Synthesis of NHC complexes by template controlled cyclization of β-functionalized isocyanides†

Aarón Flores-Figueroa, Oliver Kaufhold, Kai-Oliver Feldmann and F. Ekkehardt Hahn*

Received 24th July 2009, Accepted 1st September 2009
First published as an Advance Article on the web 24th September 2009
DOI: 10.1039/b915033a

Starting from complexes of type [Ru(Cp)Cl(P-P)] (P-P = $2PPh_3$, **3a**; P-P = $2PMe_3$, **3b**: P-P = dppe, **3c**; P-P = dppp, **3d**) isocyanide complexes [Ru(Cp)(P-P)(CNR) **4a–4d** (CNR = CN–CH_2–CH_2N_3, **1**) and **7a–7d** (CN–C_6H_4–$2N_3$, **2**) have been prepared. Reduction of the azido functions of the coordinated isocyanide ligands with Zn/NH_4Cl/H_2O in methanol leads to coordinated 2-amino functionalized isocyanides which cyclize to yield the complexes with a saturated NH,NH-stabilized NHC ligand **5a–5d** or a benzannulated NH,NH-stabilized NHC ligand **8a–8d**. The Zn/NH_4Cl/H_2O reduction method is of general applicability and allowed the generation of complex **11** bearing three saturated NH,NH-stabilized NHC ligands.

Introduction

Metal complexes containing N-heterocyclic carbene (NHC) ligands are currently studied as scaffolds for transition metal catalysts[1] and supramolecular frameworks.[2] Due to the general applicability, most syntheses of NHC complexes rely on the C2-deprotonation of N,N′-disubstituted azolium salts followed by coordination of the formed NHC to a suitable metal center.[3a–c] Other methods like the transmetallation from silver complexes,[3d] the *in situ* generation of the NHC ligands by α-elimination from 2-alkoxy-4,5-imidazolines[3e] or imidazolium-2-carboxylates[3f] and the reductive desulfurization of imidazolin-2-thiones[3g] or benzimidazolin-2- thiones[3h–i] have also been successfully employed. If the C2 deprotonation is attempted with a monosubstituted azole the formation of the complex with the NH,NR-stabilized NHC ligand competes with the coordination of the ligand through the unsubstituted nitrogen atom of the heterocycle.[4]

An alternative method for the preparation of NHC complexes with NH,O-stabilized heterocyclic carbene ligands is the cycloaddition of haloalcohols to isocyanide complexes.[5] In an extension of this approach, complexes with NH,NH-stabilized NHC ligands can be obtained by intramolecular cyclization of β-amino functionalized isocyanides at a suitable template metal.[6] Such complexes contain reactive NHC ligands which, for example, allow the linkage of the NHC to other ligands coordinated to the metal center *via* alkylation of the nitrogen atoms of the heterocycle.[7]

The free isocyanides containing an -OH or -NHR nucleophile in β-position to the isocyanide function tend to cyclize under formation of the corresponding oxazoles or azoles.[8] The use of such isocyanides in metal template controlled cyclization reactions requires the protection of the intramolecular nucleophile and its *in situ* liberation to initiate the NHC formation. We have used 2-trimethylsiloxyphenyl isocyanide which, after coordination to a suitable metal center and cleavage of the O–$SiMe_3$ bond, spontaneously cyclizes to give complexes with a benzoxazolin-2-ylidene NHC ligand.[9] We have also studied complexes of β-azido functionalized isocyanides which upon transformation of the azido function into a primary amine by the Staudinger reaction followed by hydrolysis also cyclize to give NH,NH-stabilized NHC ligands.[6,7]

Recently we noticed that the reduction of the azido function in ruthenium coordinated β-azidoethyl isocyanide by the Staudinger reaction and hydrolysis did not lead to the 2-amino functionalized isocyanide required for cyclization. Further complications arise if the phosphine used in the Staudinger reaction preferably attacks the transition metal center and not the azido group of the coordinated isocyanide ligand. An alternative reduction protocol using a mixture of $FeCl_3$ and NaI was employed in that case.[10]

Since the reduction of the azido function in coordinated β-azido isocyanides appears to depend on both the type of isocyanide (aromatic or aliphatic) and the metal center the isocyanide is coordinated to, we initiated a systematic study of this reaction. Here we report on the reduction of coordinated 2-azidoethyl isocyanide **1** and 2-azidophenyl isocyanide **2** using a Zn/NH_4Cl/H_2O mixture to give complexes with NH,NH-stabilized NHC ligands (Scheme 1)

Results and discussion

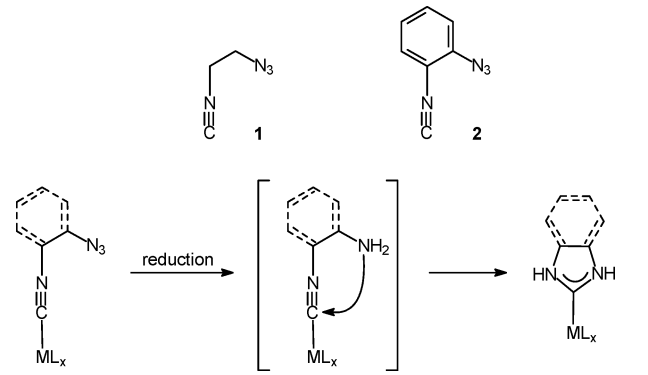
Screening of reduction methods

Since we were particularly interested in generating NH,NH-stabilized NHC ligands at Ru^{II} for the subsequent preparation of Ru^{II} complexes with cyclic [11]ane-P_2C^{NHC} ligands,[7,10] we initially studied the reduction and cyclization of Ru^{II} coordinated 2-azidoethyl isocyanide.

Organic azides are common precursors for amines since the azido group is easily introduced into different molecules and a large number of protocols for the azide reduction to a primary amine have been described.[11] From these, suitable procedures for

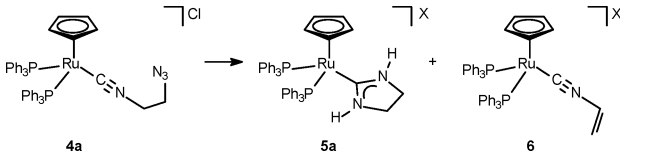
Institut für Anorganische und Analytische, Chemie, Westfälische Wilhelms-Universität Münster, Corrensstraße 30, D-48149 Münster, Germany. E-mail: fehahn@uni-muenster.de; Fax: +49-251-8333108; Tel: +49-251-8333110

† CCDC reference number 742312. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b915033a



Scheme 1 Template-controlled formation of NH,NH-stabilized NHC ligands from 2-azidoethyl isocyanide **1** or 2-azidophenyl isocyanide **2**.

Table 1 Azide reduction in complex **4a** using different reducing agents[a]



Entry	Reducing agent	Solvent	**5a** (%)	**6** (%)	Ref.
1	$FeCl_3/H_2NNH_2$	MeOH	—	—	12
2	$SiMe_3Cl/NaI$	CH_3CN	5	—	13
3	$[Sn(bdt)_2]^b/NaBH_4$	MeOH	—	—	14
4	$[Sn(bdt)_2]^b/NaBH_4$, pH = 7	$MeOH/H_2O$	59	17	14
5	$[Sn(bdt)_2]^b/NaBH_4$, pH = 10	$MeOH/H_2O$	27	17[c]	14
6	$CuSO_4{\cdot}5H_2O/NaBH_4$	MeOH	—	40	15
7	$NHEt_3[Sn(SPh)_3]$	MeOH	33	5[d]	16
8	In/NH_4Cl	MeOH	10	—	17
9	In/NH_4Cl	$MeOH/H_2O$	—	—	17
10	In/NH_4Cl	EtOH	80	—	17
11	PMe_3/H_3O^+	MeOH	90	—	6c
12	Zn/NH_4Cl	$MeOH/H_2O$	85	—	18

[a] The anion X is dependent on the reducing agent. [b] Catalytic amount, bdt = benzene-*o*-dithiolato anion. [c] A control reaction using only $NaBH_4$ and pH = 10 buffer gave no conversion. [d] An unidentified byproduct (m/z = 776) was obtained in a yield of 40%.

the azide reduction in a metal coordinated 2-azidoethyl isocyanide had to be selected. Limiting factors are the reaction temperature and the use of a reducing agent which would not require chemical quenching during workup, both of which are important to avoid isocyanide complex decomposition. In addition, a diamagnetic ruthenium template center facilitating complex analysis by NMR and MS spectrometry had to be used.

With these limitations in mind $[Ru(Cp)Cl(PPh_3)_2]$ **3a** was selected as the metal precursor for the initial studies. The reaction of **3a** with a slight excess of isocyanide **1** in boiling methanol for 12 h produced complex **4a** in good yield. Complex **4a** was characterized by ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectroscopy and by HRMS spectrometry. Reduction of the azido function in **4a** was attempted under the conditions and with the reagents listed in Table 1.

In the case of a successful reduction, the formed 2-aminoethyl isocyanide ligand cyclized by intramolecular attack of the amine function at the isocyanide carbon atom and the NHC complex **5a** was obtained as the reaction product.[6] Under certain conditions, the formation of complex **6** with the vinyl isocyanide ligand was observed together with other minor components which were not further characterized due to their low abundance and irrelevance for our purposes.

All reduction reactions were carried out over 48 h after which the most efficient reduction methods could be identified. The composition of the product mixture was determined by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy which allowed the determination of the relative amounts of complexes **5a** and **6**.

Analysis of the raw reaction mixtures showed the predominance of the two ruthenium complexes **5a** and **6** as reaction products if conversion was achieved. Some well established reducing agents did not lead to conversion in the case of the metal coordinated 2-azidoethyl isocyanide. For example, the reactions of **4a** with $FeCl_3$/hydrazine, $SiMe_3Cl/NaI$ or $[Sn(bdt)_2]/NaBH_4$ in MeOH did not yield complex **5a** or any other reduction products (entries 1–3). Using catalytic amounts of $[Sn(bdt)_2]$ in basic or neutral media led to the reduction of the azido function but also produced a considerable amount of the vinyl isocyanide complex **6** (entries 4 and 5). Complex **6** was also found to be the main reaction product in the reduction of **4a** with $CuSO_4{\cdot}5H_2O/NaBH_4$, (entry 6) and a minor product in the reaction of **4a** with $NHEt_3[Sn(SPh)_3]$ (entry 7).

The best results in terms of conversion and selectivity were observed for the reduction of **4a** with stoichiometric amounts of In/NH_4Cl, Zn/NH_4Cl and in the Staudinger reaction (entries 10–12). While the Staudinger reaction and the reduction with Zn/NH_4Cl proceeded satisfactorily in MeOH, the reduction with In/NH_4Cl gave only in EtOH an acceptable yield. It was also observed that the reductions with indium or zinc gave almost quantitative conversion to **5a** when carried out in refluxing solvents (*vide infra*).

In spite of the successful reduction of the azido function in **4a** under Staudinger conditions, we noticed previously that the Staudinger reaction at the isocyanide ligand of $[RuCl_2(p\text{-cymene})(\mathbf{1})]$ did not lead to the desired 2-aminoethyl isocyanide or its cyclization product.[10] In addition, complex **4a** contains two phosphine ligands which are not easily substituted by PMe_3 used to initiate the Staudinger reaction (Table 1, entry 11). Complexes with more labile ligands may react more readily with the Staudinger agent PR_3 which makes the Staudinger reaction not always the method of choice for the reduction of the azido group in coordinated β-azido functionalized isocyanide.

We therefore became interested in the azide reduction with alternative reducing agents like indium or zinc. Due to the lower cost of the metal, the reduction of ruthenium(II) coordinated 2-azidoethyl isocyanide with Zn/NH_4Cl was subsequently studied in detail and the results were compared to the results obtained by the Staudinger reaction (Table 2). For that purpose the reported conditions for the Staudinger reaction[6a,c] were slightly modified. The protocol employed for the reduction of the azido group in **4a** by a Staudinger reaction involved the dropwise addition of a methanolic solution of PMe_3 over 12 h to a methanol solution of complex **4a**. The resulting phosphinimine was not isolated but directly hydrolyzed with triflic acid/water at the end of the reaction.

Table 2 illustrates that omission of any of the components of the reduction mixture $Zn/NH_4Cl/H_2O$ reduces the yield in the azide reduction (entries 7–9). Absence of water in the reaction mixture allowed the reduction to proceed only in moderate yield (entry 6).

Table 2 Azide reduction in complex **4a** under varying reaction conditions[a]

Entry	Reducing agent	Amount of H_2O	Time/h	Yield **5a** (%)
1	PMe_3/TfOH	Excess	48	100 (77)
2	Zn, NH_4Cl	Excess	48	100 (90)
3	Zn, NH_4Cl	0.5 eq.	24	60
4	Zn, NH_4Cl	1 eq.	24	86
5	Zn, NH_4Cl	2 eq.	24	17
6	Zn, NH_4Cl	—	48	70
7	Zn	—	48	—
8	NH_4Cl	Excess	48	—
9	Zn	Excess	48	—

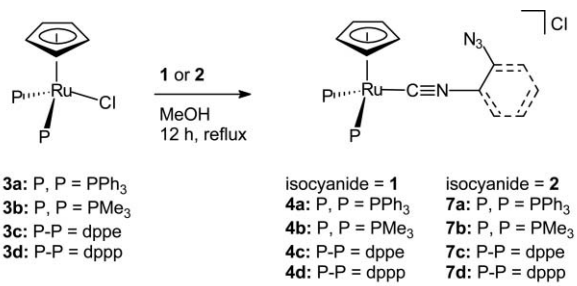
[a] 0.12 mmol **4a**, 0.16 mmol Zn, 0.27 mmol NH_4Cl, 20 mL MeOH refluxing. Yields were determined by NMR spectroscopy, isolated yields in parentheses.

To elucidate the role of the water, three reductions were carried out with varying amounts of water present (entries 3–5). No clear picture emerged from these experiments and we assume that there might exist an interplay between the water and the surface of the zinc particles as has been reported for the reduction of other substrates with zinc.[19]

Addition of an excess of water and a reaction time of 48 h, however, led to a reproducible reduction of the azido function in very good yield (entry 2). We concluded that the complete reduction of the azido group using zinc and ammonium chloride required an excess of water and should be performed in refluxing methanol over a period of 1–2 d. While the Staudinger reaction also works for the reduction of the azido group in **4a** (Table 2, entry 1), the reduction of the azido function of ruthenium(II) coordinated 2-azidoethyl isocyanide using $Zn/NH_4Cl/H_2O$ emerged as an interesting alternative procedure which does not require the addition of a ligand like PR_3 potentially causing undesired side reactions at the metal center.

Synthesis of complexes with 2-azido substituted isocyanides

In order to test the versatility of the $Zn/NH_4Cl/H_2O$ reduction protocol, a systematic variation of the phosphine ligands at ruthenium and of the 2-azido substituted isocyanide ligands was carried out. A total of four different ruthenium complexes **3a–d** were prepared by displacement of the two triphenylphosphine ligands in $[Ru(Cp)Cl(PPh_3)_2]$ **3a** by PMe_3 (**3b**), dppe (**3c**) and dppp (**3d**) ligands (Scheme 2). The substitution of the chloro ligand in complexes **3a–d** is an established procedure for the introduction of an isocyanide ligand.[20] This method was used for the generation of complexes **4a–d** (with the aliphatic 2-azidoethyl isocyanide) and **7a–d** (with the aromatic 2-azidophenyl isocyanide) (Scheme 2). Coordination of the isocyanides gave stable ruthenium complexes in all cases except for the complexes with the PMe_3 ligand **4b** and **7b**. The instability of complex $[Ru(Cp)Cl(PMe_3)_2]$ has been noticed previously.[20b] In fact, PMe_3 dissociated from the ruthenium center reacted with the azido function of the isocyanide ligand leading to the Staudinger product and prevented the isolation of analytically pure samples of the two isocyanide complexes **4b** and **7b**.



Scheme 2 Synthesis of isocyanide complexes **4a–d** and **7a–d**.

Complexes **4a–d** and **7a–d** were identified by NMR and IR spectroscopy as well as by mass spectrometry and, except for **4b** and **7b**, by microanalytical data. $^{13}C\{^1H\}$ NMR spectra of complexes **4a–d** exhibit the resonance for the isocyanide carbon atom at $\delta \approx 154$ ppm with a characteristic $^2J_{C-P}$ coupling constant of about 20 Hz. The chemical shift of the isocyanide carbon atom in complexes **4a–d** is only slightly shifted upfield compared to the value recorded for the free ligand[6c] ($\delta = 160.3$ ppm). Even smaller differences in the chemical shift were measured for the isocyanide carbon resonance in complexes **7a–d** (range $\delta = 165.6$ to $\delta = 170.3$ ppm) compared to the resonance for the free ligand **2** ($\delta = 168.8$ ppm).[6a]

The IR stretching frequencies for the C≡N groups in complexes of types **4** and **7** serve as an indicator for the propensity of the coordinated isocyanide ligand to undergo a nucleophilic attack at the isocyanide carbon atom. Reduction of the azido groups in these complexes leads to complexes with a 2-amino substituted isocyanide which can cyclize by an intramolecular nucleophilic attack of the amino group at the isocyanide carbon atom to give complexes with NH,NH-stabilized NHC ligands (Scheme 1). We have previously studied this type of cyclization with complexes bearing the 2-hydroxyphenyl isocyanide ligand.[9] It was observed that the intramolecular nucleophilic attack is obstructed when the isocyanide ligand is deactivated by metal to ligand d → π* backbonding which can be detected by a drop in the wavenumber for the C≡N stretching vibration for the coordinated isocyanide relative to the free isocyanide ligand.[9e] It can be expected that in electron-rich ruthenium complexes of types **4** and **7** such backbonding from the metal to the isocyanide ligand also exists which might deactivate the isocyanide ligand for cyclization after reduction of the azido group.

Table 3 lists the wavenumbers for the isocyanide stretching vibrations found for complexes **4a–d** and **7a–d**. For all complexes of type **7** bearing the aromatic 2-azidophenyl isocyanide ligand, a significant drop in the wavenumber for the C≡N stretching vibration upon coordination of the isocyanide was observed in accord with the good π-acceptor properties of aryl isocyanides. For the complexes with the aliphatic isocyanide ligand **1**, a significant drop in the wavenumber was observed for the particularly electron-rich complexes **4b** and **4d**. The adverse effects of Ru → $C_{isocyanide}$

Table 3 Wavenumbers of the IR stretching vibrations for the isocyanides **1** and **2** and isocyanide complexes **4a–d** and **7a–d**[a]

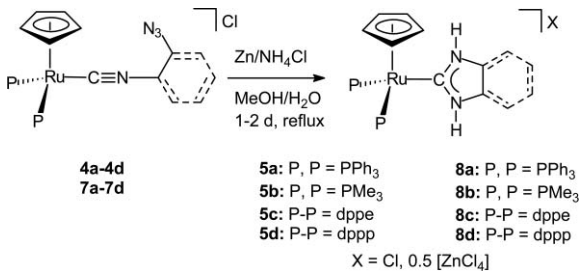
Compound	ν(C≡N)/cm^{-1}	Compound	ν(C≡N)/cm^{-1}
1	2152[b]	**2**	2142
4a	2155	**7a**	2122
4b	2122	**7b**	2124
4c	2154	**7c**	2122
4d	2141	**7d**	2123

[a] Measured in KBr. [b] Measured in CH_2Cl_2.

d–π* backbonding in complexes of type **4** and **7** which could obstruct the cyclization after reduction of the azido group in these complexes may, however, become offset by the high nucleophilicity of the liberated amino group.

Synthesis of NHC complexes

The azido groups in complexes **4a–d** and **7a–d** were reduced quantitatively in refluxing methanol over a period of 1–2 d using $Zn/NH_4Cl/H_2O$ as the reducing agent. Following the reduction, cyclization of the isocyanide by intramolecular nucleophilic attack at the isocyanide carbon atom to give complexes **5a–d** and **8a–d** bearing the NH,NH-stabilized carbene ligands was observed in all cases (Scheme 3).



Scheme 3 Reduction of the azido groups in complexes **4a–d** and **7a–d** followed by cyclization of the isocyanide ligand.

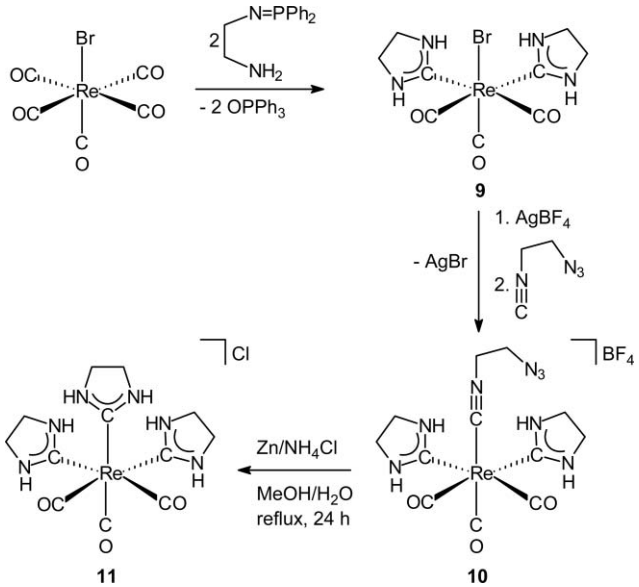
Reduction of the azido groups in complexes **4a** and **7a** with the sterically demanding PPh_3 ligands took 34 h while the reduction for the other complexes was completed in 24 h. These reaction times are longer than those observed for the reduction of related free organic azides (10–120 min)[11] suggesting that the steric conditions around the azido function determine the ease and rate of reduction. As was observed for the isocyanide complexes **4** and **7** the carbene complexes **5** and **8** are air stable solids with the exception of complexes **5b** and **8b** with the PMe_3 ligands.[20b]

Formation of the carbene complexes was confirmed by NMR and IR spectroscopy. The IR spectra were free of absorptions for isocyanide or azido groups and instead showed the absorptions of the N–H vibrations around $\nu = 3400$ cm^{-1}. The $^{13}C\{^1H\}$ NMR resonances for the isocyanide carbon atoms in complexes of type **4** ($\delta \approx 154$ ppm) and **7** ($\delta = 165.6$ to $\delta = 170.3$ ppm) were absent in the carbene complexes and new resonances for the carbene carbon atoms were found in the range of $\delta = 202.6$ to $\delta = 206.3$ ppm (for complexes of type **5**) and $\delta = 183.4$ to $\delta = 188.7$ ppm (for complexes of type **8**). Conversion of the isocyanide to a NH,NH-stabilized NHC ligand leads also to a slight upfield shift for the resonances in the $^{31}P\{^1H\}$ NMR spectra. The ^1H NMR spectra exhibit the signals for the NH protons in the expected range of $\delta =$ 6.63–7.08 ppm (for complexes of type **5**) and $\delta = 10.53$–11.37 ppm (for complexes of type **8**).

Complexes of type **5** and **8** are difficult to crystallize as the reaction conditions allow for the formation of chloride and tetrachloro zincate salts. This also caused problems regarding reproducible microanalytical data. Analytically pure samples of compounds **5a–d** and **8a–d** can be obtained by anion exchange with $NaBPh_4$.

Synthesis of a tris(NHC) complex

To further test the applicability of the azide reduction in complexes bearing 2-azido functionalized isocyanides using $Zn/NH_4Cl/H_2O$, the type of template metal and the co-ligands at the metal center were modified. The strong donors (Cp and phosphines) in complexes of type **4** and **7** were substituted by three strong π-acceptor ligands (CO) and two strong σ-donating carbene ligands and the template metal center was changed from divalent ruthenium(II) to monovalent rhenium(I). These changes led us to the preparation of the previously described complex **9** (Scheme 4). Complex **9** was obtained by the elegant method described by Liu *et al.* involving the deoxygenation reaction of two carbonyl ligands with a phosphinimine followed by cyclization of the intermediate isocyanide ligand.[21] Abstraction of the bromo ligand in **9** with $AgBF_4$ followed by coordination of 2-azidoethyl isocyanide yielded the mixed biscarbene isocyanide complex **10** (Scheme 4).



Scheme 4 Synthesis of the isocyanide complex **10** followed by reduction of the azido group and cyclization to give **11**.

Complex **10** was identified by the $^{13}C\{^1H\}$ NMR resonance for the carbene carbon atoms ($\delta = 191.6$ ppm in DMSO-d_6, $\delta =$ 211.1 ppm in CD_3OD) and the isocyanide carbon atom ($\delta =$ 141.2 ppm in CD_3OD). The resonance for the isocyanide carbon atom could not be detected in DMSO-d_6. The wavenumbers for the isocyanide stretching modes ($\nu = 2212$ and 2200 cm^{-1}), which are higher than the value for the free ligand ($\nu = 2152$ cm^{-1}) indicate an activation of the isocyanide for a nucleophilic attack upon coordination to the Re^{I} center in spite of the reduced formal charge at the metal atom in **10** compared to the ruthenium(II) complexes.

Consequently, reduction of the azido function in **10** with $Zn/NH_4Cl/H_2O$ gave the 2-aminoethyl isocyanide ligand which spontaneously cyclized leading to the tris(NHC) complex **11**. The IR spectrum of **11** exhibits only absorptions for the CO ligands and for the NH groups of the carbene ligands. Only one resonance ($\delta = 202.2$ ppm) was detected for all three carbene carbon atoms of **11** in CD_3OD.

Compound **11** was crystallized as a chloride salt by diffusion of diethyl ether into a methanol solution of the salt. The molecular structure was determined by X-ray diffraction showing the formation of a tris(NHC) complex cation (Fig. 1). The complex cation resides on a three-fold crystallographic axis.

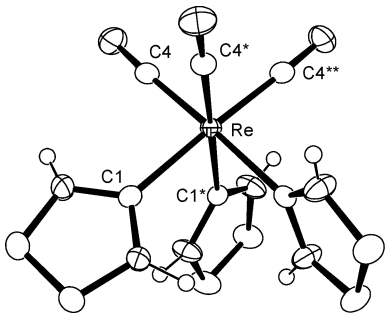


Fig. 1 Molecular structure of the cation of **11**. The molecule resides on a crystallographic three-fold axis and the asymmetric unit contains 1/3 of the cation. Selected bond lengths (Å) and bond angles (°): Re–C1 2.183(2), Re–C4 1.950(2), N1–C1 1.322(3), N2–C1 1.335(3); C1–Re–C1* 86.0(7), C1–Re–C4 92.09(8), Cl–Re–C4* 93.38(8), C1–Re–C4** 177.57(8), C4–Re–C4* 89.49(9), N1–C1–N2 106.5(2).

The metric parameters in the cation of **11** compare well to those observed for related rhenium(I) complexes bearing NH,NH-stabilized saturated NHC ligands.[7c,21] Due to steric reasons, values larger than 90° are observed for the $C_{carbene}$–Re–$C_{carbene}$ angles and values of about 90° for the OC–Re–CO angles.

Experimental

General

Caution organic azides might be explosive! Although compound **1** has been heated up to 100 °C without observation of any violent decomposition and **2** has been shown to be stable up to 60 °C, care must be taken when handling organic azides.

All reactions were carried out under an argon atmosphere using conventional Schlenk techniques. Solvents were dried and degassed by standard methods prior to use. Isocyanides **1**[6a] and **2**[6c] were prepared as described. Complexes **3a–d**[20] and **9**[21] were synthesized by literature methods. NMR spectra were recorded with a Bruker Avance I 400 NMR spectrometer. ^{1}H and ^{13}C{^{1}H} NMR chemical shifts are reported as parts per million relative to tetramethylsilane, ^{31}P{^{1}H} NMR chemical shifts are reported relative to 85% H_3PO_4. IR spectra were measured with a Bruker Vector 22 spectrometer. Mass spectra were recorded on a Finnigan MAT 4200S, a Bruker Daltonics Micro TOF, a Waters-Micromass QuatroLCZ (ESI) or a Varian MAT 212 (MALDI). Elemental analysis was performed with an Elementar, Vario EL III microanalyzer. In the description of the carbene complexes SNHC refers to the saturated imidazolidin-2-ylidene ligand and BNHC to the benzannulated benzimidazolin-2-ylidene ligand.

General procedure for the synthesis of isocyanide complexes 4a–4d and 7a–7d

A slight excess (0.37 mmol, 1.05 eq.) of the isocyanide ligand was added to a suspension of the appropriate [Ru(Cp)(Cl)P–P] precursor complex (0.35 mmol, 1.0 eq.) in methanol (20 mL). The reaction mixture was stirred for 12 h under reflux. The solvent was then removed *in vacuo*. The resulting yellow solid was washed with a minimum amount of diethyl ether (7 mL) to yield compounds **4a–4d** as yellow powders and **7a–7d** as brown powders. All complexes containing PMe_3 ligands are unstable and were difficult to isolate in pure form. Yields for these complexes were therefore determined by NMR spectroscopy and satisfactory microanalytical data could not be obtained.

[Ru(Cp)(PPh$_3$)$_2$(1)]Cl 4a. Yield: 0.288 g, 85%. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.32 (m, 6 H, PPh_3), 7.21 (m, 12 H, PPh_3), 7.04 (m, 12 H, PPh_3), 4.69 (s, 5 H, Cp), 4.13 (t, $^3J_{H-H}$ = 5.2 Hz, 2 H, $CNCH_2$), 3.52 (t, $^3J_{H-H}$ = 5.2 Hz, 2 H, CH_2N_3). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 °C): δ 153.9 (t, $^2J_{C-P}$ = 20.2 Hz, C≡N), 135.4 (PPh_3), 132.9 (PPh_3), 130.1 (PPh_3), 128.2 (PPh_3), 87.5 (Cp), 50.0 (CH_2N_3), 45.8 ($CNCH_2$). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 25 °C): δ 45.39. IR (KBr): ν 2155 (s, CN), 2103 (s, N_3) cm^{-1}. MS (MALDI): *m/z* (%) 787 (100) [M – Cl]$^+$. HRMS (ESI, positive ions): *m/z* 787.1696 [M – Cl]$^+$, calcd for $C_{44}H_{39}N_4P_2Ru$ 787.1700.

[Ru(Cp)(PMe$_3$)$_2$(1)]Cl 4b. Yield: 70% (by NMR spectroscopy). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 4.83 (s, 5 H, Cp), 3.95 (t, $^3J_{H-H}$ = 4.9 Hz, 2 H, $CNCH_2$), 3.55 (t, $^3J_{H-H}$ = 4.9 Hz, 2 H, CH_2N_3), 1.46–1.36 (m, 18 H, PMe_3). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 °C): δ 157.0 (t, $^2J_{C-P}$ = 20.0 Hz, C≡N), 83.8 (Cp), 50.4 (CH_2N_3), 44.8 ($CNCH_2$), 22.7 (dd, J_{C-P} = 18.0 Hz, J_{C-P} = 15.8 Hz, PMe_3). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 25 °C): δ 8.79. IR (KBr): ν 2122 (s, CN), 2097 (s, N_3) cm^{-1}. MS (MALDI): *m/z* (%) 415 (100) [M – Cl]$^+$.

[Ru(Cp)(dppe)(1)]Cl 4c. Yield: 0.191 g, 78%. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.71–7.62 (m, 4 H, PPh_2), 7.54–7.44 (m, 6 H, PPh_2), 7.41–7.32 (m, 6 H, PPh_2), 7.22–7.13 (m, 4 H, PPh_2), 4.94 (s, 5 H, Cp), 3.38 (t, $^3J_{H-H}$ = 5.1 Hz, 2 H, $CNCH_2$), 2.81 (t, $^3J_{H-H}$ = 5.1 Hz, 2 H, CH_2N_3), 2.75–2.64 (m, 2 H, PCH*H*CH*H*P), 2.64–2.63 (m, 2 H, PC*H*HC*H*HP). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 °C): δ 152.5 (t, $^2J_{C-P}$ = 19.9 Hz, C≡N), 137.3, 133.0, 132.7, 131.1, 130.6, 130.6, 129.0, 128.9 (PPh_2), 84.9 (Cp), 49.6 (CH_2N_3), 44.7 ($CNCH_2$), 28.6 (dd, J_{C-P} = 24.1 Hz, J_{C-P} = 21.8 Hz, PCH_2CH_2P). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 25 °C): δ 79.90. IR (KBr): ν 2154 (s, CN), 2091 (s, N_3) cm^{-1}. MS (MALDI): *m/z* (%) 661 (100) [M – Cl]$^+$. HRMS (ESI, positive ions): *m/z* 661.1226 [M – Cl]$^+$, calcd for $C_{34}H_{33}N_4P_2Ru$ 661.1228. Anal. calcd for $C_{34}H_{33}N_4ClP_2Ru$: C, 58.66; H, 4.78; N, 8.05. Found: C, 58.37; H, 4.59; N, 8.22.

[Ru(Cp)(dppp)(1)]Cl 4d. Yield: 0.210 g, 85%. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.45–7.32 (m, 12 H, PPh_2), 7.25–7.19 (m, 4 H, PPh_2), 7.18–7.10 (m, 4 H, PPh_2), 4.87 (s, 5 H, Cp), 4.34 (t, $^3J_{H-H}$ = 5.1 Hz, 2 H, $CNCH_2$), 3.61 (t, $^3J_{H-H}$ = 5.1 Hz, 2 H, CH_2N_3), 2.73–2.59 (m, 2 H, PCH*H*CH_2CH*H*P), 2.58–2.46 (m, 3 H, PC*H*HCH*H*C*H*HP), 1.74–1.55 (m, 1 H, CH_2C*H*HCH_2). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 °C): δ 153.8 (t, $^2J_{C-P}$ = 19.3 Hz, C≡N), 138.5, 136.1, 132.3, 131.3, 130.5, 130.3, 128.7, 128.4 (PPh_2), 86.1 (Cp), 49.5 (CH_2N_3), 46.1 ($CNCH_2$), 28.1 (m, $CH_2CH_2CH_2$), 20.6 ($CH_2CH_2CH_2$). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 25 °C): δ 39.43. IR (KBr): ν 2137 (s, CN), 2096 (s, N_3) cm^{-1}. MS (MALDI): *m/z* (%) 675 (100) [M – Cl]$^+$. HRMS (ESI, positive ions): *m/z* 675.1384 [M – Cl]$^+$, calcd for $C_{35}H_{35}N_4P_2Ru$ 675.1384.

Anal. calcd for $C_{35}H_{35}N_4ClP_2Ru$: C, 59.19; H, 4.97; N, 7.89. Found: C, 58.88; H, 5.22; N, 4.79.

[Ru(Cp)(PPh$_3$)$_2$(2)]Cl 7a. Yield: 0.304 g, 90%. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.41–7.31 (m, 7 H, $CNPhN_3$ and PPh_3), 7.25–7.04 (m, 26 H, $CNPhN_3$ and PPh_3), 6.91 (m, 1 H, $CNPhN_3$), 4.82 (s, 5 H, Cp). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C): δ 167.6 (t, $^2J_{C-P} = 20.7$ Hz, C≡N), 136.0 ($CNPhN_3$), 135.0, 133.0, 130.5 (PPh_3), 129.8 ($CNPhN_3$), 128.4 (PPh_3), 127.0, 125.8, 120.0, 119.0 ($CNPhN_3$), 88.6 (Cp). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 25 °C): δ 44.65. IR (KBr): ν 2122 (s, CN), 2085 (s, N_3) cm^{-1}. MS (MALDI): m/z (%) 835 (100) $[M - Cl]^+$. HRMS (ESI, positive ions): m/z 835.1691 $[M - Cl]^+$, calcd for $C_{48}H_{39}N_4P_2Ru$ 835.1701. Anal. calcd for $C_{48}H_{39}N_4ClP_2Ru$: C, 66.24; H, 4.52; N, 6.44. Found: C, 64.69; H, 4.63; N, 6.92.

[Ru(Cp)(PMe$_3$)$_2$(2)]Cl 7b. Yield: 73% (determined by NMR spectroscopy). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.31–7.01 (m, 4 H, $CNPhN_3$), 5.06 (s, 5 H, Cp), 1.56 (d, $J_{H-P} = 8.9$ Hz, 18 H, PMe_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C): δ 170.3 (t, $^2J_{C-P} = 19.4$ Hz, C≡N), 135.7, 134.9, 129.0, 126.9, 125.6, 118.9 ($CNPhN_3$), 85.2 (Cp), 22.9 (dd, $J_{C-P} = 18.3$ Hz, $J_{C-P} = 15.9$ Hz, PMe_3). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 25 °C): δ 8.66. IR (KBr): ν 2124 (s, CN), 2075 (s, N_3) cm^{-1}. MS (MALDI): m/z (%) 463 (100) $[M - Cl]^+$.

[Ru(Cp)(dppe)(2)]Cl 7c. Yield: 0.210 g, 81%. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.80–7.68 (m, 4 H, PPh_2), 7.49–7.36 (m, 12 H, PPh_2), 7.29–7.19 (m, 4 H, PPh_2), 7.18–7.11 (m, 1 H, $CNPhN_3$), 6.93–6.82 (m, 2 H, $CNPhN_3$), 6.30–6.24 (m, 1 H, $CNPhN_3$), 5.07 (s, 5 H, Cp), 2.96–2.70 (m, 4 H, PCH_2CH_2P). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C): δ 165.6 (t, $^2J_{C-P} = 19.0$ Hz, C≡N), 137.0 (PPh_2), 135.4 ($CNPhN_3$), 133.0, 132.8, 131.1, 130.8, 130.7, (PPh_2), 129.2 ($CNPhN_3$), 129.1, 128.9 (PPh_2), 127.0, 125.8, 125.2, 118.6 ($CNPhN_3$), 86.0 (Cp), 29.0 (dd, $J_{C-P} = 24.0$ Hz, $J_{C-P} = 21.8$ Hz, PCH_2CH_2P). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 25 °C): δ 78.59. IR (KBr): ν 2122 (s, CN), 2090 (s, N_3) cm^{-1}. MS (MALDI): m/z (%) 709 (100) $[M - Cl]^+$. HRMS (ESI, positive ions): m/z 709.1232 $[M - Cl]^+$, calcd for $C_{38}H_{33}N_4P_2Ru$ 709.1229. Anal. calcd for $C_{38}H_{33}N_4ClP_2Ru$: C, 61.33; H, 4.47; N, 7.53. Found: C, 60.33; H, 4.66; N, 7.40.

[Ru(Cp)(dppp)(2)]Cl 7d. Yield: 0.240 g, 90%. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.47–7.14 (m, 24 H, $CNPhN_3$ and PPh_2), 5.03 (s, 5 H, Cp), 2.89–2.78 (m, 2 H, $CHHCH_2CHH$), 2.76–2.49 (m, 1 H, CH_2CHHCH_2), 2.45–2.32 (m, 2 H, $PCHHCH_2CHHP$), 1.87–1.68 (m, 1 H, CH_2CHHCH_2). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C): δ 167.2 (t, $^2J_{C-P} = 19.5$ Hz, C≡N), 138.1 (PPh_2), 136.0 ($CNPhN_3$), 135.1, 132.4, 131.4, 131.0, 130.7 (PPh_2), 129.8 ($CNPhN_3$), 128.8, 128.7 (PPh_2), 127.5, 126.0, 125.1, 119.1 ($CNPhN_3$), 87.3 (Cp), 28.4 (m, $CH_2CH_2CH_2$), 20.7 ($CH_2CH_2CH_2$). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 25 °C): δ 38.32. IR (KBr): ν 2123 (s, CN), 2083 (s, N_3) cm^{-1}. MS (MALDI): m/z (%) 723 (100) $[M - Cl]^+$. HRMS (ESI, positive ions): m/z 723.1383 $[M - Cl]^+$, calcd for $C_{39}H_{35}N_4P_2Ru$ 723.1385. Anal. calcd for $C_{39}H_{35}N_4P_2Ru$: C, 61.78; H, 4.65; N, 7.39. Found: C, 61.03; H, 4.95; N, 7.39.

General procedure for the synthesis of carbene complexes 5a–d and 8a–d

A mixture of one of the isocyanide complexes **4a–d** or **7a–d** (0.25 mmol, 1.0 eq.), fine powdered zinc (0.32 mmol, 1.3 eq.) and NH_4Cl (0.57 mmol, 2.3 eq.) were suspended in a mixture of methanol (20 mL) and degassed water (0.1 mL). The mixture was then stirred under reflux for 24 h (**4b–d**, **7b–d**) or 34 h (**4a**, **7a**). At the end of the selected reaction time (conversion was monitored by MALDI MS), the solvent was removed *in vacuo* and dichloromethane (40 mL) was added to the residue. The obtained suspension was filtered and the solvent was removed *in vacuo*. Spectroscopic data were recorded for the compounds obtained this way. Due to the presence of chloride and tetrachloro zincate anions it was difficult to obtain satisfactory microanalytical data. Anion exchange with $NBPh_4$ gave the tetraphenyl borate salts. Yields and microanalytical data are therefore given for the tetraphenyl borate salts. The tetraphenyl borate anions would give a large number of NMR resonances in the aromatic region and were therefore not used for the spectroscopic characterization of the compounds. X in the formulae therefore corresponds to the chloride and/or tetrachloro zincate anion. All complexes containing PMe_3 ligands are unstable and were difficult to isolate in pure form. Yields for these complexes were therefore determined by NMR spectroscopy and satisfactory microanalytical data could not be obtained.

[Ru(Cp)(PPh$_3$)$_2$(SNHC)]X 5a. Yield: 0.246 g, 90%. ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ 7.52–7.41 (m, 6 H, PPh_3), 7.35 (m, 12 H, PPh_3), 7.11–6.96 (m, 12 H, PPh_3), 6.64 (s, 2 H, NH), 4.55 (s, 5 H, Cp), 3.09 (s, 4 H, CH_2CH_2). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6, 25 °C): δ 202.6 (t, $^2J_{C-P} = 16.3$ Hz, NCN), 137.0–136.1 (PPh_3), 132.9, 129.1, 128.2, (PPh_3), 86.2 (Cp), 44.6 (CH_2CH_2). δ $^{31}P\{^1H\}$ NMR (162 MHz, DMSO-d_6, 25 °C): δ 48.44. IR (KBr): ν 3442 (w, NH) cm^{-1}. MS (MALDI): m/z (%) 761 (100) $[M - Cl]^+$. HRMS (ESI, positive ions): m/z 761.1790 $[M - Cl]^+$, calcd for $C_{44}H_{41}N_2P_2Ru$ 761.1795. Anal. calcd for $C_{68}H_{61}N_2BP_2Ru$: C, 75.62; H, 5.69; N, 2.59. Found: C, 75.38; H, 5.75; N 2.21.

[Ru(Cp)(PMe$_3$)$_2$(SNHC)]X 5b. Yield: 73% (determined by NMR spectroscopy). ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ 7.08 (s br, 2 H, NH), 4.80 (s, 5 H, Cp), 3.40 (s, 4 H, CH_2CH_2), 1.45–1.40 (m, 18 H, PMe_3). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6, 25 °C): δ 206.3 (t, $^2J_{C-P} = 15.9$ Hz, NCN), 82.2 (Cp), 44.4 (NCH_2CH_2N), 22.5 (dd, $J_{C-P} = 16.02$, $J_{C-P} = 14.05$ Hz, PMe_3). $^{31}P\{^1H\}$ NMR (162 MHz, DMSO-d_6, 25 °C): δ 11.17. HRMS (ESI, positive ions): m/z 389.850 $[M - Cl]^+$, calcd. for $C_{14}H_{29}N_2P_2Ru$ 389.0848.

[Ru(Cp)(dppe)(SNHC)]X 5c. Yield: 0.222 g, 93%. ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ 7.74–7.57 (m, 4 H, PPh_2), 7.52–7.38 (m, 6 H, PPh_2), 7.37–7.19 (m, 6 H, PPh_2), 7.19–7.02 (m, 4 H, PPh_2), 6.40 (s, 2 H, NH), 4.68 (s, 5 H, Cp), 3.07–2.86 (m, 2 H, $PCHHCHHP$), 2.86–2.68 (m, 2 H, $PCHHCHHP$), 2.64 (s, 4 H, NCH_2CH_2N). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6, 25 °C): δ 203.0 (t, $^2J_{C-P} = 15.2$ Hz, NCN), 141.8, 134.1, 133.0, 130.3, 129.9, 129.1, 128.3, 128.1, (PPh_2), 85.1 (Cp), 44.0 (NCH_2CH_2N), 28.1 (m, PCH_2CH_2P). $^{31}P\{^1H\}$ NMR (162 MHz, DMSO-d_6, 25 °C): δ 90.73. IR (KBr): ν 3448 (m, NH) cm^{-1}. MS (MALDI): m/z 635 (100) $[M - Cl]^+$. HRMS (ESI, positive ions): m/z 635.1331 $[M - Cl]^+$, calcd for $C_{34}H_{35}N_2P_2Ru$ 635.1323. Anal. calcd for

$C_{58}H_{55}N_2BP_2Ru$: C, 73.03; H, 5.81; N, 2.94. Found: C, 72.74; H, 5.79; N, 2.07.

[Ru(Cp)(dppp)(SNHC)]X 5d. Yield: 0.212 g, 88%. ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ 7.51–7.38 (m, 16 H, PPh_2), 7.27–7.19 (m, 4 H, PPh_2), 6.63 (s, 2 H, NH), 4.65 (s, 5 H, Cp), 3.01 (s, 4 H, NCH_2CH_2N), 2.71–2.29 (m, 5 H, PCH_2CHHCH_2P), 1.89–1.78 (m, 1 H, PCH_2CHHCH_2P). ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C): δ 202.7 (t, $^2J_{C-P}$ = 15.3 Hz, NCN), 142.1, 138.0, 131.9, 131.3, 129.5, 129.3, 128.0, 127.0 (PPh_2), 85.8 (Cp), 44.5 (NCH_2CH_2N), 25.4 (m, $PCH_2CH_2CH_2P$), 20.6 ($PCH_2CH_2CH_2P$). ^{31}P NMR (162 MHz, DMSO-d_6, 25 °C): δ 43.3. IR (KBr): ν 3422 (m, NH) cm^{-1}. MS (MALDI): m/z (%) 649 (100) [M – Cl]$^+$. HRMS (ESI, positive ions): m/z 649.1492 [M – Cl]$^+$, calcd for $C_{35}H_{37}N_2P_2Ru$ 649.1485. Anal. calcd for $C_{59}H_{57}N_2BP_2Ru$: C, 73.21; H, 5.93; N, 2.89. Found: C, 73.34; H, 5.85; N, 1.87.

[Ru(Cp)(PPh_3)$_2$(BNHC)]X 8a. Yield: 0.250 g, 89%. ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ 10.62 (s br, 2 H, NH), 7.51–6.93 (m, 34 H, PPh_2 + BNHC), 4.74 (s, 5 H, Cp). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6, 25 °C): δ 183.4 (t, $^2J_{C-P}$ = 17.3 Hz, NCN), 136.3 (PPh_3), 133.3 (BNHC), 132.8, 129.9, 128.3 (PPh_3), 122.2, 110.0 (BNHC), 86.4 (Cp). ^{31}P{^{1}H} NMR (162 MHz, DMSO-d_6, 25 °C): δ 47.64. IR (KBr): ν 3414 (m, NH) cm^{-1}. MS (MALDI): m/z (%) 809 (100) [M – Cl]$^+$. HRMS (ESI, positive ions): m/z 809.1802 [M – Cl]$^+$, calcd for $C_{48}H_{41}N_2P_2Ru$ 809.1802. Anal. calcd for $C_{72}H_{61}N_2BP_2Ru$: C, 76.66; H, 5.45; N, 2.48. Found: C, 76.63; H, 5.43; N 2.53.

[Ru(Cp)(PMe_3)$_2$(BNHC)]X 8b. Yield: 90% (determined by NMR spectroscopy). ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ 11.37 (s br, 2 H, NH), 7.51–7.39 (m, 2 H, BNHC), 7.13–7.06 (m, 2 H, BNHC), 4.92 (s, 5 H, Cp), 1.48–1.40 (m, 18 H, PMe_3). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6, 25 °C): δ 188.7 (t, $^2J_{C-P}$ = 16.7 Hz, NCN), 134.1, 121.6, 110.0 (BNHC), 82.6 (Cp), 22.7 (dd, J_{C-P} = 15.7 Hz, J_{C-P} = 14.6 Hz, PMe_3). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 25 °C): δ 10.77 (PMe_3). HRMS (ESI, positive ions): m/z (%) 437.0844 [M – Cl]$^+$, calcd for $C_{18}H_{29}N_2P_2Ru$, 437.0849.

[Ru(Cp)(dppe)(BNHC)]X 8c. Yield: 0.233 g, 93%. ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ 10.53 (s, 2 H, NH), 7.63–7.55 (m, 4 H, PPh_2), 7.49–7.40 (m, 6 H, PPh_2), 7.31–7.19 (m, 10 H, PPh_2), 7.04–6.98 (m, 2 H, BNHC), 6.96–6.89 (m, 2 H, BNHC), 4.87 (s, 5 H, Cp), 3.30–3.08 (m, 2H, $PCHHCHHP$), 3.05–2.84 (m, 2 H, $PCHHCHHP$). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6, 25 °C): δ 184.3 (t, $^2J_{C-P}$ = 15.9 Hz, NCN), 141.6, 133.7 (m, PPh_2), 133.4 (BNHC), 132.9, 130.1, 129.9, 129.2, 128.3, 127.8 (PPh_2), 121.3, 109.4 (BNHC), 85.4 (Cp), 28.0 (m, PCH_2CH_2P). ^{31}P{^{1}H} NMR (162 MHz, DMSO-d_6, 25 °C): δ 88.74. IR (KBr): ν 3404 (m, NH) cm^{-1}. MS (MALDI): m/z (%) 683 (100) [M – Cl]$^+$. HRMS (ESI, positive ions): m/z 683.1314 [M – Cl]$^+$, calcd for $C_{38}H_{35}N_2P_2Ru$ 683.1324. Anal. calcd for $C_{62}H_{55}N_2BP_2Ru$: C, 74.32; H, 5.53; N, 2.79. Found: C, 76.02; H, 5.66; N, 2.28.

[Ru(Cp)(dppp)(BNHC)]X 8d. Yield: 0.230 g, 94%. ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ 10.67 (s, 2 H, NH), 7.50–7.37 (m, 6 H, PPh_2), 7.36–7.28 (m, 2 H, BNHC), 7.27–7.18 (m, 14 H, PPh_2), 7.09–7.03 (m, 2 H, BNHC), 4.81 (s, 5 H, Cp), 2.79–1.72 (m, 6 H, $PCH_2CH_2CH_2P$). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6, 25 °C): δ 184.0 (t, $^2J_{C-P}$ = 16.1 Hz, NCN), 141.6, 138.0 (PPh_2), 134.1 (BNHC), 131.7–131.3 (PPh_2), 129.6–129.3 (PPh_2), 128.1–127.7 (PPh_2), 121.7, 109.9 (BNHC), 86.0 (Cp), 25.6 (m, $CH_2CH_2CH_2$), 20.6 ($CH_2CH_2CH_2$). ^{31}P{^{1}H} NMR (162 MHz, DMSO-d_6, 25 °C): δ 42.47. IR (KBr): ν 3424 (m, NH) cm^{-1}. MS (MALDI): m/z (%) 697 (100) [M – Cl]$^+$. HRMS (ESI, positive ions): m/z 697.1480 [M – Cl]$^+$, calcd for $C_{39}H_{37}N_2P_2Ru$ 697.1480. Anal. calcd for $C_{63}H_{57}N_2BP_2Ru$: C, 74.48; H, 5.65; N, 2.76. Found: C, 73.25; H, 5.78; N 2.76.

Preparation of the vinyl isocyanide complex 6

Compound **6** was identified as the product in the reduction of **4a** using $CuSO_4$/$NaBH_4$ as the reducing agent. It was identified in the reaction mixture by NMR spectroscopy and MALDI MS spectrometry. An authentic sample of **6** was obtained by stirring 50 mg (0.0636 mmol, 1 eq.) of **4a** and 7 mg (0.0636 mmol, 1 eq.) of KO*t*Bu in THF (20 mL) for 14 h. After removal of the solvent the solid residue was dried *in vacuo*, redissolved in CH_2Cl_2 and filtered over Celite. Removal of the solvent gave compound **6** as a yellow solid. Yield: 0.44 g, 90%. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.35–6.24 (m, 30 H, PPh_3), 6.38 (dd, 1H, $^3J_{H-H}$ = 15.3 Hz, $^3J_{H-H}$ = 8.0 Hz, $CHCH_2$), 5.13 (d, 1 H, $^3J_{H-H}$ = 8.0 Hz, $CHCHH$), 5.08 (d, 1 H, $^3J_{H-H}$ = 15.3 Hz, $CHCHH$), 4.81 (s, 5 H, Cp). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 °C): δ 162.3 (t, $^2J_{C-P}$ = 20.8 Hz, C≡N), 135.1, 133.0, 130.4, 128.5 (PPh_3), 122.1 ($CHCH_2$), 118.3 ($CHCH_2$), 88.3 (Cp). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 25 °C): δ 45.17 (PPh_3). IR (KBr): ν 2107 (m, CN), 2036 (s, CN) 2008 (m, CN) cm^{-1}. MS (MALDI): m/z (%) 744 (100) [M – Cl]$^+$.

Synthesis of the tris(NHC) complex 11

***fac*-[Re(CO)$_3$(SNHC)$_2$(1)]BF$_4$ 10.** To a mixture of 100 mg of biscarbene complex **9** (0.20 mmol, 1 eq.) and 40 mg of $AgBF_4$ (0.20 mmol, 1 eq.) was added acetonitrile (40 mL). The reaction mixture was stirred for 12 h in the dark. The solids were removed by filtration and solid residue was washed with acetonitrile (5 mL). To the combined acetonitrile fractions was added isocyanide **1** (23 mg, 0.25 mmol, 1.2 eq.). The reaction mixture was stirred for 16 h at ambient temperature. Subsequently, all solvents were removed *in vacuo* and the solid residue was dissolved in dichloromethane (5 mL). Compound **10** precipitated from this solution upon addition of diethyl ether (20 mL) and cooling to –20 °C overnight.

Yield: 0.105 g, 88%. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.20 (s br, 4 H, NH), 4.05 (t, $^3J_{H-H}$ = 5.3 Hz, 2 H, $CNCH_2$), 3.71 (t, $^3J_{H-H}$ = 5.3 Hz, 2 H, CH_2N_3), 3.49 (s, 8 H, NCH_2CH_2N). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 191.6 (NCN), 191.4, 189.8 (CO), 48.9 (CH_2N_3), 44.4 (NCH_2CH_2N), 44.1 ($CNCH_2$); the resonance for the isocyanide carbon atom could not be detected. ^{13}C{^{1}H} NMR (100 MHz, CD_3OD): δ 211.1 (NCN), 193.8, 193.0 (CO), 141.2 (br, CN), 51.7 (CH_2N_3), 46.9 (NCH_2CH_2N), 46.1 ($CNCH_2$). ^{19}F NMR (376 MHz, DMSO-d_6): δ –148.3 (d, BF_4). IR (KBr): ν 3478, 3452, 3404 (NH), 2212 (m, CN), 2200 (m, CN), 2144 (s, N_3), 2108 (s, N_3), 2018 (m, CO), 1945 (m, CO), 1922 (m, CO) cm^{-1}. MS (MALDI): m/z 507 (100) [M – BF_4]$^+$.

***fac*-[Re(CO)$_3$(SNHC)$_3$]Cl 11.** A Schlenk flask was charged with 240 mg of compound **10** (0.41 mmol, 1 eq.), 35 mg of zinc powder (0.53 mmol, 1.3 eq.) and 50 mg of NH_4Cl (0.93 mmol, 2.3 eq.). Methanol (20 mL) and degassed water (0.1 mL) were added to the mixture. The resulting suspension was heated under reflux for 24 h. Subsequently, all solids were

removed by filtration and the resulting solution was brought to dryness under reduced pressure. The solid residue obtained was thoroughly washed with dichloromethane (30 mL). Filtration and removal of the solvent gave the tris(NHC) complex **11**. Salt **11** could contain different anions (Cl^-, $[ZnCl_4]^{2-}$, BF_4^-). This prevented the microanalytical characterization of the compound. Crystallization of **11** from methanol/diethyl ether gave exclusively the chloride salt $[Re(CO)_3(SNHC)_3]Cl$ which was characterized by X-ray diffraction in 60%. ^{1}H NMR (400 MHz, CD_3OD): δ 4.87 (s br, 6 H, NH), 3.63 (s, 8 H, 2 × NCH_2CH_2N), 3.61 (s, 2 H, 1 × NCH_2CH_2N). $^{13}C\{^1H\}$ NMR (100 MHz, CD_3OD): δ 204.2 (NCN), 198.2, 194.7 (CO), 46.0 (2 × NCH_2CH_2N), 45.8 (1 × NCH_2CH_2N). IR (KBr): ν 3416 (NH), 1999 (m, CO), 1914 (m, CO) cm^{-1}. MS (MALDI): m/z (%) 481 (100) $[M - Cl]^+$.

Crystal structure determinations

X-Ray diffraction data were collected with a Bruker AXS APEX diffractometer equipped with a rotation anode at 153(2) K using graphite monochromated Mo Kα radiation, λ = 0.71073 Å. Diffraction data were collected over the full sphere and were corrected for absorption. The data reduction was performed with the Bruker SMART[22] program package. Structure solutions were found with the SHELXS-97 package[23] using the heavy-atom method and were refined with SHELXL-97[24] against F^2 using first isotropic and later anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were added to the structure models on calculated positions.

Crystal data for 11. Formula $C_{12}H_{28}N_6ClO_3Re$, M = 519.97, colorless crystal, 0.16 × 0.16 × 0.09 mm, cubic, space group $Pa\bar{3}$, a = 14.8438(3), V = 3270.66(11) Å^3, ρ_{calc} = 2.096 g cm^{-3}, μ = 7.617 mm^{-1}, ω- and ϕ-scans, 35 498 measured intensities ($4.6 \leq 2\theta \leq 59.1°$), semi-empirical absorption correction ($0.3453 \leq T \leq 0.5034$), 1541 independent ($R_{int}$ = 0.031) and 1383 observed ($I \geq 2\sigma(I)$) intensities, Z = 8, R(all) = 0.0185, wR(all) = 0.0356, refinement of 70 parameters against all $|F^2|$. The cation resides on a crystallographic three-fold axis. The asymmetric unit contains 1/3 of the formula unit.

Conclusions

We have described a new method for the reduction/cyclization of β-azido functionalized ethyl and phenyl isocyanides using a mixture of $Zn/NH_4Cl/H_2O$ as the reducing agent. The method is of general applicability and a total of eight new cationic $[Ru^{II}(Cp)(P–P)(NHC)]^+$ complexes and $[Re(CO)_3(NHC)_3]Cl$ have been obtained by this method from the corresponding isocyanide complexes. The new reduction method can be employed instead of the Staudinger reaction which has been demonstrated to fail in the reduction of ruthenium(II) coordinated 2-azidoethyl isocyanide **1** in $[RuCl_2(p\text{-cymene})(\mathbf{1})]$.[10] No additional phosphines, which are required for the Staudinger reaction and which can interact unfavourably with the template metal, are required in the $Zn/NH_4Cl/H_2O$ reduction. The major drawback of the $Zn/NH_4Cl/H_2O$ reduction in the synthesis of charged complexes is the formation of salt mixtures containing Cl^- and $[ZnCl_4]^{2-}$ anions. These anions, however, can be exchanged. We are currently studying the reduction of β-azido functionalized isocyanides coordinated to kinetically labile metal centers like iron(III) where the reduction under Staudinger conditions could lead to an undesirable reaction of the required phosphines with the iron(III) template.

Acknowledgements

We thank the Graduate School of Chemistry Münster (GSC-MS) and DGRI-SEP Mexico for a predoctoral grant to A. F. F. and GSC-MS for a predoctoral grant to K. O. F. Our work was supported by the Deutsche Forschungsgemeinschaft (IRTG 1444) through a predoctoral grant for O. K.

Notes and references

1 *N-Heterocyclic Carbenes in Transition Metal Catalysis: Top. Organomet. Chem.*, ed. F. Glorius, Springer Verlag, Berlin/Heidelberg, 2007, vol. 21.
2 (*a*) F. E. Hahn, C. Radloff, T. Pape and A. Hepp, *Organometallics*, 2008, **27**, 6408–6410; (*b*) C. Radloff, F. E. Hahn, T. Pape and R. Fröhlich, *Dalton Trans.*, 2009, 7215–7222; (*c*) C. Radloff, J. J. Weigand and F. E. Hahn, *Dalton Trans.*, 2009, in press, 10.1039/b916651c.
3 (*a*) F. E. Hahn and M. C. Jahnke, *Angew. Chem., Int. Ed.*, 2008, **47**, 3122–3172; (*b*) O. Kaufhold and F. E. Hahn, *Angew. Chem., Int. Ed.*, 2008, **47**, 4057–4061; (*c*) F. E. Hahn, *Angew. Chem., Int. Ed.*, 2006, **45**, 1348–1352; (*d*) J. C. Y. Lin, R. T. W. Huang, C. S. Lee, A. Bhattacharyya, W. S. Hwang and I. J. B. Lin, *Chem. Rev.*, 2009, **109**, 3561–3598; (*e*) M. Scholl, D. Ding, C. W. Lee and R. H. Grubbs, *Org. Lett.*, 1999, **1**, 953–956; (*f*) A. M. Voutchkova, M. Feliz, E. Clot, O. Eisenstein and R. H. Crabtree, *J. Am. Chem. Soc.*, 2007, **129**, 12834–12846; (*g*) N. Kuhn and T. Kratz, *Synthesis*, 1993, 561–562; (*h*) F. E. Hahn, L. Wittenbecher, R. Boese and D. Bläser, *Chem.–Eur. J.*, 1999, **5**, 1931–1935; (*i*) F. E. Hahn, L. Wittenbecher, D. Le Van and R. Fröhlich, *Angew. Chem., Int. Ed.*, 2000, **39**, 541–544.
4 (*a*) N. Meier, F. E. Hahn, T. Pape, C. Siering and S. R. Waldvogel, *Eur. J. Inorg. Chem.*, 2007, 1210–1214; (*b*) M. A. Huertos, J. Pérez, L. Riera and A. Menéndez-Velázquez, *J. Am. Chem. Soc.*, 2008, **130**, 13530–13531.
5 R. A. Michelin, A. J. L. Pombeiro and M. F. C. Guedes da Silva, *Coord. Chem. Rev.*, 2001, **218**, 75–112.
6 (*a*) F. E. Hahn, V. Langenhahn, N. Meier, T. Lügger and W. P. Fehlhammer, *Chem.–Eur. J.*, 2003, **9**, 704–712; (*b*) F. E. Hahn, C. García-Plumed, M. Münder and T. Lügger, *Chem.–Eur. J.*, 2004, **10**, 6285–6293; (*c*) F. E. Hahn, V. Langenhahn and T. Pape, *Chem. Commun.*, 2005, 5390–5392; (*d*) For a review on this type of cyclization reaction see: M. Tamm and F. E. Hahn, *Coord. Chem. Rev.*, 1999, **182**, 175–209.
7 (*a*) F. E. Hahn, V. Langenhahn, T. Lügger, T. Pape and D. Le Van, *Angew. Chem., Int. Ed.*, 2005, **44**, 3759–3763; (*b*) O. Kaufhold, A. Stasch, P. G. Edwards and F. E. Hahn, *Chem. Commun.*, 2007, 1822–1824; (*c*) O. Kaufhold, A. Stasch, T. Pape, A. Hepp, P. G. Edwards, P. D. Newman and F. E. Hahn, *J. Am. Chem. Soc.*, 2009, **131**, 306–317.
8 W. P. Fehlhammer, K. Bartel, B. Weinberger and U. Plaia, *Chem. Ber.*, 1985, **118**, 2220–2234.
9 (*a*) F. E. Hahn, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 650–665; (*b*) F. E. Hahn and M. Tamm, *J. Chem. Soc., Chem. Commun.*, 1993, 842–844; (*c*) F. E. Hahn and M. Tamm, *J. Organomet. Chem.*, 1993, **456**, C11–C14; (*d*) F. E. Hahn, M. Tamm and T. Lügger, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1356–1359; (*e*) F. E. Hahn and M. Tamm, *Organometallics*, 1995, **14**, 2597–2600; (*f*) M. Tamm, T. Lügger and F. E. Hahn, *Organometallics*, 1996, **15**, 1251–1256; (*g*) F. E. Hahn and L. Imhof, *Organometallics*, 1997, **16**, 763–769.
10 O. Kaufhold, A. Flores-Figueroa, T. Pape and F. E. Hahn, *Organometallics*, 2009, **28**, 896–901.
11 S. Bräse, C. Gil, K. Knepper and V. Zimmermann, *Angew. Chem., Int. Ed.*, 2005, **44**, 5188–5240.
12 A. Kamal and B. S. N. Reddy, *Chem. Lett.*, 1998, 593–594.
13 A. Kamal, N. V. Rao and E. Laxman, *Tetrahedron Lett.*, 1997, **38**, 6945–6948.
14 I. Bosch, A. M. Costa, M. Martín, F. Urpí and J. Vilarrasa, *Org. Lett.*, 2000, **2**, 397–399.
15 H. S. P. Rao and P. Siva, *Synth. Commun.*, 1994, **24**, 549–555.

16 M. Bartra, P. Romea, F. Urpí and J. Vilarrasa, *Tetrahedron*, 1990, **46**, 587–594.
17 G. V. Reddy, G. V. Rao and D. S. Iyengar, *Tetrahedron Lett.*, 1999, **40**, 3937–3938.
18 W. Lin, X. Zhang, Z. He, Y. Jin, L. Gong and A. Mi, *Synth. Commun.*, 2002, **32**, 3279–3284.
19 (*a*) F. A. J. Kerdesky, R. J. Ardecky, M. V. Lakshmikantham and M. P. Cava, *J. Am. Chem. Soc.*, 1981, **103**, 1992–1996; (*b*) T. Carofiglio, D. Marton and G. Tagliavini, *Organometallics*, 1992, **11**, 2961–2963.
20 (*a*) R. J. Haines and A. L. Du Preez, *J. Organomet. Chem.*, 1975, **84**, 357–367; (*b*) M. I. Bruce, F. S. Wong, B. W. Skelton and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1981, 1398–1405; (*c*) F. M. Conroy-Lewis and S. J. Simpson, *J. Organomet. Chem.*, 1987, **322**, 221–228; (*d*) G. S. Ashby, M. I. Bruce, I. B. Tomkins and R. C. Wallis, *Aust. J. Chem.*, 1979, **32**, 1003–1016.
21 C.-Y. Liu, D.-Y. Chen, G.-H. Lee, S.-M. Peng and S.-T. Liu, *Organometallics*, 1996, **15**, 1055–1061.
22 *SMART*, Bruker AXS, 2000.
23 SHELXS-97, G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 1990, **46**, 467–473.
24 SHELXL-97, G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, **64**, 112–122.

