Ruthenium(II) pincer complexes featuring an anionic CNC bis(1,2,3-triazol-5-ylidene)carbazolide ligand coordinated in a meridional fashion

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ABSTRACT

The preparation of a new neutral ruthenium(II) pincer complexes with formula [RuCl(CO)$_2$(C^{TRZ}NC^{TRZ})] (CNC = bis(1,2,3-triazol-5-ylidene)carbazolide) is described. Access to the hydrido complex [RuH(CO)$_2$(C^{TRZ}NC^{TRZ})] was attained by reaction of the pincer ligand precursor with base and with [RuCl(H)(AsPh$_3$)$_3$(CO)] in the presence of CO atmosphere. The meridional geometry pincer ligand in the complexes is confirmed by a single crystal X-ray diffraction study of [RuCl(CO)$_2$(C^{TRZ}NC^{TRZ})]. Preliminary results of the use of [RuCl(CO)$_2$(C^{TRZ}NC^{TRZ})] as catalyst in the transfer hydrogenation reaction of ketones, are reported.

Keywords: ruthenium(II), mesoionic carbene (MIC), pincer ligands, 1,2,3-triazol-5-ylidene (TRZ), meridional coordination

Graphical abstract

L = CO, AsPh₃
X = Cl, H
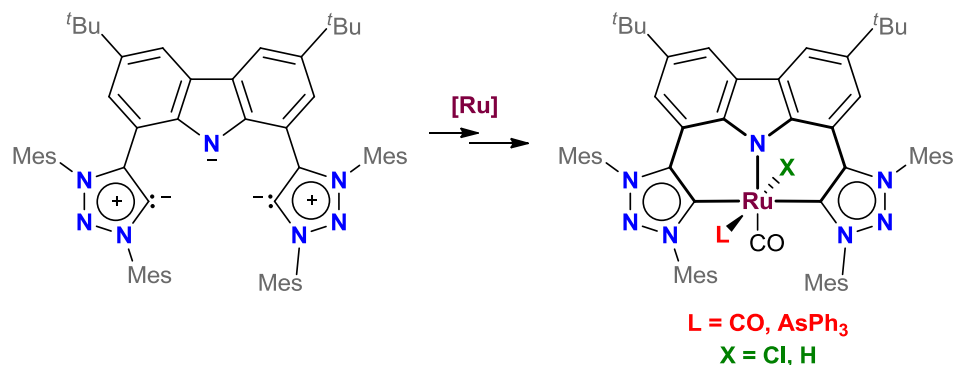
Synopsis

Synthesis and structure of CNC-pincer complexes of Ru(II) based on a bis(triazolylidene)carbazolide scaffold to enforce meridional geometry.

1. Introduction

The advantages of combining the steric and electronic directing effects of tridentate pincer ligands with coordination to ruthenium(II), have led to the development of a plethora of ruthenium(II) pincer complexes, with applications ranging from (mostly) catalysis, to photophysical and biological [1]. For the transfer hydrogenation (TH) reaction - a convenient alternative to direct hydrogenation reactions to access this fundamental organic transformation - catalysts have included Ru(II) pincer complexes almost from the onset [2]. With the advent of N-heterocyclic carbenes (NHCs) [3], robust metal catalysts have been accessible by exploitation of the strong carbene carbon-metal bond. The first NHC-based pincer complexes of Ru(II) utilized in TH contained tridentate CNC-ligands with a central pyridine as N-donor group, and flanking NHCs as C-donors, see **A** [4] and **B** [5], Fig. 1.
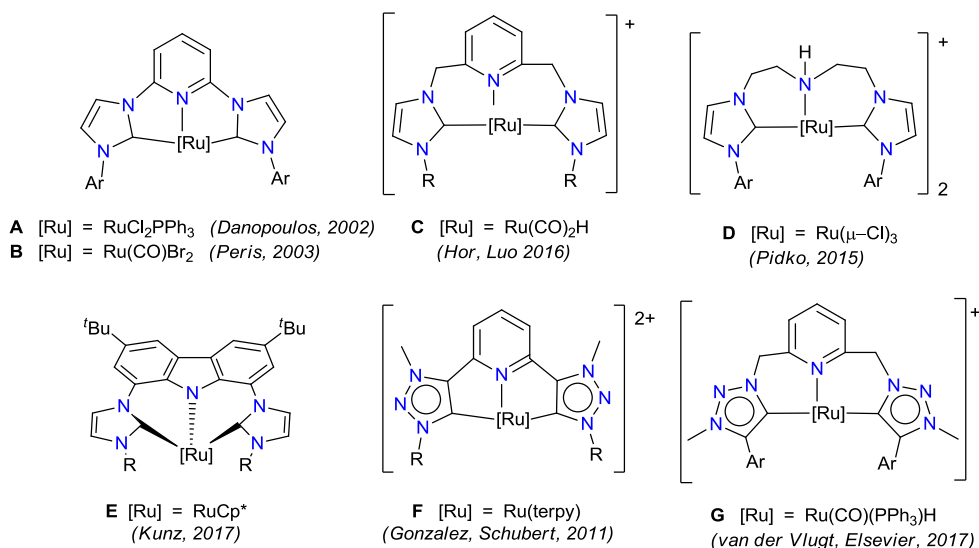
Figure 1. Examples of previously reported carbene-based CNC-Ru(II) complexes

This structural motif of a neutral CNC-tridentate ligand that coordinates to the ruthenium metal central at three adjacent co-planar sites, has been exploited also recently in the design of a bis(imidazolylidene)-lutidine based hydroboration catalyst (**C**) [6] and a bis[(imidazolylidene)alkyl]amino pincer ruthenium complex as a direct hydrogenation catalyst (**D**) [7]. In contrast, the ruthenium complex **E**, (Figure 1) featuring the rigid carbene-based CNC pincer ligand (bimca), (bimca = bis(imidazolylidene)carbazolide) reported by Kunz et al. is the only example, where the *anionic* CNC pincer ligand coordinates as a tripodal cyclopentadienyl analogue to a RuCp* precursor (Cp* = pentamethylcyclopentadienyl), and not in the usual meridional fashion [8]. The use of other Ru(II) precursors yielded octahedral complexes with coordination of two of the monoanionic pincer ligands [9]. Parallel to this, pincer ligands based on abnormal NHCs (*a*NHCs) or mesoionic carbenes (MICs) [10] have been much less explored. This class of carbenes include the 1,2,3-triazolylidenes (TRZs), which are stronger donors than NHCs and yield more electron-rich metal complexes upon coordination [11]. The only examples of pincer-TRZ ruthenium(II) complexes reported, feature an extension of the central pyridine (**F**) [12] / lutidine motif (**G**) [13] to include the TRZs as the co-planar wing-tip groups in neutral ligand scaffolds. We have recently reported the preparation of the monoanionic CNC-pincer ligand, [**C**$^{\text{TRZ}}$**NC**$^{\text{TRZ}}$]⁻, featuring a rigid carbazolide flanked by two 1,2,3-triazol-5-ylidenes as the co-planar C-donors, which is readily accessible from its salt precursor

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[H₃C^{TRZ}NC^{TRZ}]PF₆.Cl (Scheme 1), after deprotonation with KHMDS [14]. The strongly donating character of the central amido-group and the strong sigma-donating 1,2,3-triazol-5-ylidene moieties, and the steric bulk of the ligand scaffold, allowed for the isolation of reactive transition metal complexes [14a, 15] and the use of the CNC-pincer metal complexes as highly selective alkyne functionalization catalysts [14b]. It was therefore reasoned that similar steric and electronic direction could be achieved in the coordination of **[C^{TRZ}NC^{TRZ}]⁻** to an appropriate ruthenium(II) precursor.

Herein, we report the synthesis of three octahedral Ru(II)-pincer complexes with the complexation of one CNC-ligand, the TRZ-analogue of the bimca ligand (see Scheme 1).

2. Experimental

2.1 Solvents and reagents

All synthetic manipulations, unless otherwise stated, were performed under N₂ gas or Ar gas atmosphere using oven or flame dried glassware and standard Schlenk or vacuum line techniques. Air sensitive solids where stored and handled in a PureLab HE glove box. Preparation of NMR and crystallization samples that also require an inert atmosphere were done in the glove box. [RuCl(H)(AsPh₃)₃(CO)] was prepared as previously reported [16]. All other reagents were obtained from commercial sources and were used without any further purification.

Unless otherwise stated, only anhydrous solvents were used during experimental procedures. Solvents were dried using a solvent purification system (MBraun SPS). Anhydrous THF and Et₂O were obtained after distillation over sodium and benzophenone ketyl under a N₂ gas atmosphere. Anhydrous PhMe and hexane were obtained after distillation over sodium under a N₂ gas atmosphere. Anhydrous CH₂Cl₂ was obtained after distillation over calcium hydride under a N₂ gas atmosphere. Deuterated benzene was dried over sodium and distilled under an Ar gas atmosphere.

2.2 Characterisation Techniques

Nuclear magnetic resonance (NMR) spectra were obtained using either a Bruker AVANCE-III-300 operating at 300.13 MHz for ^{1}H, 75.47 MHz for ^{13}C, 121.49 MHz for ^{31}P and 282.40 MHz for ^{19}F; AVANCE-III-400 operating at 400.21 MHz for ^{1}H, 100.64 MHz for ^{13}C, 162.01 MHz for ^{31}P and 376.57 MHz for ^{19}F; or on on a Varian Mercury 300 MHz, Varian NMR System 500 MHz. ^{1}H Chemical shifts are reported as δ (ppm) values downfield from Me$_4$Si and chemical shifts where referenced to residual non-deuterated solvents peaks (CD$_3$CN, 1.94 ppm; CDCl$_3$, 7.26 ppm; C$_6$D$_6$, 7.16 ppm). ^{13}C chemical shifts are also reported as δ (ppm) values downfield from Me$_4$Si and chemical shifts where referenced to residual non-deuterated solvents peaks (CD$_3$CN, 1.32 ppm; CDCl$_3$, 77.16 ppm; C$_6$D$_6$, 128.06 ppm). Proton coupling constants (J) are given in Hz. The spectral coupling patterns are designated as follows: s/S - singlet; d/D - doublet; t/T - triplet; q/Q - quartet; sept-septet; m - multiplet; br - broad signal. Quaternary carbons are designated as C$_q$.

Chemical shift assignment in the ^{1}H NMR spectra is based on first-order analysis and when required were confirmed by two-dimensional (2D) (^{1}H-^{1}H) homonuclear chemical shift correlation (COSY) experiments. The ^{13}C shifts were obtained from proton-decoupled ^{13}C NMR spectra. Where necessary, the multiplicities of the ^{13}C signals were deduced from proton-decoupled DEPT-135 spectra. The resonances of the proton-bearing carbon atoms were correlated with specific proton resonances using 2D (^{13}C-^{1}H) heteronuclear single-quantum coherence (HSQC) and heteronuclear multiple bond correlations (HMBC) experiments. Standard Bruker pulse programs were used in the experiments.

Solution IR spectra (ν(CO), and ν(Ru-H)) were recorded on a Bruker ALPHA FT–IR or on a JASCO FT/IR-6200 spectrometer with a NaCl cell, using CH$_2$Cl$_2$ as solvent, or as a KBr pellet. The range of absorption measured was from 4000-600 cm$^{-1.}$

Electrospray mass spectra (ESI-MS) were recorded on a Micromass Quatro LC instrument or on a Bruker QTOF Mass spectrometer with positive electron spray as the ionization techniques; nitrogen was employed as drying and nebulizing gas at a flow of 4 L/min. The m/z values were measured in the range of 100-1500 with acetonitrile as

solvent. Accurate mass measurements were performed by use of a Q-TOF premier mass spectrometer with electrospray source (Waters, Manchester, UK) operating at a resolution of ca. 16 000 (fwhm). Elemental analyses were carried out on a EuroEA3000 Eurovector Analyzer. Single crystal X-ray diffraction data were collected on a Agilent SuperNova difractometer equipped with an Atlas CCD detector using Cu Kα radiation (λ = 1.54184 Å). The single crystal was mounted on a MicroMount polymer tip (MiteGen) in a random orientation.

The yields of the catalytic reactions were calculated by GC using anisole as an internal standard. (Shimadzu GC-2010, NF-5225, 30 m, 0.25 mm, 0.25 µm, He at 1.0 mL/min, constant Flow 40 °C for 2 min, ramp to 100°C at 30 °C/min, ramp to 240°Cat 45 °C/min (hold 0.5 min).

2.3 Crystal structure determination

A single crystal of **1** was selected and mounted on a SuperNova, Dual, Cu at zero, Atlas diffractometer. The crystal was kept at 293(2) K during data collection. Using Olex2 [17], the structure was solved with the XS [18] structure solution program using Direct Methods and refined with the ShelXL [18] refinement package using Least Squares minimisation.

Crystal Data for **1**: $C_{63}H_{68}Cl_3N_7O_2Ru$ (M =1162.66 g/mol): triclinic, space group P-1 (no. 2), $a =$ 11.68915(13) Å, $b =$ 14.9965(2) Å, $c =$ 19.5138(3) Å, $\alpha =$ 69.4553(14)°, $\beta =$ 81.5229(11)°, $\gamma =$ 68.4617(12)°, $V =$ 2978.81(8) Å^3,$Z =$ 2, $T =$ 293(2) K, µ(MoKα) = 0.446 mm^{-1}, $Dcalc =$ 1.296 g/cm^3, 58667 reflections measured (5.666° $\leq$ 2Θ $\leq$ 52°), 11710 unique (R_{int} = 0.0423, R_{sigma} = 0.0284) which were used in all calculations. The final R_1 was 0.0338 (I > 2σ(I)) and wR_2 was 0.0939 (all data).

2.4 Synthesis of complex 1, [RuCl(CO)$_2$(C^{TRZ}NC^{TRZ})]

A Schlenk tube was loaded with [**H$_3$C^{TRZ}NC^{TRZ}]PF$_6$.Cl** (1.00 g, 9.4 x 10^{-4} mol) and (bicyclo[2.2.1]hepta-2,5-diene)dichlororuthenium(II) polymer (352.9 mg, 1.4 x 10^{-3} mol). The tube was evacuated and purged with N$_2$ (g), with subsequent addition of

degassed ethanol (60 mL). Degassed Et$_3$N (1.56 mL, 1.1 x 10^{-2} mol) was added to the mixture. The reaction mixture was then heated up and refluxed at 95 °C for 5 days in the absence of light. The solvent was evaporated under reduced pressure. The product was extracted with Et$_2$O (3 x 30 mL), and the solvent removed *in vacuo* to obtain a dark yellow solid. The solid was first washed with hexanes (5 x 30 mL), followed by CH$_3$CN (10 mL) and finally dried under reduced pressure to yield 145.0 mg of **1** (1.3 x 10^{-4} mol, yield 14%) as a yellow solid. **^{1}H NMR** δ_H (CD$_2$Cl$_2$, 300 MHz) 8.20 (d, *J* = 2.1 Hz, 2H, Ar**H**$_{carb}$), 7.31 (d, *J* = 1.8 Hz, 2H, Ar**H**$_{carb}$), 7.25 (s, 2H, Ar**H**$_{Mes}$), 7.18 (s, 2H, Ar**H**$_{Mes}$), 7.00 (s, 2H, Ar**H**$_{Mes}$), 6.98 (s, 2H, Ar**H**$_{Mes}$), 2.45 (s, 6H, Ar**CH$_3$**), 2.35 (s, 6H, Ar**CH$_3$**), 2.34 (s, 6H, Ar**CH$_3$**), 2.20 (s, 6H, Ar**CH$_3$**), 2.09 (s, 6H, Ar**CH$_3$**), 1.98 (s, 6H, Ar**CH$_3$**), 1.14 (s, 18H, C(**CH$_3$**)$_3$). **^{13}C NMR** δ_C (CD$_2$Cl$_2$, 75 MHz) 198.7 (Ru**C**O), 196.0 (Ru**C**O), 165.2 (**C**$_{Carbene}$), 143.4, 142.2, 142.0, 141.3, 138.9, 137.9, 137.1, 135.9, 135.6, 135.6, 135.3, 130.8, 130.5, 130.0, 129.2, 126.8, 118.2, 117.7, 111.6, 34.7 (**C**(CH$_3$)$_3$), 31.9 (C(**C**H$_3$)$_3$), 21.5 (Ar**C**H$_3$), 21.4 (Ar**C**H$_3$), 18.7 (Ar**C**H$_3$), 18.0 (Ar**C**H$_3$), 17.8 (Ar**C**H$_3$), 17.6 (Ar**C**H$_3$). **FTIR** (KBr): 2028 cm^{-1} (v**CO**), 1957 cm^{-1} (v**CO**). **HRMS** (ESI-TOF): Calculated for C$_{62}$H$_{66}$N$_7$O$_2$Ru$^+$ [M]$^+$: 1042.4321, found: 1042.4343. Elemental analysis calc. (%) for C$_{62}$H$_{66}$N$_7$O$_2$RuCl: C 69.1, H 6.1, N 9.1; found 68.3, H 6.0, N 8.6.

2.5 Synthesis of complex **2**, [**RuH(AsPh$_3$)(CO)(C^{TRZ}NC^{TRZ})**]

A Schlenk tube was charged with [**H$_3$C^{TRZ}NC^{TRZ}**]**PF$_6$.Cl** (400.0 mg, 3.7 x 10^{-4} mol), [RuCl(H)(AsPh$_3$)$_3$(CO)] (487.0 mg, 4.5 x 10^{-4} mol) and KN[Si(CH$_3$)$_3$]$_2$ (373.3 mg, 1.9 x 10^{-3} mol) under a N$_2$ (g) atmosphere. The solids were cooled down to -78 °C, before the addition of THF (25 mL), which had also been cooled down to -78 °C. The mixture was stirred at -78 °C for one hour, before it was allowed to gradually warm up to room temperature whilst stirring the solution overnight in the absence of light. The solvent was evaporated *in vacuo* and compound **2** was extracted with hexanes (4 x 30 mL). The solvent was evaporated under reduced pressure to yield a red residue, which was characterized by NMR spectroscopy as being complex **2** accompanied by a residual amount of AsPh$_3$. **^{1}H NMR** δ_H (C$_6$D$_6$, 300 MHz) 8.28 (d, *J* = 1.8 Hz, 2H, Ar**H**$_{carb}$), 7.34

(br s, 45H, As(C_6H_5)$_3$), 7.05 - 7.03 (m, 15H, As(C_6H_5)$_3$, overlapping with uncoordinated AsPh$_3$), 6.94 (s, 2H, Ar**H**$_{Mes}$), 6.90 (s, 2H, Ar**H**$_{Mes}$), 6.80 (s, 2H, Ar**H**$_{Mes}$), 6.57 (s, 2H, Ar**H**$_{Mes}$), 2.60 (s, 6H, Ar**CH**$_3$), 2.28 (s, 12H, Ar**CH**$_3$), 2.11 (s, 6H, Ar**CH**$_3$), 1.95 (s, 6H, Ar**CH**$_3$), 1.44 (s, 6H, Ar**CH**$_3$), 1.27 (s, 18H, C(**CH**$_3$)$_3$), -8.82 (s, 1H, Ru**H**). **^{13}C NMR** δ_C (C_6D_6, 75 MHz) 205.9 (Ru**C**O), 178.8 (**C**$_{Carbene}$), 146.0, 141.6, 140.3 (As(C_6H_5)$_3$), 140.2, 139.1, 138.5, 136.7, 136.1, 136.1, 135.8, 135.4, 135.3, 134.1 (As(C_6H_5)$_3$), 131.8, 131.6, 130.1, 129.5, 129.3, 129.2, 128.9 (As(C_6H_5)$_3$), 128.6 (As(C_6H_5)$_3$), 127.2, 117.4, 116.5, 113.7, 34.4 (**C**(CH$_3$)$_3$), 32.1 (C(**CH**$_3$)$_3$), 21.5 (Ar**CH**$_3$), 21.5 (Ar**CH**$_3$), 21.1 (Ar**CH**$_3$), 21.0 (Ar**CH**$_3$), 19.4 (Ar**CH**$_3$), 18.2 (Ar**CH**$_3$), 18.1 (Ar**CH**$_3$), 18.0 (Ar**CH**$_3$), 18.0 (Ar**CH**$_3$), 17.2 (Ar**CH**$_3$).

## 2.6 *Synthesis of complex 3, [RuH(CO)$_2$($C^{TRZ}NC^{TRZ}$)]*

The red residue obtained from the reaction to prepare **2**, was dissolved in diethyl ether at room temperature. In the absence of light, CO (g) was bubbled through the red solution for 10 min. The vessel was sealed, and the reaction stirred overnight, at which point a slight color change occurred from red to orange-brown. The reaction was left to settle, and the solution filtered off from the precipitate. The solvent was evaporated *in vacuo*, and the residue was washed with hexanes (4 x 20 mL). The solid was dried under reduced pressure, to yield **3** (68.0 mg, 6.5 x 10^{-5} mol, overall yield 17%) as a yellow brown solid. **^{1}H NMR** δ_H (C_6D_6, 300 MHz) 8.52 (d, *J* = 1.8 Hz, 2H, Ar**H**$_{carb}$), 7.27 (d, *J* = 2.1 Hz, 2H, Ar**H**$_{carb}$), 6.84 (s, 2H, Ar**H**$_{Mes}$), 6.77 (s, 2H, Ar**H**$_{Mes}$), 6.73 (s, 2H, Ar**H**$_{Mes}$), 6.59 (s, 2H, Ar**H**$_{Mes}$), 2.49 (s, 6H, Ar**CH**$_3$), 2.23 (s, 6H, Ar**CH**$_3$), 2.22 (s, 6H, Ar**CH**$_3$), 2.09 (s, 6H, Ar**CH**$_3$), 2.06 (s, 6H, Ar**CH**$_3$), 1.57 (s, 6H, Ar**CH**$_3$), 1.24 (s, 18H, C(**CH**$_3$)$_3$), -3.83 (s, 1H, Ru**H**). **^{13}C NMR** δ_C (C_6D_6, 75 MHz) 201.3 (Ru**C**O), 196.4 (Ru**C**O), 170.6 (**C**$_{Carbene}$), 146.2, 141.8, 140.6, 139.6, 137.7, 137.1, 136.3, 136.2, 135.5, 135.3, 130.1, 129.8, 129.3, 129.1, 127.5, 117.9, 117.5, 112.9, 34.5 (**C**(CH$_3$)$_3$), 32.0 (C(**CH**$_3$)$_3$), 21.3 (Ar**CH**$_3$), 21.3 (Ar**CH**$_3$), 21.0 (Ar**CH**$_3$), 20.9 (Ar**CH**$_3$), 19.0 (Ar**CH**$_3$), 19.0 (Ar**CH**$_3$), 17.6 (Ar**CH**$_3$), 17.6 (Ar**CH**$_3$), 17.5 (Ar**CH**$_3$), 17.2 (Ar**CH**$_3$), 17.2 (Ar**CH**$_3$). **FTIR** (CH$_2$Cl$_2$): 2040 cm^{-1} (υ-Ru**H**), 2008 cm^{-1} (υ-**CO**), 1944 cm^{-1} (υ-**CO**). **HRMS** (ESI-

TOF): Calculated for $C_{62}H_{66}N_7O_2Ru^+$ [M-H]$^+$: 1042.4321, found: 1042.4374, and calculated for $C_{62}H_{67}N_7O_2Ru^+$ [M]$^+$: 1043.4399, found: 1043.4391.

3. Results and discussion

3.1 Synthesis and characterisation of dicarbonylchloridobis(1,2,3-triazol-5-ylidene)carbazolideruthenium(II) complex

Complex [RuCl(CO)$_2$(C^{TRZ}NC^{TRZ})], **1**, was prepared following the reaction procedure depicted in Scheme 1. The dicationic bis(triazolium)carbazole precursor, [**H$_3$C^{TRZ}NC^{TRZ}]PF$_6$.Cl** [14] was reacted with (bicyclo[2.2.1]hepta-2,5-diene)dichlororuthenium(II) polymer ([RuCl$_2$(NBD)]$_n$, NBD = norbornadiene) in the absence of light (Scheme 1), yieldiong complex **1** in low yield (14%). The synthetic procedure is similar to previously reported routes making use of the [RuCl$_2$(COD)]$_n$ polymer (COD = 1,5-cyclooctadiene) as precursor to yield *dihalo* monocarbonyl pincer complexes.[5, 19] In our case the *dicarbonyl* monochloride CNC complex **1** was formed due to the anionic (and electron donating) nature of the CNC ligand.
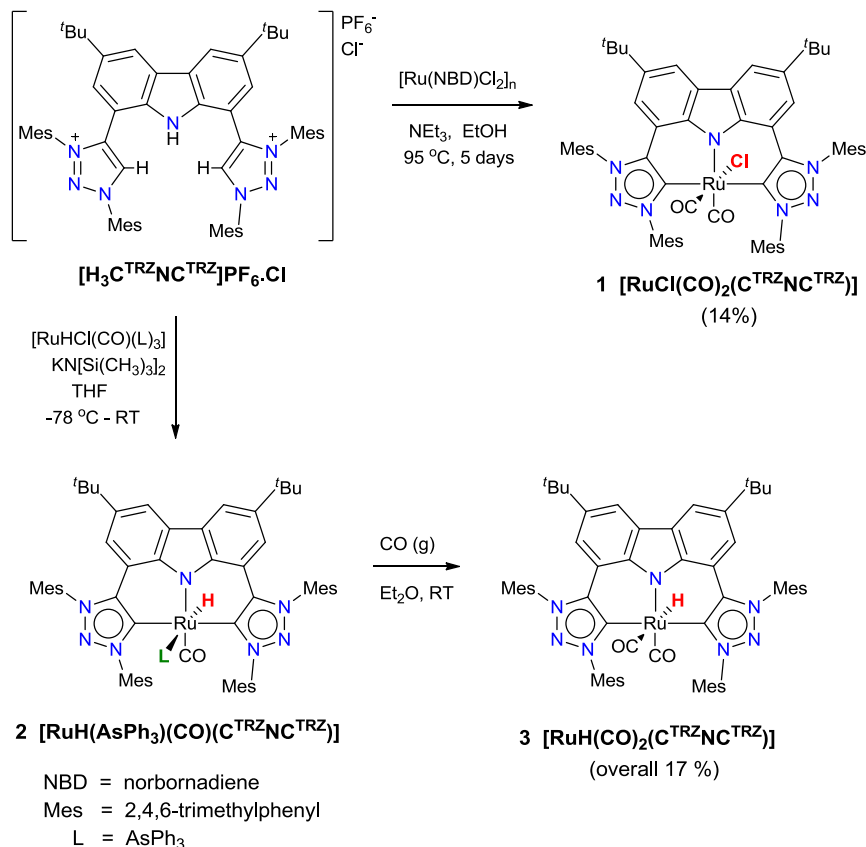
Scheme 1. Synthesis of complexes **1**−**3**.

Unlike the other two examples of Ru-bisTRZ-pyridine/lutidine pincer complexes reported previously, transmetallation from a Ag-precursor was not required for successful complexation. [10, 11] The disappearance of the acidic triazolium CH and carbazole NH proton resonances in the ^{1}H NMR spectrum of **1** confirmed coordination of the ligand to Ru(II), as well as the carbene carbon resonance at 165.2 ppm in the ^{13}C NMR spectrum. This value corresponds to the TRZ-$C_{carbene}$ resonances for other reported Ru-TRZ complexes, ranging from 161−185 ppm, although occurring on the high field end of the range due to the overall neutral charge of the complex compared to mono- and dicationic Ru-TRZ complexes previously reported. [10, 11, 20] Similarly, the signals due to the carbonyl carbons also display relatively upfield chemical shifts, at 198.7 ppm and 196.0 ppm, compared to, for example, cationic complex **F** (Fig. 1) where the carbonyl carbon atom resonates at 208.5 ppm [11], and the carbonyl stretching frequencies are observed at 2028 cm^{-1} and 1957 cm^{-1}.
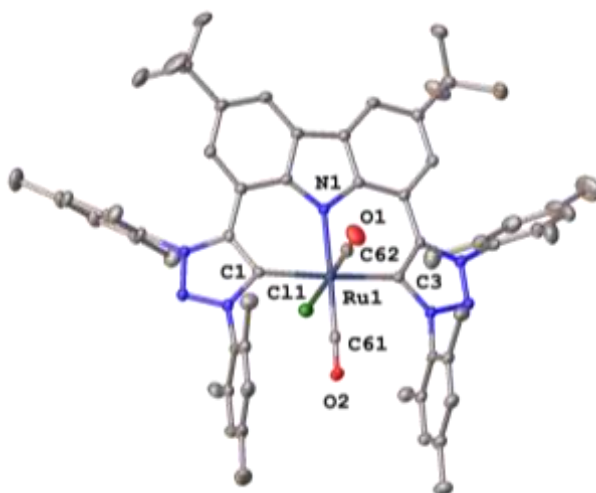
Figure 2. Molecular structure of complex **1** with 50% probability ellipsoids. Hydrogens and one solvent molecule of CH_2Cl_2 have been omitted for clarity. Selected bond distances (Å) and bond angles (°): Ru(1)–C(1) = 2.132 (2); Ru(1)–C(3) = 2.119 (2); Ru(1)–N(1) = 2.1308 (17); Ru(1) –C(61) = 1.888(2); Ru(1)–C(62) = 1.853(2); Ru(1)–Cl(1) = 2.460(5); C(1)–Ru(1)–C(3) = 169.4(8); N(1)–Ru(1)–C(61)= 176.7(8); N(1)–Ru(1)–Cl(1) = 88.1(5).

The molecular structure of **1** (Figure 2), displays a slightly distorted octahedral geometry around the ruthenium(II) metal centre, with meridional geometry of the **$C^{TRZ}NC^{TRZ}$** ligand, similar to the *mer*-geometry enforced by the coordination of two different tridentate ligands of **F** [12]. However, other Ru-pincer carbene complexes (**E** [8], **G** [13]) displayed deviation from this mode of coordination if not supported by secondary chelating/pincing ligand scaffolds. The Ru–$C_{carbene}$ bond lengths (Ru(1)–C(1) = 2.132 (2) Å; Ru(1)–C(3) = 2.119 (2) Å), and the Ru–N_{amido} bond distance (Ru(1)–N(1) = 2.1308 (17)), are longer than reported for other Ru-NHC/TRZ pincer complexes (Ru–$C_{carbene}$ = 1.97 – 2.09 Å; Ru–N = 2.06 – 2.20 Å) [6, 7, 10, 12]. This observation is in all probability a result of the steric crowding around the central Ru-atom, with the bite angle of the CNC-pincer ligand (C(1)–Ru(1)–C(3)) being 169.4(8)°. As expected, the two π-acceptor carbonyl ligands are coordinated *cis* to each other, and *trans* to the carbazolide amido and chlorido ligands, respectively.

3.2 Synthesis and characterisation of dicarbonylhydridoridebis(1,2,3-triazol-5-ylidene)carbazolide ruthenium(II) complex

The bis(triazolium) precursor **[$H_3C^{TRZ}NC^{TRZ}$]PF$_6$.Cl** was triply deprotonated by adding an excess of potassium hexamethyldisilazide (KHMDS). The *in situ* generated free

bis(triazolylidene) reacted with the [RuCl(H)(AsPh₃)₃(CO)] to yield complex **2**, with a triphenyl arsine co-ligand (see Scheme 1). Purification of this complex proved non-trivial, and all our attempts to isolate complex **2** in the pure form were unsuccessful – the complex was always accompanied by a residual amount of AsPh$_s$. Nevertheless, we were able to characterize the comple by NMR techniques (see Fig. S3-S4, Supplementary data). Complex [RuH(CO)₂(CNC)], **3**, was generated by bubbling carbon monoxide through an ethereal solution of **2**. After workup, **3** was obtained in low yield (overall yield from precursor triazolium salt 17 %, Scheme 1).
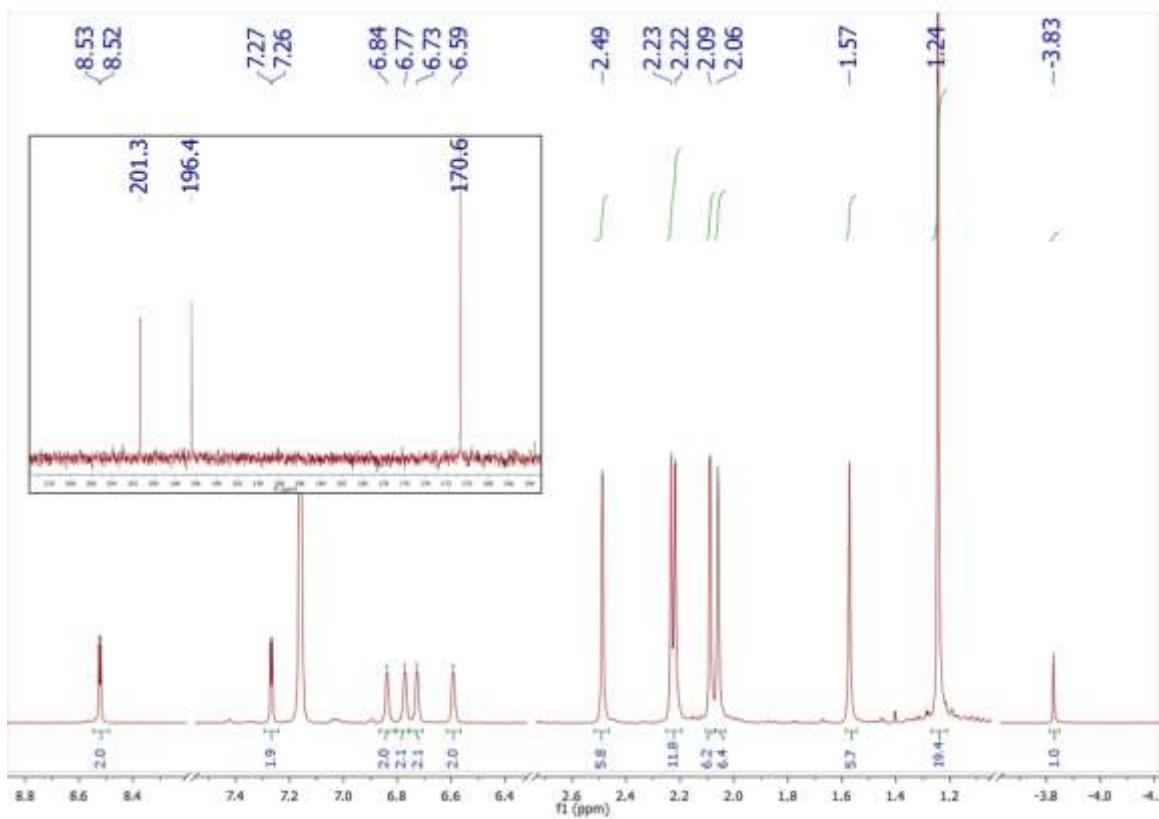

Figure 3. ¹H and ¹³C (inset) NMR spectrum of **3**.

The ¹H NMR spectrum of **3** displays the signal due to the hydrido ligand at -3.83 ppm (see Figure 3). This value is downfield shifted compared to the hydrido resonances reported for **D** and **G**, ranging from -7.15 – -5.10 ppm [6, 11], and also compared to the hydrido chemical shift of **2** (-8.82 ppm). Correspondingly, the ¹³C NMR spectrum of **3** shows that both the carbonyl and carbene carbon resonances are observed at 201.3, 196.4

and 170.6 ppm, respectively, therefore downfield shifted compared to the same signals in **1.** In addition, the strongly σ-donating hydrido ligand induces lower carbonyl stretching frequencies observed for **3** (ν_{CO} = 2008, 1944 cm^{-1}) in the FT-IR spectrum, than for **1**. The Ru-H band observed in the IR spectrum vibrates at a high energy of 2040 cm^{-1}, although such a high wavenumber ν_{Ru-H} is not unprecedented in the literature [21]. In the case of complex **2**, carbene and carbonyl carbon resonances were observed at 205.9 and 178.8 ppm, respectively.

3.3 Transfer hydrogenation of ketones

The structural similarity of **1** to the transfer hydrogenation catalysts **A** and **B** (Figure 1), prompted us to test the catalytic activity of **1** in the transfer hydrogenation of acetophenone to 1-phenylethanol, using isopropanol as sacrificial H-donor. The reaction conditions were optimized using different bases (potassium *tert*-butoxide or cesium carbonate), different substrate:base:catalyst ratios and by varying the temperature and time of the reaction (See Table S1, SI). The optimized conditions of 1 mol% catalyst loading, 10 mol% Cs$_2$CO$_3$ as base at 95 °C for 14 hours, yielded quantitative reduction of acetophenone (entry 6, Table S1). In the case of the reaction with 4-bromoacetophenone, the substrate was reduced to its related alcohol in 20 % yield under the same reaction conditions (entry 8, Table S1). The possibility of the low activity of **1** as catalytic precursor due to steric factors is discarded[14b], and is rather ascribed to the presence of two carbonyls and a chloride ligand to complete the octahedral coordination sphere of the catalyst precursor as well as the absence of ligand cooperativity, unlike the transfer hydrogenation catalyst **G** described by van der Vlugt, Elsevier et al. [13], where the presence of more labile phosphine and reactive hydrido ligands bonded to the Ru(CNC)-moiety combined with the pincer ligand cooperativity yield a more active catalyst.

4. Conclusions

We synthesized and characterized a new Ru(II) CNC-pincer complex, with a bis(1,2,3-triazol-5-ylidene)carbazolide ligand with two carbonyls and a chloride as ancillary ligands. The synthetic procedure to this complex circumvents the use of a silver complex intermediate as transmetallation agent. The rigidity of the central carbazole moiety, together with the presence of

bulky mesityl substituents at the triazolylidene rings, enforce a *mer*-geometry of the CNC pincer ligand. This finding contrasts with the recent example reported by Kunz and co-workers, in which a related CNC di-NHC ligand with a carbazole linker displays a CNC-*fac* conformation.[8] In our case, the steric bulk produced by the mesityl fragments may disfavor the coordinating in the tripodal (*fac*) form. Our complex constitutes the first example of a CNC-pincer complex of ruthenium where the central N-donor coordinates as a monoanionic X-type ligand flanked by 1,2,3-triazol-5-ylidene moieties. Access to the hydrido-analogue of the complex was attained by the *in situ* reaction of the ligand precursor with KHMDS to yield the triply deprotonated ligand, which could then be reacted with an appropriate ruthenium(II) carbonyl hydrido precursor and then with carbon monoxide to afford $[RuH(CO)_2(CNC)]$. Preliminary studies of the dicarbonyl chloride Ru(II) pincer complex **1** as a catalyst for the transfer hydrogenation of ketones did not yield results as satisfactory as expected. We are currently exploring the use of these complexes as catalysts in other model organic transformations, including amination reactions.

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