Polyhedron 29 (2010) 3097–3102

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Synthesis and characterization of ruthenium *p*-cymene complexes bearing bidentate P–N and E–N ligands (E = S, Se) based on 2-aminopyridine

Wolfgang Lackner-Warton [a], Shinji Tanaka [a], Christina M. Standfest-Hauser [a], Özgür Öztopcu [a], Jen-Chieh Hsieh [a], Kurt Mereiter [b], Karl Kirchner [a,*]

[a] Institute of Applied Synthetic Chemistry, Vienna University of Technology, Getreidemarkt 9, A-1060 Vienna, Austria
[b] Institute of Chemical Technologies and Analytics, Vienna University of Technology, Getreidemarkt 9, A-1060 Vienna, Austria

ARTICLE INFO

Article history:
Received 12 July 2010
Accepted 12 August 2010
Available online 20 August 2010

Keywords:
Ruthenium
Half sandwich complexes
Aminophosphines
Hemilabile ligands
Transfer hydrogenation

ABSTRACT

The syntheses and characterization of a series of cationic of Ru(II) halfsandwich complexes of the types $[Ru(\eta^6\text{-}p\text{-cymene})(\kappa^2(P,N)\text{-PN})Cl]^+$ (PN = *N*-diphenylphosphino-2-aminopyridine, *N*-di-*iso*-propylphosphino-2-aminopyridine, 2-[(2-pyridyl)amino]dibenzo[d,f][1,2,3]dioxaphosphepine, *N*-(diisopropylphosphino)-2,6-diaminopyridine) and $[Ru(\eta^6\text{-}p\text{-cymene})(\kappa^2(E,N)\text{-EN})Cl]^+$ (EN = *N*-(2-pyridinyl)amino-diphenylphosphine sulfide, *N*-(2-pyridinyl)amino-diisopropylphosphine sulfide, *N*-(2-pyridinyl)amino-diphenylphosphine selenide, *N*-(2-pyridinyl)amino-diisopropylphosphine selenide) is described. Some of these complexes were tested as precatalysts for the transfer hydrogenation of acetophenone to give 1-phenyl ethanol.

1. Introduction

Heterodifunctional ligands are intensively studied and applied in coordination and organometallic chemistry owing to the often unique properties of their metal complexes and their ability to generate so called hemilabile systems which often display enhanced reactivity [1]. According to this concept introduced by Jeffrey and Rauchfuss, such ligands provide different electronegativities at their coordination sites [2]. In particular soft/hard, e.g., P/N and P/O assemblies, are able to coordinate reversibly to a metal center providing or protecting temporarily a vacant coordination site a feature very desirable for catalysts.

In this context, we have become interested in heterodifunctional PN ligands based on 2-aminopyridine in which the donor atoms are separated by an amino group [3,4]. These types of ligands are easily constructed by reacting 2-aminopyridine with R_2PCl in the presence of base (Scheme 1). R_2PCl may contain both bulky and/or electron-rich dialkyl phosphines as well as P–O and P–N bond containing achiral and chiral phosphite units derived from diols, aminoalcohols, and diamines [5]. Due to the comparative ease of phosphorus–nitrogen bond forming reactions in comparison with those in which phosphorus–carbon bonds are formed it is not surprising that several examples of transition metal complexes featuring this type of PN ligands have emerged over the last decades [6–15]. With a few exceptions [16], however, *N*-diphenylphosphino-2-aminopyridine (PN-Ph) is the most prominent member of these ligand family. Another interesting aspect of PN ligands is the fact that they can be further functionalized by oxidation with H_2O_2, sulfur, and grey selenium, respectively, to give the chalcogen O, S, and Se derivatives according to Scheme 1 (EN ligands). Although these heterodifunctional ligands have been known for some time [12], transition metal complexes thereof are relatively scarce [8,11,17,18].

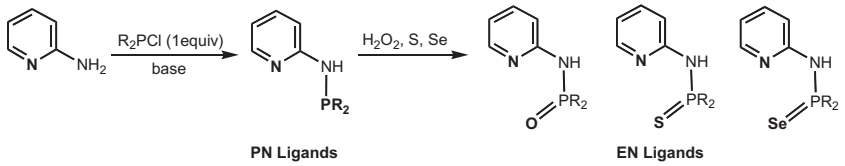
In the present contribution we report on the reactions of $[Ru(\eta^6\text{-}p\text{-cymene})(\mu\text{-Cl})Cl]_2$ with the PN and EN ligands shown in Scheme 2 resulting, with the exception of the ON ligands, in the formation of a series of cationic *p*-cymene Ru(II) complexes of the types $[Ru(\eta^6\text{-}p\text{-cymene})(PN)Cl]^+$ and $[Ru(\eta^6\text{-}p\text{-cymene})(EN)Cl]^+$. The X-ray structures of two representative complexes are presented. In addition, some of these complexes were tested as precatalysts for the transfer hydrogenation of acetophenone to give 1-phenyl ethanol.

2. Results and discussion

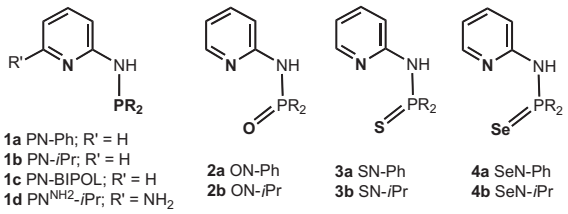
Similarly to the known ligands PN-Ph (**1a**) [19], PN-*i*Pr (**1b**), and 2-[(2-pyridyl)amino]dibenzo[d,f][1,2,3]dioxaphosphepine (PN-BIPOL) (**1c**) [3], the new ligand PN^{NH2}-*i*Pr (**1d**) was prepared in 45% yield by treatment of 2,6-diaminopyridine with 1 equiv. of $PiPr_2Cl$ in the presence of a base NEt_3. This compound had to be purified by chromatography due to the formation of the doubly phosphorylated PNP-*i*Pr ligand (Scheme 3) [20]. The EN ligands **2** were prepared according to the literature by the addition of a small

* Corresponding author. Tel.: +43 1 58801 15340; fax: +43 1 58801 16399.
E-mail address: kkirch@mail.zserv.tuwien.ac.at (K. Kirchner).

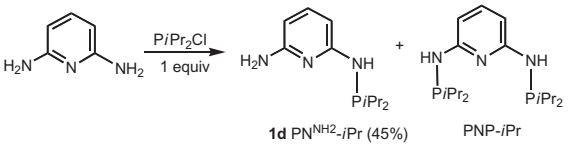
0277-5387/$ - see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.poly.2010.08.014



Scheme 1.



Scheme 2.



Scheme 3.

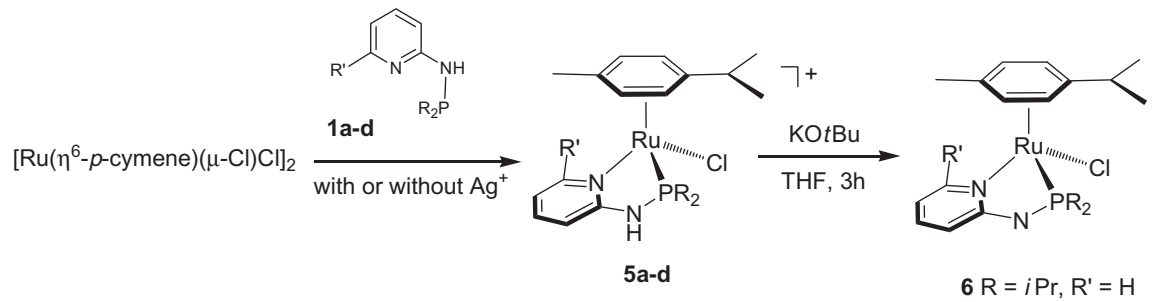
excess of aqueous H_2O_2 (30%) to a THF solution of the respective PN ligands **1** [12a]. The EN ligands **3** and **4** were also prepared following the literature method [8,12a] by refluxing the PN ligands **1** with a stoichiometric quantity of sulfur and grey selenium, respectively, in toluene.

Treatment of $[Ru(\eta^6\text{-}p\text{-cymene})(\mu\text{-Cl})Cl]_2$ with 2 equiv. of the respective ligands **1a–d** in the presence of 2 equiv. of Ag^+ salts (SbF_6^- or $CF_3SO_3^-$) in CH_2Cl_2 at room temperature afforded the cationic complexes $[Ru(\eta^6\text{-}p\text{-cymene})(\kappa^2(P,N)\text{-PN-Ph})Cl]^+$ (**5a**), $[Ru(\eta^6\text{-}p\text{-cymene})(\kappa^2(P,N)\text{-PN-}i\text{Pr})Cl]^+$ (**5b**), $[Ru(\eta^6\text{-}p\text{-cymene})(\kappa^2(P,N)\text{-PN-BIPOL})Cl]^+$ (**5c**), and $[Ru(\eta^6\text{-}p\text{-cymene})(\kappa^2(P,N)\text{-PN}^{NH2}\text{-}i\text{Pr})Cl]^+$ (**5d**) in 59–88% isolated yields (Scheme 4). In the absence of a silver salt the same reaction took place yielding the respective complexes with chloride as counterion. There was no evidence for the formation of intermediates of the type $[Ru(\eta^6\text{-}p\text{-cymene})(\kappa^1(P)\text{-PN})Cl_2]$ bearing a $\kappa^1(P)$-coordinated PN ligand. Deprotonation of the PN-*i*Pr ligand was achieved by reacting **5b** with 2 equiv. of KO*t*Bu in THF for 3 h affording the neutral complex $[Ru(\eta^6\text{-}p\text{-cymene})(\kappa^2(P,N)\text{-PN}^{dep}\text{-}i\text{Pr})Cl]$ (**6**) in 37% isolated yield (Scheme 4).

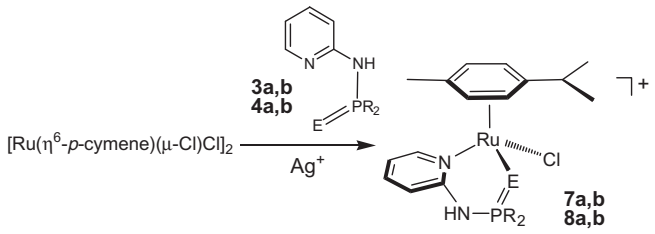
The complexes $[Ru(\eta^6\text{-}p\text{-cymene})(\kappa^2(S,N)\text{-PN-Ph})Cl]^+$ (**7a**), $[Ru(\eta^6\text{-}p\text{-cymene})(\kappa^2(S,N)\text{-SN-}i\text{Pr})Cl]^+$ (**7b**), $[Ru(\eta^6\text{-}p\text{-cymene})(\kappa^2(Se,N)\text{-SeN-Ph})Cl]^+$ (**8a**), and $[Ru(\eta^6\text{-}p\text{-cymene})(\kappa^2(Se,N)\text{-SeN-}i\text{Pr})Cl]^+$ (**8b**) were prepared in similar fashion by reacting $[Ru(\eta^6\text{-}p\text{-cymene})(\mu\text{-Cl})Cl]_2$ with 2 equiv. of the ligands **3** and **4** in the presence of 2 equiv. of $AgSbF_6$ in 78–86% isolated yields (Scheme 5). It has to be noted that in the absence of a silver salt no clean reaction took place. Moreover, in the case of the ON ligands ON-Ph (**2a**) and ON-*i*Pr (**2b**) we were unable to obtain complexes of the type $[Ru(\eta^6\text{-}p\text{-cymene})(\kappa^2(O,N)\text{-ON})Cl]^+$ and only intractable materials were obtained. It has to be also noted that several attempts to deprotonate complexes **7** and **8** with KO*t*Bu failed and intractable materials were obtained only.

All complexes are air-stable orange compounds which were characterized by ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy as well as elemental analysis. The ^1H NMR spectra contain in most cases a set of four well-resolved high-field-shifted doublets characteristic of an η^6-*p*-cymene ring attached to a metal center coordinated to three different donor atoms. The methyl groups of the *i*Pr moiety are diastereotopic exhibiting typically two distinct doublets centered at about 1.1 and 0.9 ppm. The $^{13}C\{^1H\}$ NMR spectrum does not bear any unusual features and is not discussed here. In the $^{31}P\{^1H\}$ NMR spectra, **5a–d** exhibit singlets which show the expected low-field shifts of the $\kappa^2(P,N)$-coordinated PN ligands relative to the free uncoordinated ligands [**5a**: 97.5 ppm ($\Delta\delta$ = 70.0 ppm), **5b**: 123.6 ppm ($\Delta\delta$ = 73.7 ppm), **5c**: 165.7 ppm ($\Delta\delta$ = 25.7 ppm), **5d**: 117.3 ppm ($\Delta\delta$ = 69.8 ppm)]. This trend is reversed in the case of complexes **7a**, **7b**, **8a**, and **8b**. The $\kappa^2(S,N)$- and $\kappa^2(Se,N)$-coordinated EN ligands give rise to signals at 52.6, 83.6, 44.5, and 77.3 ppm, whereas the uncoordinated ligands are shifted to lower fields exhibiting singlets at 63.5, 103.4, 54.4, and 102.0 ppm, respectively. In the case of the SeN complexes **8a** and **8b**, the phosphorus signals exhibit a pair of Se satellites with ^{31}P–^{77}Se coupling constants of 663 and 640 Hz, respectively. The deprotonated complex **6** also displays a sharp single $^{31}P\{^1H\}$ NMR resonance at 132.7 ppm which is shifted slightly to higher field than the starting material **5b** (cf. 134.1 ppm). The ^1H spectrum of **6** is also very similar to that of **5b** except that the NH resonance is now absent.

The molecular structures of **5a′** (with chloride as counter ion) and **7b** (with SbF_6^- as counter ion) were determined by X-ray crystallography. ORTEP diagrams of the two Ru-complexes are depicted in Figs. 1 and 2 with selected bond distances and angles reported in the captions. Both complexes adopt the typical three



Scheme 4.



Scheme 5.

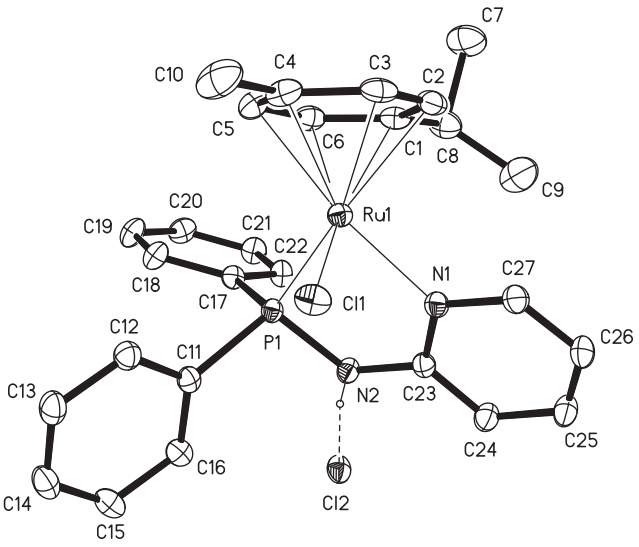


Fig. 1. Molecular structure of **5a**′ (50% displacement ellipsoids, most H atoms omitted for clarity). Selected bond lengths (Å) and angles (°): <Ru1–C_{cymene}> = 2.237(2), Ru1–N1 = 2.099(2), Ru1–P1 = 2.283(1), Ru1–Cl1 = 2.394(1), N1–Ru1–P1 = 79.84(4), N1–Ru1–Cl1 = 83.23(4), P1–Ru1–Cl1 = 91.56(2), N2···Cl2 = 3.032(2).

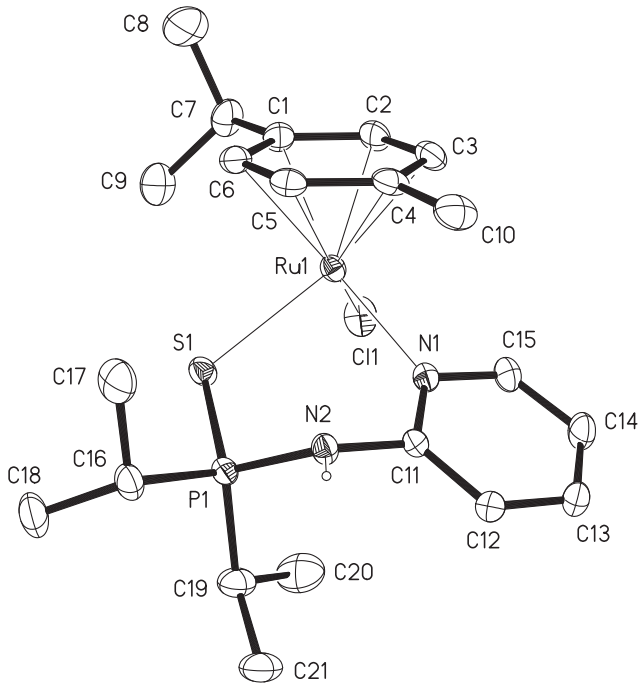


Fig. 2. Molecular structure of **7b** (50% displacement ellipsoids, SbF_6^- anion and most H atoms omitted for clarity). Selected bond lengths (Å) and angles (°): <Ru1–C_{cymene}> = 2.189(2), Ru1–N1 = 2.138(1), Ru1–S1 = 2.4394(6), Ru1–Cl1 = 2.4043(6), N1–Ru1–S1 = 92.56(5), N1–Ru1–Cl1 = 84.71(5), S1–Ru1–Cl1 = 85.80(2); N2···Cl1 = 3.183(2) (not shown).

legged piano stool configuration with Cl and the N and P atoms and the N and S atoms of the bidentate PN-Ph and SN-*i*Pr ligands, respectively, as the legs. The *p*-cymene ring is essentially planar with C–C bond distances in the range 1.392(3)–1.435(3) Å, giving a mean value of 1.417(3) Å. The Ru–C distances range from 2.173(2) to 2.201(2) Å (mean 2.189(2) Å) in **5a**′ and from 2.192(2) to 2.261(2) Å (mean 2.237(2) Å) in **7b**. In the case of **5a**′ the NH group of the complex forms a characteristic hydrogen bond to the free chloride ion Cl2 with a comparatively short distance N2···Cl2 = 3.032(2) Å. Further coherence of the solid state structure is provided by four C–H···Cl interactions to Cl2 (not Cl1) with C···Cl distances from 3.321(2) to 3.726(2) Å. In the case of **7b** the NH group forms a N–H···Cl hydrogen bond to the chloride of a neighbouring Ru complex, N2···Cl1 = 3.183(2) Å, thus giving rise to infinite chains parallel to [1 0 1] of H-bonded Ru-complexes. The SbF_6 counter ions are located between these chains and are anchored via a five different C–H···F interactions with C···F distances between 3.120(2) and 3.464(2) Å.

Transfer hydrogenation of acetophenone to give 1-phenyl ethanol in refluxing 2-propanol was carried out to test the catalytic activity of complexes **5b**, **7b**, and **8b** using typically 0.1 M acetophenone solution, 0.5 mol% of the complex as catalyst, and 10 mol% of KO*t*Bu as the base. Under these conditions all four complexes acted as efficient catalyst reaching 99% conversion within 22 h (Table 1, entries 1, 8, and 10). Under the same conditions, but with 0.1 mol% of **5b** the conversion dropped to 75% (entry 3). Performing the reaction at room temperature with 0.5 mol% of the precatalysts **5b**, **7b**, and **8b**, and 10 mol% of KO*t*Bu resulted in either very poor (entry 5) or no conversion (entries 9 and 11). With 5 mol% of **5b** the yield of 1-phenyl ethanol was 75% (entry 3). Performing the catalysis with the deprotonated complex **6** gave the same results as with **5b** (entry 7). The catalytic effect of the ruthenium complexes was confirmed by running the reaction without catalyst. No product was formed and only starting materials were isolated from the reaction mixture.

Table 1
Catalytic transfer hydrogenation of acetophenone.[a]

Entry	C	S:C:B	*T* (°C)	Time (h)	Conv. (%)
1	**5b**	200:1:20	75	22	99
2	**5b**	200:1:20	75	2.2	25
3	**5b**	2000:1:20	75	22	75
4	**5b**	200:1:20	25	44	99
5	**5b**	200:1:20	25	22	20
6	**5b**	20:1:20	25	22	75
7	**6**	200:1:20	75	22	99
8	**7b**	200:1:20	75	22	99
9	**7b**	200:1:20	25	22	–
10	**8b**	200:1:20	75	22	99
11	**8b**	200:1:20	25	22	–

[a] S = acetophenone, C = catalyst, B = KO*t*Bu.

The nature of the catalytically active species is not clear at the moment. On the one hand *p*-cymene ligand displacement may not be dismissed, on the other hand the PN and SN ligands may be hemilabile under the reaction conditions forming reactive 16e$^-$ intermediates with $\kappa^1(P)$-bonded or $\kappa^1(N)$-bonded ligands. However, both ^{1}H and ^{31}P{^{1}H} NMR spectra of **5b**, **6**, **7b**, and **8b** in CD_3NO_2 at 100 °C did not significantly change as compared to the room temperature spectra and there was no indication of any dynamic processes. Moreover, it has to be noted that the addition of $AgSbF_6$ (stoichiometric with respect to the catalyst) as chloride

scavenger had no effect on both reaction rates and conversions and it thus seems that the chloride ligand is not removed from the metal center during the catalysis.

In sum we have shown that the dimeric complex [Ru(η^6-*p*-cymene)(μ-Cl)Cl]$_2$ reacts readily with PN and EN ligands to give cationic *p*-cymene Ru(II) complexes of the types [Ru(η^6-*p*-cymene)(PN)Cl]$^+$ and [Ru(η^6-*p*-cymene)(EN)Cl]$^+$. In the case of [Ru(η^6-*p*-cymene)(PN)Cl]$^+$ with PN = PN-*i*Pr we have also demonstrated that deportonation of the acidic NH proton of the PN ligand is possible yielding the neutral complex [Ru(η^6-*p*-cymene)(κ^2(P,N)-PN^{dep}-*i*Pr)Cl]. Some of these complexes act as moderately active precatalysts for the transfer hydrogenation of acetophenone to give 1-phenyl ethanol.

3. Experimental section

3.1. General procedure

All manipulations were performed under an inert atmosphere of argon by using Schlenk techniques. The solvents were purified according to standard procedures [21]. [Ru(η^6-*p*-cymene)-(μ-Cl)Cl]$_2$ [22], *N*-diphenylphosphino-2-aminopyridine (PN-Ph) (**1a**), *N*-diisopropylphosphino-2-aminopyridine (PN-*i*Pr) (**1b**), 2-[(2-pyridyl)amino]dibenzo[d,f][1,2,3]-dioxaphosphepine (PN-BIPOL) (**1c**) [4], *N*-(2-pyridinyl)amino-diphenylphosphine oxide (ON-Ph) (**2a**), *N*-(2-pyridinyl)amino-diisopropylphosphine oxide (ON-*i*Pr) (**2b**), *N*-(2-pyridinyl)amino-diphenylphosphine sulfide (SN-Ph) (**3a**), *N*-(2-pyridinyl)amino-diisopropylphosphine sulfide (SN-*i*Pr) (**3b**), *N*-(2-pyridinyl)amino-diphenylphosphine selenide (SeN-Ph) (**4a**), and *N*-(2-pyridinyl)amino-diisopropylphosphine selenide (SN-*i*Pr) (**4b**) were prepared according to the literature [9d]. The deuterated solvents were purchased from Aldrich and dried over 4 Å molecular sieves. ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra were recorded on a Bruker AVANCE-250 spectrometer and were referenced to $SiMe_4$ and H_3PO_4 (85%), respectively.

3.2. Synthesis

3.2.1. N-(Diisopropylphosphino)-2,6-diaminopyridine (PN^{NH2}-iPr) (**1d**)

P*i*Pr$_2$Cl (3.35 g, 22 mmol) was added dropwise to a solution of 2,6-diaminopyridine (2.18 g, 20 mmol) and triethylamine (2.2 g, 22 mmol) in THF (30 mL) at 0 °C. The mixture was stirred for 20 h at room temperature. After that ethyl acetate was added and the solution was filtered over neutral Al_2O_3. The solvent was removed under reduced pressure and the crude product was chromatographed with an ethyl acetate/hexane mixture (1:1) as eluent in order to remove the doubly phosphorylated PNP-*i*Pr ligand [20]. Yield: 2.02 g (45%). *Anal.* Calc. for $C_{11}H_{20}N_3P$: C, 58.65; H, 8.95; N, 18.65. Found: C, 58.74; H, 8.70; N, 18.79%. ^{1}H NMR (δ, $CDCl_3$, 20 °C): 7.18 (t, J = 7.75 Hz, 1H, py^4), 6.40 (dd, J = 6.25 Hz, J = 1.75 Hz, 1H, py^3), 5.83 (d, J = 7.75 Hz, 1H, py^5), 4.47 (d, J = 11.0 Hz, 1H, N*H*), 4.32 (b, 2H, NH_2) 1.70 (m, J = 5.25 Hz, 2H, C*H*(CH$_3$)$_2$), 1.06–0.96 (m, 12H, CH(CH_3)$_2$). ^{13}C{^{1}H} NMR (δ, $CDCl_3$, 20 °C): 169.8 (d, J = 20.8 Hz, py^2), 157.3 (py^6), 139.5 (d, J = 1.9 Hz, py^4), 98.0 (py^3), 97.7 (py^5), 26.3 (d, J = 11.3 Hz, C*H*(CH$_3$)$_2$), 18.6 (d, J = 19.5 Hz, CH(CH_3)$_2$), 17.0 (d, J = 7.5 Hz, CH(CH_3)$_2$). ^{31}P{^{1}H} NMR (δ, $CDCl_3$, 20 °C): 47.5.

3.2.2. [Ru(η^6-p-cymene)(κ^2(P,N)-PN-Ph)Cl]CF_3SO_3 (**5a**)

To a solution of [Ru(η^6-*p*-cymene)(μ-Cl)Cl]$_2$ (0.290 g, 0.474 mmol) in CH_2Cl_2 (10 mL) PN-Ph (0.263 g, 0.947 mmol) and $AgCF_3SO_3$ (0.243 g, 0.947 mmol) were added and the mixture was stirred at room temperature for 3 h. After that insoluble materials (AgCl) were removed by filtration through Celite, and the solvent was removed under reduced pressure. The resulting orange solid was washed with diethyl ether and dried under vacuum. Yield: 0.514 g (78%). *Anal.* Calc. for $C_{28}H_{29}ClF_3N_2O_3PRuS$: C, 48.17; H, 4.19; N, 4.01. Found: C, 48.24; H, 4.11; N, 4.09%. ^{1}H NMR (δ, CD_2Cl_2, 20 °C): 9.28 (d, J_{HH} = 2.92 Hz, 1H, NH), 8.70 (d, J_{HH} = 5.48 Hz, 1H, py^6), 7.90–7.20 (m, 11H, Ph, py^4), 7.12 (s, 1H, py^5), 6.84 (t, J_{HH} = 6.28 Hz, 1H, py^3), 6.02 (d, J_{HH} = 6.17 Hz, 1H, cym), 5.74 (d, J_{HH} = 6.62 Hz, 1H, cym), 5.62 (d, J_{HH} = 5.71 Hz, 1H, cym), 4.82 (d, J_{HH} = 3.65 Hz, 1H, cym), 2.88 (m, J_{HH} = 7.08 Hz, 1H, C*H*(CH$_3$)$_2$), 2.09 (s, 3H, CH$_3$), 1.06 (d, J_{HH} = 6.85 Hz, 3H, CH(CH_3)$_2$), 0.87 (d, J_{HH} = 6.85 Hz, 3H, CH(CH_3)$_2$). ^{13}C{^{1}H} NMR (δ, CD_2Cl_2, 20 °C): 161.5 (d, $^2J_{CP}$ = 12.07 Hz, py^2), 154.7 (s, py^6), 140.1 (s, py^4), 136.3–128.2 (Ph), 117.5 (s, py^5), 112.3 (d, $^3J_{CP}$ = 9.20 Hz, py^3), 108.8 (s, cym), 101.5 (s, cym), 98.4 (d, $^2J_{CP}$ = 7.47 Hz, cym), 93.1 (d, $^2J_{CP}$ = 5.75 Hz, cym), 88.7 (d, $^2J_{CP}$ = 2.30 Hz, cym), 86.8 (d, $^2J_{CP}$ = 1.46 Hz, cym), 30.6 (s, C*H*(CH$_3$)$_2$), 22.4 (s, CH(C*H*$_3$)$_2$), 21.3 (s, CH(C*H*$_3$)$_2$), 18.1 (s, CH$_3$). ^{31}P{^{1}H} NMR (δ, CD_2Cl_2, 20 °C): 97.5.

3.2.3. [Ru(η^6-p-cymene)(κ^2(P,N)-PN-Ph)Cl]Cl (**5a′**)

This complex has been prepared analogously to **5a** with [Ru(η^6-*p*-cymene)(μ-Cl)Cl]$_2$ (0.500 g, 0.817 mmol) and PN-Ph (0.344 g, 2.64 mmol) as starting materials but in the absence of a silver salt. Yield: 0.420 g (88%). *Anal.* Calc. for $C_{27}H_{29}Cl_2N_2PRu$: C, 55.48; H, 5.00; N, 4.79. Found: C, 55.24; H, 5.10; N, 4.88%. The NMR spectra of this complex are virtually the same as those of **5a**·CF_3SO_3 except that the NH proton is shifted from 9.28 to 9.43 ppm.

3.2.4. [Ru(η^6-p-cymene)(κ^2(P,N)-PN-iPr)Cl]SbF_6 (**5b**)

This complex has been prepared analogously to **5a** with [Ru(η^6-*p*-cymene)(μ-Cl)Cl]$_2$ (0.808 g, 1.32 mmol), PN-*i*Pr (0.555 g, 2.64 mmol), and $AgSbF_6$ (0.907 g, 2.64 mmol) as starting materials. Yield: 1.61 g (85%) *Anal.* Calc. for $C_{21}H_{33}ClF_6N_2PRuSb$: C, 35.19; H, 4.64; N, 3.91. Found: C, 35.00; H, 4.51; N, 4.04%. ^{1}H NMR (δ, CD_2Cl_2, 20 °C): 8.63 (d, J_{HH} = 5.4 Hz, 1H, py^6), 7.59 (t, J_{HH} = 6.7 Hz, 1H, py^4), 7.03 (d, J_{HH} = 8.0 Hz, 1H, py^3), 6.83 (t, J_{HH} = 5.0 Hz, 1H, py^5), 6.76 (s, 1H, NH), 6.15 (d, J_{HH} = 4.97 Hz, 1H, cym), 5.96 (d, J_{HH} = 4.97 Hz, 2H, cym), 5.80 (d, J_{HH} = 1.91 Hz, 1H, cym), 2.89 (m, J_{HH} = 6.31 Hz, 2H, C*H*(CH$_3$)$_2$), 2.56 (m, J_{HH} = 5.55 Hz, 1H, C*H*(CH$_3$)$_2$), 2.11 (s, 3H, CH$_3$), 1.50–1.00 (m, 18H, CH(CH_3)$_2$). ^{13}C{^{1}H} NMR (δ, CD_2Cl_2, 20 °C): 161.3 (d, $^2J_{CP}$ = 9.20 Hz, py^2), 154.7 (s, py^6), 140.1 (s, py^4), 117.1 (s, py^5), 111.2 (d, $^3J_{CP}$ = 6.90 Hz, py^3), 107.4 (s, cym), 99.0 (s, cym), 96.4 (d, $^2J_{CP}$ = 5.75 Hz, cym), 92.5 (d, $^2J_{CP}$ = 5.75 Hz, cym), 88.3 (d, $^2J_{CP}$ = 2.87 Hz, cym), 87.1 (d, $^2J_{CP}$ = 2.87 Hz, cym), 31.6 (d, $^1J_{CP}$ = 28.16 Hz, C*H*(CH$_3$)$_2$), 31.3 (s, C*H*(CH$_3$)$_2$), 28.4 (d, $^1J_{CP}$ = 28.74 Hz, C*H*(CH$_3$)$_2$), 22.1 (d, $^2J_{CP}$ = 20.12 Hz, CH(C*H*$_3$)$_2$), 18.1 (s, CH(C*H*$_3$)$_2$), 17.9 (d, $^2J_{CP}$ = 14.94 Hz, CH(C*H*$_3$)$_2$), 16.8 (d, J_{CP} = 2.87 Hz, CH$_3$). ^{31}P{1H} NMR (δ, acetone-d_6, 20 °C): 134.1.

3.2.5. [Ru(η^6-p-cymene)(κ^2(P,N)-PN-iPr)(Cl)]Cl (**5b′**)

This complex has been prepared analogously to **5a** with [Ru(η^6-*p*-cymene)(μ-Cl)Cl]$_2$ (0.223 g, 0.364 mmol) und PN-*i*Pr (0.153 g, 0.728 mmol) as starting materials but in the absence of a silver salt. Yield: 0.317 g (84%). *Anal.* Calc. for $C_{21}H_{33}Cl_2N_2PRu$: C, 48.84; H, 6.44; N, 5.42. Found: C, 48.69; H, 6.54; N, 5.38%. The NMR spectra of this complex are virtually the same as those of **5a** except that the NH proton is shifted from 6.76 to 10.61 ppm.

3.2.6. [Ru(η^6-p-cymene)(κ^2(P,N)-PN-BIPOL)Cl]CF_3SO_3 (**5c**)

This complex has been prepared analogously to **5a** with [Ru(η^6-*p*-cymene)(μ-Cl)Cl]$_2$ (0.199 g, 0.324 mmol), PN-BIPOL (0.200 g, 0.649 mmol), and $AgCF_3SO_3$ (0.167 g, 0.649 mmol) as starting materials. Yield: 0.280 g (59%). *Anal.* Calc. for $C_{28}H_{27}ClF_3N_2O_5PRuS$: C, 46.19; H, 3.74; N, 3.85. Found: C, 46.14; H, 3.80; N, 3.99%. ^{1}H NMR (δ, CD_2Cl_2, 20 °C): 9.49 (d, J_{HH} = 7.54 Hz, 1H, py^6), 8.74 (d, J_{HH} = 5.71 Hz, 1H, py^4), 7.80–7.10 (m, 9H, Ph, py^5), 7.12 (s, 1H, NH), 6.95 (t, J_{HH} = 6.62 Hz, 1H, py^3), 6.16 (d, J_{HH} = 5.03 Hz, 2H, cym), 5.63 (d, J_{HH} = 5.03 Hz, 1H, cym), 5.13 (d, J_{HH} = 5.94 Hz, 1H,

cym), 2.51 (m, J_{HH} = 6.80 Hz, 1H, C*H*(CH_3)$_2$), 2.05 (s, 3H, CH_3), 1.07 (d, J_{HH} = 6.85 Hz, 3H, CH(C*H*$_3$)$_2$), 0.97 (d, J_{HH} = 6.85 Hz, 3H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (δ, CD_2Cl_2, 20 °C): 161.5 (d, $^2J_{CP}$ = 20.69 Hz, py^2), 155.2 (s, py^6), 149.2 (d, $^2J_{CP}$ = 15.52 Hz, Ph), 147.6 (d, $^2J_{CP}$ = 6.32 Hz, Ph), 140.6 (s, py^4), 134.3–121.4 (Ph), 119.8 (s, py^5), 112.4 (d, $^3J_{CP}$ = 10.92 Hz, py^3), 109.8 (s, cym), 109.0 (s, cym), 99.5 (d, $^2J_{CP}$ = 10.92 Hz, cym), 97.5 (d, $^2J_{CP}$ = 5.75 Hz, cym), 89.3 (d, $^2J_{CP}$ = 2.30 Hz, cym), 85.7 (s, cym), 30.8 (s, *C*H(CH_3)$_2$), 22.5 (s, CH(*C*H$_3$)$_2$), 21.0 (s, CH(*C*H$_3$)$_2$), 18.6 (s, *C*H$_3$). ^{31}P{^{1}H} NMR (δ, CD_2Cl_2, 20 °C): 165.7.

3.2.7. [Ru(η^6-*p*-cymene)(κ^2(*P*,*N*)-PN^{NH2}-iPr)Cl]CF_3SO_3. (**5d**)

This complex has been prepared analogously to **5a** with [Ru(η^6-*p*-cymene)(μ-Cl)Cl]$_2$ (0.200 g, 0.327 mmol), PN^{NH2}-*i*Pr (0.147 g, 0.653 mmol), and $AgCF_3SO_3$ (0.168 g, 0.654 mmol) as starting materials. Yield: 0.374 g (87%). *Anal.* Calc. for $C_{22}H_{34}ClF_3N_3O_3PRuS$: C, 40.96; H, 5.31; N, 6.51. Found: C, 40.87; H, 5.54; N, 6.49%. ^{1}H NMR (δ, CD_2Cl_2, 20 °C): 7.55 (d, J_{HH} = 5.00 Hz, 1H, py^5), 7.30 (t, J_{HH} = 6.50 Hz, 1H, py^4), 6.51 (d, J_{HH} = 5.00 Hz, 1H, py^3), 6.23 (m, 2H, cym), 6.11 (b, 1H, NH), 5.97 (m, 2H, cym), 5.82 (d, J_{HH} = 13.38 Hz, 2H, NH), 3.08 (m, 1H, C*H*(CH_3)$_2$), 2.63 (m, 1H, C*H*(CH_3)$_2$), 2.55 (m, 1H, C*H*(CH_3)$_2$), 1.92 (s, 3H, CH_3), 1.65–1.00 (m, 18H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (δ, CD_2Cl_2, 20 °C): 162.3 (s, py^6), 160.2 (d, $^2J_{CP}$ = 7.98 Hz, py^2), 145.9 (s, cym), 141.0 (s, py^4), 135.1 (s, cym), 102.0 (s, py^5), 99.5 (d, $^3J_{CP}$ = 6.98 Hz, py^3), 128.8 (s, cym), 126.2 (s, cym), 31.0 (s, *C*H(CH_3)$_2$), 30.4–29.7 (m, *C*H(CH_3)$_2$), 23.8–16.8 (m, *C*H$_3$). ^{31}P{^{1}H} NMR (δ, CD_2Cl_2, 20 °C): 117.3.

3.2.8. [Ru(η^6-*p*-cymene)(κ^2(*P*,*N*)-PN^{dep}-iPr)Cl] (**6**)

A solution of **5b** (200 mg, 0.28 mmol) in THF (15 mL) was treated with KO*t*Bu (38 mg, 0.33 mmol) for 2 h at room temperature. After removal of the solvent under reduced pressure the residue was dissolved in benzene (20 mL). Insoluble materials were removed by filtration and the solvent was again removed under reduced pressure affording an orange solid which was dried under vacuum. Yield: 50 mg (37%). *Anal.* Calc. for $C_{21}H_{32}ClN_2PRu$: C, 52.55; H, 6.72; N, 5.89. Found: C, 51.90; H, 6.84; N, 5.79%. ^{1}H NMR (δ, acetone-d_6, 20 °C): 8.49 (d, J = 6.6 Hz, 1H, py^6), 7.00 (t, J = 7.5 Hz, 1H, py^4), 6.48 (d, J = 8.3 Hz, 1H, py^3), 6.21 (d, J = 6.6 Hz, 1H, cym), 6.02 (d, J = 6.6 Hz, 1H, cym), 5.95 (t, J = 6.6 Hz, 1H, py^5), 5.70 (d, J = 6.6 Hz, 1H, cym), 5.59 (d, J = 6.6 Hz, 1H, cym), 2.66–2.50 (m, 3H, C*H*(CH_3)$_2$), 2.01 (s, 3H, C*H*$_3$), 1.42–1.00 (m, 18H, CH(C*H*$_3$)$_2$). ^{31}P{^{1}H} NMR (δ, acetone-d_6, 20 °C): 132.7.

3.2.9. [Ru(η^6-*p*-cymene)(κ^2(*S*,*N*)-SN-Ph)Cl]SbF_6. (**7a**)

This complex has been prepared analogously to **5a** with [Ru(η^6-*p*-cymene)(μ-Cl)Cl]$_2$ (0.100 g, 0.163 mmol), SN-Ph (0.106 g, 0.332 mmol), and $AgSbF_6$ (0.114 g, 0.342 mmol) as starting materials. Yield: 0.223 g (84%). *Anal.* Calc. for $C_{27}H_{29}ClF_6N_2PRuSSb$: C, 39.70; H, 3.58; N, 3.43. Found: C, 39.74; H, 3.64; N, 3.59%. ^{1}H NMR (δ, CD_2Cl_2, 20 °C): 9.50 (br, 1H, NH), 9.08 (d, J_{HH} = 5.03 Hz, 1H, py^6), 8.50–7.30 (m, 13H, Ph, py), 5.90 (d, J_{HH} = 5.48 Hz, 1H, cym), 5.65 (d, J_{HH} = 5.63 Hz, 1H, cym), 5.35 (d, J_{HH} = 5.18 Hz, 1H, cym), 5.25 (d, J_{HH} = 5.33 Hz, 1H, cym), 2.77 (m, J_{HH} = 6.66 Hz, 1H, C*H*(CH_3)$_2$), 1.75 (s, 3H, CH_3), 1.25 (d, J_{HH} = 7.01 Hz, 3H, CH(C*H*$_3$)$_2$), 1.23 (d, J_{HH} = 6.85 Hz, 3H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (δ, CD_2Cl_2, 20 °C): 155.6 (s, py^6), 155.3 (d, $^2J_{CP}$ = 5.39 Hz, py^2), 141.2 (s, py^4), 134.6–129.2 (Ph), 120.7 (s, py^5), 119.5 (d, $^3J_{CP}$ = 4.72 Hz, py^3), 102.1 (s, cym), 101.8 (s, cym), 89.7 (s, cym), 84.1 (s, cym), 83.7 (s, cym), 81.4 (s, cym), 30.8 (s, *C*H(CH_3)$_2$), 21.7 (s, CH(*C*H$_3$)$_2$), 21.5 (s, CH(*C*H$_3$)$_2$), 17.3 (s, *C*H$_3$). ^{31}P{^{1}H} NMR (δ, CD_2Cl_2, 20 °C): 52.6.

3.2.10. [Ru(η^6-*p*-cymene)(κ^2(*S*,*N*)-SN-iPr)Cl]SbF_6. (**7b**)

This complex has been prepared analogously to **5a** with [Ru(η^6-*p*-cymene)(μ-Cl)Cl]$_2$ (0.100 g, 0.163 mmol), SN-*i*Pr (0.080 g, 0.326 mmol), and $AgSbF_6$ (0.112 g, 0.330 mmol) as starting materials. Yield: 0.195 g (80%). *Anal.* Calc. for $C_{21}H_{33}ClF_6N_2PRuSSb$: C, 33.68; H, 4.44; N, 3.74. Found: C, 33.59; H, 4.51; N, 3.71%. ^{1}H NMR (δ, CD_2Cl_2, 20 °C): 9.24 (br, 1H, NH), 9.08 (d, J_{HH} = 6.00 Hz, 1H, py^6), 7.99 (t, J_{HH} = 7.42 Hz, 1H, py^4), 7.70 (d, J_{HH} = 7.90 Hz, 1H, py^3), 7.31 (t, J_{HH} = 6.48 Hz, 1H, py^5), 6.01 (d, J_{HH} = 6.00 Hz, 1H, cym), 5.97 (d, J_{HH} = 5.69 Hz, 1H, cym), 5.55 (d, J_{HH} = 5.69 Hz, 1H, cym), 5.53 (d, J_{HH} = 5.37 Hz, 1H, cym), 3.01 (m, J_{HH} = 7.27 Hz, 1H, C*H*(CH_3)$_2$), 2.95 (m, J_{HH} = 6.63 Hz, 1H, C*H*(CH_3)$_2$), 2.32 (m, J_{HH} = 7.06 Hz, 1H, C*H*(CH_3)$_2$), 1.66 (s, 3H, CH_3), 1.64–1.33 (m, 12H CH(C*H*$_3$)$_2$), 1.14 (dd, J = 19.27 Hz, $^1J_{HH}$ = 6.63 Hz, 3H, CH(C*H*$_3$)$_2$), 0.70 (dd, J = 18.64 Hz, J_{HH} = 6.95 Hz, 3H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (δ, CD_2Cl_2, 20 °C): 157.8 (d, $^2J_{CP}$ = 5.98 Hz, py^2), 156.2 (s, py^6), 140.9 (s, py^4), 120.2 (s, py^5), 119.7 (d, $^3J_{CP}$ = 3.99 Hz, py^3), 102.0 (s, cym), 101.5 (s, cym), 90.2 (s, cym), 86.1 (s, cym), 83.6 (s, cym), 82.4 (s, cym), 32.3 (d, J_{CP} = 49.37 Hz, *C*H(CH_3)$_2$), 30.8 (s, *C*H(CH_3)$_2$), 25.9 (d, J_{CP} = 54.35 Hz, *C*H(CH_3)$_2$), 22.2–15.7 (CH(*C*H$_3$)$_2$), 14.6 (s, *C*H$_3$). ^{31}P{^{1}H} NMR (δ, CD_2Cl_2, 20 °C): 83.6.

3.2.11. [Ru(η^6-*p*-cymene)(κ^2(*Se*,*N*)-SeN-Ph)Cl]SbF_6. (**8a**)

This complex has been prepared analogously to **5a** with [Ru(η^6-*p*-cymene)(μ-Cl)Cl]$_2$ (0.100 g, 0.163 mmol), SN-Ph (0.114 g, 0.319 mmol), and $AgSbF_6$ (0.115 g, 0.335 mmol) as starting materials. Yield: 0.238 g (86%). *Anal.* Calc. for $C_{27}H_{29}ClF_6N_2PRuSbSe$: C, 37.55; H, 3.38; N, 3.24. Found: C, 37.54; H, 3.41; N, 3.19%. ^{1}H NMR (δ, CD_2Cl_2, 20 °C): 9.47 (br, 1H, NH), 9.18 (d, J_{HH} = 6.00 Hz, 1H, py^6), 8.48 (d, J_{HH} = 7.90 Hz, 1H, py^4), 8.42 (d, J_{HH} = 7.90 Hz, 1H, py^3), 8.10–7.10 (m, 11H, Ph, py^5), 5.82 (d, J_{HH} = 6.63 Hz, 1H, cym), 5.68 (d, J_{HH} = 5.37 Hz, 1H, cym), 5.35 (d, J_{HH} = 6.00 Hz, 1H, cym), 5.20 (d, J_{HH} = 5.37 Hz, 1H, cym), 2.77 (m, J_{HH} = 6.87 Hz, 1H, C*H*(CH_3)$_2$), 1.75 (s, 3H, CH_3), 1.24 (d, J_{HH} = 6.95 Hz, 3H, CH(C*H*$_3$)$_2$), 1.21 (d, J_{HH} = 6.95 Hz, 3H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (δ, CD_2Cl_2, 20 °C): 155.9 (d, $^2J_{CP}$ = 4.72 Hz, py^2), 155.5 (s, py^6), 141.2 (s, py^4), 134.6–128.4 (Ph), 120.9 (s, py^5), 120.2 (d, $^3J_{CP}$ = 4.04 Hz, py^3), 102.1 (s, cym), 101.6 (s, cym), 88.7 (s, cym), 84.1 (s, cym), 83.3 (s, cym), 79.2 (s, cym), 31.0 (s, *C*H(CH_3)$_2$), 22.1 (s, CH(*C*H$_3$)$_2$), 21.3 (s, CH(*C*H$_3$)$_2$), 17.3 (s, *C*H$_3$). ^{31}P{^{1}H} NMR (δ, CD_2Cl_2, 20 °C): 44.5 (with satellites $J_{P\text{-}Se}$ = 663 Hz).

3.2.12. [Ru(η^6-*p*-cymene)(κ^2(*Se*,*N*)-SeN-iPr)Cl]SbF_6. (**8b**)

This complex has been prepared analogously to **5a** with [Ru(η^6-*p*-cymene)(μ-Cl)Cl]$_2$ (0.100 g, 0.163 mmol), SeN-*i*Pr (0.096 g, 0.332 mmol), and $AgSbF_6$ (0.124 g, 0.361 mmol) as starting materials. Yield: 0.202 g (78%). *Anal.* Calc. for $C_{21}H_{33}ClF_6N_2PRuSbSe$: C, 31.70; H, 4.18; N, 3.52. Found: C, 31.68; H, 4.08; N, 3.55%. ^{1}H NMR (δ, CD_2Cl_2, 20 °C): 9.20 (d, J_{HH} = 4.87 Hz, 1H, py^6), 8.45 (br, 1H, NH), 8.03 (t, J_{HH} = 7.61 Hz, 1H, py^4), 7.58 (d, J_{HH} = 7.77 Hz, 1H, py^3), 7.37 (t, J_{HH} = 5.48 Hz, 1H, py^5), 6.08 (d, J_{HH} = 4.72 Hz, 1H, cym), 5.97 (d, J_{HH} = 5.18 Hz, 1H, cym), 5.62 (d, J_{HH} = 4.87 Hz, 1H, cym), 5.46 (d, J_{HH} = 4.72 Hz, 1H, cym), 2.95 (m, 2H, C*H*(CH_3)$_2$), 2.45 (m, 1H, C*H*(CH_3)$_2$), 1.60 (s, 3H, CH_3), 1.54–1.08 (m, 15H CH(C*H*$_3$)$_2$), 0.79 (dd, J = 19.26 Hz, J_{HH} = 6.93 Hz, 3H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (δ, CD_2Cl_2, 20 °C): 157.8 (d, $^2J_{CP}$ = 5.39 Hz, py^2), 156.2 (s, py^6), 141.1 (s, py^4), 120.7 (s, py^5), 120.4 (d, $^3J_{CP}$ = 4.04 Hz, py^3), 101.9 (s, cym), 101.5 (s, cym), 90.3 (s, cym), 85.5 (s, cym), 83.8 (s, cym), 81.3 (s, cym), 32.6 (d, J_{CP} = 39.07 Hz, *C*H(CH_3)$_2$), 30.9 (s, *C*H(CH_3)$_2$), 26.2 (d, J_{CP} = 47.16 Hz, *C*H(CH_3)$_2$), 22.0–15.7 (CH(*C*H$_3$)$_2$), 14.9 (s, *C*H$_3$). ^{31}P{^{1}H} NMR (δ, CD_2Cl_2, 20 °C): 77.3 (with satellites $J_{P\text{-}Se}$ = 640 Hz).

3.3. X-ray structure determination of **5a′** and **7b**

X-ray data of **5a′** and **7b** were collected on a Bruker Smart APEX CCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) and 0.3° ω-scan frames. Corrections for absorption and λ/2 effects were applied [23]. After structure

solution with program SHELXS97 refinement on F^2 was carried out with the program SHELXL97 [24]. Non-hydrogen atoms were refined anisotropically. H atoms were placed in calculated positions and thereafter treated as riding. Important crystallographic data are: **5a′**: $C_{27}H_{29}Cl_2N_2PRu$, M_r = 584.46, orange block from CD_2Cl_2, 0.59 × 0.38 × 0.30 mm, monoclinic, space group $P2_1/n$ (no. 14), a = 9.2754(5) Å, b = 18.7332(10) Å, c = 15.1296(8) Å, β = 106.380(1)°, V = 2522.2(2) Å^3, Z = 4, μ = 0.916 mm^{-1}, d_x = 1.539 g cm^{-3}, T = 100(2) K. 22820 reflections were collected up to θ_{max} = 30.0° and, after applying absorption corrections, merged to 7261 independent data (R_{int} = 0.018); final R indices: R_1 = 0.0306 (6781 reflections with $I > 2\sigma(I)$), wR_2 = 0.0789 (all data), 298 parameters. **7b**: $C_{21}H_{33}ClF_6N_2PRuSSb$, M_r = 748.79, orange plates from CD_2Cl_2, 0.34 × 0.26 × 0.22 mm, monoclinic, space group $P2_1/n$ (no. 14), a = 11.1387(2) Å, b = 20.6898(3) Å, c = 12.5233(2) Å, β = 104.463(1)°, V = 2794.63(8) Å^3, Z = 4, μ = 1.788 mm^{-1}, d_x = 1.780 g cm^{-3}, T = 100(2) K. 41994 reflections were collected up to θ_{max} = 30.0° and, after applying absorption corrections, merged to 8266 independent data (R_{int} = 0.027); final R indices: R_1 = 0.0306 (8266 reflections with $I > 2\sigma(I)$), wR_2 = 0.0777 (all data), 317 parameters.

3.4. Hydrogen transfer catalysis with the precatalysts **5b**, **6**, **7b**, and **8b**

In a typical procedure, to a 0.1 M solution of acetophenone in 2-propanol the pre-catalyst (0.5 mol%) and KO*t*Bu (10 mol%) were added (acetophenone:precatalyst:KO*t*Bu = 200:1:20) to a Schlenk tube and heated at 75 °C for 22 h unless otherwise noted (see Table 1). After the reaction time the solvent was removed under pressure and the product distribution was determined by ^{1}H NMR spectroscopy.

4. Supplementary material

Crystallographic data for the crystal structures of **5a′** and **7b** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication under reference CCDC 771456 (**5a′**) and 782837 (**7b**). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

References

[1] (a) A. Bader, E. Lindner, Coord. Chem. Rev. 108 (1991) 27. and references cited therein;
(b) M. Bassetti, Eur. J. Inorg. Chem. (2006) 4473;
(c) G. Helmchen, A. Pfaltz, Acc. Chem. Res. 33 (2000) 336;
(d) H.A. McManus, P. Guiry, Chem. Rev. 104 (2004) 4151;
(e) P. Braunstein, Chem. Rev. 106 (2006) 134;
(f) V.V. Grushin, Chem. Rev. 104 (2004) 1629;
(g) T.Q. Ly, J.D. Woollins, Coord. Chem. Rev. 176 (1998) 451.
[2] J.C. Jeffrey, T.B. Rauchfuss, Inorg. Chem. 18 (1979) 2658.
[3] D. Benito-Garagorri, K. Mereiter, K. Kirchner, Collect. Czech. Chem. Commun. 72 (2007) 527.
[4] C.M. Standfest-Hauser, G. Dazinger, J. Wiedermann, K. Mereiter, K. Kirchner, Eur. J. Inorg. Chem. (2009) 4085.
[5] J. Ansell, M. Wills, Chem. Soc. Rec. 31 (2002) 259.
[6] W.-J. Zhao, S.-J. Zhang, Y. Deng, Z.-Z. Zhang, Y.-F. Ma, W.-P. Huang, H.-G. Wang, Jiegou Huaxue 15 (1996) 44.
[7] W. Seidel, H. Schöler, Z. Chem. 11 (1967) 431.
[8] W. Ainscough, L.K. Peterson, Inorg. Chem. 9 (1970) 2699.
[9] H. Brunner, H. Weber, Chem. Ber. 118 (1985) 3380.
[10] (a) W. Schirmer, U. Flörke, H.J. Haupt, Z. Anorg. Allg. Chem. 545 (1987) 83;
(b) W. Schirmer, U. Flörke, H.J. Haupt, Z. Anorg. Allg. Chem. 574 (1989) 239.
[11] S.M. Aucott, A.M.Z. Slawin, J.D. Woollins, Phosphorus Sulfur Silicon 124–125 (1997) 473.
[12] (a) S.M. Aucott, A.M.Z. Slawin, J.D. Woollins, J. Chem. Soc., Dalton Trans. (2000) 2559;
(b) A.M.Z. Slawin, J. Wheatley, M.V. Wheatley, J.D. Woollins, Polyhedron 22 (2003) 1397.
[13] G. Sanchez, J. Garcia, D. Meseguer, J.L. Serrano, L. Garcia, J. Perez, G. Lopez, Inorg. Chim. Acta 357 (2004) 4568.
[14] (a) E. Smolensky, M. Kapon, J.D. Woollins, M.S. Eisen, Organometallics 24 (2005) 3255;
(b) E. Smolensky, M. Kapon, M.S. Eisen, Organometallics 26 (2007) 4510.
[15] S.M. Nabavizadeh, E.S. Tabei, F.N. Hosseini, N. Keshavarz, S. Jamali, M. Rashidi, New J. Chem. 34 (2010) 495.
[16] I. Macías-Arce, M.C. Puerta, P. Valerga, Eur. J. Inorg. Chem. (2010) 1767.
[17] H.-G. Henning, U. Ladhoff, Z. Chem. 13 (1973) 6.
[18] For related tridentate ENE ligands see for example: N. Biricik, Z. Fei, R. Scopelliti, P.J. Dyson, Helv. Chim. Acta 86 (2003) 3281.
[19] (a) W.J. Knebel, R.J. Angelici, Inorg. Chim. Acta 7 (1973) 713;
(b) W.J. Knebel, R.J. Angelici, Inorg. Chem. 13 (1974) 632;
(c) E.W. Ainscough, A.M. Brodie, S.T. Wong, J. Chem. Soc., Dalton Trans. (1977) 915.
[20] D. Benito-Garagorri, E. Becker, J. Wiedermann, W. Lackner, M. Pollak, K. Mereiter, J. Kisala, K. Kirchner, Organometallics 25 (2006) 1900.
[21] D.D. Perrin, W.L.F. Armarego, Purification of Laboratory Chemicals, third ed., Pergamon, New York, 1988.
[22] M.A. Bennett, A.K. Smith, J. Chem. Soc., Dalton Trans. (1974) 233.
[23] Bruker Programs: SMART, Version 5.625; SAINT, Version 6.54; SADABS, Version 2.10; SHELXTL, Version 6.1, Bruker AXS Inc., Madison, WI, 2003.
[24] G.M. Sheldrick, Acta Crystallogr., Sect. A 64 (2008) 112.