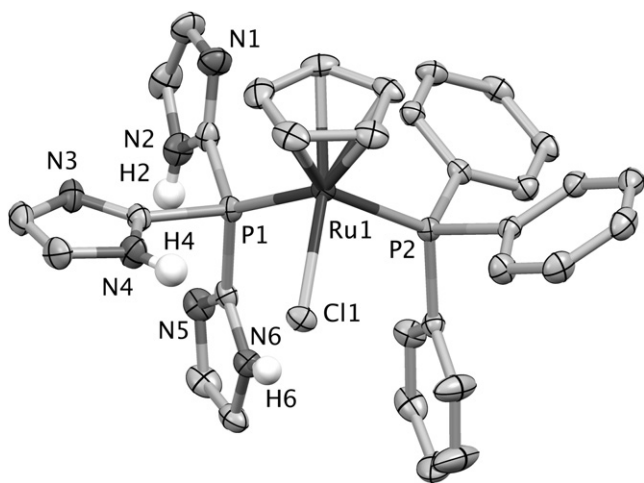
Fig. 4. Solid-state structure of [CpRu(κ^1P-**3a**)(PPh$_3$)]Cl·CH$_2$Cl$_2$ (**9**·CH$_2$Cl$_2$). Displacement ellipsoids are drawn at 50% level. Hydrogen atoms are drawn at arbitrary radius and non-acidic hydrogen atoms are omitted for clarity.

of the type [CpRu(L)$_2$(NCCH$_3$)]PF$_6$ [25,56]. The corresponding CpRu-precursor and two equivalents of the corresponding ligand were stirred at 60 °C in an oil bath over night (monitored by ^{31}P NMR, see ESI). The results of the various catalytic hydration reactions with different ligands were unexpectedly disappointing (for details see ESI). None of the investigated complexes showed substantial catalytic activity in the hydration of 1-octyne. The highest conversion with 9% after 22 h at 60 °C was found in a trial with [CpRu(C$_{10}$H$_8$)]PF$_6$ and 4-MIP^{iPrNMe} (**1i**) at a catalyst loading of 5 mol%.

4. Conclusions

We prepared CpRu-complexes with imidazole-based PN ligands. Three types of coordination modes for the PN ligands have been found in the corresponding CpRu complexes: κ^1P-monodentate, κ^2P,N-, κ^2N,N- and κ^3N,N,N- chelating and μ-κP:κ^2N,N-brigding. We have screened 11 imidazole-based PN ligands in the CpRu(II)-catalysed hydration of 1-octyne. Although the observed conversion rates are low to zero, some complexes show high selectivity for the formation of aldehyde over ketone. When poly(imidazolyl) ligands are used, the formation of coordinatively saturated complexes seems to prevent catalytic activity. The conditions for the catalytic trials will be further explored, as Hintermann et al. recently described a procedure for hydration reactions of alkynes in water/acetone as solvent [25].

Appendix. Supplementary material

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2011.10.006.

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