ChemPubSoc Europe

DOI: 10.1002/chem.201504709

CHEMISTRY
A European Journal
Full Paper

Synthesis Design

NNP-Type Pincer Imidazolylphosphine Ruthenium Complexes: Efficient Base-Free Hydrogenation of Aromatic and Aliphatic Nitriles under Mild Conditions

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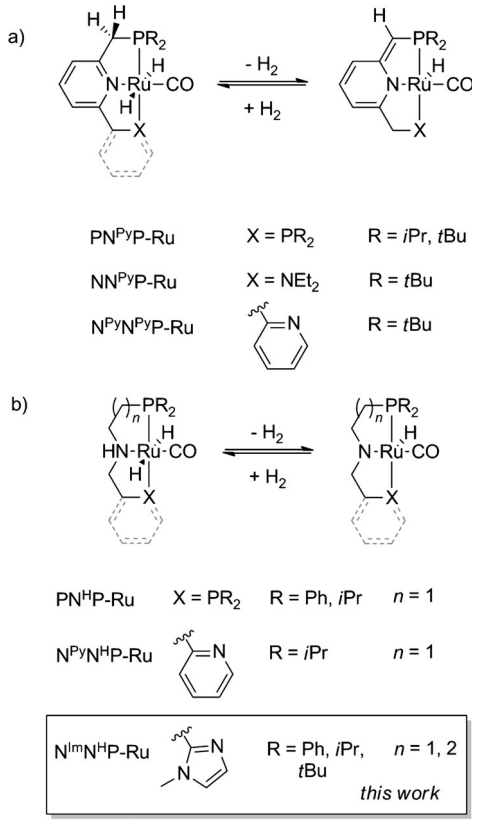
Abstract: A series of seven novel $N^{Im}N^{H}P$-type pincer imidazolylphosphine ruthenium complexes has been synthesized and fully characterized. The use of hydrogenation of benzonitrile as a benchmark test identified [RuHCl(CO)($N^{Im}N^{H}P^{tBu}$)] as the most active catalyst. With its stable Ru–BH_4 analogue, in which chloride is replaced by BH_4, a broad range of (hetero)aromatic and aliphatic nitriles, including industrially interesting adiponitrile, has been hydrogenated under mild and base-free conditions.

Introduction

Pincer ligands and their complexes are of high interest to organometallic and organic chemists, since they are widely and successfully applied in catalysis.[1] Their tridentate and, in the majority of cases, planar coordination to the metal center confers improved stability to the resulting catalysts, which are therefore also suitable for reactions that might require forcing conditions. Clearly, the design of pincer ligands serves to modulate the steric and electronic properties of the corresponding metal center. In addition, the ligand often participates actively in several elementary steps of the catalytic cycle through reversible bond activation (bifunctional catalysis).[2] This paved the way to alternative reactivities, and thus, several redox transformations could be achieved under milder conditions.[3] The majority of today's pincer ligands, which allow for bifunctional catalysis, are built upon a 2,6-lutidine skeleton[4a] (Scheme 1 a) or possesses a central aliphatic NH group[4b] (Scheme 1 b). Structural diversity in these systems is then achieved by introducing different donor sets on the pincer arms. Several versatile catalysts have been prepared, in which pincer ligands of each class are symmetrically substituted by



Scheme 1. Representative examples of pincer ruthenium complexes, the ligands of which are built upon a 2,6-lutedine skeleton (a) or possess a central aliphatic NH group (b). For both classes, the reversible activation of dihydrogen is enabled by metal–ligand cooperation. Py = pyridine, Im = imidazole.

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*Supporting information and the ORCID for the author of this article can be found under http://dx.doi.org/10.1002/chem.201504709. It contains experimental procedures for the synthesis of ligands **1a–2c** and complexes **3–6** and **8–10**, their characterization and NMR spectra, crystallographic information, additional tables, and characterization of isolated amines.*

alkyl- or aryl-substituted phosphino groups ($PN^{Py}P$, $PN^{H}P$): yet, replacement of a phosphino group with either a dialkylamino ($NN^{Py}P$) or pyridino group ($N^{Py}N^{Py}P$, $N^{Py}N^{H}P$) has been shown to improve catalyst activity in ester hydrogenation,[5] amide hydrogenolysis to alcohol and amine,[6] dehydrogenations of secondary alcohols to ketones,[7] dehydrogenative couplings of primary alcohols to afford esters,[5a,8] acylation of secondary alcohols with esters,[9] and dehydrogenative couplings of alcohols and amines to form amides.[10]

In the last case, the authors ascribed the enhanced activity of the ruthenium–$NN^{Py}P^{tBu}$ catalyst to the potentially hemilabile nature[11] of the ligated amino group. By providing a temporary vacant coordination site at the metal, dehydrogenation of the coordinated alcohol (and of the hemiaminal formed from the reaction of the resulting aldehyde with amine) is facilitated. However, DFT calculations have questioned this partial dissociation of the pincer ligand and shown that, under the applied experimental conditions, dehydrogenation of the alcohol (and hemiaminal) through a bifunctional double hydrogen transfer in the metal outer coordination sphere is likewise feasible and indeed energetically favored.[12] Even more interesting is the observation that, when the Ru–$P^{tBu}N^{Py}P^{tBu}$ catalyst is used instead, the dehydrogenative coupling of primary alcohols and primary amines affords imines rather than amides.[13] Imines arise from dehydration of the intermediate hemiaminal, which, for the Ru–$P^{tBu}N^{Py}P^{tBu}$-mediated process, is, in general, kinetically more favorable than the metal-mediated dehydrogenation of the same intermediate to the corresponding amide.[14] The switch in product selectivity is ruled by the diverse steric and electronic properties of the side donor in the pincer ligand, either a phosphino or an amino group, rather than the ability of the latter to reversibly dissociate from the metal around the catalytic cycle.[14] Furthermore, recent work by Langer and Xu addressed the effect of varying the nature of the heterocyclic group in Ru–$XN^{H}P$-type catalysts: replacing the side arm pyridino group with weaker coordinating heterocycles, such as a furanyl or thiophenyl group, negatively affects the activity of the corresponding catalyst in the acceptorless dehydrogenation of alcohols and hydrogenation of ketones.[15]

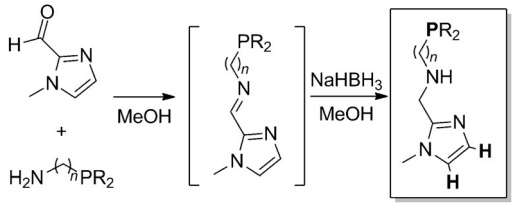
Following our previous work on the synthesis of bidentate imidazolyl phosphines and their successful application in the ruthenium-catalyzed hydrogenation of carboxylic acid derivatives,[16] we considered adding to the diversity of $NN^{H}P$-type pincer ligands by introducing a 1-methylimidazolyl group.[17] 1-Methylimidazole, with a pK_{aH} of 7.0, has a basicity that is intermediate between that of the side-arm nitrogen donors so far employed in NNP pincer ligands, such as a pyridine (pyridine $pK_{aH} = 5.2$), or an amine moiety NR_2 (fully saturated aliphatic amines have pK_{aH} values mostly within the range 9–11).[18] Its coordinating properties are expected to be likewise intermediate.[19] Because of the commercial availability of the corresponding building blocks and the ease of synthesis, ligands with different substituents at phosphorus and either a two- or three-carbon chain connecting the central aliphatic nitrogen and phosphorus donor have been prepared.[20]

Although increasing effort is being put into the design of catalysts based on more abundant, cheaper, and less toxic first-row metals,[21] in this area ruthenium still remains the benchmark metal to probe the ability of new ligands to provide efficient catalysts.[1a,b] In a preliminary report, we showed the synthesis of one member of this new complex family and its catalytic behavior in base-free hydrogenation of amides to alcohols and amines.[22] Herein, we describe the general synthesis of a number of ruthenium complexes with the new ligands and their application to the hydrogenation of nitriles.

Results and Discussion

Synthesis of complexes

The $N^{Im}N^{H}P$ pincer ligands, **1a–2c** (Scheme 2), were easily assembled in a one-pot, two-step procedure starting from commercially available 1-methyl-2-imidazolecarboxaldehyde and the respective aminophosphine. After condensation, the resulting imine was reduced with sodium borohydride. Relevant ligand NMR spectroscopy data are reported in Table 1.



			Yield (%)
$n = 2$	R = Ph	**1a**	77
	*i*Pr	**1b**	78
$n = 3$	Ph	**2a**	91
	*i*Pr	**2b**	71
	*t*Bu	**2c**	89

Scheme 2. General synthetic procedure to access the novel $N^{Im}N^{H}P$ pincer ligands **1a–2c**. The chemical shifts of the highlighted atoms are reported in Table 1. The synthesis of **2c** has been already described, see ref. [22].

Table 1. Selected NMR spectroscopy data of pincer ligands **1a–2c**.[a]

Ligand	P δ (^{31}P)[ppm]	CH_{Im} δ (^{1}H)[ppm]	CH_{Im} δ (^{1}H)[ppm]
1a	−20.40	6.83	6.82
1b	−1.17	6.83	6.82
2a	−15.80	6.87	6.83
2b	4.06	6.83	6.82
2c[b]	28.71	6.87	6.86

[a] Spectra were recorded in CD_2Cl_2 at 298 K. [b] Data of **2c**, the synthesis of which has been already described (ref. [22]), are reported herein for comparison.

To prepare the corresponding ruthenium complexes, the ligands were reacted with two different precursors: $[RuHCl(CO)(PPh_3)_3]$ or $[RuCl_2(PPh_3)_3]$.

The type of complex arising from the reaction with $[RuHCl(CO)(PPh_3)_3]$ turned out to depend on the length of the tether between the central nitrogen atom and the phosphino group in the corresponding pincer ligand, either a two- (**1a**, **1b**) or three-carbon chain (**2a–c**). When either ligand **1a** or **1b** was

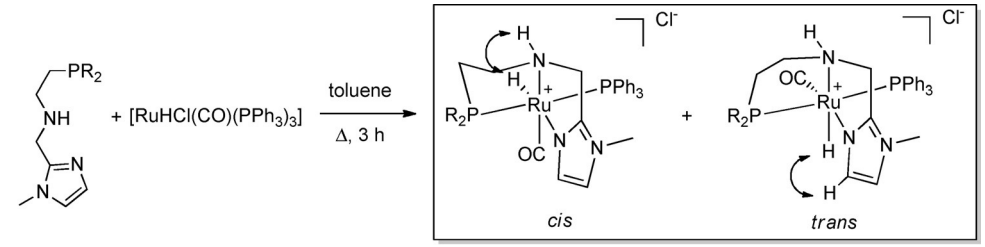
reacted with [RuHCl(CO)(PPh_3)$_3$] in toluene at reflux for 3 h, the corresponding cationic complexes **3** and **4** were isolated as a mixture of *cis* and *trans* isomers, so defined based on the relative orientation of the ruthenium hydride and the hydrogen on the aliphatic nitrogen (Scheme 3).[23,24]

All complexes were fully characterized and their NMR spectroscopy data revealed similar structural features (Table 2).

The *trans* orientation of the two phosphorus donors and the ensuing facial coordination of the pincer ligand is established for all complexes based on the value of the *J*(P,P) coupling constants (260–283 Hz) in the ^{31}P NMR spectrum.[25] In the ^{1}H NMR spectrum, the hydride appeared as a triplet due to the almost equivalent coupling to the two adjacent *cis*-oriented phosphino groups. For both **3** and **4**, the structure of each isomer, either *cis* or *trans*, was assigned based on diagnostic NOE contacts between H4 of the imidazolyl group (*trans*) or the hydrogen on the aliphatic nitrogen (*cis*) and the hydride, respectively (see the Supporting Information).

In solution, the binding of the imidazolyl sp^2-N donor to ruthenium was inferred by changes in the ^{1}H chemical shifts of the imidazolyl H4 and H5 resonances relative to those in the free ligands. Whereas in the latter case they give rise to an AB system with very close chemical shifts, in the complexes the relative signals move apart, both to higher fields.

Crystals of *cis*-**4** suitable for XRD were grown by slow diffusion of diethyl ether into a concentrated solution of the two isomers in dichloromethane (ratio of *cis*-**4** and *trans*-**4** in solution 96:4; Figure 1). The solid structure confirmed the ligand facial coordination deduced from NMR spectroscopy data with the two phosphorus donors arranged *trans* to each other and to the metal center and CO ligand coordinated *trans* to the aliphatic nitrogen. For both complexes, the *cis* isomer appears to



R = Ph **1a**
*i*Pr **1b**

		Yield (%)
R = Ph	*cis*-**3** + *trans*-**3**	84
*i*Pr	*cis*-**4** + *trans*-**4**	65

Scheme 3. Synthesis of complexes **3** and **4**: NOE contacts allowed assignment of the *cis* and *trans* structures of the two isomers (see the Supporting Information).

Table 2. Selected NMR spectroscopy data of complexes **3**–**10**.[a]

Complex	m	PR_2 δ (^{31}P) [ppm]	*m*	PPh_3 δ (^{31}P) [ppm]	*J*(P,P) [Hz]	m	Ru*H* δ (^{1}H) [ppm]	*J*(H,PR_2) [Hz]	*J*(H,PPh_3) [Hz]	C*H*$_{Im}$5 δ (^{1}H) [ppm]	C*H*$_{Im}$4 δ (^{1}H) [ppm]
cis-**3**	d	62.30	d	42.77	272.4	t	−12.39	20.1	20.1	6.43	6.33
trans-**3**	d	54.21	d	44.41	283.5	dd	−12.27	20.7	17.1	6.28	6.06
cis-**4**	d	80.19	d	46.61	260.3	t	−13.08	19.6	19.6	6.68	6.70
trans-**4**	d	72.72	d	44.93	269.2	t	−12.60	18.8	18.8	6.59	6.42
maj-**5**	s	50.85	–	–	–	d	−15.04	23.9	–	6.89	7.16
maj-**6**	br s	65.12	–	—	–	d	−15.73	19.5	–	6.90	7.17
min-**6**	br s	65.1206	–	–	–	d	−15.80	21.4	–	6.90	7.14
cis-**7**[b]	s	78.11	–	–	–	d	−15.91	25.2	–	6.90	7.15
trans-**7**[b]	s	74.19	–	–	–	d	−16.25	23.0	–	6.89	7.15
maj-**8**	d	51.60	d	51.94	31.3	–	–	–	–	6.62	6.10
min-**8**	d	55.60	d	50.35	31.2	–	–	–	–	n.d.	n.d.
maj-**9**	d	55.38	d	52.63	29.0	–	–	–	–	6.59	6.12
min-**9**	d	63.63	d	50.25	29.0	–	–	–	–	6.40	6.14
maj-**10**	d	28.86	d	53.87	33.6	–	–	–	–	6.54	6.14
min-**10**	d	39.47	d	47.79	29.0	–	–	–	–	6.48	6.00

[a] Spectra were recorded in CD_2Cl_2 at 298 K. [b] The synthesis and characterization of **7** have been reported elsewhere, see ref. [22]. Selected NMR spectroscopy data are included here for comparison.

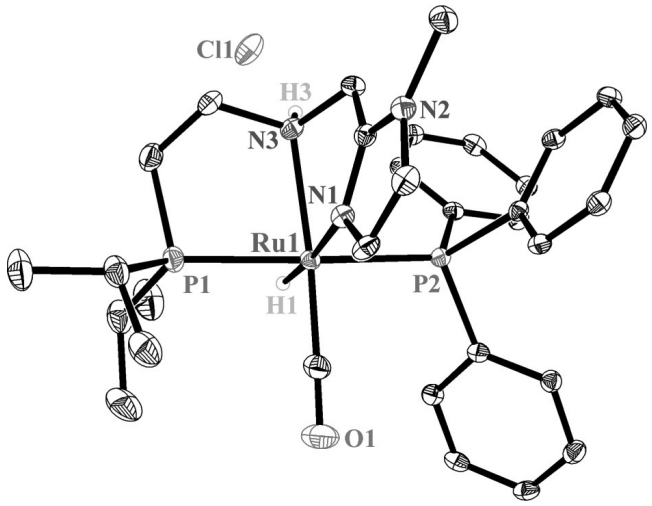
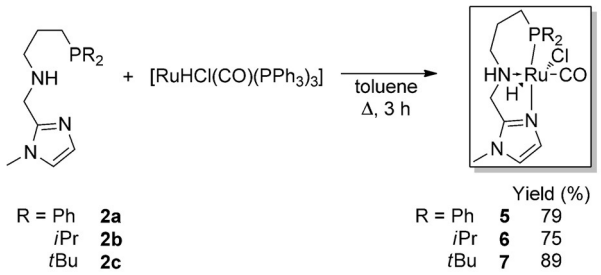


Figure 1. X-ray structure of *cis*-**4** with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms other than H1 and H3 are omitted for clarity. H1 and H3 were refined based on electron density. Selected bond lengths and angles are reported in Table 3.

be the thermodynamic product because its relative amount increases upon standing in solution (see the Supporting Information).

When ligands **2a**–**c** were reacted with $[RuHCl(CO)(PPh_3)_3]$ in toluene at reflux for 3 h, the corresponding neutral complexes **5**–**7** were isolated as mixtures of isomers, the relative amounts of which depended on the ligand (Scheme 4). In this case, the ratio of isomers obtained following the chosen standard synthetic procedure could not be altered by extending the reaction time of the latter, neither by prolonged standing nor heating in solution. For **5**, the most abundant isomer, *maj*-**5**, represents 88% of the total content; the rest is equally distributed among three minor isomers, of which only the hydride signals and the corresponding phosphorus signals could be assigned. Complex **6** afforded two isomers in a ratio of 57:43 but, because of extensive overlapping, complete assignment of NMR signals to either *maj*-**6**, the most abundant of the two isomers, or *min*-**6**, the less abundant one, was not possible. For complex **7**, the configuration of the two isomers, in a ratio of 74:26, was confidently assigned.[22] Despite the difficulty in establishing the relative orientation of all coordinated ligands in the various isomers, some important structural features of the complexes could be established based on 1D and 2D NMR spectra. For each complex, regardless of the substituents at phosphorus or the isomer, only one signal, a singlet, was detected in the $^{31}P\{^1H\}$ NMR spectrum, which indicated that PPh_3 had been completely displaced from the ruthenium coordination sphere (Table 2). The hydride signal appears as a doublet ranging from $\delta = -15.04$ ppm in *maj*-**5** to $\delta = -16.25$ ppm in *trans*-**7**.[26] For **6** and **7**, the chemical shifts of the hydrides in the two isomers are quite close, which suggests that the hydride must be coordinated *trans* to either the same ligand or a ligand of comparable *trans* influence.[27] In all cases, the hydride is located *cis* to the phosphorus donor, as determined from the value of J(H,P), which falls in the range of 19.4–25.2 Hz (Table 2). For each complex, one strong broad band in the IR attenuated total reflectance (ATR) spectrum corroborates the presence of one coordinated CO, the stretching frequency of which shifts from $\tilde{\nu} = 1906$ cm^{-1} in **5**, to $\tilde{\nu} = 1892$ cm^{-1} in **6**, to $\tilde{\nu} = 1890$ cm^{-1} in **7**; these values clearly reflect the more pronounced back-donation in the complexes **6** and **7**, which is made possible by the presence of the more σ-donating P*i*Pr$_2$ and P*t*Bu$_2$ ligands in **6** and **7**, respectively, relative to PPh_2 in **5**.



Scheme 4. Synthesis of complexes **5**–**7**: for the ratio of isomers, see text and the Supporting Information.

For **7**, the most abundant isomer could be assigned the *cis* configuration.[28] Complexes **5**–**7** are not soluble or poorly soluble in solvents such as 1,2-dichloroethane, toluene, THF, acetone, MeOH, and CH_3CN. However, they are perfectly soluble in CD_2Cl_2. Hence, this solvent was used to record their NMR spectra. Unfortunately, in this solvent, the hydride ligand of **5** and **6** is gradually substituted by chloride, as shown by the steady disappearance of the hydride resonances with concomitant growth of a signal at $\delta = 2.99$ ppm (pent, J(H,D) = 1.6 Hz), which is assigned to CHD_2Cl (see the Supporting Information).[29] Likewise, in the ^{31}P NMR spectra, the signals relative to the ruthenium monohydride species are gradually replaced by a signal due to the corresponding ruthenium dichloride species **Cl$_2$-5** ($^{31}P\{^1H\}$ NMR: $\delta = 41.27$ ppm (s)) and **Cl$_2$-6** ($^{31}P\{^1H\}$ NMR: $\delta = 46.03$ ppm (s)). Although a kinetic investigation was not performed, the rate of nucleophilic substitution of chloride in CD_2Cl_2 by the ruthenium hydride, as determined from monitoring of the process by NMR spectroscopy, decreases upon going from **5** to **6**: the ruthenium dichloride complex forms within hours once **5** or **6** are dissolved in dichloromethane; H/Cl exchange does not take place in **7**. For **5**, yellow crystals of **Cl$_2$-5**, $[RuCl_2(CO)(PPh_3)\{3\text{-(diphenylphosphino)-}N\text{-[(1-methyl-1}H\text{-imidazol-2-yl)methyl]-propylamine}\}]$, suitable for XRD formed from a solution of **5** in CD_2Cl_2 inside the J-Young NMR tube after a few days. The X-ray structure revealed that **Cl$_2$-5** possessed a distorted octahedral geometry with the pincer ligand coordinated in a meridional fashion and the CO ligand bound to ruthenium *trans* to the central aliphatic nitrogen (Figure 2). The two chlorides occupy the apical positions and are disposed *trans* to each other.

Next, the synthesis of neutral ruthenium complexes with an ancillary PPh_3 in place of CO was considered, as a further possibility to modulate the electronic and steric properties of the metal center (Scheme 5). Thus, complexes **8**–**10** were obtained

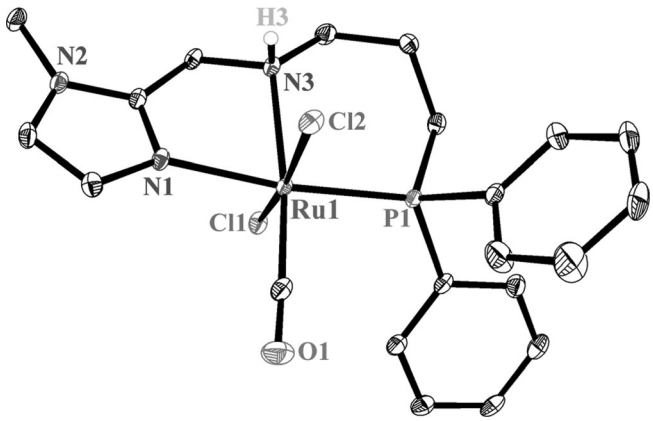
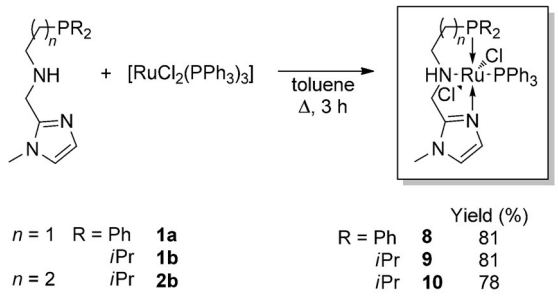


Figure 2. X-ray structure of **Cl_2-5** with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms other than H3 are omitted for clarity. Selected bond lengths and angles are reported in Table 3.



Scheme 5. Synthesis of complexes **8**–**10**: each complex was obtained as a mixture of two isomers: maj-**8**/min-**8** 91:9; maj-**9**/min-**9** 93:7; maj-**10**/min-**10** 80:20. The structure of the *trans*-(Cl)(Cl)-isomer, as established by X-ray analysis for all complexes, is drawn.

in good yields through ligand exchange reactions with the precursor $[RuCl_2(PPh_3)_3]$ to afford, in all cases, a mixture of two isomers, in a ratio ranging from 93:7 to 80:20, as red–orange crystalline solids.[30] In all complexes, regardless of the isomer, the *J*(P,P) coupling constant falls between 29 and 34 Hz, which indicates that the phosphorus donor on the pincer ligand and the ancillary triphenylphosphine are coordinated *cis* to each other (Table 3).

For all complexes, it was possible to grow crystals suitable for XRD, which revealed in every case a meridional arrangement of the pincer ligand with PPh_3 coordinated *trans* to the central aliphatic nitrogen and the two chlorides bound to ruthenium *trans* to each other (Figures 3–5). However, it was not possible to correlate the solid-state structure with that of either isomer in solution. Interestingly, by comparing the structures of complexes **3** and **8**, or **4** and **9**, it is clear that ligands **1a** and **1b** can adopt both the facial and meridional coordination modes.[31]

Nitrile hydrogenation

The potential of the new complexes as catalysts was tested in the hydrogenation of nitriles.[32] This chemical transformation was chosen because of its synthetic importance and the possibility to directly compare the activity of the new catalysts with that of analogous PNP–Ru ones.[33] The hydrogenation of nitriles allows for a direct synthesis of amines, which are valuable organic compounds that have wide industrial applications as solvents, additives, antifoam agents, corrosion inhibitors, detergents, dyes, and bactericides.[34] Moreover, the amino group is widespread in agrochemicals and pharmaceuticals.[34] On an industrial level, nitriles are reduced by using heterogeneous catalysts,[35] mainly Raney®-Ni and -Co; however, these reactions require the presence of ammonia or ammonium salts to prevent

Table 3. Selected bond lengths [Å] and angles [°] for complexes *syn*-**4**, **Cl_2-5**, *syn*-**7**, **8**, **9**, and **10**.

	cis-**4**	**Cl_2-5**	*cis*-**7**[a]	**8**[b]	**9**[b]	**10**[b]
Ru1–Cl1	–	2.4015(6)	2.5741(7)	2.4216(4)	2.4376(10)	2.4173(10)
Ru1–Cl2	–	2.3881(6)	–	2.4033(4)	2.4147(10)	2.4477(10)
Ru1–H1	1.71(3)	–	1.52(2)	–	–	–
Ru1–$N1^{Im}$	2.196(2)	2.1248(18)	2.1137(15)	2.1564(14)	2.1694(14)	2.1611(15)
Ru1–N3	2.240(3)	2.208(2)	2.2219(16)	2.1631(14)	2.1592(16)	2.2161(16)
Ru1–P1	2.3044(9)	2.2882(6)	2.2995(6)	2.2965(5)	2.3168(8)	2.3063(6)
Ru1–CO1	1.811(4)	1.841(3)	1.809(2)	–	–	–
Ru1–P2	2.3825(8)	–	–	2.3126(5)	2.3021(7)	2.3062(7)
C–O1	1.166(4)	1.125(3)	1.161(3)	–	–	–
P1-Ru1-N3	81.79(7)	95.81(5)	94.14(4)	82.88(4)	83.56(4)	88.70(5)
N3-Ru1-$N1^{Im}$	74.39(9)	75.91(7)	77.15(6)	75.75(5)	75.66(6)	76.75(6)
P1-Ru1-$N1^{Im}$	99.26(7)	171.61(6)	169.28(4)	158.33(4)	158.36(4)	165.02(4)
P1-Ru1-P2	165.31(3)	–	–	104.080(16)	102.17(3)	98.10(3)
P1-Ru1-CO1	93.29(11)	92.29(8)	92.89(6)	–	–	–
CO1-Ru1-P2	90.08(11)	–	–	–	–	–
N3-Ru1-P2	96.30(7)	–	–	–	–	–
Cl1-Ru1-Cl2	–	171.35(2)	–	169.439(14)	166.185(17)	165.371(17)
$N1^{Im}$-Ru1-CO1	–	96.06(9)	95.18(7)	–	–	–

[a] The X-ray structure has been reported elsewhere; see ref. [22]. Selected bond lengths and angles are included herein for comparison. [b] Data refer, for each complex, to the isomer in which the two chloride ligands are coordinated to ruthenium *trans* to each other.

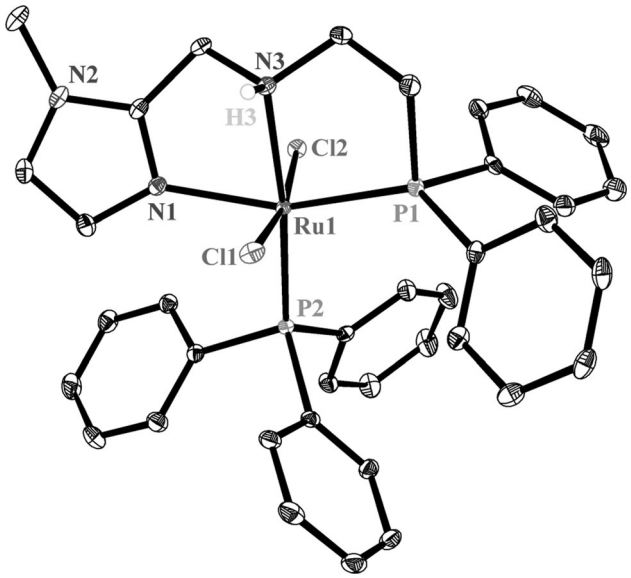


Figure 3. X-ray structure of *trans*-Cl_2-**8** with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms other than H3 are omitted for clarity. Selected bond lengths and angles are reported in Table 3.

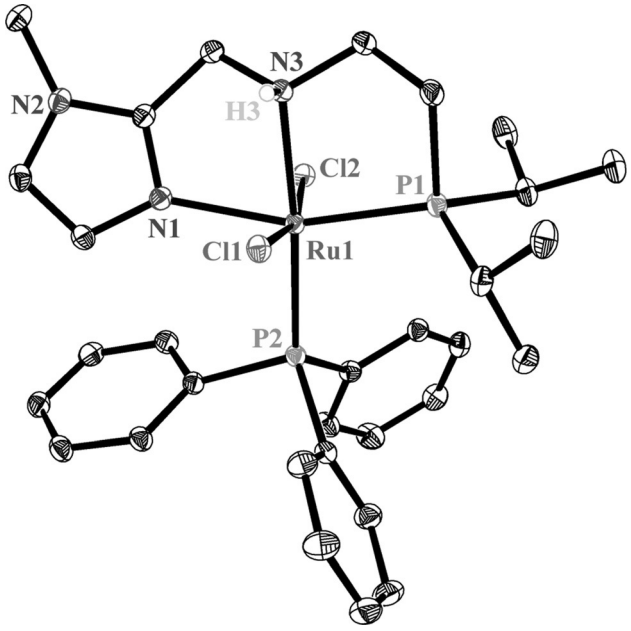


Figure 4. X-ray structure of *trans*-Cl_2-**9** with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms other than H3 are omitted for clarity. Selected bond lengths and angles are reported in Table 3.

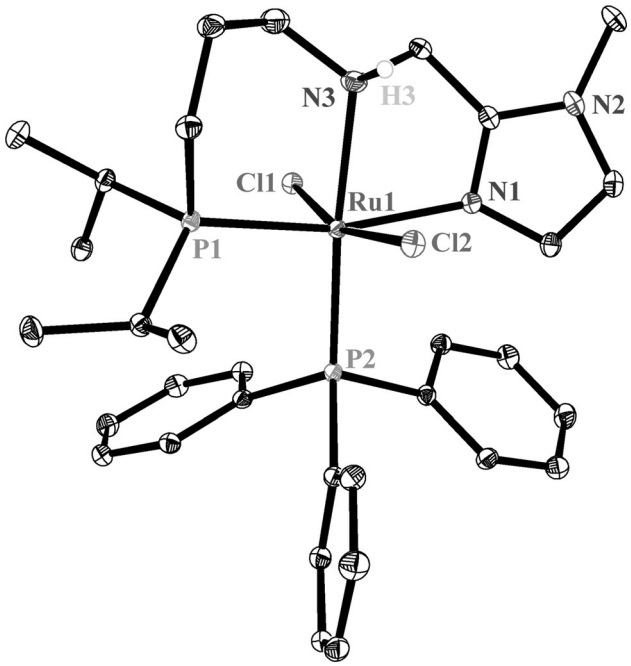
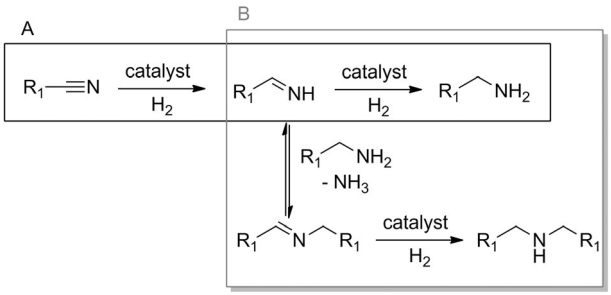


Figure 5. X-ray structure of *trans*-Cl_2-**10** with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms other than H3 are omitted for clarity. Selected bond lengths and angles are reported in Table 3.



Scheme 6. Catalytic hydrogenation of nitriles and possible side reactions.

the formation of byproducts (secondary and tertiary amines/imines).[36] For small-scale preparations, nitriles are usually reduced by using metal hydrides or boranes;[37] a methodology that suffers from low atom economy because it generates (over)stoichiometric amounts of difficult to dispose waste byproducts. In this respect, the possibility of carrying out the same transformation with molecular hydrogen is highly desirable. The key for the efficient synthesis of primary amines from nitriles is control of the catalytic hydrogenation of the primary imine (Scheme 6). This crucial intermediate can be further hydrogenated to afford the desired amine (Scheme 6, path A), or can react with a molecule of the latter to provide a secondary imine with release of ammonia (Scheme 6, path B). Hydrogenation of the secondary imine leads to the secondary amine. Classically, side-product formation has been mitigated by the addition of base.

Several reports have appeared on the homogeneous hydrogenation of nitriles promoted by ruthenium,[16a,38] rhodium,[39] iridium,[40] molybdenum,[41] and rhenium[42] complexes. More recently, successful systems based on the use of non-noble metals, such as iron[43] and cobalt,[44] in combination with PNP pincer ligands, have been also disclosed. With the exception of the Fe–PNP complex[43b] and a few other Ru–pincer catalysts,[33,38a,c] most of the reported systems require a basic additive to hamper the formation of secondary products, which can be a drawback in terms of functional group tolerance. Therefore, efforts are being devoted to the development of

novel catalytic systems that allow the hydrogenation of nitriles to be performed under mild conditions, without additives, while providing a high selectivity in the desired amines.

To assess the catalytic activity of the novel complexes in nitrile hydrogenation, benzonitrile (**11**) was chosen as a standard substrate (Figure 6 and Table S1 in the Supporting Information). To begin with, reactions were carried out for 3 h in *i*PrOH at 70 °C under 30 bar of hydrogen with 1 mol% of the catalyst

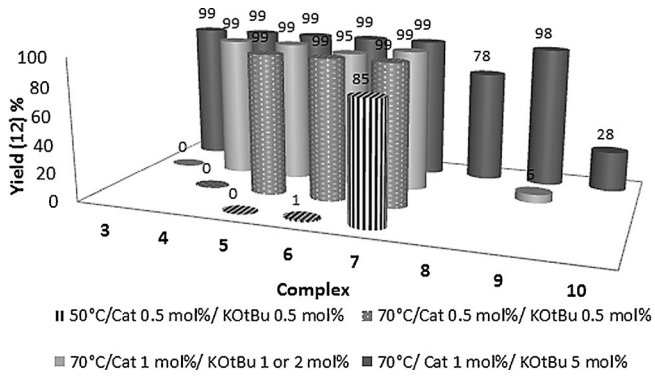


Figure 6. Comparison of the catalytic activity of complexes **3**–**10** in the hydrogenation of **11** to afford **12** in 30 bar hydrogen.

and a minimum amount of base (5 mol% of KO*t*Bu). Under these conditions, all catalysts afforded quantitative yields of benzylamine (**12**), with the exception of **8** and **10**, which gave the product in moderate to low yield (Table S1, entries 1–8, in the Supporting Information). To probe the influence of base, the best performing catalysts were tested with the amount of base strictly necessary to generate the catalytic active species by their dehydrochlorination: one equivalent to ruthenium for **3**–**7**; two for **9**, under otherwise identical conditions.[45] Indeed complexes **4**, **5**, **6**, and **7** catalyzed the formation of **12** in excellent yields, whereas **3** and **9** showed a lower activity and selectivity, which resulted in the preferential formation of the secondary imine **S1** (Table S1, entries 9–14, in the Supporting Information). At a lower catalyst loading (0.5 mol%), only complexes **5**–**7** were active enough to secure the quantitative and selective formation of **12** over the 3 h of reaction time (Table S1, entries 16–18, in the Supporting Information). Catalyst **4** was less efficient and afforded exclusively the secondary imine **S1** (Table S1, entries 15, in the Supporting Information). Finally, by decreasing the temperature to 50 °C, it was possible to identify **7**, among the structurally related catalysts **5**–**7**, as the most active catalyst for the reduction of **11** to **12**, which proceeded in 85% yield (Table S1, entries 19–20, in the Supporting Information). Also, in a similar screening, complex **7** was the most active and selective catalyst for the hydrogenation of the aliphatic nitrile 1-heptanenitrile (**13**) as well (Table S2 in the Supporting Information).

Notably, catalyst **7** requires only one equivalent of base to promote the reduction of **11**. This means that base might be needed only in the initial stage of the process to generate the catalytic active species. Therefore, for subsequent experiments, catalyst **BH_4-7**,[46] in which the Cl ligand was replaced by BH_4^-, was used with no added base.[47]

Indeed, compound **11** was quantitatively hydrogenated over 3 h under base-free conditions with 1 mol% of **BH_4-7** at 70 °C and 30 bar of hydrogen (Table 4, entry 1). To our delight, the reaction proceeded smoothly, even at lower catalyst loadings (Table 4, entries 2–5), reaching a TON of about 2000 at 0.05 mol%; this is the highest TON reported so far for this reaction. When either the catalyst loading (Table 4, entry 6) or the hydrogen pressure were reduced further (Table 4, entry 7), the reaction became slower thus favoring the formation of the secondary imine in moderate yields.

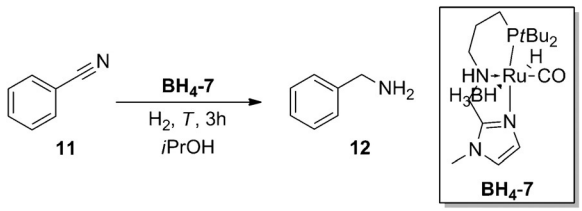
Quantitative yields of **12** were obtained, even at 50 °C, when using 0.1 mol% **BH_4-7** (Table 4, entry 9). By comparing the results in entries 9 and 11 in Table 4 (reaction times of 3 and 1 h, respectively, under otherwise identical conditions), it is evident that in the initial stages of the reaction the main product is the secondary imine, which, through the equilibria described in Scheme 6, reverts back to the primary imine as the reaction proceeds and is eventually hydrogenated to the primary amine.[33b]

A few solvents, other than *i*PrOH, were screened (Table S3 in the Supporting Information): complex **BH_4-7** was only active in THF; however, the yield of **12** was quite low. The reaction did not proceed in the absence of hydrogen (Table 4, entry 8). Similar experiments were carried out to study the influence of catalyst loading, pressure, and temperature on the reduction of **13** in the presence of **BH_4-7** (Table 5). As for **11**, the screening results show that for better selectivity the three parameters have to be adjusted to secure a fast enough reaction to prevent the intermediate imine from reacting with the product amine (Table 5, entries 3 and 6). The best compromise was obtained when using 0.5 mol% of catalyst at 70 °C under 15 bar of H_2, affording heptylamine (**14**) in excellent yield (98%; Table 5, entry 4) over 3 h. Even in this case, no reaction took place in the absence of hydrogen (Table 5, entry 5).

Having assessed to which extent reaction conditions might be mitigated without compromising yield and selectivity, the general applicability of the new system was evaluated in the hydrogenation of several aromatic and aliphatic nitriles. Table 6 summarizes the results obtained with aromatic and heteroaromatic nitriles. All experiments were carried out under 30 bar of hydrogen. In most cases, excellent yields of primary amines were obtained at 50 °C with 0.5 mol% of **BH_4-7**. Both electron-donating (Table 6, entries 3–8) and -withdrawing groups (Table 6, entries 9–12) are tolerated, including *ortho*-substituted derivatives.

Benzonitriles with either an ester or an amido group are selectively hydrogenated, too. For methyl 4-cyanobenzoato, selectivity was achieved by shortening the reaction time (Table 6, entry 13). In case of *N*-(4-cyanophenyl)acetamide, reduction of the sole cyano group was achieved at 70 °C over 3 h.[22] Gratifyingly, selected heteroaromatic nitriles were efficiently hydrogenated to the corresponding amines (Table 6, entries 15–20). Under mild reaction conditions, 3- and 4-pyridinecarbonitrile, but not 2-pyridinecarbonitrile, afforded the corresponding picolylamines in high yields (Table 6, entries 15 and 16). The 2-

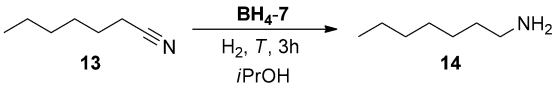
Table 4. Optimization of reaction conditions for the hydrogenation of **11** with ruthenium complex **BH_4-7**.[a]



Entry	H_2 [bar]	T [°C]	**BH_4-7** [mol%]	Conversion [%][b]	Yield **12** [%][b]	TON[c]
1	30	70	1	100	>99	99
2	30	70	0.5	100	>99	198
3	30	70	0.25	100	>99	396
4	30	70	0.1	100	>99	990
5	30	70	0.05	100	>99	1980
6[d]	30	70	0.025	70	–	–
7[d]	15	70	0.05	87	5	100
8	–	70	0.5	–	–	–
9	30	50	0.1	100	>99	990
10[d]	30	50	0.05	91	20	400
11[d,e]	30	50	0.1	54	–	–
12[d]	30	40	0.1	79	–	–

[a] Standard reaction conditions at 1–0.5 mol% of Ru: **11** (0.5 mmol, 51.6 mg), **BH_4-7** (1–0.5 mol%), dry *i*PrOH (2 mL) under H_2 over 3 h; standard reaction conditions at 0.25 mol% of Ru: **11** (1 mmol, 103.1 mg), **BH_4-7** (0.25 mol%), dry *i*PrOH (2 mL) under H_2 over 3 h; standard reaction conditions at 0.1 mol% of Ru: **11** (2 mmol, 206.2 mg), **BH_4-7** (0.1 mol%), dry *i*PrOH (2 mL) under H_2 over 3 h; standard reaction conditions at 0.05 mol% of Ru: **11** (4 mmol, 412.5 mg), **BH_4-7** (0.025 mol%), dry *i*PrOH (4 mL) under H_2 over 3 h; standard reaction conditions at 0.025 mol% of Ru: **11** (10 mmol, 1.0 g), **BH_4-7** (0.1 mol%), dry *i*PrOH (10 mL) under H_2 over 3 h. [b] The conversion of **11** and yield of **12** were calculated by GC with hexadecane as an external standard. [c] Turnover number (TON) was calculated by dividing the yield of product by mol% of catalyst. [d] Intermediate **S1** formed in yields of 65 (entry 6), 75 (entry 7), 71 (entry 10), 37 (entry 11), and 61% (entry 12). [e] The reaction time was 1 h.

Table 5. Optimization of the reaction conditions for the hydrogenation of **13** with ruthenium complex **BH_4-7**.[a]



Entry	H_2 [bar]	T [°C]	**BH_4-7** [mol%]	Conv. [%][b]	Yield **14** [%][b]
1	30	70	1	100	>99
2	30	70	0.5	100	>99
3[c]	30	70	0.25	85	67
4	15	70	0.5	100	98
5	–	70	0.5	–	–
6[c]	30	50	0.5	80	49
7[d]	30	70	0.5	95	90

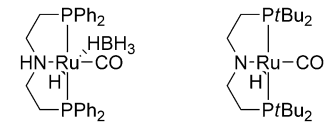
[a] Standard reaction conditions: **13** (0.5 mmol, 55.6 mg), **BH_4-7** (1-0.25 mol%), dry *i*PrOH (2 mL) under H_2 over 3 h. [b] The conversion of **13** and yield of **14** were calculated by GC with hexadecane as an external standard. [c] *N*-Heptylideneheptan-1-amine was formed as a side product. [d] The reaction time was 1 h.

and 3-(thiophen-2-yl)acetonitrile derivatives, as well as 2-(furan-2-yl)acetonitrile and 1*H*-indole-5-carbonitrile, could be also hydrogenated (Table 6, entries 17–20), although for these substrates higher temperatures and/or higher catalyst loadings were required. Finally, the hydrogenation of terephthalodinitrile afforded the corresponding diamine in high yield (86%; Table 6, entry 21).

Next, the scope of **BH_4-7** in aliphatic nitrile hydrogenation was explored (Table 7). With 0.5 mol% catalyst, at 70 °C under 15 bar of hydrogen, linear, branched, and cyclic nitriles were successfully hydrogenated to the corresponding primary alkyl amines over 3 h in high yields, regardless of the alkyl chain length (Table 7, entries 1–5) or steric bulk close to the cyano group (Table 7, entries 6–9). Additionally, benzyl-substituted nitriles and 3-phenylpropanenitrile also smoothly afforded the corresponding amines (Table 7, entries 10–12). Remarkably, the industrially relevant hexane-1,6-diamine, used for the production of Nylon-6,6, was obtained in high yield by the hydrogenation of adiponitrile at 70 °C (Table 7, entry 13).

Compared with previously known reduction of nitriles promoted by pincer ruthenium complexes (Figure 7), the novel catalyst **BH_4-7** allowed reaction conditions to be mitigated further.

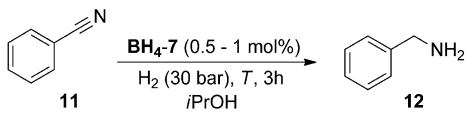
In the case of the Ru–$P^{tBu}N^HP^{tBu}$ catalyst **17**, which represents a pertinent example because it carries the same *t*Bu substituents at phosphorus as **BH_4-7**, the reported substrate scope is less broad.[33b] The system



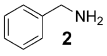
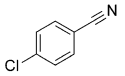
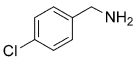
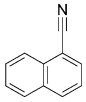
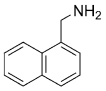
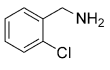
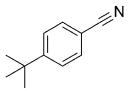
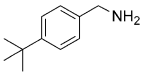
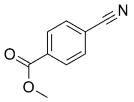
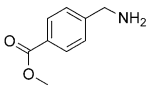
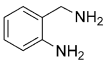
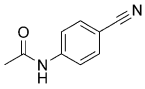
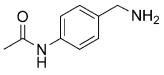
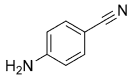
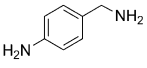
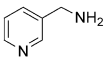
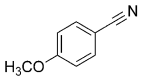
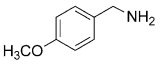
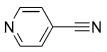
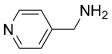
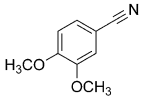
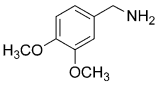
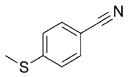
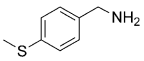
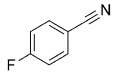
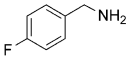
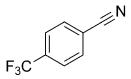
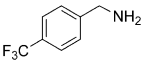
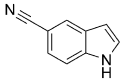
Ru-Macho™-BH **17**

Figure 7. Ru–PN^HP pincer complexes used for the hydrogenation of nitriles.

Table 6. Substrate scope for the hydrogenation of various aromatic nitriles with **BH_4-7**.[a]



11 **12**

Entry	Nitrile	Amine	*T* [°C]	Conversion [%][b]	Yield **12** [%][b]	Entry	Nitrile	Amine	*T* [°C]	Conversion [%][b]	Yield **2** [%][b]
1	 **1**	 **2**	50	>99	99[c]	11[d]			70	>99	99
2			50	>99	98	12			130	>99	92
3			50	>99	99	13[e]			50	>99	85[c]
4			50	>99	98	14[d]			70	>99	84[c]
5			70	>99	88	15			50	>99	86
6[d]			50	>99	90	16			50	>99	95
7[d]			50	>99	99	17			70	>99	89
8			50	>99	90[c]	18[d]			130	>99	82
9			50	>99	92	19[f]			150	>99	75
10[d]			50	>99	89	20[g]			150	>99	98
						21			50	>99	86[c]

[a] Standard reaction conditions: nitrile (0.5 mmol), **BH_4-7** (0.5 mol%), *i*PrOH (2 mL), 30 bar H_2, 3 h. [b] The conversion and yields were calculated by GC with hexadecane as an external standard. [c] Yield of product isolated as the ammonium salt. [d] 1 mol% of **BH_4-7**. [e] 1 hour. [f] 1 mol% of **BH_4-7**, KO*t*Bu 10 mol%, 15 h. [g] 1 mol% of **BH_4-7**, 15 h.

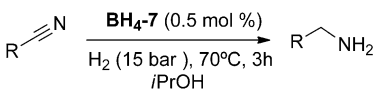
is remarkable because it operates at very low pressure, only 4 bar, which, in the case of **11**, provides an almost quantitative yield of the corresponding secondary imine in the first hour, but longer reactions times are necessary to convert it into the primary amine.[33b]

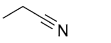
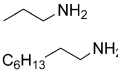
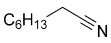
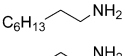
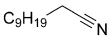
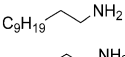
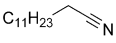
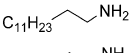
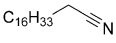
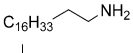
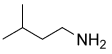
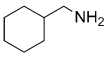
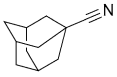
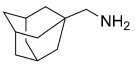
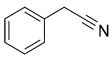
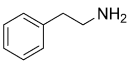
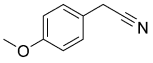
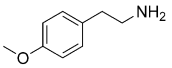
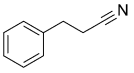
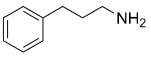
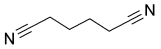
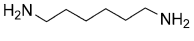
A direct comparison of catalysts **BH_4-7**, Ru-Macho^{TM}-BH, and **17** in the reduction of both **11** and **13** under the same reaction conditions was performed (Table 8). Ru-Macho^{TM}-BH was less active than **BH_4-7** for the hydrogenation of **11** affording low conversions under the tested conditions (Table 8, entries 2 and 5), whereas for the hydrogenation of **13** the two catalysts showed a similar performance at 70 °C (Table 8, entry 8). In the case of complex **17**, high conversions were detected for the hydrogenation of both **11** and **13**. However, this catalyst was not selective to the primary amine and the corresponding secondary imine was detected as a side product (Table 8, entries 3, 6, and 9).

Conclusions

A small family of novel pincer ruthenium complexes was prepared and tested in the hydrogenation of nitriles. The novel hybrid NNP imidazolylphosphino pincer ligands were easily assembled from commercially available building blocks that al-

Table 7. Substrate scope for the hydrogenation of various aliphatic nitriles with BH_4-**7**.[a]



Entry	Nitrile	Amine	Conversion [%][b]	Yield [%][b]
1			>99	98[d]
2			>99	88
3			>99	88
4			>99	99
5			>99	88[d]
6			>99	99
7			>99	76[d]
8			>99	99
9			>99	99
10			>99	91
11[c]			>99	94
12			>99	99
13			>99	87[d]

[a] Standard reaction conditions: nitrile (0.5 mmol), BH_4-**7** (0.5 mol%), *i*PrOH (2 mL), 15 bar H_2, 3 h. [b] The conversion of RCN and yield of RCH_2NH were calculated by GC with hexadecane as an external standard. [c] 1 mol% of BH_4-**7**. [d] Yield of product isolated as the ammonium salt.

lowed for structural diversity. The complexes had different steric and electronic properties, which manifested in their different performances as catalysts for the homogeneous hydrogenation of nitriles. Indeed catalyst BH_4-**7**, with bulky *t*Bu substituents at phosphorus and a molecule of CO as an ancillary ligand at ruthenium, stood out as an efficient catalyst for the reduction of a range of (hetero)aromatic and aliphatic nitriles in high yield and selectivity. No added base was necessary to promote the reaction. Although the catalyst was able to hydrogenate esters and amides,[22] through modulation of reaction conditions, it was possible to selectively reduce the cyano group in the presence of either an ester or amide functionality.

Experimental Section

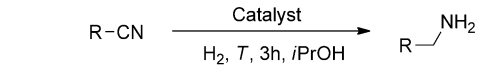
General procedure for the hydrogenation of nitriles with BH_4-7

A 4 mL glass vial containing a stirrer bar was charged with BH_4-**7** (1.1 mg, 0.0025 mmol, 0.5 mol%). The vial, sealed with a septum equipped with a syringe needle, was evacuated and subsequently flushed with argon three times. Dry isopropanol (2 mL) and **11** (0.5 mmol, 51.56 μL) were added under argon. The vial was set in an alloy plate and introduced into a 300 mL autoclave (Parr instrument) filled with argon. The autoclave was sealed, purged three times (20 bar of H_2), and pressurized with H_2 (30 bar). The autoclave was placed into an aluminum block and heated to 50 °C for 3 h with magnetic stirring. After the desired reaction time, the autoclave was quickly cooled with an ice-water bath and the gas carefully released. The reaction mixture was analyzed by GC-MS and GC with *n*-hexadecane as an internal standard.

Isolation of reaction products as HCl salts

HCl (1 M in MeOH, 1 mL) was added to the reaction mixture and stirring was maintained for 30 min at room temperature. Then, the reaction mixture was transferred to a 100 mL round-bottomed flask containing diethyl ether (50 mL). The resulting precipitate was filtered and washed with diethyl ether and ethyl acetate.

Table 8. Hydrogenation of **11** and **13** with **BH_4-7**, Ru-Macho™-BH, and **17** under standard reaction conditions.[a]



R = C_6H_5 **11** → **12**; C_6H_{13} **13** → **14**

Entry	H_2 [bar]	T [°C]	Catalyst ([mol%])	Nitrile	Conversion [%][b]	Yield [%][b]
1	30	50	**BH_4-7** (0.5)	**11**	100	>99
2	30	50	Ru-Macho™-BH (0.5)	**11**	14	13
3[c]	30	50	**17**[d] (0.5)	**11**	100	59
4	30	70	**BH_4-7** (0.05)	**11**	100	>99
5	30	70	Ru-Macho™-BH (0.05)	**11**	–	–
6[e]	30	70	**17**[d] (0.05)	**11**	100	15
7	15	70	**BH_4-7** (0.5)	**13**	100	>99
8	15	70	Ru-Macho™-BH (0.5)	**13**	100	85
9[f]	15	70	**17**[d] (0.5)	**13**	100	15

[a] Standard reaction conditions for the hydrogenation of **11** at 0.5 mol% of Ru: **11** (0.5 mmol, 51. 6 mg), catalyst (0.5 mol%), dry *i*PrOH (2 mL) over 3 h; standard reaction conditions for the hydrogenation of **11** at 0.05 mol% of Ru: **11** (4 mmol, 412.5 mg), catalyst (0.05 mol%), dry *i*PrOH (4 mL) over 3 h; standard reaction conditions for the hydrogenation of **13** at 0.5 mol% of Ru: **13** (0.5 mmol, 55.6 mg), catalyst (0.5 mol%), dry *i*PrOH (2 mL) over 3 h. [b] The conversion of **11** and **13** and yields of the corresponding amines, **12** and **14**, respectively, were calculated by GC with hexadecane as an external standard. [c] Intermediate **S1** formed in a yield of 41%. [d] Catalyst **17** was prepared in situ by dehydrochlorination of [RuHCl(CO){$HN(CH_2CH_2P\{C(CH_3)_3\}_2)_2$}] with one equivalent of *t*BuOK. [RuHCl(CO){$HN(CH_2CH_2P\{C(CH_3)_3\}_2)_2$}] was prepared by following a published procedure.[48] [e] Intermediate **S1** was formed in a yield of 33% together with an unidentified polymer. [f] *N*-Heptylideneheptan-1-amine was formed as side product.

Acknowledgements

We would like to thank Dr. C. Fischer, S. Buchholz, S. Schareina, K. Fiedler, and S. Rossmeisl (all at the Leibniz-Institut für Katalyse e.V.) for excellent analytical and technical support. Financial support from the State of Mecklenburg–Vorpommern and the BMBF is gratefully acknowledged. R.A. thanks the Ramon Areces Foundation for a postdoctoral fellowship.

Keywords: homogeneous catalysis · hydrogenation · N,P ligands · ruthenium · synthesis design

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Received: November 23, 2016
Published online on February 19, 2016