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Cationic Rh and Ir complexes containing bidentate imidazolylidene–1,2,3-triazole donor ligands: synthesis and preliminary catalytic studies†

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A series of new cationic Rh(I), Rh(III) and Ir(III) complexes containing hybrid bidentate N-heterocyclic carbene–1,2,3-triazolyl donor of general formulae [Rh(CaT)(COD)]BPh_4 (**2a–d**), [Rh(CaT)$(CO)_2$]BPh_4 (**3a–d**) and [M(CaT)(Cp*)Cl]BPh_4 (M = Rh, **4a–d**; M = Ir, **5a–c**), where CaT = bidentate N-heterocyclic carbene–triazolyl ligands, COD = 1,5-cyclooctadiene and Cp* = 1,2,3,4,5-pentamethylcyclopentadienyl, were synthesised. The imidazolium–1,2,3-triazolyl pre-ligands (**1a–c** and **1e–i**) were readily prepared using the Cu(I) catalysed 'click reaction' between phenyl azide or benzyl azides with propargyl functionalised imidazolium salts. The single crystal solid state structures of complexes **2a–d**; **3a–b**; **4a–d** and **5a–b** confirm the bidentate coordination of the NHC–1,2,3-triazolyl ligand with the NHC coordinating *via* the 'normal' C2-carbon and the 1,2,3-triazolyl donor coordinating *via* the N3' atom to form six membered metallocycles. These complexes are the first examples of Rh and Ir complexes containing the hybrid NHC–1,2,3-triazolyl ligands which exhibit a bidentate coordination mode. A number of these complexes showed limited efficiency as catalysts for the intramolecular hydroamination of 4-pentyn-1-amine to 2-methylpyrroline.

Introduction

The success of metal complexes as catalysts for organic transformation has been largely attributed to the variety of different ligands available to coordinate and tune the reactivity of the metal centre. Easy access to ligand architectures that can be readily functionalised is crucial not only in catalysis but also in areas of research relying on the use of metal complexes, including metallopharmaceuticals, bioimaging and metallosupramolecular chemistry.[1,2] The highly versatile and modular Cu(I) catalysed Huisgen 1,3-cycloaddition reaction between an alkyne and an azide (CuAAC "click" reaction) leading to the formation of 1,2,3-triazole is an excellent method for the synthesis of a variety of different ligands containing the 1,2,3-triazole donor. The 1,2,3-triazolyl ring system can coordinate to a metal centre *via* one of the N3, N2 or C5 positions of the triazole ring and to date a diverse number of bi-, tri-, and polydentate ligands incorporating 1,4-disubstituted-1,2,3-triazole moieties have been reported.[1,2]

Metal complexes with N-heterocyclic carbene (NHC) donor ligands have been successfully used in catalysis, where the use of the NHC donor ligand has led to the formation of highly active and stable catalysts.[3] One of the most well-known examples is the Grubbs 2nd generation olefin metathesis catalyst where the replacement of a phosphine donor with an NHC donor led to a remarkable increase in the catalytic activity of the resulting Ru complex.[4] The combination of a strong NHC-**C** donor and a weak 1,2,3-triazolyl-**N** donor is expected to lead to the formation of a hybrid hemilabile donor ligand, which can be highly desirable in catalysis as these ligands are expected to have influence on both the stability as well as selectivity of the resulting metal complexes. There have been only two reports of late transition metal complexes containing mixed NHC–1,2,3-triazolyl bidentate ligands, and each of these reported the synthesis of palladium complexes.[5,6] More recently, Cowie and co-workers reported the synthesis of a number of imidazolium–1,2,3-triazolyl salts but then alkylated the 1,2,3-triazolyl moiety to triazolium. They

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†Electronic supplementary information (ESI) available: Syntheses and characterization of ligands **1b–c** and **1e–g**; Rh(I) complexes **2b–d** and **3b–d**; Rh(III) complexes **4b–d**; Ir(III) complexes (**5b–c**). Table S1: summary of IR ν CO and ^{13}C (CO) NMR chemicals shifts of complexes **3a–d**. Crystallographic data (Tables S2 and S3). CCDC 934035–934047 for X-ray structures of **1c**, **2a–d**, **3a–b**, **4a–d** and **5a–b**. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt51440d

successfully used the imidazolium–1,2,3-triazolyl dicationic salt for the synthesis of mixed metal Pd/Rh complexes where Pd coordinates to the NHC and Rh coordinates to the mesoionic 1,2,3-triazolyl-5-ylidene donor ligands respectively.[7]

The hydroamination of alkynes and alkenes is an atom economical method for the synthesis of C–N bonds and can be catalysed by lanthanides, actinides as well as early and late transition metal complexes.[8–19] Finding catalysts that are stable as well as effective for promoting a range of different hydroamination reactions remains an important challenge. Late transition metal complexes have lower oxophilicity and higher functional group tolerance in comparison to lanthanides, actinides and early transition metal complexes, and hence have great potential for a wider application as hydroamination catalysts.

We have previously reported Rh and Ir complexes containing hybrid NHC–phosphine[20] and NHC–pyrazole[12] bidentate donor ligands and shown that these complexes are efficient as catalysts for the hydroamination reaction.[20] Here we report the modular synthesis of a series of mixed NHC–1,2,3-triazolyl donor ligands and their Rh(I), Ir(III) and Rh(III) complexes (Fig. 1). The bidentate coordination of these mixed carbene–1,2,3-triazolyl-N donor ligands was confirmed using NMR, MS and single crystal X-ray diffraction studies, and preliminary catalytic results on the intramolecular hydroamination of aminoalkynes are presented.

Results and discussion

Synthesis of ligands

A series of imidazolium–1,2,3-triazole salts (**1a–c**; **1e–i**) was prepared by the Cu(I) catalysed alkyne–azide cycloaddition reaction (CuAAC) between either 1-propargyl-3-methylimidazolium bromide or 1-propargyl-3-mesitylimidazolium bromide and the corresponding azide. Standard CuAAC reaction conditions with $CuSO_4{\cdot}5H_2O$ and sodium L-ascorbate (Scheme 1) were used. In most cases, a counter-anion exchange using $NaBPh_4$ was performed to facilitate the isolation of the desired product. A saturated aqueous sodium EDTA solution (preferred) or saturated aqueous ammonium chloride solution was used to remove the copper catalyst. During the course of our studies, Elsevier *et al.*[5] and Chen *et al.*[6] reported the synthesis of a number of analogous imidazolium–1,2,3-triazole ligands with either Br or PF_6^- as the counter anion and their complexes with palladium. Ligand **1d** with an aniline functional group (n = 1; R^2 = NH_2, Scheme 1) was synthesised by the reduction of the corresponding nitro compound **1c** with hydrazine hydrate in the presence of palladium on activated carbon.[21,22]

All of the imidazolium–1,2,3-triazole salts **1a–g** were fully characterised using NMR spectroscopy and elemental analysis. In the ^{1}H NMR spectra, the imidazolium-*H*2 proton resonances appear at approximately 9.5 ppm (in dmso-d_6) for compounds which have a mesityl substituent on the imidazolium ring (**1a–d**, **1f** and **1h–i**) and for the compounds with a methyl substituent on the imidazolium ring (**1e** and **1g**) these

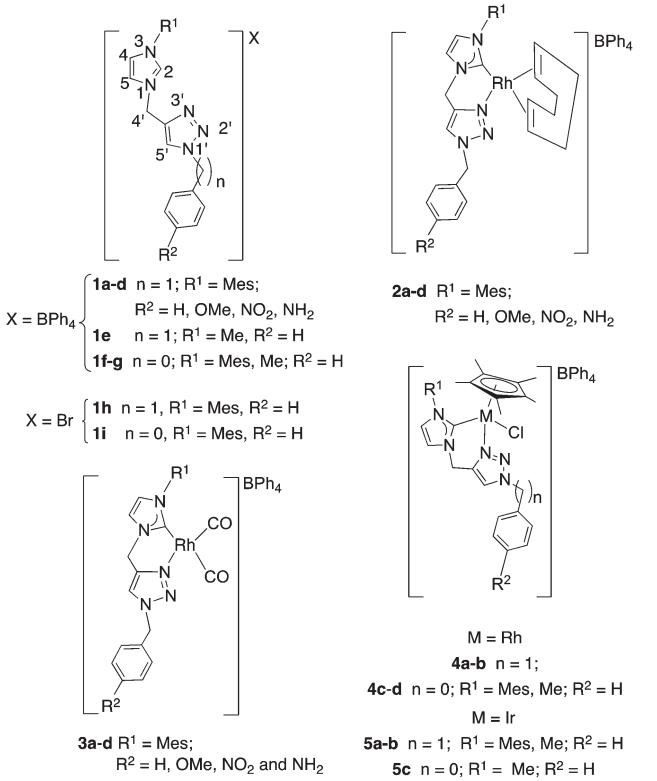
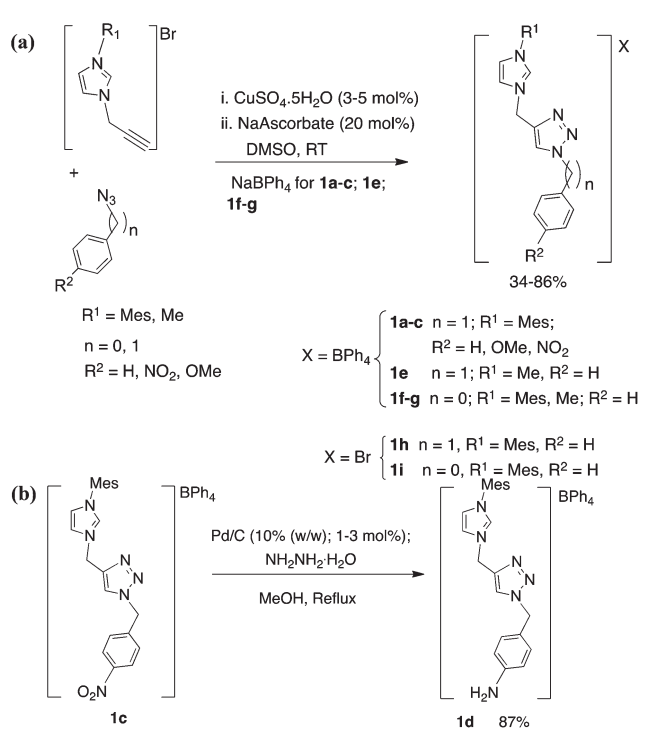


Fig. 1 Imidazolium–1,2,3-triazole pre-ligands and their Rh(I), Rh(III) and Ir(III) complexes.



Scheme 1 Synthesis of imidazolium–1,2,3-triazole as precursors to bidentate NHC–1,2,3-triazole ligands (a) **1a–c**, **1e–i** and (b) **1d**.

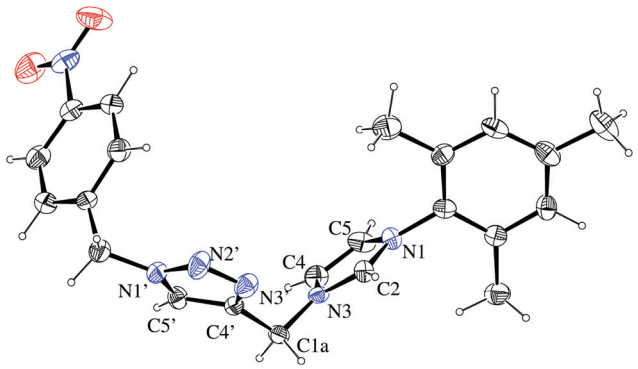


Fig. 2 ORTEP depiction of cationic fragment of the solid state single X-ray structure of [MesCaTBnNO$_2$]BPh$_4$ (**1c**) at 40% thermal ellipsoid for the non-hydrogen atoms.

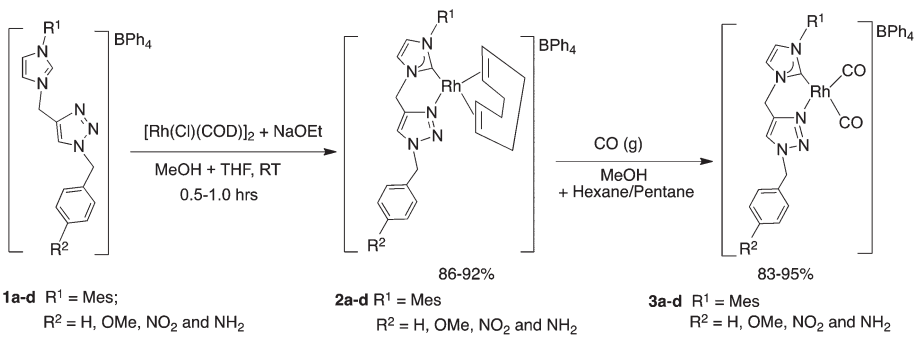
resonances appear at approximately 9.2 ppm (in dmso-d_6). The down-field shift of the imidazolium-*H*2 resonance in the mesityl substituted compounds **1a–d** and **1f–i** when compared with the methyl substituted compounds **1e** and **1g** was attributed to the ring current effect imposed by the aromatic mesityl ring. The solid state structure of **1c** was determined (Fig. 2) using X-ray crystallography, and this structure showed that in the solid state the mesityl ring and the imidazolium ring are orthogonal to each other. Crystal structure data for **1c** is provided in the ESI (ESI, Table S2†).

Synthesis of Rh(I) complexes. A series of Rh(I) complexes of the general formula [Rh(CaT)(COD)]BPh$_4$ (**2a–d**; CaT = carbene–1,2,3-triazole bidentate ligands; COD = 1,5-cyclooctadiene) were prepared in excellent yields (86–92%) by the reaction of the imidazolium–1,2,3-triazole pre-ligands **1a–d** with suspension of [Rh(OR)(COD)]$_2$ (R = Me, Et) in a mixture of tetrahydrofuran and methanol. [Rh(OR)(COD)]$_2$ (R = Me, Et) was generated *in situ* by the reaction of [Rh(Cl)(COD)]$_2$ with an excess of NaOEt in methanol. The synthetic approach used here has been reported previously for the synthesis of a range of analogous Rh(I) and/or Ir(I) complexes containing bidentate NHC–pyrazolyl,[23,24] NHC–phosphine[20,25] and NHC–NHC[26] donor ligands. Complexes **2a–c** were found to be air stable in the solid state. Complex **2d** which contains an aniline substituent on the 1,2,3-triazolyl ring was less stable and decomposed in a dcm-d_2 solution over several days at room temperature.

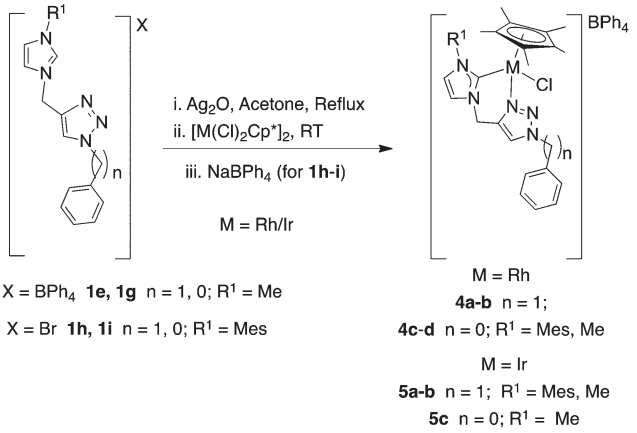
All of the complexes [Rh(CaT)(COD)]BPh$_4$ (**2a–d**) were fully characterised using a combination of NMR spectroscopy, electrospray mass spectrometry and elemental analysis. The ^{1}H NMR spectra showed the disappearance of the imidazolium-***H***2 resonances as would be expected. Resonances of the imidazole-**C**2 appeared at *ca.* 176 ppm with coupling to ^{103}Rh, ^1J(Rh-C) = 51–53 Hz, in the ^{13}C{^{1}H} NMR spectra[27] (dcm-d_2) confirming that the coordination of the NHC donor to the Rh centre is *via* the 'normal' C2 carbon. The observed chemical shifts and coupling constants for the carbene resonance are similar to those that have been reported previously for square planar Rh(I) complexes with NHC ligands.[20,23,24,26,28–31] For each complex, the positive electrospray mass spectrum obtained contained the parent ions corresponding to the entire cationic metal complex with one NHC–1,2,3-triazolyl ligand and one COD co-ligand. This suggests that the NHC–triazolyl ligands coordinate to the Rh(I) centre in a bidentate fashion and together with the COD co-ligands form the expected square planar Rh(I) complexes. The suggested coordination mode was confirmed by single crystal diffraction analysis (see below).

Attempts to synthesise the iridium complex [Ir(MesCaTBn)(COD)]BPh$_4$ using a method analogous to that used for the synthesis of the rhodium complex [Rh(MesCaTBn)(COD)]BPh$_4$ (**2a**), where [Ir(Cl)(COD)]$_2$ was used in place of [Rh(Cl)(COD)]$_2$, resulted in the formation of a complex mixture of products.

Cationic Rh(I) complexes with the NHC–1,2,3-triazole bidentate ligand and dicarbonyl co-ligands, [Rh(CaT)(CO)$_2$]BPh$_4$ **3a–d**, were synthesised in excellent yields by the displacement of COD from the corresponding [Rh(CaT)(COD)]BPh$_4$ precursors **2a–d** with carbon monoxide (Scheme 2). Complexes **3a–b** are orange solids and complexes **3c–d** are greenish yellow solids. In dichloromethane solution, complexes **3a–b** and **3d** are pale yellow and complex **3c** gave the solution a greenish yellow colour. Complexes **3a–c** are stable in the solid state and in solution while complex **3d** with an aniline substituent decomposed in a dichloromethane solution overnight. All of the complexes were fully characterised using a combination of NMR, IR, MS and elemental analysis. The IR absorptions due to the CO stretches and the ^{13}C NMR chemical shifts of complexes **3a–d** are all extremely similar or identical indicating



Scheme 2 Synthesis of Rh(I) complexes containing bidentate NHC–1,2,3-triazole donor ligands.



Scheme 3 Synthesis of Rh(III) and Ir(III) complexes containing bidentate NHC–1,2,3-triazole donor ligands.

that the substituents on the *para* position in ligands **1a–d** have minimal effect on the electronic properties of the Rh(I) centre (see Table S1, ESI†).

Synthesis of Rh(III) and Ir(III) complexes. A number of Rh(III) and Ir(III) complexes (**4a–d**; **5a–c**) were synthesised by the transmetallation of the metal precursor $[M(Cl)_2Cp^*]_2$ (M = Rh or Ir) with the *in situ* generated Ag(I)–NHC complexes, which were formed by the reaction between the imidazolium–1,2,3-triazole pre-ligands, **1e** and **1g–i** and silver oxide in acetone (Scheme 3). The Rh(III) and Ir(III) complexes (**4a–d**; **5a**, **c**) were isolated as bright orange and yellow solids respectively. In the case of the iridium complex **5b**, a limited number of X-ray quality crystals were isolated and used to undertake X-ray diffraction analysis and full characterization using NMR and elemental analysis was not performed. All of these complexes, (**4a–d**; **5a**, **c**) are highly stable in air both as solids and in solution (dichloromethane, 1,1′,2,2′-tetrachloroethane). Attempts to prepare these Rh(III) and Ir(III) complexes by the reaction between the pre-ligand and $[M(Cl)_2Cp^*]_2$ (M = Rh/Ir) in the presence of NaOEt led to the formation of an intractable mixture of products.

The Rh(III) and Ir(III) complexes (**4a–d**; **5a** and **5c**) were fully characterized using NMR spectroscopy, mass spectrometry and elemental analyses. Upon coordination to the metal centre, the rotation of the mesityl ring substituent on the imidazolydene ring in complexes **4a**, **4c**, **5a** and **5c** becomes restricted due to steric hindrance between the *ortho*-CH_3 groups on the mesityl ring and the Cp* co-ligand. This restricted rotation led to the observation in the ^{1}H NMR spectrum of two distinct resonances attributed to the two inequivalent *ortho*-CH_3 groups, as well as two distinct resonances that were attributed to the two *meta*-CH protons of the mesityl moiety. In the ^{1}H–^{1}H NOESY spectra of complexes **4a**, **4c**, **5a** and **5c**, exchange cross-peaks were observed between each pair of *ortho*-CH_3 and *meta*-CH resonances indicating that rotation of the mesityl group around the N–C bond between the mesityl and imidazolyl ring is taking place on the NMR time scale. The two resonances attributed to the protons of the methylene group, CH_2, linking the NHC and the 1,2,3-triazole moieties appear as two AB doublets with ^2J = ~16 Hz with significantly different chemical shifts. The difference in chemical shifts of these two resonances is likely due to the fact that one of these two protons is orientated towards the Cp* ring and hence subjected to the strong ring current effect of the aromatic Cp* ring while the other proton is pointed away from the Cp* ring.

Solid state structures of Rh(I), Rh(III) and Ir(III) Complexes

Rh(I) complexes. Single crystals of Rh(I) complexes, [Rh(CaT)(COD)]BPh_4 (**2a–d**) and [Rh(CaT)$(CO)_2$]BPh_4 (**3a–b**) were obtained by layering a concentrated dichloromethane solution of each of the complexes with pentane. The ORTEP depictions of complexes [Rh(MesCaTBn)(COD)]BPh_4 (**2a**) and [Rh(MesCaTBn)$(CO)_2$]BPh_4 (**3a**) are shown in Fig. 3. A summary of relevant bond lengths and bond angles of the inner coordination spheres of these complexes are given in Table 1. The ORTEP depictions of the structures of complexes **2b–d** and **3b** are given in the ESI (Fig. S1–S4†). Crystal data for each of these complexes are given in Table S2 (ESI†).

The solid state structures of the Rh(I) complexes [Rh(CaT)(COD)]BPh_4 (**2a–d**) and [Rh(CaT)$(CO)_2$]BPh_4 (**3a–b**) all show the expected square planar coordination around the Rh(I) centre. The 1,2,3-triazolyl donor is coordinated to the Rh centre *via* the N3′ donor, and together with the C2 of the NHC donor form six membered metallocycles. These metallocycles adopt a distorted boat conformation. The N3′–Rh1–C2 bite angles in complexes **2a–2b** and **3a**, vary between 85.1–86.4° (Table 1), which deviate slightly from the ideal angle of 90°. The sum of the angles around the Rh centre in all of these complexes is

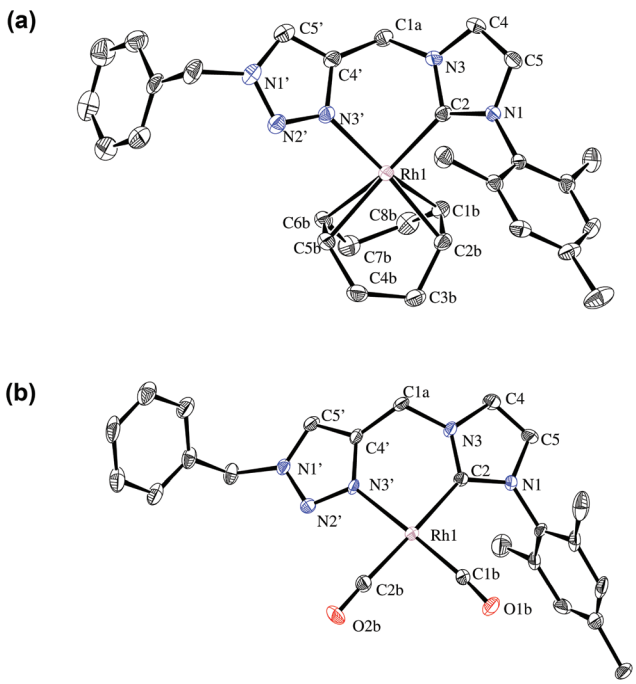


Fig. 3 ORTEP depictions of the cationic fragments of the single crystal solid state structures of (a) [Rh(MesCaTBn)(COD)]BPh_4 (**2a**) and (b) [Rh(MesCaTBn)$(CO)_2$]BPh_4 (**3a**) at 40% thermal ellipsoids for the non-hydrogen atoms.

Table 1 Selected bond lengths and bond angles[a] of the inner coordination spheres of [Rh(MesCaTBn)(COD)]BPh_4 (**2a**), [Rh(MesCaTBnOMe)(COD)]BPh_4 (**2b**), [Rh(MesCaTBnNO_2)(COD)]BPh_4 (**2c**), [Rh(MesCaTBnNH_2)(COD)]BPh_4 (**2d**), [Rh(MesCaTBn)$(CO)_2$]BPh_4 (**3a**) and [Rh(MesCaTBnOMe)$(CO)_2$]BPh_4 (**3b**)

Atoms[b]	2a	2b	2c	2d	3a	3b
Bond lengths (Å)						
Rh1–N3′	2.085(2)	2.090(2)	2.088(5)	2.087(3)	2.060(5)	2.100(3)
Rh1–C2	2.047(2)	2.052(2)	2.053(4)	2.045(3)	2.052(6)	2.010(3)
Rh1–C1b*/C1b	2.029	2.036	2.036	2.027	1.840(6)	1.887(3)
Rh1–C5b*/C2b	2.079	2.079	2.079	2.090	1.889(7)	1.860(3)
Bond angles (°)						
N3′–Rh1–C2	85.57(9)	85.12(8)	85.1(2)	85.9(1)	86.4(2)	88.7(1)
C2–Rh1–C1b*	95.75	97.36	96.25	95.74	94.9(3)	92.5(1)
C1b*/C1b–Rh1–C5b*/C2b	86.92	86.99	86.78	86.82	88.4(3)	91.5(1)
C5b*/C2b–Rh1–N3′	91.59	91.05	91.59	91.40	90.2(3)	87.2(1)

[a] Standard deviations in the least significant figures are given in parentheses. [b] C1b* and C5b* are the centroids of (C1b, C2b) and (C5b, C6b) in complexes **2a–d**.

360 ± 2° confirming the expected square planar coordination in these Rh(I) complexes. In complexes **2a**, **2b** and **3a**, the Rh1–C5b*/C2b (*trans* to NHC) bond lengths are slightly longer than the Rh1–C1b*/C1b (*trans* to 1,2,3-triazole) as a consequence of the stronger *trans* influence of NHC donor than the triazolyl-N3′ donor (Table 1). Varying the substituent on the *para* position of the benzyl group from H to OCH_3, NO_2 and NH_2 did not lead to any significant differences in the bond lengths and angles of the solid structures of complexes [Rh(CaT)(COD)]BPh_4 (**2a–d**).

The solid state structure of complex **3b** shows the presence of two molecules in each unit cell and these two molecules have very strong interactions with each other with the Rh–Rh distance measured at only 3.277 Å (Fig. S4, ESI†). This strong Rh–Rh interaction might have led to: (i) the N3′–Rh1–C2 bite angle of 88.7° being significantly larger than the bite angles observed for the analogous complexes **2a–2b** and **3a** and (ii) the Rh1–C1b (CO *trans* to triazole) bond being longer than Rh1–C2b (CO *trans* to NHC) and this is opposite to the trend observed for the equivalent bonds observed in the structures of complexes **2a–d** (Table 1). The Rh–C, Rh–N bonds and N–Rh–C bite angles in complexes **2a–d** and **3a–b** are comparable to the values observed in analogous Rh(I) complexes with bidentate NHC–pyrazole, pyrazole–1,2,3-triazole or NHC–NHC donors.[23,24,32–34]

Rh(III) and Ir(III) complexes. Crystals of Rh(III), **4a–d** and Ir(III), **5a–b** complexes suitable for single crystal X-ray diffraction analysis were grown by the slow diffusion of *n*-pentane into a concentrated dichloromethane or 1,1′,2,2′-tetrachloroethane solution of each of the complexes. The ORTEP depictions of the cationic fragments of [Rh(MesCaTBn)Cp*Cl]BPh_4 (**4a**) and [Ir(MesCaTBn)Cp*Cl]BPh_4 (**5a**) are shown in Fig. 4. The ORTEP depictions of complexes **4b–d** and **5b** are provided in the ESI (Fig. S5–S8†). Selected bond lengths and bond angles are given in Table 2. Crystal data for complexes **4a–d** and **5a–b** are provided in Table S3, ESI.†

In the solid state, complexes **4a–d** and **5a–b** display a piano stool octahedral coordination environment around the metal centre. The coordination of the 1,2,3-triazolyl donor is *via* the N3′ nitrogen atom. The 6-membered metallocycles

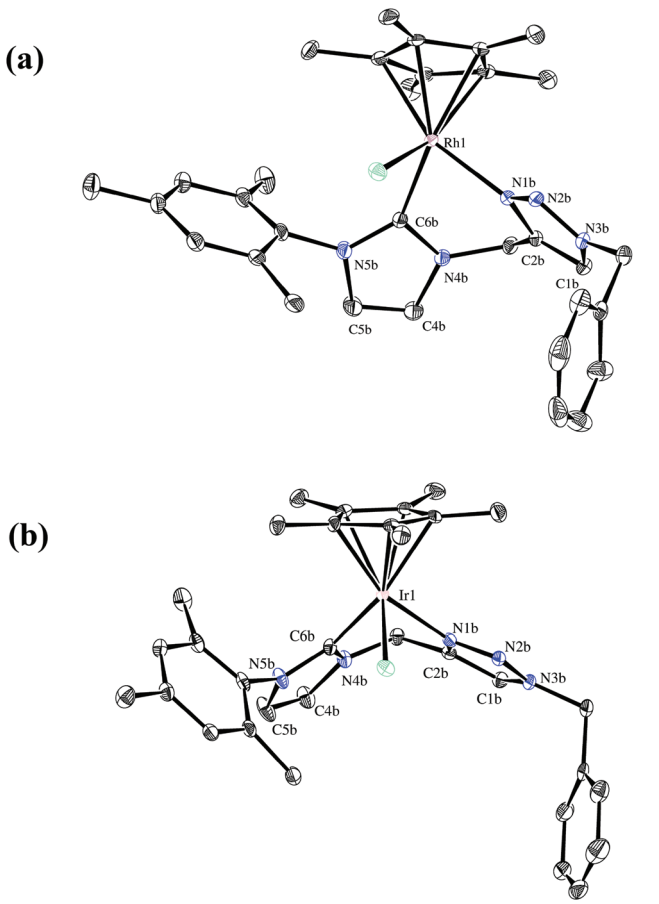


Fig. 4 ORTEP depictions of the cationic fragments of the single crystal solid state structures of (a) [Rh(MesCaTBn)Cp*Cl]BPh_4 (**4a**) and (b) [Ir(MesCaTBn)-Cp*Cl]BPh_4 (**5a**) at 40% thermal ellipsoids for the non-hydrogen atoms.

formed upon the coordination of the bidentate NHC–triazolyl ligands to the metal centre display a distorted boat conformation. The N3′–M–C2 (M = Rh1/Ir1) bite angles are within the range of 83.29(9)–84.67(7)° (Table 2). These angles are slightly smaller than the ideal values in octahedral complexes indicating some level of strain associated with the chelation of the NHC–1,2,3-triazolyl ligands to the metal centre. The M–C*

Table 2 Selected bond lengths and bond angles[a] in the inner coordination sphere of [Rh(MesCaTBn)Cp*Cl]BPh_4 (**4a**), [Rh(MeCaTBn)Cp*Cl]BPh_4 (**4b**), [Rh(MesCaTPh)Cp*Cl]BPh_4 (**4c**), [Rh(MeCaTPh)Cp*Cl]BPh_4 (**4d**), [Ir(MesCaTBn)Cp*Cl]BPh_4 (**5a**) and [Ir(MesCaTBn)Cp*Cl]BPh_4 (**5b**)

Atoms[b]	4a	4b	4c	4d	5a	5b
Bond lengths (Å)						
Rh1–N3′(Tz)	2.1090(19)	2.0802(16)	2.138(4)	2.0666(16)	2.098(2)	2.090(2)
Rh1–C(carbene)	2.076(3)	2.0306(19)	2.067(6)	2.022(2)	2.059(2)	2.026(3)
Rh1–C*	1.812	1.812	1.811	1.815	1.817	1.805
Rh1–Cl1	2.3774(6)	2.4089(5)	2.409(1)	2.4089(5)	2.3853(5)	2.4409(7)
Bond angles (°)						
N3(Tz)–Rh1–C(carbene)	83.97(9)	84.64(7)	84.0(2)	84.27(7)	83.29(9)	84.1(1)
Cl1–Rh1–C(carbene)	90.79(7)	89.37(6)	91.8(2)	91.51(6)	90.03(7)	89.74(8)
N3(Tz)–Rh1–Cl1	88.82(6)	89.56(5)	89.9(1)	88.86(5)	86.97(6)	86.39(6)

[a] Standard deviations in the least significant figures are given in parentheses. [b] C* is the centroid of the Cp* ring.

(M = Rh or Ir with C* = the centroid of the Cp* ring) bond lengths are similar in Rh, **4a–d**, and Ir, **5a–b** complexes. The M–C2 and M–N bond lengths (Table 2) are within the range reported in the literature for analogous Rh(III) and Ir(III) complexes with Cp* co-ligands.[12,32,35–39] The M–C2 bond in complexes **4b**, **4d** and **5b** with the small methyl substituent on the imidazolyl ring is significantly shorter than the equivalent bond in the analogous complexes with the mesityl substituent **4a**, **4c** and **5a** (Table 2). The longer M–C2 bond in complexes with a mesityl substituent is likely to be due to steric repulsion between the Cp* and the bulky mesityl group.

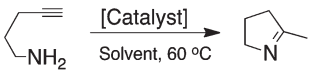
Catalysis

The intramolecular hydroamination of aminoalkynes and aminoalkenes is an efficient method for the synthesis of N-containing heterocycles. A number of late transition metal complexes are efficient catalysts for the intramolecular hydroamination of alkynes. Rh(I)/Rh(III) and Ir(I)/Ir(III) complexes have been demonstrated by us and others to be efficient catalysts for this transformation.[12,20,32,40–48]

We have found that small variations in donor ability of the ligands can lead to significant variations in the catalytic efficiency of the resulting metal complexes.[32,41,49] We tested a number of the Rh(I), Rh(III) and Ir(III) complexes containing the NHC–1,2,3-triazolyl donor ligands described here as catalysts for the intramolecular hydroamination of 4-pentyn-1-amine to form 2-methyl-1-pyrroline (Table 3).

As can be seen in Table 3, the Rh(III) complex [Rh(MesCaTBn)Cp*Cl]BPh_4 (**4a**) was the most efficient catalyst for the cyclisation of 4-pentyn-1-amine to 2-methyl-1-pyrroline with 91% conversion achieved in 18 hours and complete conversion reached after 42 hours. The catalytic activity of **4a** is significantly higher than that of the analogous Rh(III) complex [Rh(MeCaTPh)Cp*Cl]BPh_4 (**4d**) which only gave 21% conversion under analogous reaction conditions, most likely due to the effect of the mesityl substituent on the NHC donor which

Table 3 Intramolecular cyclisation of 4-pentyn-1-amine to 2-methyl-1-pyrroline using Rh(I), Rh(III) and Ir(III) complexes containing NHC–1,2,3-triazolyl bidentate donor ligands as catalysts[a]



Entry	Complex	Solvent	% Conversion[b] (time/h)	Reference
1	[Rh(MesCaTBn)(COD)]BPh_4, **2a**	$CDCl_3$	32 (45)	This work
2	[Rh(MesCaTBn)$(CO)_2$]BPh_4, **3a**	$CDCl_3$	23 (45)	
3	[Rh(MesCaTBn)(COD)]BPh_4, **2a**	THF-d_8	37 (45)	
4	[Rh(MesCaTBn)$(CO)_2$]BPh_4, **3a**	THF-d_8	45 (45)	
5	[Rh(MesCaTBn)Cp*Cl]BPh_4, **4a**	THF-d_8	91 (18)	
6	[Rh(MeCaTPh)Cp*Cl]BPh_4, **4d**	THF-d_8	21 (17)	
7	[Ir(MesCaTPh)Cp*Cl]BPh_4, **5c**	THF-d_8	15 (18)	
8	[Rh(bpm)$(CO)_2$]BPh_4[c]	THF-d_8	90 (12)	49
9	[Rh(PyT)$(CO)_2$]BPh_4[c]	THF-d_8	88 (22)	32
10	[Ir(PyT)$(CO)_2$]BPh_4[c]	THF-d_8	98 (2.5)	32
10	[Rh(bim)$(CO)_2$]BPh_4[c]	THF-d_8	>97 (14)	49
11	[Rh(PC)$(CO)_2$]BPh_4[c]	THF-d_8	>97 (14)	20
12	[Rh(mdd)$(CO)_2$]BPh_4[c]	THF-d_8	76 (16)	26

[a] Catalytic hydroamination reactions were conducted in Youngs' NMR tubes with [4-pentyn-1-amine] = 0.56–0.64 M at 60 °C with 1.6–2.0 mol% of catalyst. [b] The reaction progress was monitored by ^{1}H NMR spectroscopy. [c] bpm = bis(1-pyrazolyl)methane; PyT = 4-((1*H*-pyrazoly-1-yl)methyl-1*H*-1,2,3-triazole; bim = bis(1-methylimidazol-2-yl)methane; PC = 3-[2-diphenylphosphino)ethyl]-1-methylimidazol-2-ylidene and mdd = 1,1′ = methylene-3,3′-dimethylimidazol-2,2′-diylidene.

led to more stable complexes. THF-d_8 is a better solvent for this cyclisation than $CDCl_3$ when Rh(I) complexes (**2a**, **3a**) were used as the catalysts.

In comparison with results using similar Rh(I) and Ir(I) complexes having N–N, NHC–phosphine or NHC–NHC bidentate ligands[20,26,32,49] for the cyclisation of 4-pentyn-1-amine to 2-methyl-1-pyrroline (entries 8–12, Table 3) the catalytic efficiency of the complexes reported here (entries 1–7) were much lower. The catalytic results obtained in this work appear to confirm the general trend that complexes with ligands with more basic donors that bind more strongly to the metal centre are less active catalysts for the hydroamination reaction.[40] Rh(III) and Ir(III) complexes (**4a**, **4d** and **5c**, entries 5–7, Table 3) were not very efficient as catalysts for this hydroamination reaction possibly due to the fact that these complexes are coordinately saturated. We recently demonstrated that similar Ir(III) complexes with bidentate N–N or N(pyrazolyl)–NHC donor ligands in the presence of $AgBF_4$ could efficiently promote the intramolecular hydroamination of aminoalkynes.[12] This improvement in catalytic reactivity in the presence of Ag^+ was attributed to the generation of a vacant coordination site on the Ir(III) *via* Cl^- abstraction with Ag^+ ion.[12] In that paper, the catalytic reactivity was found to be better using an N(pyrazolyl)–NHC donor ligand than when N–N donor ligands were used.[12] Analogous catalytic work using Ir(III) and Rh(III) complexes prepared in this work in combination with Ag^+ ion as catalysts for hydroamination is being investigated in our laboratory.

Conclusions

A series of imidazolium–1,2,3-triazole salts were successfully synthesised in a modular fashion using the copper catalyzed 'click' (CuAAC) reactions. These salts were successfully coordinated to Rh(I), Rh(III) and Ir(III) centres to form complexes of the general formulae [Rh(CaT)(COD)]BPh_4 (**2a–d**), [Rh(CaT)$(CO)_2$]BPh_4 (**3a–d**), [Rh(CaT)Cp*Cl]BPh_4 (**4a–d**) and [Ir(CaT)Cp*Cl]BPh_4 (**5a–c**). The ligand coordinates to the metal centre in a bidentate manner in each complex as confirmed by NMR spectroscopy, mass spectrometry and single crystal X-ray diffraction analysis.

In all of the 12 solid state X-ray structures of Rh and Ir metal complexes reported here, the 6-membered metallocycles formed upon the coordination of the NHC–1,2,3-triazolyl ligand to the metal centre adopt distorted boat conformations. The coordination modes around the metal centre are square planar for Rh(I) complexes, **2a–d** and **3a–b**, and octahedral for Rh(III) and Ir(III) complexes, **4a–d** and **5a–b**, respectively. The NHC donor has a stronger *trans*-influence in comparison with the 1,2,3-triazolyl *N*′3 donor. This is the first time Rh and Ir complexes with bidentate NHC–1,2,3-triazolyl donors have been reported. The work here will enhance our understanding of the coordination chemistry of the 1,2,3-triazolyl ring which has seen significant recent interest.

These complexes showed only limited activity as catalysts for the intramolecular hydroamination of alkyne using 4-pentyn-1-amine as the substrate. The activity of these complexes as hydroamination catalysts is significantly lower than the activity of analogous complexes having bidentate sp^2 N–N donor ligands where the sp^2 N-donors are pyrazole and/or imidazole. This variation in catalysis reactivity might be attributed to the stronger donating ability of the NHC donor in comparison with sp^2-N donors.

Experimental

All manipulations of metal complexes and air sensitive reagents were performed using either standard Schlenk techniques or in a nitrogen or argon filled Braun glove-box. Reagents were purchased from Aldrich Chemical Company Inc. or Alfa Aesar Inc. and were used without further purification unless otherwise stated. Iridium(III) chloride hydrate and rhodium(III) chloride hydrate were obtained from Precious Metals Online, PMO P/L. $[IrCl_2Cp^*]_2$,[50] $[RhCl_2Cp^*]_2$,[50] phenylazide,[51] benzyl azide,[52] 4-methoxybenzyl azide,[52,53] 4-nitrobenzyl azide,[52,54] and mesitylimidazole[55] were prepared using literature methods. 1-Methyl-3-propargylimidazolium bromide[56] 1-mesityl-3-propargylimidazolium bromide[57] were prepared using modifications of literature methods where acetonitrile was used as the reaction solvent instead of ethyl acetate and toluene as reported respectively.

For the purposes of air sensitive manipulations and in the preparation of air sensitive complexes, pentane, hexane, dichloromethane and tetrahydrofuran were dispensed from a PuraSolv solvent purification system. Acetone and methanol were distilled under nitrogen or argon from calcium sulfate and magnesium methoxide respectively. The bulk compressed gases argon (>99.999%) and carbon monoxide (>99.5%) were obtained from Air Liquide and used as received. Nitrogen gas for Schlenk line operation comes from in-house liquid nitrogen boil-off.

^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on Bruker DPX300, DMX400, DMX500 and DMX600 spectrometers operating at 300, 400, 500 and 600 MHz (^1H) respectively and 75, 100, 125 and 150 MHz (^{13}C) respectively. Unless otherwise stated, spectra were recorded at 25 °C and chemical shifts (δ) are quoted in ppm. Coupling constants (J) are quoted in Hz and have uncertainties of ±0.05 Hz for ^1H and ±0.5 Hz for ^{13}C. ^1H and ^{13}C NMR chemical shifts were referenced internally to residual solvent resonances. Deuterated solvents were purchased from Cambridge Stable Isotopes and used as received. Air sensitive NMR samples were prepared in an inert gas glovebox or by vacuum transfer of deuterated solvents into NMR tubes fitted with a Young's Teflon valve. For air sensitive NMR samples, dcm-d_2 and $CDCl_3$ were distilled over calcium hydride. Acetone-d_6 was distilled from calcium sulfate.

Infrared spectra were measured as solutions in dichloromethane using a Nicolet 380 Avatar FTIR spectrometer. Melting points were measured using a Stanford Research

Systems Optimelt melting point apparatus in glass capillaries and are uncorrected. Microanalyses were carried out at the Campbell Micro-analytical Laboratory, University of Otago, New Zealand or at the Research School of Chemistry, the Australian National University, Canberra, Australia. Mass spectra were acquired using a Thermo LTQ Orbitrap XL located in the Bio-analytical Mass Spectrometry Facility (BMSF) of the Mark Wainwright Analytical Centre, UNSW or on a Micromass ZQ (ESI-MS) mass spectrometer located in the School of Chemistry, UNSW. M is defined as the molecular weight of the compound of interest or cationic fragment for cationic metal complexes.

Synthesis of ligands

The syntheses of ligands **1a** and **1d** are presented here. The syntheses of **1b–c** and **1e–g** were performed following a similar method to that used for the synthesis of **1a** and the full description of these syntheses is provided in the supporting information (ESI†).

Synthesis of [MesCaTBn]BPh$_4$ (1a). Sodium L-ascorbate (0.30 g, 1.5 mmol), $CuSO_4{\cdot}5H_2O$ (0.08 g, 0.32 mmol) benzyl azide (0.66 g, 5.0 mmol) and 1-mesityl-3-propargylimidazolium bromide (1.53 g, 5.00 mmol) were added to a deoxygenated solution of dimethyl sulfoxide (30 mL) in a Schlenk flask under an atmosphere of nitrogen and the reaction mixture was then stirred overnight at RT. The mixture was poured into a conical flask containing water (200 mL) with vigorous stirring. Sodium tetraphenylborate (2.0 g, 5.8 mmol) was added to the reaction mixture with vigorous stirring, and a white solid precipitate formed. The solid was collected by filtration, washed with saturated aqueous ammonium chloride solution (3 × 20 mL), water (2 × 30 mL), methanol (2 × 15 mL) and air dried. The solid product was recrystallised from dichloromethane–hexane and was collected as a white solid and dried *in vacuo*. Yield: 2.60 g, 77%. Elemental analysis: found: C, 81.56; H, 6.63 and N, 10.56; calculated for $C_{46}H_{44}BN_5$: C, 81.53; H, 6.54 and N, 10.33%. ESI-MS (ESI$^+$, CH_3CN) *m*/*z* (assignment, %): 358.20 (M, 100); Calculated for $[C_{22}H_{24}N_5]^+$: 358.20 amu. ^{1}H NMR (500 MHz, dmso-d_6): δ 9.51 (apparent t, ^3J = 1.6 Hz, 1H, **H**2), 8.32 (s, 1H, Tz-**H**5), 8.04 (t, ^3J = 1.6 Hz, 1H, Im-**H**4), 7.91 (t, ^3J = 1.6 Hz, 1H, **H**5), 7.40–7.33 (m, 3H, *m* and *p*-C**H**s of CH_2Ph), 7.32–7.31 (m, 2H, *o*-C**H** of CH_2Ph), 7.18 (br m, 8H, *o*-C**H** of BPh_4), 7.14 (s, 2H, *m*-C**H** of Mes), 6.92 (t, ^3J = 7.4 Hz, 8H, *m*-C**H** of BPh_4), 6.79 (t, J = 7.4 Hz, 4H, *p*-C**H** of BPh_4), 5.61 (s, 2H, C**H**$_2$Ph), 5.62 (s, 2H, Im-NC**H**$_2$), 2.32 (s, 3H, *p*-C**H**$_3$ of Mes), 1.98 (s, 6H, *o*-C**H**$_3$ of Mes) ppm. ^{13}C{^{1}H} NMR (125 MHz, dmso-d_6): δ 166.33 (q, ^1J = 49.6 Hz, *ipso*-C of BPh_4), 140.70 (Tz-**C**5′), 140.32 (*p*-C**H** of Mes), 137.78 (**C**2), 135.75 (*p*-**C**H), 135.55 (*o*-C**H** of BPh_4), 134.27 (*o*-**C**H of Mes), 131.15 (N-**C** of Mes), 129.26 (*m*-**C**H of Mes), 128.83 (*m*-**C**H of CH_2Ph), 128.29 (*p*-**C**H of Ph), 128.02 (*o*-**C**H of CH_2Ph), 125.33 (q, $^3J_{B-C}$ = 2.3 Hz, *m*-**C**H of BPh_4), 124.56 (Tz-**C**4′), 124.14 (Im-**C**5), 123.34 (Im-**C**4), 121.54 (*p*-**C**H of BPh_4), 53.03 (**C**H$_2$Ph), 44.33 (Im-NCH$_2$), 20.60 (*p*-CCH$_3$), 16.86 (*o*-CCH$_3$) ppm.

Synthesis of [MesCaTBnNH$_2$]BPh$_4$ (1d). Methanol (20 mL) and tetrahydrofuran, THF, (10 mL) were added to a Schlenk flask containing [MesCaTBnNO$_2$]BPh$_4$, **1c**, (0.729 g, 1.00 mmol) under an atmosphere of nitrogen. Hydrazine monohydrate (2.0 mL excess) and Pd on carbon (10% (w/w), 10 mg) were added to the reaction mixture and the reaction was heated at reflux under nitrogen overnight. The reaction was cooled to room temperature, extra THF (20 mL) was added and the reaction mixture was filtered through a pad of Celite and rinsed with THF (3 × 15 mL). The solvent was removed *in vacuo* to afford an off white solid which was collected by filtration and washed with diethyl ether (3 × 15–20 mL) and dried in a vacuum desiccator overnight. Yield: 0.602 g, 87%. Elemental analysis, found: C, 78.17; H, 6.61 and N, 12.37; calculated for $C_{46}H_{45}BN_6{\cdot}0.5H_2O$: C, 78.14; H, 6.61 and N, 11.98%. ESI-MS (ESI$^+$, MeOH) *m*/*z* (assignment, %): 372.95 ([M]$^+$, 100); calculated for $C_{22}H_{25}N_6^+$: 372.21 amu. ^{1}H NMR (500 MHz, dmso-d_6): δ 9.51 (br s, 1H, Im-**H**2), 8.18 (s, 1H, Tz-**H**5), 8.02 (apparent t, ^3J = 1.5 Hz, 1H, Im-**H**5), 7.91 (apparent t, ^3J = 1.5 Hz, 1H, Im-**H**4), 7.18 (br m, 8H, *o*-C**H** of BPh_4), 7.13 (s, 2H, *m*-C**H** of Mes), 7.04 (d, ^3J = 8.5 Hz, 2H, *o*-C**H** of $PhNH_2$), 6.92 (t, ^3J = 7.5 Hz, 8H, *m*-C**H** of BPh_4), 6.79 (t, ^3J = 7.5 Hz, 4H, *p*-C**H** of BPh_4), 6.53 (d, ^3J = 8.5 Hz, 2H, *m*-C**H** of $PhNH_2$), 5.59 (s, 2H, Im-NC**H**$_2$), 5.39 (s, 2H, Tz-NC**H**$_2$), 5.19 (s, 2H N**H**$_2$), 2.33 (s, 3H, *p*-CC**H**$_3$), 1.98 (s, 6H, *o*-CC**H**$_3$) ppm. ^{13}C{^{1}H} NMR (125 MHz, dmso-d_6): δ 163.36 (q, $^1J_{B-C}$ = 49.7 Hz, *ipso*-**C** of BPh_4), 148.93 (**C**NH$_2$), 140.49 (Tz-C4′) 140.29 (*p*-C of Mes), 137.74 (**C**2), 135.53 (*o*-**C**H of BPh_4), 134.25 (*o*-**C** of Mes), 131.14 (N-**C** of Mes), 129.42 (*o*-**C**H of $PhNH_2$), 129.23 (*m*-**C**H of Mes), 125.29 (*m*-**C**H of BPh_4), 124.11 (Im-**C**4), 123.86 (Tz-**C**H), 123.29 (Im-**C**5), 122.05 (*ipso*-**C**-C of $PhNH_2$), 121.52 (*p*-**C**H of BPh_4), 113.75 (*m*-**C**H), 53.15 (Tz-NCH$_2$), 44.32 (Im-NCH$_2$), 20.58 (*p*-CCH$_3$), 16.85 (*o*-CCH$_3$) ppm.

Synthesis of Rh(I) complexes

The syntheses of [Rh(MesCaTBn)(COD)]BPh$_4$ (**2a**) and [Rh(MesCaTBn)(CO)$_2$]BPh$_4$ (**3a**) are presented here. The syntheses of **2b–d** and **3–d** were carried out using methods similar to those used for **2a** and **3a** respectively and are provided in the supporting information (ESI†).

Synthesis of [Rh(MesCaTBn)(COD)BPh$_4$ (2a). Sodium ethoxide (0.06 g, 0.90 mmol) was added to a suspension of [Rh(Cl)(COD)]$_2$ (0.123 g, 0.250 mmol) in ethanol (25 mL) and the reaction mixture was stirred for 10 minutes at room temperature, during which time the colour of the solid changed from yellow orange to pale yellow. A solution of [MesCaTBn]BPh$_4$ (**1a**, 0.339 g, 0.500 mmol) in THF (25 mL) was added slowly and the reaction mixture was stirred for 30 minutes at RT. The solvent was removed *in vacuo* until 1 mL of solvent remained. The residue was washed with methanol (4 × 3 mL) and dried under vacuum. The crude solid product was recrystallised using dichloromethane (10 mL)–pentane (35 mL) to afford a bright yellow solid, which was collected by filtration and dried under vacuum overnight. Yield: 0.382 g, 86%. Elemental analysis, Found: C, 71.58, H, 6.17 and N, 7.86; calculated for $C_{54}H_{55}BN_5Rh.\ 0.25CH_2Cl_2$: C, 71.68; N, 6.15 and N, 7.70%. ESI-MS (ESI$^+$, CH_3CN): *m*/*z* (assignment, %): 568.06 (M, 100); expected for $[C_{30}H_{55}N_5Rh]^+$: 568.21 amu. ^{1}H NMR (500 MHz,

CD_2Cl_2): δ 7.40–7.39 (m, 11H, *o*-C**H** of BPh_4 and *m*- and *p*-C**H** of Ph), 7.17 (m, 2H, *o*-C**H** of Ph), 7.03 (s, 2H, *m*-C**H** of Mes), 6.99 (t, J = 7.34 Hz, 8H, *m*-C**H** of BPh_4), 6.86–6.85 (m, 4H, *p*-C**H** of BPh_4), 6.83 (s, 1H, Im-**H**4), 6.73 (d, ^3J = 1.89 Hz, 1H, Im-**H**5), 6.64 (s, 1H, Tz-C**H**), 5.24 (s, 2H, PhC$\mathbf{H}_2$), 4.83 (br s, 2H, COD-C**H** *trans* N), 4.68 (s, 2H, Im-NC$\mathbf{H}_2$), 3.62 (br s, 2H, COD-C**H** *trans* to NHC), 2.37 (s, 3H, *p*-CC$\mathbf{H}_3$), 2.25–2.20 (m, 2H, COD-CH**H**), 2.07 (s, 6H, *o*-CC$\mathbf{H}_3$), 2.05–1.87 (m, 6H, COD-CH**H** and COD-C**H**H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, CD_2Cl_2): δ 176.21 (d, ^1J(Rh-C2) = 50.9 Hz, Im-**C**2), 164.45 (q, $^1J_{B-C}$ 49.3 Hz, *ipso*-**C** of BPh_4), 140.17 (*p*-**C** of Mes), 140.08 (Tz-**C**4′) 136.34 (*o*-**C**H of BPh_4), 135.90 (*ipso*-**C** of Mes), 135.52 (*o*-**C** of Mes), 133.53 (*ipso*-**C** of Ph) 129.64 (*m*-**C**H of Mes and *p*-**C**H of Ph), 129.55 (*m*-**C**H of Ph), 128.64 (*o*-**C**H of Ph), 126.19 (*m*-**C**H of BPh_4), 123.57 (Im-**C**4), 123.16 (Tz-**C**5′), 122.62 (Im-**C**5), 122.32 (*p*-**C**H of BPh_4), 96.60 (**C**H of COD *trans* N), 79.10 (d, ^1J (Rh-C) = 10.2 Hz, COD-**C**H *trans* NHC), 55.71 (s, **C**H_2Ph), 45.12 (s, Im-N**C**H_2), 32.59 (COD-**C**H_2 *trans* N), 29.24 (COD-**C**H_2 *trans* NHC), 21.21 (*o*-C**C**H_3), 18.56 (*p*-C**C**H_3) ppm.

Synthesis of [Rh(MesCaTBn)(CO)$_2$]BPh$_4$ (3a). A suspension of [Rh(MesCaTBn)(COD)]BPh_4, **2a**, (0.160 g, 0.174 mmol) in methanol (4 mL) and pentane (20 mL) was degassed *via* three cycles of freeze–pump–thaw. The reaction mixture was placed under an atmosphere of carbon monoxide using a balloon, the colour of the solid changed from bright yellow to pale yellow then turned dark orange. The CO balloon was removed and the orange solid was collected by filtration and washed with pentane (3 × 5 mL) and dried *in vacuo*. Yield: 0.138 g; 95%. ESI-MS (ESI$^+$, MeOH) *m*/*z* (assignment, %): 520.07 ([M − CO + MeOH]$^+$, 46), 516.04 ([M]$^+$, 63), 488.06 ([M − CO]$^+$, 100), 460.08 ([M − 2 × CO]$^+$, 67) amu. Elemental analysis: found: C, 69.22; H, 5.29 and N, 8.55; calculated for $C_{48}H_{43}BN_5O_2Rh$: C, 68.99; H, 5.19 and N, 8.38%. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.42–7.39 (br m, 11H, *o*-C**H** of BPh_4 and *p*- and *m*-CH of Ph), 7.25 (d, ^3J = 6.9 Hz, 2H, *o*-C**H** of Ph), 7.05 (s, 2H, *m*-C**H** of Mes), 6.98 (t, ^3J = 7.2 Hz, 8H, *m*-C**H** of BPh_4), 6.94 (s, 1H, Im-**H**4), 6.86 (s, 1H, Im-**H**5), 6.82 (t, ^3J = 6.8 Hz, 4H, *p*-C**H** of BPh_4), 6.37 (s, 1H, Tz-**H**5′), 5.28 (s, 2H, Tz-NC$\mathbf{H}_2$), 4.32 (s, 2H, Im-NC$\mathbf{H}_2$), 2.37 (s, 3H, *p*-CC$\mathbf{H}_3$), 2.02 (s, 6H, *o*-CC$\mathbf{H}_3$) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, CD_2Cl_2): δ 184.29 (d, $^1J_{Rh-C}$ = 60.5 Hz, **C**O), 184.23 (d, $^1J_{Rh-C}$ = 68.8 Hz, **C**O), 171.74 (d, ^1J = 46.8 Hz, Im-**C**2), 164.01 (q, $^1J_{B-C}$ = 49.3 Hz, *ipso*-**C** of BPh_4), 140.75 (*p*-CCH_3 of Mes), 139.95 (Tz-**C**4′), 135.87 (br s, *o*-**C**H of BPh_4), 135.62 (*o*-**C**CH_3 of Mes), 132.42 (*ispo*-**C** of Ph), 129.54 (*p*-**C**H and *ipso*-**C** of Mes), 129.47 (*m*-**C**H of Ph), 129.32 (*m*-**C**H of Mes), 128.60 (*o*-**C**H of Mes), 125.88 (br s, *m*-**C**H of BPh_4), 123.74 (s, Tz-**C**5′), 123.54 (Im-**C**5), 122.91 (Im-**C**4), 122.02 (*p*-**C**H of BPh_4), 55.73 (Tz-N**C**H_2), 44.20 (Im-N**C**H_2), 20.87 (*p*-C**C**H_3), 17.92 (*o*-C**C**H_3) ppm. FTIR (dcm): ν (CO): 2095 and 2034 cm^{-1}.

Synthesis of Rh(III) complexes

The synthesis of [Rh(Cp*)(MesCaTBn)Cl]BPh_4 (**4a**) is presented here. The syntheses of the Rh(III) complexes **4b–d** were performed using an analogous method and the details are provided in the ESI.

Synthesis of [Rh(MesCaTBn)Cp*Cl]BPh$_4$ (4a). To a solution of **1h** (0.219 g, 0.5 mmol) in acetone (25 mL), silver oxide (0.08 g, 0.35 mmol) was added and the reaction mixture was refluxed for 3 hours under nitrogen. $[RhCp^*Cl_2]_2$ (0.155 g, 0.25 mmol) was added and reaction mixture was refluxed for 1 h and stirred overnight at room temperature. $NaBPh_4$ (0.171 g, 0.50 mmol) was added and the reaction mixture was stirred for another 30 min, followed by filtration through Celite. The solvent was removed *in vacuo* to afford a brown solid. The solid was redissolved in dichloromethane (4 mL) and pentane (*ca*. 15 mL) was added to form a yellow precipitate. This suspension was cooled down in an ice bath to induce further precipitation of the product, which was filtered and dried under vacuum. Yield: 0.413 g, 87%; m.p. 132 °C; ESI-MS (ESI$^+$, MeOH), *m*/*z* (assignment, %): 630.2 (M, 71), 631.2 (M, 24), 632.2 (M, 22) amu; calculated for $[C_{32}H_{38}ClN_5Rh]^+$ = 630.19 amu. Elemental analysis: found: C, 69.94; H, 5.90; N, 7.35; calculated for $C_{56}H_{58}BClN_5Rh$: C, 69.46; H, 6.25; N, 7.23%. ^{1}H NMR (500 MHz, $C_2D_2Cl_4$): δ 7.48 (br s, 8H, *o*-C**H** of BPh_4), 7.45 (m, 3H, *m*-C**H** and *p*-C**H** of Ph), 7.26 (m, 2H, *o*-C**H**), 7.02 (m, 8H, *m*-C**H** of BPh_4) 6.98 (s, 1H, m_2-C**H** of Mes), 6.96 (s, 1H, m_1-C**H** of Mes), 6.88 (m, 5H, *p*-C**H** of BPh_4 and **H**4), 6.80 (d, $^3J_{H4-H5}$ = 1.7 Hz, 1H, **H**5), 6.57 (s, 1H, Tz-**H**5′), 5.48 (d, $^2J_{H'-H''}$ = 14.4 Hz, 1H, Tz-NC**H**′H″), 5.27 (d, $^2J_{H''-H'}$ = 14.4 Hz, 1H, TzN-CH′**H**″, 4.58 (d, $^2J_{H'-H''}$ = 15.9 Hz, 1H, Im-C**H**′H″), 4.18 (d, $^2J_{H''-H'}$ = 15.9 Hz, 1H, Im-NCH′**H**″, 2.37 (s, 3H, *p*-CH_3 of Mes), 2.10 (s, 3H, o_1-CC$\mathbf{H}_3$ of Mes), 1.98 (s, 3H, o_2-CC$\mathbf{H}_3$ of Mes), 1.31 (s, 15H, CH_3 of Cp*) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $C_2D_2Cl_4$): δ 168.0 (d, ^1J(Rh-C) ~ 55 Hz, **C**2), 163.6 (q, ^1J (B-C) ~ 50 Hz, *ipso*-**C** of BPh_4), 140.6 (Tz-**C**4′), 140.0 (*p*-**C** of Mes), 138.5 (o_2-**C** of Mes), 136.3 (*o*-**C** of BPh_4), 135.3 (*ipso*-**C** of Mes), 134.5 (o_1-**C** of Mes), 132.9 (*m*-**C**H of Ph), 132.8 (*ipso*-**C** of Ph), 129.8 (m_2-**C** of Mes), 129.6 (*p*-**C**H of Ph), 128.6 (*o*-**C**H of Ph), 128.3 (m_1-**C** of Mes), 125.9 (*m*-**C**H of BPh_4), 125.5 (Im-**C**5), 124.2 (Im-**C**4), 123.8 (Tz-**C**5′), 122.0 (*p*-**C** of BPh_4), 98.6 (**C**CH_3 of Cp*), 55.8 (Tz-N**C**H′H″), 44.5 (Im-N**C**H′H″), 21.3 (*p*-C**C**H_3 of Mes), 19.8 (o_2-C**C**H_3 of Mes), 19.0 (o_1-CCH_3 of Mes), 9.5 (**C**H_3 of Cp*) ppm.

Synthesis of Ir(III) complexes

The synthesis of [Ir(Cp*)(MesCaTBn)Cl]BPh_4 (**5a**) is presented here. The syntheses of other Ir(III) complexes (**5b–c**) were performed using an analogous method and are provided in the ESI.†

Synthesis of [Ir(MesCaTBn)Cp*Cl]BPh$_4$ (5a). To a solution of **1h** (0.219 g, 0.50 mmol) in acetone (25 mL), silver oxide (0.08 g, 0.35 mmol) was added and the reaction mixture was refluxed for 3 h under nitrogen. $[IrCp^*Cl_2]_2$ (0.199 g, 0.25 mmol) was added, the reaction mixture was refluxed for 1 h and stirred overnight at room temperature. $NaBPh_4$ (0.171 g, 0.50 mmol) was added and reaction mixture was stirred for another 30 min, followed by filtration through Celite. The solvent was removed *in vacuo* to afford a brown solid. The solid was dissolved in DCM (4 mL) and pentane (*ca*. 20 mL) was added to form a yellow precipitate. This suspension was cooled down in an ice bath to further precipitation of

the product, which was filtered and dried under vacuum. Yield: 0.177 g; 34%. ES-MS (ESI^+, MeOH), *m/z* (assignment, %): 720.24 (M, 100), 718.24 (M, 50), 721.25 (M, 35); calculated for $C_{32}H_{38}BClIrN_5$: 720.24 amu. Elemental analysis, found: C, 63.04; H, 5.61; N, 6.49; calculated for $C_{56}H_{58}BClIrN_5$ + 0.5 CH_2Cl_2: C, 62.72; H, 5.50; N, 6.47%. ^{1}H NMR (500 MHz, $C_2D_2Cl_4$): δ 7.43 (m, 3H, *m*-C**H** and *p*-C**H** of Ph), 7.38 (br s, 8H, *o*-C**H** of BPh_4), 7.26 (m, 2H, *o*-C**H**), 7.00 (m, 8H, *m*-C**H** of BPh_4), 6.95 (s, 2H, m_1-C**H** and m_2-C**H** of Mes), 6.78 (d, $^3J_{H4-H5}$ = 1.9 Hz, 1H, **H**4), 6.86 (m, 4H, *p*-C**H** of BPh_4), 6.78 (d, $^3J_{H5-H4}$ = 1.9 Hz, 1H, Im-**H**5), 6.62 (s, 1H, Tz-**H**5′), 5.49 (d, $^2J_{H'-H''}$ = 14.6 Hz, 1H, Tz-NC**H**′H″), 5.31 (d, $^2J_{H''-H'}$ = 14.6 Hz, 1H, Tz-NCH′**H**″), 4.41 (d, $^2J_{H'-H''}$ = 15.9 Hz, 1H, Im-NC**H**′H″), 4.12 (d, $^2J_{H''-H'}$ = 15.9 Hz, 1H, Im-NCH′**H**″), 2.33 (s, 3H, *p*-C**H**$_3$ of Mes), 2.09 (s, 3H, o_2-C**H**$_3$ of Mes), 1.97 (s, 3H, o_1-C**H**$_3$ of Mes), 1.36 (s, 15H, C**H**$_3$ of Cp*) ppm. ^{13}C{^{1}H} NMR (125 MHz, $C_2D_2Cl_4$): δ 164.2 (q, *ipso*-**C** of BPh_4), 152.2 (**C**2), 140.1 (Tz-**C**4′), 139.7 (*p*-**C** of Mes), 138.7 (o_1-**C** of Mes), 135.9 (*o*-**C**H of BPh_4), 135.1 (*ipso*-**C** of Mes), 134.3 (o_2-**C** of Mes), 133.3 (*ipso*-**C** of Ph), 129.3 (*m*-**C**H and *p*-**C**H of Ph), 129.2 (m_2-**C** of Mes), 128.3 (*o*-**C**H of Ph), 127.9 (m_1-**C** of Mes), 125.8 (*m*-**C**H of BPh_4), 125.1 (Im-**C**4), 123.5 (Tz-**C**5′), 123.0 (Im-**C**5), 122.0 (m, *p*-**C**H of BPh_4), 91.2 (**C**CH_3 of Cp*), 55.8 (Tz-N**C**H′H″), 44.7 (Im-N**C**H′H″), 20.7 (*p*-**C**CH_3 of Mes), 19.6 (o_1-**C**CH_3 of Mes), 18.8 (o_2-**C**CH_3 of Mes), 9.1 (**C**H_3 of Cp*) ppm.

X-ray crystallography

Suitable single crystals of **1c**, **2a–d**, **3a–b**, **4a–d**, **5a–b** selected under the polarizing microscope (Leica M165Z), were picked up on a MicroMount (MiTeGen, USA) consisting of a thin polymer tip with a wicking aperture. The X-ray diffraction measurements were carried out on a Bruker kappa-II CCD diffractometer at 150 K by using graphite-monochromated Mo-Kα radiation (λ = 0.710723 Å). The single crystals, mounted on the goniometer using cryo loops for intensity measurements, were coated with paraffin oil and then quickly transferred to the cold stream using an Oxford Cryo stream attachment. Symmetry related absorption corrections using the program SADABS[58] were applied and the data were corrected for Lorentz and polarisation effects using Bruker APEX2 software.[59] All structures were solved by direct methods and the full-matrix least-square refinements were carried out using SHELXL.[60] The non-hydrogen atoms were refined anisotropically. The molecular graphic was generated using Mercury.[61] Key crystallographic data and refinement details are presented in the Tables S2 and S3 (ESI†).

Catalysis procedure

Catalytic hydroamination reactions were conducted using the same procedure as described previously.[20]

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