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3-Aminoquinazoline–phosphine ligands and their ruthenium(II) complexes: application in catalytic hydrogenation and transfer hydrogenation reactions

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Abstract
3-Aminoquinazolinone–phosphine proligands (**5a**–**e**) and their Ru(II) complexes (**6a**–**e**) were prepared and characterized by NMR (^{1}H, ^{13}C, ^{31}P{^{1}H}), FTIR and microanalysis. The 3-aminoquinazolinone–phosphine ligands were found to coordinate with the Ru(II) center via their phosphorus and nitrogen atoms. The Ru(II) complexes were applied as catalysts for the hydrogenation and transfer hydrogenation of prochiral ketones. The results showed that these complexes are efficient transfer hydrogenation catalysts.

Introduction

Ruthenium(II) complexes and their catalytic applications are important in the synthesis of biologically active compounds for pharmaceutical, natural and industrial applications [1]. Hydrogenation is one of these applications and serves as a useful method for the reduction of carbonyl compounds to their corresponding secondary alcohols. Hydrogenation is generally performed by two methods [2–4]. The first procedure uses high pressure with molecular H_2 [5], while the second is performed using isopropyl alcohol or formic acid as the hydrogen source [6]. The second method is eco-friendly, is safer and shows high selectivity compared to hydrogenation methods involving high pressure. The hydrogenation reactions are carried out in the presence of transition metal catalysts, whose efficiency is a critical factor in securing high product yields. Phosphine ligands are known to increase the catalytic activity of hydrogenation reactions [7–9]. In particular, after Noyori's research on hydrogenation with the chiral P_2N_2 ligand, researchers have continued to explore the use of ligands which combine soft phosphorus and hard nitrogen atoms. Such PN-based ligands and their metal complexes, especially ruthenium complexes, act as catalysts and are applied in hydrogenation and transfer hydrogenation reactions to reduce or saturate organic compounds [10–13].

In the present study, 3-aminoquinazolinones were synthesized from α-hydroxy acids or α-amino acids, as described in the literature [14], and 3-aminoquinazolinone–phosphine proligands were obtained by the reactions of 2-(diphenylphosphino)benzaldehyde with these 3-aminoquinazolinones. The corresponding $Ru(PN)_2Cl_2$ (**6a**–**e**) complexes were synthesized from these iminophosphine proligands (**5a**–**e**). Spectroscopic analysis showed that the 3-aminoquinazolinone–phosphine proligands coordinate the Ru(II) center via their phosphorus and nitrogen atoms. All the $Ru(PN)_2Cl_2$ complexes were investigated as catalysts for hydrogenation and transfer hydrogenation (TH) reactions as catalysts.

Results and discussion

3-Aminoquinazolinones (**4a**–**e**) were prepared from L-lactic acid **1a**, L-mandelic acid **1b**, L-valine **1c**, L–*t*-leucine **1d** and L-phenyl alanine **1e** via a three step synthesis [15, 16] (Scheme 1).

The 3-aminoquinazolinone–phosphine proligands (**5a**–**e**) were synthesized by reaction of 2-(diphenylphosphino)benzaldehyde with 3-aminoquinazolinones (**5a**–**e**) as shown in Scheme 2. They were characterized by elemental analysis, FTIR, and ^{1}H, ^{13}C, ^{31}P{^{1}H} NMR spectroscopy.

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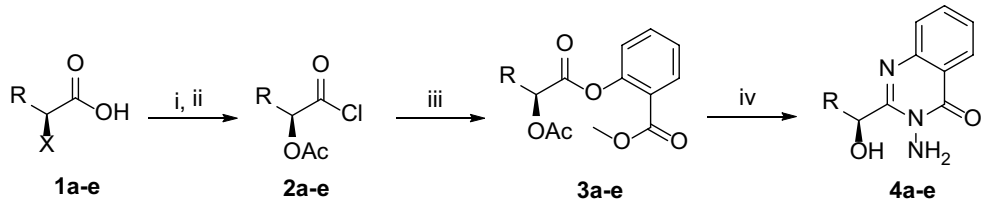
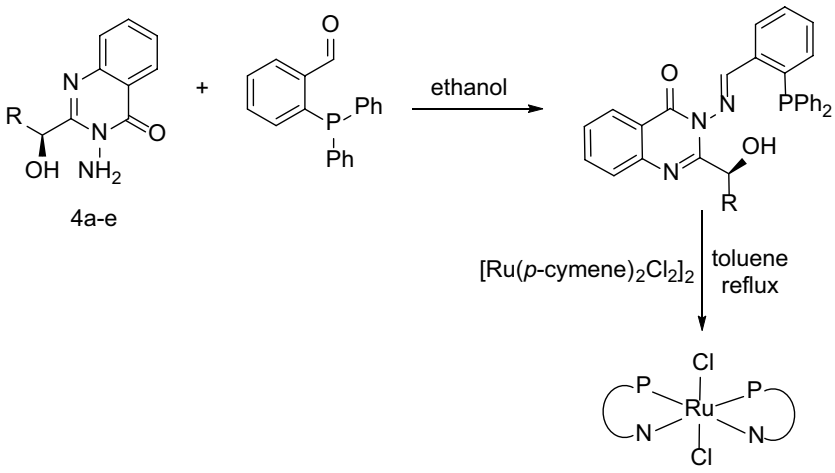


R= Me, X=OH **(a)**; R= Ph, X= NH_2 **(b)**; R= ^{i}Pr, X=NH_2 **(c)**
R= ^{t}Bu, X=NH_2 **(d)**; R= Bn, X=OH **(e)**

Scheme 1 Preparation of the 3-aminoquinazolinones **4a–e**. i) 4.0 equiv. AcCl (for **1a** and **1b**); 4.0 equiv. $NaNO_2$, AcOH (for **1c–e**), RT; ii) 3.0 equiv. $SOCl_2$, DMF, RT; iii) 2.2 equiv. methyl 2-aminobenzoate, Et_2O, RT; iv) 5.0 equiv. NH_2NH_2, EtOH, 150 °C

Scheme 2 Preparation of the 3-aminoquinazolinone–phosphine proligands and their Ru(II) complexes



5a R= CH_3
5b R= Ph
5c R= ^{i}Pr
5d R= ^{t}Bu
5e R= Bn

6a R= CH_3
6b R= Ph
6c R= ^{i}Pr
6d R= ^{t}Bu
6e R= Bn

In the IR spectra of the free proligands, peaks due to the ν(N–H) and ν(C = O) stretching vibrations of the amines and aldehydes were absent, being replaced by the imine group ν(N = CH) stretching at 1607–1603 cm^{-1} (1607 (**5a**), 1603 (**5b**), 1607 (**5c**), 1606 (**5d**) and 1606 (**5e**) cm^{-1}). The corresponding ν(N = CH) stretching vibrations of the Ru(II) complexes were observed at 1603–1569 cm^{-1}, indicating that Ru is coordinated by the imine nitrogen [17]. The P-Ph bands for the Ru(II) complexes (**6a–e**) were observed at 1436–1472 cm^{-1} [18, 19]. In the ^{1}H NMR spectra of the proligands, multiplets at 8.56–7.00 ppm were assigned to the phenyl protons. The azomethine protons (HC = N) appeared at 9.88 (**5a**), 9.59 (**5b**), 9.90 (**5c**), 10.00 (**5d**) and 9.92 (**5e**) ppm as a doublet, with a coupling constant of around J_{PH} = 6.0 Hz; the peak was shifted downfield to 9.83–10.90 ppm as a singlet after coordination to the Ru(II) center. Peaks at different values around at 5.30–1.62 ppm were assigned to the OH protons of both the free proligands and their complexes [20]. In the ^{13}C NMR spectra, azomethine carbons of the proligands were observed between 165.0 and 166.0 ppm, while the aromatic carbon signals were observed at 159–117 ppm. The ^{31}P NMR spectra of all of these 3-aminoquinazolinone–phosphine proligands show a single peak, shifted upfield compared to 2-(diphenylphosphino)benzaldehyde at − 15.35 (**5a**), − 16.26 (**5b**), − 16.18 (**5c**), − 16.35 (**5d**) and − 15.44 (**5e**) ppm [21, 22]. The ^{31}P NMR spectra of the Ru(PN)Cl_2 complexes were observed at 59.60 (**6a**), 59.61 (**6b**), 52.57 (**6c**), 61.00 (**6d**) and 59.62 ppm (**6e**). Hence, the ^{31}P NMR peaks were shifted downfield upon complexation, consistent with coordination of the P atoms to the metal [23, 24]. Overall, the spectroscopic data clearly showed that the ligands do not coordinate to the metal via the aliphatic hydroxide, which would confer chirality on the complexes, despite the fact that the reactions were carried out at different temperatures with several bases. On the other hand, from the ^{31}P NMR spectra of **6a–e**, the peaks observed at 26.71–26.97 ppm showed that the phosphorus was partially oxidized during the purification of the compounds or the NMR measurements.

Transfer hydrogenation reactions

For a series of complexes, both the chemical nature of the substituents and their positions can influence their catalytic activities. Therefore, a series of Ru(II) complexes, substituted with both aliphatic and aromatic groups having

different electronic and steric effects on the 3-aminoquinazolinone skeleton, were investigated in transfer hydrogenation reactions. To evaluate the efficiency of these Ru(II) complexes (**6a–e)** for transfer hydrogenation reactions, we have chosen acetophenone as a model substrate. Normally, in a typical transfer hydrogenation reaction, a base is used for generation of a highly active dihydride complex. This serves to deprotonate the isopropyl alcohol, resulting in an alkoxide ion that undergoes β-elimination at the Ru–H active center [2]. In order to determine the effect of base on the transfer hydrogenation reaction, we examined both inorganic and organic bases (NaOH, KO^{t}Bu and Et_3N). We did not obtain significant yields with KO^{t}Bu or Et_3N; however, NaOH gave acceptable yields. When the reaction was carried out in the absence of a base, no products were obtained.

The reaction temperature is an important parameter for the transfer hydrogenation of prochiral ketones, so we also tested different temperatures (82, 60, 40 and 25 °C). For the reaction with NaOH in 2-propanol, as the temperature was decreased from 82 °C to room temperature, both the yield and conversion decreased dramatically, such that poor results were obtained at low temperatures. Subsequent experiments were therefore carried out at 82 °C (Scheme 3).

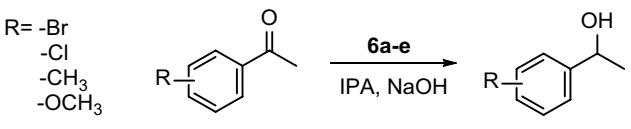
Our first investigation was into the reduction of bromo- and chloro-acetophenones with electron-withdrawing groups to secondary alcohols. Bromo-acetophenones were reduced to the corresponding secondary alcohols in good yields at 82 °C (Table 1, entries 4, 5 and 6). The same situation was observed with chloro-acetophenones, as shown in Table 1 entries 7–9. The electron-withdrawing effect of these groups reduces the electron density on the carbonyl group, increasing the affinity of the active ruthenium center for the substrate and so accelerating the catalytic reaction. As expected, the transfer hydrogenation of acetophenones with ring activating methyl and methoxy groups on the aromatic ring gave moderate yields (Table 1, entries 10 and 11). It can be concluded that electron-donating groups on the aryl ring of the ketones tend to slow the catalytic hydride transfer [2, 25].

Hydrogenation reactions

The Ru(II) complexes (**6a–e**) were also investigated for the hydrogenation of various acetophenones. Preliminary optimization of the reaction conditions was investigated for the hydrogenation of acetophenone. The system was initially investigated under 10 bar H_2 pressure for 24 h using 1% mol of complex **6a.** The results are presented in Table 2.

The use of ethanol or isopropanol as solvent failed to achieve a significant conversion. However, when methanol was used as solvent, the activity of the catalysts was increased, which can be explained by the higher polarity ($\varepsilon_{EtOH} = 25$, $\varepsilon_{iPrOH} = 20$ and $\varepsilon_{MeOH} = 33$) [26]. As given in Table 2, under 10 bar hydrogen pressure, the reduction of acetophenone to secondary alcohol gave very low yield. Therefore, in order to improve the yield, the hydrogen pressure was increased to 40 bar. Herein, we chose a substrate to catalyst (S/C) ratio of 100/1 and the racemic products were analyzed by GC (Table 3).

As shown in Table 3, different yields were obtained from the hydrogenation of acetophenone (72%), 2-methoxyacetophenone (99 and 97%) and 3-methoxyacetophenone (95%, entries 4, 6, 10 and 12) under 40 bar H_2 pressure. We conclude that long reaction times and high pressures of H_2 are required for optimum yields.



Scheme 3 Catalytic transfer hydrogenation of acetophenone derivatives

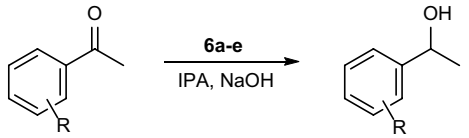
Experimental

Materials and methods

All reactions were carried out under an inert atmosphere using conventional Schlenk glassware. Solvents were dried using established procedures and then immediately distilled under argon prior to use [27]. The 3-aminoquinazolinones [15, 16] and 2-(diphenylphosphino)benzaldehyde [28] were prepared as described in the literature. Microanalyses were obtained with a LECO CHNS 932 instrument. IR spectra were recorded with a PerkinElmer RX1 spectrophotometer in the range between 4000 and 650 cm^{-1}. All ^1H NMR (400.1 MHz) and $^{31}P\{^1H\}$ NMR (162.0 MHz) spectra were recorded at 25 °C with DMSO-d_6 and $CDCl_3$ on a Bruker NMR spectrometer. The ^{13}C NMR spectra were taken on a Varian Mercury 100.6 MHz NMR spectrometer. The $^{31}P\{^1H\}$ NMR spectra were recorded with complete proton decoupling and referenced with 85% H_3PO_4 as external standard. The reaction products were analyzed with a PerkinElmer Clarus 500 series gas chromatograph equipped with a flame ionization detector and a 30 m × 0.25 mm × 0.25 µm film thickness β-Dex capillary column. Thin-layer chromatography was used for monitoring the reactions.

Preparation of 3-(2-(diphenylphosphino) benzylideneamino)-2-(1-hydroxyethyl) quinazolin-4(3H)-one (5a) A mixture of *p*-toluenesulfonic acid (10 mg), 2-(diphenylphosphino)benzaldehyde (282 mg, 0,974 mmol) and 3-amino-2-(S)-1-hydroxyethyl)-3H-quinazolin-4-one (100 mg, 0,487 mmol) in ethanol (10 mL) and heated at 120 °C for 12 h. The reaction was cooled and analyzed by

Table 1 Transfer hydrogenation of acetophenones with Ru(II) catalysts



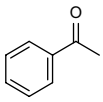
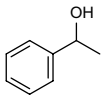
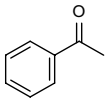
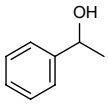
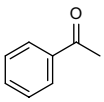
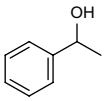
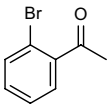
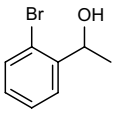
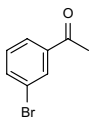
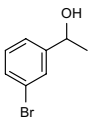
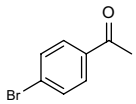
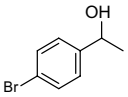
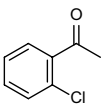
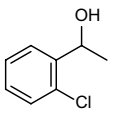
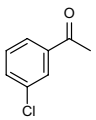
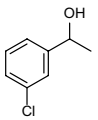
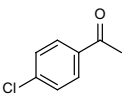
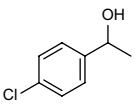
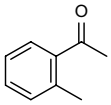
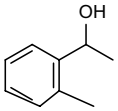
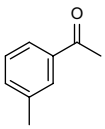
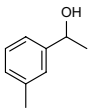
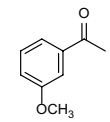
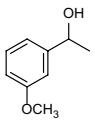
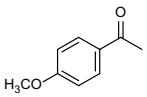
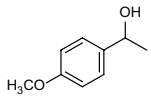
Entry	Substrate	Product	Yield[c] (%) (TON)[d]				
			6a	6b	6c	6d	6e
1			87 (435)	78 (390)	82 (410)	98 (490)	96 (480)
2			44[a] (220)	53[a] (265)	39[a] (195)	66[a] (330)	84[a] (420)
3			17[b] (85)	13[b] (65)	26[b] (130)	38[b] (190)	34[c] (170)
4			92 (460)	97 (485)	96 (480)	98 (490)	≥99 (495)
5			98 (490)	98 (490)	98 (490)	≥99 (495)	≥99 (495)
6			97(485)	96 (480)	82 (410)	97 (485)	98 (490)
7			≥99 (495)	≥99 (495)	≥99 (495)	≥99 (495)	≥99 (495)
8			99 (495)	98 (490)	96 (480)	99 (495)	98 (490)
9			96 (480)	95 (475)	97 (485)	99 (495)	99 (495)
10			≤5 (25)	6 (30)	8 (40)	12 (60)	19 (95)
11			41(205)	39 (195)	60 (300)	68 (340)	78 (390)

Table 1 (continued)

Entry	Substrate	Product	Yield[c] (%) (TON)[d]				
			6a	6b	6c	6d	6e
12			76 (380)	73 (365)	92 (460)	90 (450)	92 (460)
13			8 (40)	6 (30)	23 (115)	33 (165)	23 (115)

Reaction conditions: substrate (2 mmol), catalyst (0.004 mmol), IPA (3 mL), NaOH (0.1 mmol), 24 h.
[a]Base: KO^{t}Bu
[b]Base: Et_3N
[c]GC yield of the corresponding alcohol
[d]TON: mol of product/mol of catalyst

Table 2 Influence of solvents and temperature on the reduction of acetophenone with **6a**[a]

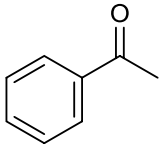
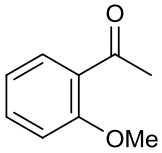
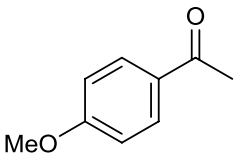
Entry	Solvent	T (°C)	Conv. (%)[b]
1	Methanol	50	10
2	Methanol	60	27
3	Methanol	80	68
4	^{i}PrOH	60	NR
5	Ethanol	80	3

[a]Reaction conditions: acetophenone (2 mmol), **6a** (0.1 mmol), solv. (3 mL), H_2:10 bar, 24 h. NR: no reaction
[b]Products were analyzed by GC

TLC [ethylacetate:hexane/1:5]. The solvent was evaporated under reduced pressure until dryness and the residue was dissolved in CH_2Cl_2. The solution was washed with $NaHCO_3$ followed by H_2O and the organic phase was dried with Na_2SO_4. The crude product, obtained by evaporation of the solvent, was purified by chromatography on silica gel using 1:9 ethylacetate:hexane as an eluent. Yield 101 mg (44%), m.p.: 130–131 °C (dec.). ^{1}H NMR (400.2 MHz, $CDCl_3$): δ (ppm) 9.88 (d, 1H, J_{PH} = 5.8 Hz, HC = N), 8.12 (m, 2H, ArCH), 7.52 (m, 2H, ArCH), 7.44–7.21 (m, 12H, ArCH), 6.84 (m, 2H, ArCH), 4.84 (m, 1H, CH), 4.35 (s, OH), 1.34 (d, 3H, J = 6.4 Hz, CH_3). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ (ppm) 165.5 (d, J_{PC} = 19.2 *Hz*, N = CH), 158.7–121.6 (Ar), 65.4 (CH), 22.1 (CH_3). ^{31}P{^{1}H} NMR (162.0 MHz, $CDCl_3$): δ (ppm) − 15.35 (s). FTIR (KBr, cm^{-1}): 3451 (OH); 1687 (C = O); 1607 (C = N); 1435 (P-Ph). Anal. calcd. for $C_{29}H_{24}N_3O_2P$: C, 72.95; H, 5.07; N, 8.80%. Found: C, 73.33; H, 5.29; N, 8.47%.

The other proligands **5b**–**5e** were prepared by the same procedure.

Table 3 Hydrogenation reaction of acetophenone and derivatives[a]

Entry	Catalyst	Substrate	Yield (%)[b]	
			10 bar H_2	40 bar H_2
1	**6a**		NR	5
2	**6b**		NR	≤ 5
3	**6c**		15	45
4	**6d**		46	72
5	**6e**		15	16
6	**6a**		16	99
7	**6b**		9	9
8	**6c**		NR	≤ 5
9	**6d**		≤ 5	59
10	**6e**		80	97
11	**6a**		52	58
12	**6b**		45	95
13	**6c**		NR	69
14	**6d**		79	77
15	**6e**		60	69

[a]Reaction conditions: substrate (2 mmol), cat. (0.004 mmol), 24 h. NR: no reaction
[b]GC yield of the corresponding alcohol

3-(2-(Diphenylphosphino)benzylideneamino)-2-(hydroxy(phenyl)methyl)quinazolin-4(3H)-one (5b) Yield 74 mg (37%), m.p.: 161–163 °C (dec.). ^{1}H NMR (400.2 MHz, $CDCl_3$): δ (ppm) 9.59 (d, 1H, J_{PH} = 6.01 Hz, HC = N), 8.20–7.00 (m, ArH, 23H), 4.20 (s, 1H, CH), 1.62 (s, OH). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ (ppm) 165.3 (d, J_{PC} = 19.2 *Hz*, N = CH), 145.50–117.0 (Ar), 68.4 (CH). ^{31}P{^{1}H} NMR (162.0 MHz, $CDCl_3$): δ (ppm) − 16.26 (s). FTIR (KBr, cm^{-1}): 3301 (OH); 1682 (C = O); 1603 (C = N); 1432 (P–Ph). Anal. calcd. for $C_{34}H_{26}N_3O_2P$: C, 75.68; H, 4.86; N, 7.79%. Found: C, 76.73; H, 5.09; N, 8.47%.

3-(2-(Diphenylphosphino)benzylideneamino)-2-(1-hydroxy-2-methylpropyl)quinazolin-4(3H)-one (5c) Yield 65 mg (30%), m.p.: 118–120 °C (dec.). ^{1}H NMR (400.2 MHz, $CDCl_3$): δ (ppm) 9.90 (d, 1H, J_{PH} = 6.00 Hz, HC = N), 8.32–7.00 (m, 18H, ArH), 4.24 (d, J = 7.6 Hz, 1H, CH), 2.68 (m, 1H, CH), 1.62 (br, OH), 1.80 (s, 6H, CH_3). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ (ppm) 165.5 (d, J_{PC} = 19.2 Hz, N = CH), 158.7–121.6 (Ar), 65.4 (CH), 23.0 (CH_3). ^{31}P{^{1}H} NMR (162.0 MHz, $CDCl_3$): δ (ppm) − 16.18 (s). FTIR (KBr, cm^{-1}): 3426 (OH); 1683 (C = O); 1607 (C = N); 1434 (P–Ph). Anal. calcd. for $C_{31}H_{28}N_3O_2P$: C, 73.65; H, 5.58; N, 8.31%. Found: C, 74.45; H, 5.86; N, 8.86%.

3-(2-(Diphenylphosphino)benzylideneamino)-2-(1-hydroxy-2,2-dimethylpropyl)quinazolin-4(3H)-one (5d) Yield 138 mg (66%), m.p.: 144 °C (dec.). ^{1}H NMR (400.2 MHz, $CDCl_3$): δ (ppm) 10.00 (d, 1H, J_{PH} = 6.24 Hz, HC = N), 8.20–7.10 (m, 18H, ArH), 4.91 (s, OH), 3.63 (s, 1H, CH), 0.82 (s, 9H, CH_3). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ (ppm) 165.0 (d, J_{PC} = 19.2 Hz, N = CH), 159.7–127.0 (Ar), 73.0 (CH), 23.0 (CH_3). ^{31}P{^{1}H} NMR (162.0 MHz, $CDCl_3$): δ (ppm) − 16.35 (s). FTIR (KBr, cm^{-1}): 3423 (OH); 1684 (C = O); 1606 (C = N); 1434 (P–Ph). Anal. calcd. for $C_{32}H_{30}N_3O_2P$: C, 73.97; H, 5.82; N, 8.09%. Found: C, 73.93; H, 6.09; N, 8.43%.

3-(2-(Diphenylphosphino)benzylideneamino)-2-(1-hydroxy-2-phenylethyl)quinazolin-4(3H)-one (5e) Yield 140 mg (71%), m.p.: 156 °C (dec.). ^{1}H NMR (400.2 MHz, $CDCl_3$): δ (ppm) 9.92 (d, 1H, J_{PH} = 5.96 Hz, HC = N), 8.25–7.13 (m, 23H, ArH), 4.91 (d, 1H, J = 9.7 Hz, CH), 4.24 (s, OH), 3.74 (d, 1H, J = 9.7 Hz, CH). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ (ppm) 166.0 (d, J_{PC} = 19.2 Hz, N = CH), 139.0–126.0 (Ar), 71.4 (CH), 41.0 (CH_3). ^{31}P{^{1}H} NMR (162.0 MHz, $CDCl_3$): δ (ppm) − 15.44 (s). FTIR (KBr, cm^{-1}): 3423 (OH); 1684 (C = O); 1606 (C = N); 1434 (P–Ph). Anal. calcd. for $C_{35}H_{28}N_3O_2P$: C, 75.94; H, 5.10; N, 7.59%. Found: C, 76.30; H, 5.69; N, 8.47%.

Preparation of Ru(II) complexes (6a–e)

Complex 6a

To a solution of [Ru(*p*-cymene)Cl_2]$_2$ (306 mg, 1 mmol) in dry toluene (10 mL), compound **5a** (960 mg, 2.1 mmol) was added. The mixture was stirred for 12 h at reflux. The solvent was removed under reduced pressure until dryness, giving a dark red solid, which was crystallized from CH_2Cl_2/hexane mixture. Yield 1.015 g (90%), mp.: 191 °C (dec.). ^{1}H NMR (400.2 MHz, $CDCl_3$): δ (ppm) 9.87 (s, 2H, N = CH), 7.89–7.28 (m, ArH, 36H), 5.30 (s, OH), 4.93 (m, 2H, CH), 2.70 (s, 6H, CH_3). ^{31}P{^{1}H} NMR (162.0 MHz, $CDCl_3$): δ (ppm) 59.60 (s). FTIR (KBr, cm^{-1}): 3426 (OH); 1678 (C = O); 1592 (C = N); 1436 (P–Ph). Anal. calcd. for $C_{58}H_{48}Cl_2N_6O_4P_2Ru$: C: 61.81, H: 4.29, N: 7.46%. Found: C: 62.34, H: 4.09, N: 7.02%.

The other complexes **6b–d** were prepared by the same procedure.

Complex 6b

Yield 913 mg (73%), m.p.: 210 °C (dec.), dark red solid. ^{1}H NMR (400.2 MHz, $CDCl_3$): δ (ppm) 10.15 (s, 2H, N = CH), 8.56–7.28 (m, ArH, 46H), 5.17 (s, 2H, CH), 1.67 (s, OH). ^{31}P{^{1}H} NMR (162.0 MHz, $CDCl_3$): δ (ppm) 59.61 (s). FTIR (KBr, cm^{-1}): 3386 (OH); 1681 (C = O); 1592 (C = N); 1468 (P–Ph). Anal. calcd. for $C_{68}H_{52}Cl_2N_6O_4P_2Ru$: C: 65.28, H: 4.19, N: 6.72%. Found: C: 66.02, H: 4.30, N: 6.10%.

Complex 6c

Yield 993 mg (84%), m.p.: 243 °C (dec.), brown solid. ^{1}H NMR (400.2 MHz, $CDCl_3$): δ (ppm) 10.15 (s, 2H, N = CH), 8.29–7.28 (m, ArH, 36H), 4.51 (s, 2H, CH), 4.51 (s, OH), 3.48 (m, 2H, CH), 1.91 (s, 12H, CH_3). ^{31}P{^{1}H} NMR (162.0 MHz, $CDCl_3$): δ (ppm) 52.57 (s). FTIR (KBr, cm^{-1}): 3418 (OH); 1680 (C = O); 1603 (C = N); 1468 (P–Ph). Anal. calcd. for $C_{62}H_{56}Cl_2N_6O_4P_2Ru$: C: 62.94, H: 4.77, N: 7.10%. Found: C: 63.85, H: 4.70, N: 6.90%.

Complex 6d

Yield 690 mg (57%), m.p.: 248 °C (dec.), brown solid. ^{1}H NMR (400.2 MHz, $CDCl_3$): δ (ppm) 10.90 (s, 2H, N = CH), 8.30–7.07 (m, ArH, 36H), 5.17 (s, 2H, CH), 4.45 (s, OH), 1.90 (s, 18H, CH_3). ^{31}P{^{1}H} NMR (162.0 MHz, $CDCl_3$): δ (ppm) 61.00 (s). FTIR (KBr, cm^{-1}): 3426 (OH); 1657 (C = O); 1602 (C = N); 1472 (P–Ph). Anal. calcd.

for $C_{64}H_{60}Cl_2N_6O_4P_2Ru$: 63.47, H:4.99, N:6.94%. Found: C: 63.95, H: 4.97, N: 6.15%.

Complex 6e

Yield 844 mg (66%), m.p.: 230 °C (dec.), brown solid. ^1H NMR (400.2 MHz, $CDCl_3$): δ (ppm) 9.83 (s, 2H, N = CH), 8.40–7.28 (m, ArH, 46H), 4.57 (m, 4H, CH_2), 3.47 (m, 2H, CH), 3.15 (s, OH). $^{31}P\{^1H\}$ NMR (162.0 MHz, $CDCl_3$): δ (ppm) 59.62 (s). FTIR (KBr, cm^{-1}): 3429 (OH); 1672 (C = O); 1569 (C = N); 1468 (P–Ph). Anal. calcd. for $C_{70}H_{56}Cl_2N_6O_4P_2Ru$: C: 65.73, H: 4.41, N: 6.57%. Found: C: 66.21, H: 4.47, N: 6.24%.

General procedure for transfer hydrogenation reactions

A mixture of the Ru(II) complex (0.004 mmol), 2-propanol (3 mL), NaOH (0.1 mmol) and the substrate (2 mmol, substrate:catalyst/500:1) was introduced into a Schlenk tube under an argon atmosphere. The resulting solution was heated at 82 °C for 24 h. The solution was cooled down and then concentrated to dryness under reduced pressure. The residue was purified by flash chromatography (ethyl acetate:hexane/1:10). The products were analyzed by GC.

General procedure for hydrogenation reactions

In a typical experiment, a stainless steel reactor was charged with acetophenone (2 mmol) and solvent (2 mL), followed by the required catalyst (1% mol, substrate:catalyst/100:1) under an N_2 atmosphere. The reaction mixture was then stirred at the required temperature for the specified time under 10 or 40 bars pressure of H_2. After the completion of the reaction, the mixture was cooled and extracted with diethyl ether (3 × 20 mL). Yields were determined by GC.

Conclusion

A series of Ru(II) complexes with 3-aminoquinazolinone–phosphine (PN donor) ligands have been synthesized and characterized by spectroscopic techniques. The ligands were shown to coordinate with the Ru(II) center via their phosphorus and nitrogen atoms. The Ru(PN)Cl_2 complexes act as catalysts for both hydrogenation and transfer hydrogenation reactions of ketones in moderate to good yields. The use of a variety of ligands with different substituents (–Me, –^{i}Pr, –^{t}Bu, –Bn and –Ph) was investigated for the Ru(II) catalyzed hydrogenation and transfer hydrogenation reactions; however, the catalytic activities were not significantly affected by the substituents. This is probably because the substituents are remote from the ruthenium active centers, such that the nature of the substituents did not contribute to the catalytic performance.

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