ORGANOMETALLICS

Article

pubs.acs.org/Organometallics

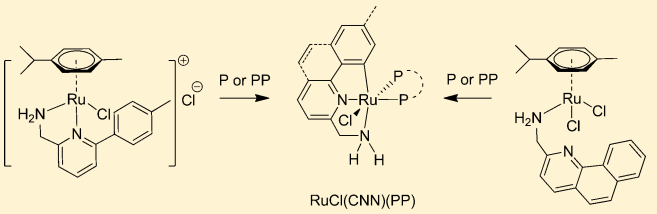
Synthesis of Pincer Ruthenium RuCl(CNN)(PP) Catalysts from [RuCl(μ-Cl)(η^6-*p*-cymene)]$_2$

Shuanming Zhang and Walter Baratta*

Dipartimento di Chimica, Fisica Ambiente, Università di Udine, Via Cotonificio 108, I-33100 Udine, Italy

Supporting Information

ABSTRACT: The cationic [RuCl(η^6-*p*-cymene)(HCNN^a)]Cl (**1a**) (HCNN^a = 1-(6-arylpyridin-2-yl)methanamine) and the neutral RuCl$_2$(η^6-*p*-cymene)(HCNN^b) (**1b**) (HCNN^b = 2-aminomethylbenzo[*h*]quinoline) complexes have been obtained by reaction of the precursor [RuCl(μ-Cl)(η^6-*p*-cymene)]$_2$ with the corresponding nitrogen ligand (HCNN^a and HCNN^b) in THF. Complex **1a** reacts cleanly with monodentate (P = PPh$_3$) and bidentate phosphines (PP = dppb, dppf) in ethanol in the presence of NEt$_3$, affording the pincer catalysts RuCl(CNN^a)(PPh$_3$)$_2$ (**2**) and RuCl(CNN^a)(PP) (PP = dppb **3**, dppf **4**). Similarly, the benzo[*h*]quinoline pincer derivative RuCl(CNN^b)(dppb) (**5**) is obtained from **1b** and dppb. Complex **3** has also been prepared in a one-pot reaction from [RuCl(μ-Cl)(η^6-*p*-cymene)]$_2$, HCNN^a, and dppb in ethanol. Similarly, the chiral complex RuCl(CNN^a)((*R*,*S*)-Josiphos) was isolated as a single stereoisomer by treatment of [RuCl(μ-Cl)(η^6-*p*-cymene)]$_2$ with HCNN^a and (*R*,*S*)-Josiphos in 1-butanol. Reaction of **1a** and **1b** with dppb affords cymene diphosphine species by displacement of the HCCN ligand.



INTRODUCTION

The reduction of carbonyl compounds to alcohols is a versatile organic transformation for the preparation of a number of industrially relevant products.[1] The catalytic hydrogenation[2] and transfer hydrogenation[3] of ketones can be achieved using dihydrogen or hydrogen donor molecules, such as formic acid or 2-propanol, mediated by transition-metal complexes based on Rh, Ir, Os,[4] and Ru, with ruthenium being the metal of choice.[2,3] On account of the ease of working, absence of the risks associated with the use of H_2, and the environmentally friendly transformation, the catalytic transfer hydrogenation of carbonyl compounds has become a valuable route for the synthesis of alcohols. Following the pioneering works of Noyori et. al on *trans*-RuCl$_2$(PP)(1,2-diamine) (PP = diphosphine)[5] and (η^6-arene)RuCl(TsNCHPhCHPhNH$_2$) (Ts = SO$_2$C$_6$H$_4$-CH$_3$)[6] for the hydrogenation and transfer hydrogenation of ketones, respectively, several Ru catalysts have been developed in the past decade. High rate ande chemo- and stereoselectivity have been achieved using ligands containing the N−H function, via bifunctional catalysis.[7] The CNN pincer complexes RuCl(CNN)(PP) (HCNN = 1-(6-arylpyridin-2-yl)-methanamine,[8] 2-aminomethylbenzo[*h*]quinoline[9]), displaying the NH$_2$ function,[7] are the most efficient catalysts for the transfer hydrogenation of aldehydes and ketones. Outstanding rate and productivity have been achieved, affording TOF and TON values of 10^6 h^{-1} and 10^5, respectively, which meet the requirements for industrial applications. These CNN pincer complexes have also been found to be highly active in hydrogenation of carbonyl compounds[8c,9b] and dehydrogenation,[10] racemization, and deuteration of alcohols[11] and hold promise for a broad use in a number of organic transformations.

The preparation of these complexes entails the reaction of RuCl$_2$(PPh$_3$)$_3$ with a diphosphine and the HCNN ligand, through orthometalation. It is worth noting that the arene complexes [RuCl(μ-Cl)(η^6-arene)]$_2$ are the common precursors used for the synthesis of the Noyori catalysts for both hydrogenation and transfer hydrogenation reactions and involve the formation of species containing the Ru(η^6-arene)(LL) moiety (LL = diphosphine, diamine).[12]

We report herein a new practical route for the preparation of the CNN pincer catalysts starting from the commercially available [RuCl(μ-Cl)(η^6-*p*-cymene)]$_2$ and from cationic and neutral HCNN cymene ruthenium complexes.

RESULTS AND DISCUSSION

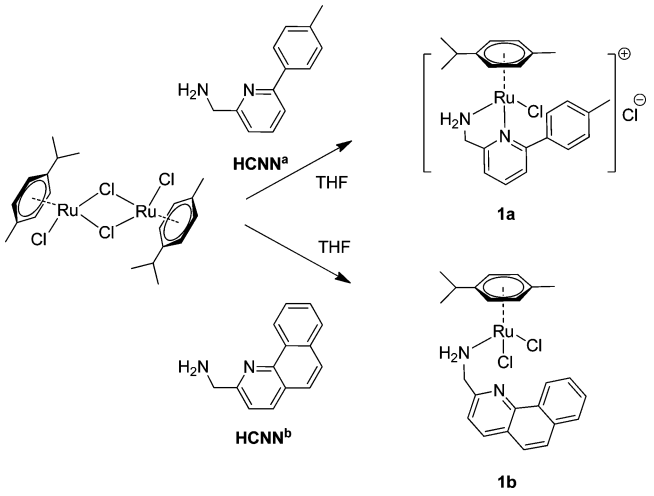
Treatment of [RuCl(μ-Cl)(η^6-*p*-cymene)]$_2$ with 2 equiv of 1-(6-arylpyridin-2-yl)methanamine (HCNN^a) in THF promptly leads to the complex [RuCl(η^6-*p*-cymene)(HCNN^a)]Cl (**1a**), which was isolated in 81% yield (Scheme 1).

The ^{1}H NMR spectrum of **1a** at 50 °C shows four doublets for the aromatic *p*-cymene protons with two doublets for the isopropyl moiety, whereas the two multiplets at δ = 4.50 are for the two diastereotopic NCH$_2$ protons. These data are consistent with a cationic complex with a chloride as counterion, as observed for analogous ruthenium complexes.[13] While one N−H proton is at δ = 3.28 and appears as a broad quartet, the second N−H is significantly low-field shifted at δ = 9.46 (broad triplet), as established through a ^{1}H−^{1}H COSY experiment, and it is consistent with an interaction of the N−H

Received: April 4, 2013

dx.doi.org/10.1021/om400280m | *Organometallics* XXXX, XXX, XXX−XXX

Scheme 1. Synthesis of the Complexes 1a and 1b



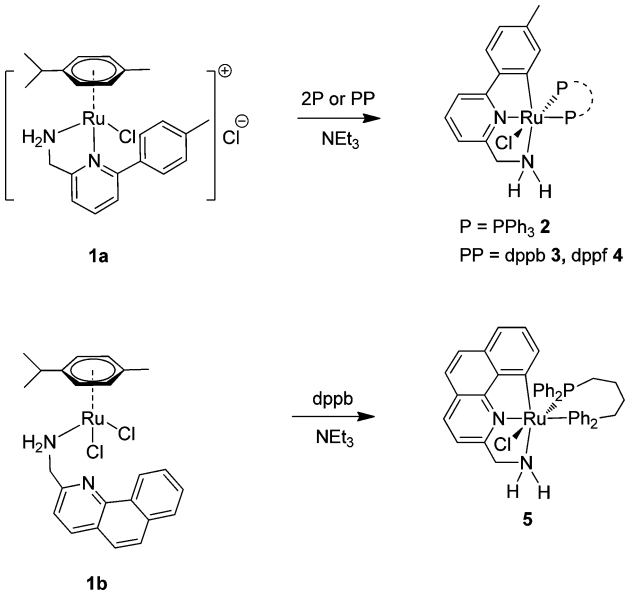
proton with the outer sphere chloride. In addition, the two broad signals at δ = 7.25 and 7.90 of the aromatic tolyl protons at 25 °C become sharper at 50 °C with a J(H,H) of 7.5 Hz, suggesting that the slow rotation of the tolyl group is due to its interaction with the *p*-cymene ligand. By contrast to HCNN[a], the reaction of 2-aminomethylbenzo[*h*]quinoline (HCNN[b]) with $[RuCl(\mu\text{-}Cl)(\eta^6\text{-}p\text{-cymene})]_2$ leads to the formation of a neutral complex **1b** in 83% yield (Scheme 1). The ^{1}H NMR spectrum of **1b** shows two doublets at δ = 5.20 and 5.06 for the aromatic *p*-cymene protons, whereas the CH_2 and NH_2 groups give two triplets at δ = 4.52 and 4.10, the latter N−H signal being low-field shifted with respect to that of the free ligand (δ = 2.90),[8d] in agreement with a benzo[*h*]quinoline acting as a monodentate ligand through the NH_2 group.[14] The different behaviors of the two HCNN ligands can be ascribed to the steric properties of the nitrogen ligands, with the benzo[*h*]-quinoline, which displays higher rigidity and hinders the coordination of the heterocyclic nitrogen to the Ru *p*-cymene moiety.

The cationic complex **1a** reacts promptly with the mono-phosphine PPh_3 in the presence of triethylamine in ethanol at reflux, affording the pincer compound $RuCl(CNN^a)(PPh_3)_2$ (**2**) through displacement of *p*-cymene and orthometalation of the HCNN ligand (Scheme 2). Under the same experimental conditions, **1a** reacts with the diphosphine $Ph_2P(CH_2)_4PPh_2$ (dppb), leading to the pincer catalysts $RuCl(CNN^a)$(dppb) (**3**),[8a] whereas the use of 1,1′-bis(diphenylphosphino)ferrocene (dppf) affords $RuCl(CNN^a)$(dppf) (**4**),[11] which were isolated in high yield (Scheme 2).

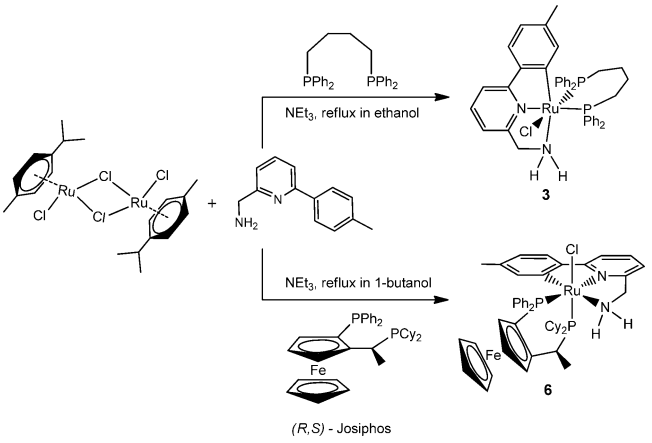
Conversely, the neutral benzo[*h*]quinoline derivative **1b** reacts cleanly with dppb in ethanol at reflux, affording the pincer complex **5**[9a] in 80% yield (Scheme 2). It is worth pointing out that the pincer complex $RuCl(CNN^a)$(dppb) (**3**) was also obtained in 64% yield by adding HCNN[a] and dppb to the ruthenium precursor $[RuCl(\mu\text{-}Cl)(\eta^6\text{-}p\text{-cymene})]_2$ in ethanol at reflux and in the presence of NEt_3, through a one-pot synthesis and without isolating the **1a** intermediate (Scheme 3).

Following this procedure, treatment of $[RuCl(\mu\text{-}Cl)(\eta^6\text{-}p\text{-cymene})]_2$ with HCNN[a] and the chiral diphosphine (*R*,*S*)-Josiphos in EtOH at refluxing conditions (8 h) results in the formation of a mixture of two $RuCl(CNN^a)$((*R*,*S*)-Josiphos) diastereoisomers and the cationic arene phosphino intermediate $[RuCl(\eta^6\text{-}p\text{-cymene})$((*R*,*S*)-Josiphos)]Cl in about a 1:3:8

Scheme 2. Synthesis of the Pincer Complexes 2−5



Scheme 3. One-Pot Synthesis of the Pincer Complexes 3 and 6



molar ratio, respectively.[15,16] Interestingly, by performing the reaction in refluxing 1-butanol, which displays a boiling point higher compared to ethanol (117 vs 78 °C), the chiral pincer complex $RuCl(CNN^a)$((*R*,*S*)-Josiphos) (**6**)[8c] was obtained as a single stereoisomer and was isolated in 62% (Scheme 3). Employment of toluene resulted in the formation of a mixture of uncharacterized products, indicating that the solvent is crucial for the synthesis of the pincer catalysts with (chiral) bulky phosphines.

To elucidate the nature of the species involved in the formation of the pincer complexes, we studied the reactivity of the arene ruthenium complexes with HCNN and phosphine ligands. It is well-established that the precursor $[RuCl(\mu\text{-}Cl)(\eta^6\text{-}p\text{-cymene})]_2$ reacts promptly with phosphines, leading to cationic or neutral complexes, depending on the stereo-electronic features of the phosphines. As a matter of fact, the reaction of $[RuCl(\mu\text{-}Cl)(\eta^6\text{-}p\text{-cymene})]_2$ with rigid diphosphines, such as BINAP, gave the cationic $[RuCl(\eta^6\text{-}p\text{-cymene})(BINAP)]Cl$ complex.[17] Cationic species $[RuCl(\eta^6\text{-}p\text{-cymene})(PP)]^+$ (e.g., for PP = dppf)[18] were easily prepared by substitution of one chloride with low coordinating anions, namely, PF_6 or BF_4, in polar solvent media. Reaction of

dx.doi.org/10.1021/om400280m | *Organometallics* XXXX, XXX, XXX−XXX

$[RuCl(\mu\text{-}Cl)(\eta^6\text{-}p\text{-cymene})]_2$ with dppb led to the isolation of the neutral dinuclear complex $[RuCl_2(\eta^6\text{-cymene})]_2(\mu\text{-dppb})$, regardless of the ruthenium/diphosphine stoichiometry, as reported by Doherty et al.[19] We found in this work that $[RuCl(\mu\text{-}Cl)(\eta^6\text{-}p\text{-cymene})]_2$ reacts with dppb in dichloromethane, leading to an equilibrium between mononuclear and dinuclear Ru complexes, according to eq 1

$$[RuCl_2(\eta^6\text{-}p\text{-cymene})]_2(\mu\text{-dppb}) + \text{dppb} \rightleftharpoons 2Rucl_2(\eta^6\text{-}p\text{-cymene})(\eta^1\text{-dppb}) \quad (1)$$

A $K = 2.2$ at 25 °C was determined through $^{31}P\{^1H\}$ NMR measurements carried out with a Ru:diphosphine molar ratio of 1:1 to 1:3.[20] As regards to the HCNN cymene derivatives, complex **1b** reacts promptly (5 min) with dppb in CD_2Cl_2 at RT, affording $RuCl_2(\eta^6\text{-}p\text{-cymene})(\eta^1\text{-dppb})$ and $[RuCl_2(\eta^6\text{-}p\text{-cymene})]_2(\mu\text{-dppb})$ in equilibrium (eq 1), by displacement of the HCNN[b] ligand. The reaction of the cationic complex **1a** gives the same phosphino complexes at 40 °C after 15 h. These results clearly indicate that the neutral complex **1b** is more labile than the cationic **1a** and that the diphosphine is a stronger ligand compared to the neutral bidentate HCNN[a] and HCNN[b] ligands. Therefore, the formation of the pincer complexes from **1a** and **1b** involves the displacement of HCNN with the phosphine, leading to the neutral or cationic species $Ru(\eta^6\text{-}p\text{-cymene})Cl_n(PP)^{0/+}$ ($n = 1, 2$). In alcohol media and under reflux conditions, these species react with the HCNN, affording $RuCl_2(HCNN)(PP)$ by elimination of *p*-cymene and leading to the final RuCl(CNN)(PP) complex via orthometalation. It is worth noting that employment of diphosphines with a short backbone (i.e., dppe) leads to the $RuCl_2(PP)_2$ species that show high stability and do not convert into the pincer complexes. Thus, the preparation of RuCl(CNN)(PP) derivatives is accomplished with a suitable combination of the HCCN and phosphine ligands. In addition, although arene phosphine derivatives can be employed for the synthesis of the pincer complexes, the Ru/phosphine stoichiometry depends on the type of the phosphine used.

■ CONCLUDING REMARKS

In summary, we have described the isolation of ionic $[RuCl(\eta^6\text{-}p\text{-cymene})(HCNN]Cl$ and neutral $RuCl_2(\eta^6\text{-}p\text{-cymene})(HCNN)$ complexes, displaying a Ru/HCNN = 1, which can be used as suitable precursors for the preparation of the pincer catalysts RuCl(CNN)(PP) by reaction with the appropriate phosphine ligand. Steric effects and the rigidity of HCNN are responsible for the different coordination modes of these ligands to the ruthenium center. Achiral and chiral pincer complexes have also been prepared from $[RuCl(\mu\text{-}Cl)(\eta^6\text{-}p\text{-cymene})]_2$, HCNN, and the appropriate (chiral) diphosphine ligand, through a one-pot reaction using EtOH or 1-BuOH as solvents. The straightforward synthesis of the pincer ruthenium complexes holds promise for a broad use of them as catalysts in organic transformations.

■ EXPERIMENTAL SECTION

All manipulations were carried out under an inert argon atmosphere, using standard Schlenk-line conditions and dried and freshly distilled solvents. The HCNN ligands 6-(4′-methylphenyl)-2-pyridylmethylamine (HCNN[a])[8d] and 2-aminomethylbenzo[*h*]quinoline (HCNN[b])[9a] were prepared according to literature procedures. All other chemicals were purchased from Aldrich and used without further purification. Unless otherwise stated, the ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded at 298 K on a Bruker AC 200 instrument at 200, 60, and 80 MHz, respectively, whereas the chemical shifts are in parts per million, using TMS or H_3PO_4 (85% in D_2O) as external standards. The elemental analyses were carried out with a Carlo Erba 1106 elemental analyzer.

Synthesis of $[RuCl(\eta^6\text{-}p\text{-cymene})(HCNN^a)]Cl$ (1a). $[RuCl(\mu\text{-}Cl)(\eta^6\text{-}p\text{-cymene})]_2$ (0.306 g, 0.5 mmol) was added to a solution of HCNN[a] (0.198 g, 1.0 mmol) in THF (5 mL). The mixture was stirred at room temperature for 10 min, affording a yellow precipitate that was filtered, washed with THF, and dried under reduced pressure (0.410 g, 81% yield). mp 139 °C. Anal. Calcd for $C_{23}H_{28}Cl_2N_2Ru$ (504.46): C, 54.76; H, 5.59; N, 5.55. Found: C, 54.65; H, 5.20; N, 5.40. ^1H NMR ($CDCl_3$, 50 °C): δ 9.46 (br, 1H, NH_2), 7.95−7.29 (m, 7H, aromatic hydrogens), 5.96 (d, 1H, $^3J(H,H) = 6.0$ Hz, C_6H_4 of cymene), 5.24 (d, 1H, $^3J(H,H) = 6.0$ Hz, C_6H_4 of cymene), 4.98 (d, 1H, $^3J(H,H) = 6.0$ Hz, C_6H_4 of cymene), 4.80 (d, 1H, $^3J(H,H) = 6.0$ Hz, C_6H_4 of cymene), 4.63 (m, 1H, NCH_2), 4.40 (m, 1H, NCH_2), 3.28 (br, 1H, NH_2), 2.72 (sept, 1H, $^3J(H,H) = 7.0$ Hz, $CH(CH_3)_2$), 2.49 (s, 3H, CH_3 of HCNN[a]), 1.93 (s, 3H, CH_3 of cymene), 1.05 (d, 3H, $^3J(H,H) = 7.0$ Hz, $CH(CH_3)_2$), 0.96 (d, 3H, $^3J(H,H) = 7.0$ Hz, $CH(CH_3)_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 164.7−119.4 (m, aromatic carbons), 103.7 (s, *ipso*-C_6H_4 of cymene), 90.1 (s, *ipso*-C_6H_4 of cymene), 83.8 (br, C_6H_4 of cymene), 82.7 (br), 54.1 (s, NCH_2), 30.7 (s, $CH(CH_3)_2$), 23.0 (s, CH_3 of HCNN[a]), 21.4 (s, $CH(CH_3)_2$), 18.6 (s, CH_3 of cymene).

Synthesis of $RuCl_2(\eta^6\text{-}p\text{-cymene})(HCNN^b)$ (1b). $[RuCl(\mu\text{-}Cl)(\eta^6\text{-}p\text{-cymene})]_2$ (0.306 g, 0.50 mmol) was added to a solution of ligand HCNN[b] (0.208 g, 1.0 mmol) in THF (5 mL). The mixture was stirred at room temperature for 10 min, affording an orange-yellow precipitate that was filtered, washed with THF, and dried under reduced pressure (0.427 g, 83% yield). mp 211 °C. Anal. Calcd for $C_{24}H_{26}Cl_2N_2Ru$ (514.45): C, 56.03; H, 5.09; N, 5.45. Found: C, 56.05; H, 5.25; N, 5.31. ^1H NMR (CD_2Cl_2): δ 7.44−9.33 (m, 8H, aromatic hydrogens of HCNN[b]), 5.20 (d, 2H, $^3J(H,H) = 6.0$ Hz, C_6H_4 of cymene), 5.06 (d, 2H, $^3J(H,H) = 6.0$ Hz, C_6H_4 of cymene), 4.52 (t, 2H, $^3J(H,H) = 4.5$ Hz, NCH_2), 4.10 (t, 2H, $^3J(H,H) = 4.5$ Hz, NH_2), 2.93 (sept, 1H, $^3J(H,H) = 7.2$ Hz, $CH(CH_3)_2$), 2.14 (s, 3H, CH_3), 1.23 (d, 6H, $^3J(H,H) = 7.2$ Hz, $CH(CH_3)_2$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 156.0−120.7 (aromatic carbons), 102.7 (s, *ipso*-C_6H_4 of cymene), 95.8 (s, *ipso*-C_6H_4 of cymene), 81.2 (s, C_6H_4 of cymene), 80.1 (s, C_6H_4 of cymene), 52.5 (s, NCH_2), 31.1 (s, $CH(CH_3)_2$), 22.2 (s, $CH(CH_3)_2$), 18.7 (s, CH_3 of cymene).

Synthesis of $RuCl(CNN^a)(PPh_3)_2$ (2). PPh_3 (0.216 g, 0.8 mmol) and NEt_3 (0.5 mL, 3.5 mmol) were added to a solution of complex $[RuCl(\eta^6\text{-}p\text{-cymene})(HCNN^a)]Cl$ (**1a**) (0.200 g, 0.4 mmol) in ethanol (5 mL). The resulting mixture was stirred under reflux for 2 h, whereupon a dark yellow precipitate formed that was filtered, washed with ethanol, and dried under reduced pressure (0.284 g, 83% yield). mp 158 °C. Anal. Calcd for $C_{49}H_{43}ClN_2P_2Ru$ (858.35): C, 68.56; H, 5.05; N, 3.26. Found: C, 68.35; H, 5.20; N, 3.07. ^1H NMR ($CDCl_3$): δ 7.95−6.84 (m, 36H, aromatic), 4.52 (br, 1H, NCH_2), 4.05 (br, 1H, NCH_2), 3.45(br, 1H, NH_2), 2.18 (s, 3H, CH_3), 1.53 (br, 1H, NH_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 56.7 (d, $^2J(P,P) = 33.6$ Hz), 50.5 (d, $^2J(P,P) = 33.6$ Hz).

Synthesis of $RuCl(CNN^a)(dppb)$ (3). The synthesis of **3** was carried out as described for **2** by addition of NEt_3 (0.5 mL, 3.5 mmol) and dppb (0.172 g, 0.4 mmol) in place of PPh_3, to a solution of $[RuCl(\eta^6\text{-}p\text{-cymene})(HCNN^a)]Cl$ (**1a**) (0.200 g, 0.4 mmol) in ethanol (5 mL). The resulting mixture was stirred under reflux for 2 h, whereupon a yellow precipitate formed that was filtered, washed with ethanol, and dried under reduced pressure (0.244 g, 80% yield).[8a]

Synthesis of $RuCl(CNN^a)(dppf)$ (4). The synthesis of **4** was carried out as described for **2** by addition of NEt_3 (0.5 mL, 3.5 mmol) and dppf (0.216 g, 0.4 mmol) in place of PPh_3, to a solution of complex $[RuCl(\eta^6\text{-}p\text{-cymene})(HCNN^a)]Cl$ (**1a**) (0.200 g, 0.4 mmol) in ethanol (5 mL). The resulting mixture was stirred under reflux for 2 h, whereupon a yellow precipitate formed that was filtered, washed with ethanol, and dried under reduced pressure (0.284 g, 79% yield).[11]

Synthesis of $RuCl(CNN^b)(dppb)$ (5). The synthesis of **5** was carried out as described for **2** by addition of NEt_3 (0.5 mL, 3.5 mmol)

dx.doi.org/10.1021/om400280m | *Organometallics* XXXX, XXX, XXX−XXX

and dppb (0.172 g, 0.4 mmol) in place of PPh_3, to a solution of complex $RuCl_2(\eta^6$-*p*-cymene)(HCNN[b]) (**1b**) (0.204 g, 0.4 mmol) in ethanol (5 mL). The resulting mixture was stirred under reflux for 2 h, whereupon a yellow precipitate formed that was filtered, washed with ethanol, and dried under reduced pressure (0.062 g, 80% yield).[9a]

One-Pot Synthesis of RuCl(CNN[a])(dppb) (3). dppb (0.214 g, 0.5 mmol), HCNN[a] (0.100 g, 0.5 mmol), and NEt_3 (0.2 mL, 1.4 mmol) were added to a solution of complex $[RuCl(\mu\text{-}Cl)(\eta^6\text{-}p\text{-cymene})]_2$ (0.153 g, 0.25 mmol) in ethanol (3 mL). The resulting mixture was stirred under reflux for 2 h, whereupon a dark yellow precipitate formed that was filtered, washed with ethanol, and dried under reduced pressure (0.243 g, 64% yield).

One-Pot Synthesis of RuCl(CNN[a])((*R*,*S*)-Josiphos) (6). (*R*,*S*)-Josiphos (0.320 g, 0.5 mmol), HCNN[a] (0.100 g, 0.5 mmol), and NEt_3 (0.5 mL, 3.5 mmol) were added to a solution of complex $[RuCl(\mu\text{-}Cl)(\eta^6\text{-}p\text{-cymene})]_2$ (0.156 g, 0.25 mmol) in 1-butanol (4 mL). The resulting mixture was stirred under reflux for 4 h, the resulting dark red solution was concentrated to 0.5 mL, and pentane (5 mL) was added. Compound **6** was obtained as a dark yellow solid through filtration and dried under reduced pressure (0.301 g, 62% yield).[8c]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The NMR spectra of **1a** and of the Ru(*p*-cymene)/dppb system. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: walter.baratta@uniud.it.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the Ministero dell'Università e della Ricerca (MIUR) and the Talents program of the AREA Science Park of Trieste for a fellowship for S.Z. We thank Johnson-Matthey/Alfa Aesar for a generous loan of ruthenium and Mr. P. Polese for carrying out the elemental analyses.

■ REFERENCES

(1) Magano, J.; Dunetz, J. R. *Org. Process Res. Dev.* **2012**, *16*, 1156.

(2) (a) Shang, G.; Li, W.; Zhang, X. In *Catalytic Asymmetric Synthesis*, 3rd ed.; Ojima, I., Ed.; John Wiley & Sons: Hoboken, NJ, 2010; Chapter 7. (b) de Vries, J. G., Elsevier, C. J., Eds. *The Handbook of Homogeneous Hydrogenation*; Wiley-VCH: Weinheim, Germany, 2007; Vols. *1*−3. (c) Beller, M., Bolm, C., Eds. *Transition Metals for Organic Synthesis*, 2nd ed.; Wiley-VCH: Weinheim, 2004; p 29. (d) Blaser, H. U., Schmidt, E., Eds. *Asymmetric Catalysis on Industrial Scale*; Wiley-VCH: Weinheim, Germany, 2004.

(3) (a) Morris, R. H. *Chem. Soc. Rev.* **2009**, *38*, 2282. (b) Baratta, W.; Rigo, P. *Eur. J. Inorg. Chem.* **2008**, 4041. (c) Wang, C.; Wu, X.; Xiao, J. *Chem.—Asian J.* **2008**, *3*, 1750. (d) Morris, D. J.; Wills, M. *Chem. Today (Chimica Oggi)* **2007**, *25*, 11. (e) Ikariya, T.; Blacker, A. J. *Acc. Chem. Res.* **2007**, *40*, 1300. (f) Samec, J. S. M.; Bäckvall, J. E.; Andersson, P. G.; Brandt, P. *Chem. Soc. Rev.* **2006**, *35*, 237. (g) Ikariya, T.; Murata, K.; Noyori, R. *Org. Biomol. Chem.* **2006**, *4*, 393.

(4) (a) Baratta, W.; Ballico, M.; Chelucci, G.; Siega, K.; Rigo, P. *Angew. Chem., Int. Ed.* **2008**, *47*, 4362. (b) Baratta, W.; Ballico, M.; Del Zotto, A.; Siega, K.; Magnolia, S.; Rigo, P. *Chem.—Eur. J.* **2008**, *14*, 2557.

(5) Doucet, H.; Ohkuma, T.; Murata, K.; Yokozawa, T.; Kozawa, M.; Katayama, E.; England, A. F.; Ikariya, T.; Noyori, R. *Angew. Chem., Int. Ed.* **1998**, *37*, 1703.

(6) Haack, K. J.; Hashiguchi, S.; Fujii, A.; Ikariya, T.; Noyori, R. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 285.

(7) (a) Yamakawa, M.; Ito, H.; Noyori, R. *J. Am. Chem. Soc.* **2000**, *122*, 1466. (b) Petra, D. G. I.; Reek, J. N. H.; Handgraaf, J. W.; Meijer, E. J.; Dierkes, P.; Kamer, P. C. J.; Brussee, J.; Schoemaker, H. E.; van Leeuwen, P. W. N. M. *Chem.—Eur. J.* **2000**, *6*, 2818.

(8) (a) Baratta, W.; Chelucci, G.; Gladiali, S.; Siega, K.; Toniutti, M.; Zanette, M.; Zangrando, E.; Rigo, P. *Angew. Chem., Int. Ed.* **2005**, *44*, 6214. (b) Baratta, W.; Siega, K.; Rigo, P. *Adv. Synth. Catal.* **2007**, *349*, 1633. (c) Baratta, W.; Chelucci, G.; Magnolia, S.; Siega, K.; Rigo, P. *Chem.—Eur. J.* **2009**, *15*, 726. (d) Baratta, W.; Bosco, M.; Chelucci, G.; Del Zotto, A.; Siega, K.; Toniutti, M.; Zangrando, E.; Rigo, P. *Organometallics* **2006**, *25*, 4611. (e) Baratta, W.; Benedetti, F.; Del Zotto, A.; Fanfoni, L.; Felluga, F.; Magnolia, S.; Putignano, E.; Rigo, P. *Organometallics* **2010**, *29*, 3563.

(9) (a) Baratta, W.; Ballico, M.; Baldino, S.; Chelucci, G.; Herdtweck, E.; Siega, K.; Magnolia, S.; Rigo, P. *Chem.—Eur. J.* **2008**, *14*, 9148. (b) Baratta, W.; Fanfoni, L.; Magnolia, S.; Siega, K.; Rigo, P. *Eur. J. Inorg. Chem.* **2010**, 1419.

(10) Baratta, W.; Bossi, G.; Putignano, E.; Rigo, P. *Chem.—Eur. J.* **2011**, *17*, 3474.

(11) Bossi, G.; Putignano, E.; Rigo, P.; Baratta, W. *Dalton Trans.* **2011**, *40*, 8986.

(12) (a) Noyori, R.; Ohkuma, T. *Angew. Chem., Int. Ed.* **2001**, *40*, 40. (b) Noyori, R.; Hashiguchi, S. *Acc. Chem. Res.* **1997**, *30*, 97.

(13) (a) Türkmen, H.; Kani, I.; Çetinkaya, B. *Eur. J. Inorg. Chem.* **2012**, 4494. (b) Zobi, F.; Mood, B. B.; Wood, P. A.; Fabbiani, F. P. A.; Parsons, S.; Sadler, P. J. *Eur. J. Inorg. Chem.* **2007**, 2783.

(14) (a) Burrell, A. K.; Steedman, A. J. *Organometallics* **1997**, *16*, 1203. (b) Govindaswamy, P.; Kollipara, M. R. *J. Coord. Chem.* **2006**, *59*, 131.

(15) $^{31}P\{^1H\}$ NMR in $CDCl_3$: δ 78.3 and 40.3 (d, $^2J(P,P)$ = 43.2 Hz, diastereomer of **6**), 68.7 and 44.3 (d, $^2J(P,P)$ = 42.8 Hz, complex **6**), 49.1 and 28.3 (d, $^2J(P,P)$ = 59.2 Hz, $[RuCl(\eta^6$-*p*-cymene)((*R*,*S*)-Josiphos)]Cl).

(16) Zanetti, N. C.; Spindler, F.; Spencer, J.; Togni, A.; Rihs, G. *Organometallics* **1996**, *15*, 860.

(17) (a) den Reijer, C. J.; Dotta, P.; Pregosin, P. S.; Albinati, A. *Can. J. Chem.* **2001**, *79*, 693. (b) Mashima, K.; Kusano, K. H.; Sate, N.; Matsumura, Y. I.; Nozaki, K.; Kumobayashi, H.; Sayo, N.; Hori, Y.; Ishizaki, T.; Akutagawa, S.; Takaya, H. *J. Org. Chem.* **1994**, *59*, 3064.

(18) Jensen, S. B.; Rodger, S. J.; Spicer, M. D. *J. Organomet. Chem.* **1998**, *556*, 151.

(19) Doherty, S.; Knight, J. G.; Rath, R. K.; Clegg, W.; Harrington, R. W.; Newman, C. R.; Campbell, R.; Amin, H. *Organometallics* **2005**, *24*, 2633.

(20) See the Supporting Information.