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Bi- and tri-metallic Rh and Ir complexes containing click derived *bis*- and *tris*-(pyrazolyl-*1,2,3*-triazolyl) N-N' donor ligands and their application as catalysts for the dihydroalkoxylation of alkynes

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Abstract

A series of bi-topic and a tri-topic pyrazolyl-*1,2,3*-triazolyl donor ligands (**1a-d**; **1a-c** = 1,X-*bis*((4-((1*H*-pyrazol-1-yl)methyl)-1*H*-1,2,3-triazol-1-yl)methyl)benzene (X = 2, 3 and 4; *o*-$C_6H_4(PyT)_2$, *m*-$C_6H_4(PyT)_2$ and *p*-$C_6H_4(PyT)_2$) and **1d** = *1,3,5-tris*((4-((1*H*-pyrazol-1-yl)methyl)-1*H*-1,2,3-triazol-1-yl)methyl)benzene, *1,3,5*-$C_6H_3(PyT)_3$) were conveniently synthesised in 'one pot' reactions using the Cu(I) catalysed 'click' reaction. Rh(I), Ir(I), Rh(III) and Ir(III) complexes with ligands **1a-d** of the general formulae $C_6H_{6-n}[(PyT)M(CO)_2]_n[BAr^F{}_4]_n$ (M = Rh, Ir; n = 2, 3; **2a-d**; **3a-d**) and $C_6H_{6-n}[(PyT)MCp^*Cl]_n[BAr^F{}_4]_n$ (M = Rh, Ir; n = 2, 3; **4a-d**; **5a-d**) were synthesised and fully characterised. In solution each of the bi- or tri-metallic complexes **4a-d** and **5a-d** exists as a mixture of two (**4a-c**, **5a-c**) or three (**4d** and **5d**) diastereomers due to the presence of a chiral centre at each metal centre in these complexes. The solid state structures of complexes **2b-c** and **4a** were determined using single crystal X-ray crystallography and showed that each bidentate arm of these multitopic ligands coordinates to the Rh or Ir centre in a bidentate fashion *via* the pyrazolyl-**N**2 and *1,2,3*-triazolyl **N**3' donors. The intermetallic distances in these solid state structures vary from 8.66 Å to 15.17 Å. These complexes were assessed as catalysts for the dihydroalkoxylation of alkynes using the cyclisation of 2-(5-hydroxypent-1-ynyl)benzyl alcohol, **S** to a mixture of two spiroketals, 2,3,4,5-tetrahydro-spirol[furan-2,3'-isochroman], **P1** and 3',4',5',6'-tetrahydro-spiro[isobenzofuran-1(3*H*),2'(2*H*)pyran], **P2** as the model reaction. The Rh(I) complexes (**2a-d**), with the highest TOF of 2052 h^{-1} for complex **2d**, were the most active catalysts when compared with the other complexes under investigation here. The Ir(I) complexes (**3a-d**) were moderately active as catalysts for the same transformation. No significant enhancement in catalytic reactivity was observed with the Rh(I) series bi- and trimetallic complexes (**2a-d**) when compared with their monometallic analogue. The bi- and trimetallic Ir(I) complexes (**3a-d**) were much more efficient as catalysts for this transformation than their monometallic analogue, suggesting some intermetallic cooperativity. Rh(III), **4a-d** and Ir(III), **5a-d** complexes were not active as catalysts for this transformation.

Introduction

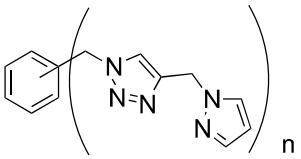
The Cu(I) catalysed Huisgen cycloaddition reaction (CuAAC) or 'click' reaction between an alkyne and an azide is a highly versatile reaction.[1, 2] The reaction is a convenient and expedient way to increase the complexity of organic compounds. The product of the reaction, 1,4-disubstituted *1,2,3*-triazole, has been widely used as a linker for biological applications and in the modification of surfaces and nanoparticles.[2] More recently, *1,2,3*-triazole has also been shown to be a highly versatile sp^2 N donor ligand. The *1,2,3*-triazolyl moiety has two potential *N*-donors N2 and N3, of which the N3 donor is the more common donor and appears to have higher electron donating ability than the *N2* donor on binding to transition metals.[3,4,5] Using 'click' chemistry a variety of bi- and tridentate triazolyl containing donor ligands and their metal complexes have been prepared.[3, 4] These 'click' derived ligands include bi-triazolyl,[6] triazolyl-pyridine,[7, 8] triazolyl-pyrazolyl, [9, 10] triazolyl-NHC,[11] and triazolyl-phosphine[12] donors. Metal complexes containing these ligands have been shown to be active as catalysts for a number of reactions including ethylene oligomerisation,[7] allylic alkylation,[12a-b] hydrogenation of alkenes[12b] and hydroamination.[9, 10]

In recent years, here has been a significant increase in the number reports of bimetallic and trimetallic complexes in which the metal centres are tethered together on a bridging ligand scaffold.[13,14,15,16,17,18,19,20] A number of these homo multi-metallic complexes have been demonstrated to be highly efficient as catalysts for a variety of chemical reactions including hydroformylation,[14] olefin polymerization,[13] hydroamination[18] and Suzuki-Miyaura coupling.[17h, 18] Significant enhancement in catalytic reactivity and selectivity achieved by the multimetallic catalysts in comparison with their monometallic analogues has been observed and this enhancement has been attributed to cooperative interactions between proximate metal centres in the multi-metallic complexes.[15, 18, 19, 21] On the other hand, there have also been cases where the use of multi-metallic complexes did not lead to any enhancement in catalytic reactivity in comparison with their monometallic counterparts. Examples of these 'unsuccessful' enhancement attempts include bimetallic Hoveyda-Grubbs metathesis catalysts reported by Barbasiewicz *et al.*[20] and bimetallic

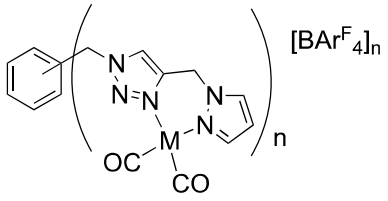
lanthanide hydroamination catalysts reported by the Marks' group.[16] A full understanding of the cooperative effect is still not available but factors such as the intermetallic distance, the rigid three dimensional geometry of the scaffold as well as the integrity of the multi-metallic structure during the catalytic cycle are all thought to play important roles. [15, 18, 19, 21] In addition to homo multi-metallic complexes, a number of hetero-bimetallic complexes which could promote two mechanistically distinct reactions in a tandem have been reported in the literature.[22]

The catalysed tandem dihydroalkoxyation of alkyne diols is an efficient, atom economical method for the synthesis of *O,O*-acetals including *O,O*-spiroketals which are an important class of biologically active compounds.[23,24]A number of metal complexes with a variety of metal centres are efficient catalysts for the dihydroalkoxylation reaction including complexes of Pd(II),[25] Pt(II),[26] Rh(I),[27,28,29] Ir(I),[28, 29] Ir(III),[30] Hg(II)[31] and Au(I) and Au(III).[24, 32]

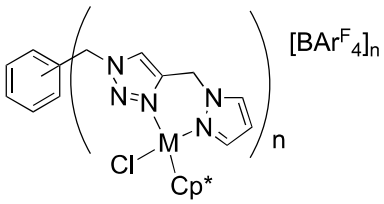
We have recently shown that Rh(I) and Ir(I) complexes containing bidentate pyrazolyl-triazolyl donor ligands are effective catalysts for the intramolecular hydroamination of alkynes and alkenes,[9] and Ir(III) complexes with these ligands are active catalysts for tandem C-N/C-C bond formations in the synthesis of tricyclic indoles.[10] We have also shown that bimetallic Rh(I) and Ir(I) complexes containing *bis*(pyrazolyl) bidentate donor ligands lead to remarkable enhancements in catalytic activity for the dihydroalkoxylation of alkyne reactions relative to the activity of the corresponding monometallic complex.[28, 29, 33, 34] In this paper, we have used the CuAAC reaction to conveniently synthesise a series of bi- and tri-topic bidentate pyrazolyl-triazolyl donor ligands in 'one pot'. Rh(I), Ir(I), Rh(III) and Ir(III) bi- and trimetallic complexes with these multi-topic ligands (Figure 1) were synthesised, characterised and assessed as catalysts for the tandem dihydroalkoxylation of alkynes using 2-(5-hydroxypent-1-ynyl)benzyl alcohol (**S**) as the substrate.



n = 2, *o*-$C_6H_4(PyT)_2$, **1a**
m-$C_6H_4(PyT)_2$, **1b**
p-$C_6H_4(PyT)_2$ **1c**
n = 3, *1,3,5*-$C_6H_3(PyT)_3$ **1d**



n = 2, *o*-$C_6H_4[(PyT)M(CO)_2]_2[BAr^F{}_4]_2$, **2a** (Rh) and **3a** (Ir)
m-$C_6H_4[(PyT)M(CO)_2]_2[BAr^F{}_4]_2$, **2b** (Rh) and **3b** (Ir)
p-$C_6H_4[(PyT)M(CO)_2]_2[BAr^F{}_4]_2$, **2c** (Rh) and **3c** (Ir)
n = 3, *1,3,5*-$C_6H_3[(PyT)M(CO)_2]_3[BAr^F{}_4]_3$, **2d** (Rh) and **3d** (Ir)



n = 2, *o*-$C_6H_4[(PyT)M(Cp^*)Cl][BAr^F{}_4]_2$, **4a** (Rh) and **5a** (Ir)
m-$C_6H_4[(PyT)MCp^*)Cl]_2[BAr^F{}_4]_2$, **4b** (Rh) and **5b** (Ir)
p-$C_6H_4[(PyT)M(Cp^*)Cl]_2[BAr^F{}_4]_2$, **4c** (Rh) and **5c** (Ir)
n = 3, *1,3,5*-$C_6H_3[(PyT)M(Cp^*)Cl]_3[BAr^F{}_4]_3$, **4d** (Rh) and **5d** (Ir)

o- = *ortho*, *m-* = *meta* and *p-* = *para*
$BAr^F{}_4$ = [*tetrakis*(3,5-*bis*(trifluoromethyl)phenyl]borate
M = Rh or Ir

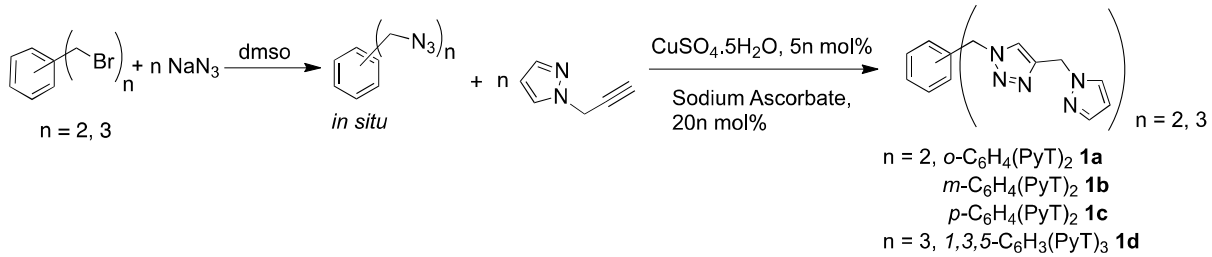
Figure 1: Bi- and tri-topic bidentate pyrazolyl-*1,2,3*-triazolyl donor ligands and their rhodium and iridium complexes.

Results and Discussion

Synthesis of ligands

Bi- and tri-topic bidentate pyrazolyl-*1,2,3*-triazolyl donor ligands were synthesised using the Cu(I) catalysed alkyne-azide cycloaddition reaction between *bis* and *tris*(azidomethyl)benzene and two or three molar equivalents of 1-propargylpyrazole to afford the desired multi-topic ligands **1a-d** in good yields (57–88%). The *bis* and *tris*(azidomethyl)benzene intermediates were generated *in situ* by the reaction between sodium azide and commercially available *bis* and *tris*(bromomethyl)benzene in dimethylsulfoxide.[1, 2] The isolation of these *bis* and *tris*(azidomethyl)benzene intermediates was not performed due to the potential danger in handling neat samples of polyazido organic compounds. The Cu catalyst was removed from the reaction

mixture by multiple washings with saturated aqueous Na_2EDTA (disodium ethylenediaminetetraacetic acid) until the filtrate turned colourless.



Scheme 1: Synthesis of *bi*- and *tri*-topic pyrazole-*1,2,3*-triazole donor ligands.

The ^{1}H NMR spectra of each of the bi and tri-topic bidentate pyrazolyl-triazolyl donor ligands **1a-1d** each contains only one set of resonances due to protons on the pyrazolyl and *1,2,3*-triazolyl rings as each of the bidentate donors are equivalent to each other due to the symmetry of these ligands. X-ray quality crystals of *m*-$C_6H_4(PyT)_2$ (**1b**) and *p*-$C_6H_4(PyT)_2$ (**1c**) were obtained by re-crystallisation of each of the compounds from hot methanol and the ORTEP diagrams of three dimensional structures determined in the solid state using X-ray crystallography are presented in Figure 2. Crystal data are given in the electronic supporting information (ESI, Table S3).

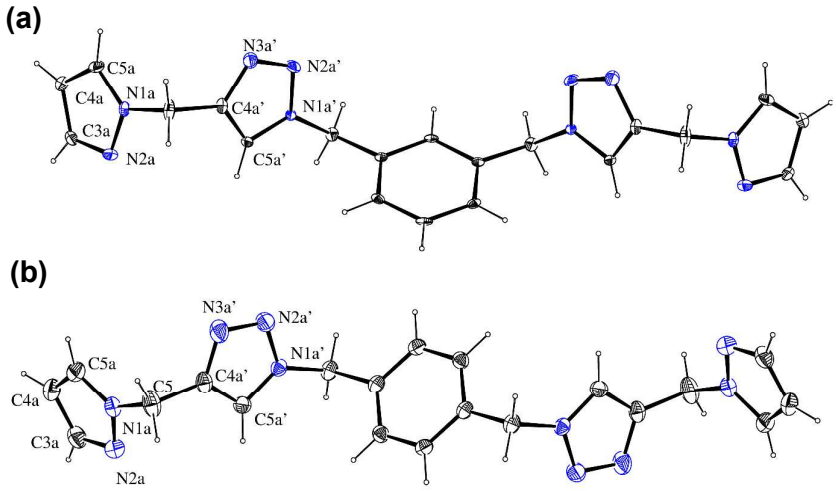


Figure 2: ORTEP diagrams of the solid state structures of *m*-$C_6H_4(PyT)_2$ (**1b**) and *p*-$C_6H_4(PyT)_2$ (**1c**) at 40% thermal ellipsoid for the non-hydrogen atoms.

Synthesis of metal complexes

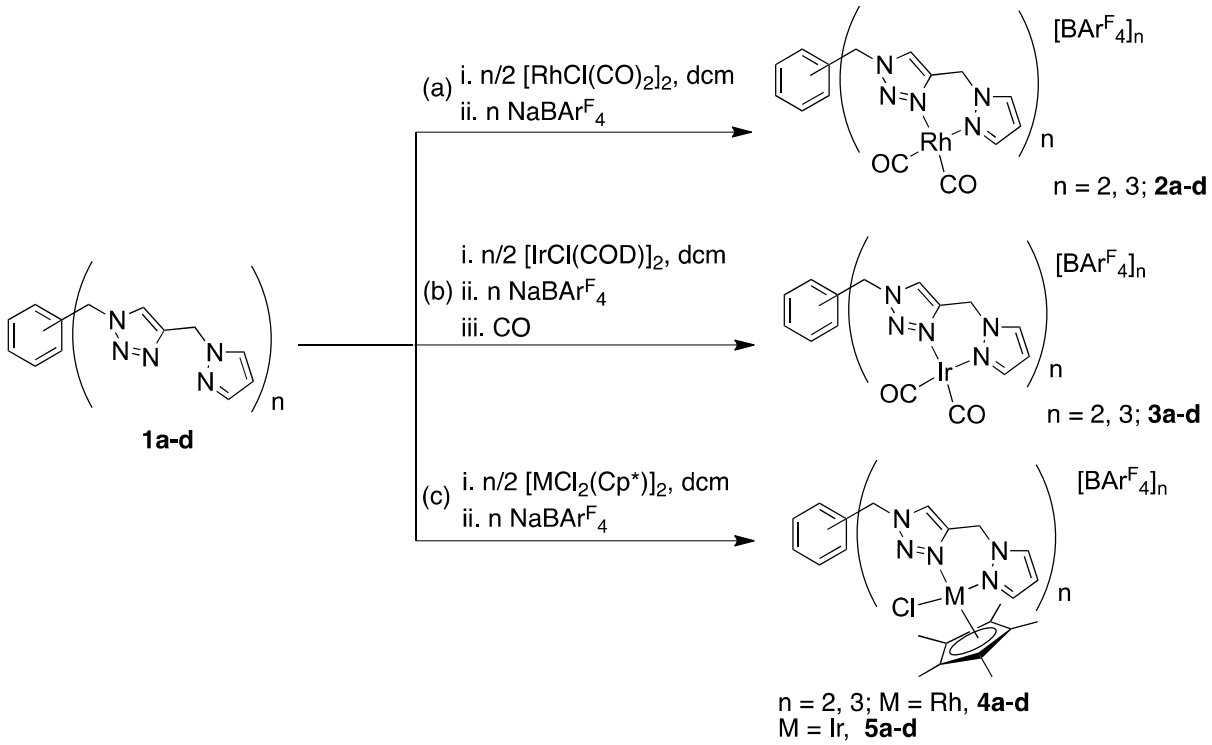
Rh(I) and Ir(I) complexes

Cationic bi- and trimetallic Rh(I) complexes $C_6H_{6-n}[(PyT)Rh(CO)_2]_n[BAr^F{}_4]_n$ (**2a-d**; Scheme 2(a)) were synthesised by the reaction of the appropriate ligands with 0.5 x n molar equivalents of the Rh precursor $[Rh(Cl)(CO)_2]_2$ (n is the number of PyT, motifs on the ligands **1a-d**, n = 2 or 3) in dichloromethane followed by a counteranion exchange using $NaBAr^F{}_4$. The products were collected as very pale yellow (**2c**) or yellow solids (**2a**, **2b** and **2d**) in very good to excellent yields (79-92%).

The analogous cationic Ir(I) complexes, **3a-d**, were prepared in a similar fashion (Scheme 2(b)) using the $[IrCl(COD)]_2$ (COD = 1,5-cyclooctadiene) precursor in place of $[RhCl(CO)_2]_2$. The iridium 1,5-cyclooctadiene intermediates were not isolated and the COD co-ligand was displaced with carbon monoxide to form the Ir dicarbonyl complexes $C_6H_{6-n}[(PyT)Ir(CO)_2]_n[BAr^F{}_4]_n$ (**3a-d**). The desired products **3a-d** were collected as orange solids in very good yields (75-91%). All of these complexes (Rh(I), **2a-d** and Ir(I), **3a-d**) are air stable in the solid state and in solution.

Complexes **2a-d** and **3a-d** were fully characterised using NMR spectroscopy, mass spectrometry, infrared spectroscopy and elemental analyses. In each of the ^1H and ^{13}C NMR spectra of each of these complexes, only one set of resonances due to the protons of the metal complexes was observed, as would be expected from the symmetry of these bi- and trimetallic complexes. The IR spectra (in dichloromethane solution) of these complexes each contain two strong ν(CO) bands of similar intensity, as is to be expected in the case of dicarbonyl complexes where two CO substituents are coordinated in a *cis* manner (Table S1, Electronic Supporting Information, ESI). No notable difference in the ν(CO) values was observed in each of the Rh (**2a-d**) and Ir (**3a-d**) series of complexes and also when compared with the values for the corresponding monometallic complexes[9] suggesting that there is little interaction between the pairs of metal centres in these bi- and trimetallic complexes. In the same way, the chemical shift (***δ***) values of the

^{13}CO resonances in each of the Rh and Ir series of the complexes **2a-d** and **3a-d** (in the same solvents) are very similar.



Scheme 2: Synthesis of Rh(I), Ir(I), Rh(III) and Ir(III) complexes.

Rh(III) and Ir(III) complexes

Cationic Rh(III) and Ir(III) complexes $C_6H_{6-n}[(PyT)M(Cp^*)Cl]_n[BAr^F{}_4]_n$ (M = Rh, **4a-d** and M = Ir, **5a-d**, Scheme 2 (c)) were synthesised by the reaction of the bi- or tri-topic ligand (**1a-d**) with the metal precursor $[MCp^*Cl_2]_2$ (M = Rh or Ir) in dichloromethane, followed by a counteranion exchange with $NaBAr^F{}_4$. The desired metal complexes **4a-d** and **5a-d** were collected as air stable orange (Rh) or yellow (Ir) solids in good to excellent yields (73-95%). These complexes were also found to be stable in solution (dichloromethane or acetone). All of the complexes **4a-d** and **5a-d** were fully characterised by NMR spectroscopy, mass spectrometry and elemental analysis.

The chemical shifts of the ^{1}H and ^{13}C resonances of complexes $C_6H_{6-n}[M(PyT)(Cp^*)Cl]_n[BAr^F{}_4]_n$ (M = Rh, **4a-d** or Ir, **5a-d**) are similar to those reported for the analogous monometallic complexes $[M(PyT)(Cp^*)Cl][BAr^F{}_4]$ (M = Rh or Ir).[10] However, due to

the fact that each of the metal centres in complexes **4a-d** and **5a-d** is chiral, two (**4a-c** and **5a-c**) and three (**4d** and **5d**) sets of resonances were observed for the ^{1}H and ^{13}C resonances of the cationic fragment in each of the complexes. The observation of two and three separate sets of resonances where there are two and three metal complexes bound to the scaffold respectively is due the formation of diastereomers where there are two or three chiral centres in the bimetallic and trimetallic complexes. In order to confirm that the presence of multiple sets of NMR resonances is due to the presence of groups of diastereomers and not due to the presence of different steric conformers, ^{1}H NMR spectra of a sample of *m*-$C_6H_4[(PyT)Rh(Cp^*)Cl]_2[BAr^F{}_4]_2$ (**4c**) in $CDCl_2CDCl_2$ were acquired over a range of temperatures (235K to 355K) in 10° intervals. No significant change either in the ratios of the intensities or the chemical shifts of the two sets of resonances attributed to the two metal complex substituents was observed over this temperature range, confirming that the presence of different sets of resonances arises from the chirality of the individual metal complex substituents.

The ratios of the diastereoisomers in these complexes (as determined by integration of the ^{1}H NMR spectra at room temperature) are summarised in Table S2 (ESI). In the case of the bimetallic complexes, four diastereomers are expected; two of which are pairs of enantiomers which will pairwise give rise to identical chemical shifts in the NMR spectra. A close to 1.0 : 1.0 ratio of the two pairs of diastereomers formed was observed for all of the bimetallic complexes containing two chiral centres, however an exact 1.0 : 1.0 ratio was only observed for the pair of diastereomers formed for *p*-$C_6H_4[(PyT)MCp^*Cl]_2[BAr^F{}_4]_2$ (M = Rh, **4c** and M = Ir, **5c**) where the two metal centres are the furthest apart. In the case of the trimeric complexes, 8 diastereomers could form, however by symmetry only three different sets of NMR resonances would be expected in an ideal ratio of 1:2:1. The observed ratios of formation of the groups of diastereomers of the trimeric complexes by NMR were all close to 1.0 : 2.0 : 1.0, as expected by symmetry. The fact that the relative amount of diastereomers formed varies from the expected 1 : 1 (for dimeric complexes) and 1 : 2 : 1 (trimeric complexes) suggests that upon the coordination of a MCp*Cl motif to a set of

pyrazolyl-triazolyl donor, the newly formed intermediate complex may have a diastereo-selective 'directing effect' on the coordination of the next metal precursor fragment to the remaining 'vacant' ligand donor site(s). This stereo-directing effect could be attributed to the steric interactions between the newly formed complex and the approaching Cp*M fragment, both of which have the bulky Cp* moiety. However, the variation from the expected ratio could also be due to the epimerization of the chiral metal centres leading to an equilibrium between diastereomers particularly in coordinating solvents (see below).

The ^{1}H-^{1}H NOESY spectra of complexes **4a-d** and **5a-d** in acetone-d_6 contain exchange cross-peaks between resonances due to protons of magnetically different diastereomers (Figure 2). Analogous exchange cross-peaks were not observed in the ^{1}H-^{1}H NOESY spectra of similar complexes when the spectra were acquired in dichloromethane-d_2. The ^{1}H-^{1}H NOESY spectra of the *o*-$C_6H_4[(PyT)Rh(Cp^*)Cl]_2[BAr^F{}_4]_2$ (**4a**) were acquired in both acetone-d_6 and in dcm-d_2. Exchange cross-peaks were observed only where the spectrum was acquired in acetone-d_6. This observation indicates that the chiral metal centres in these complexes epimerize constantly in coordinating solvents such as acetone-d_6. However, the diastereomers are in dynamic equilibrium with each other and no change in diasteromeric ratios were observed upon prolonged storage in solution at room temperature, specifically for samples of *o*-$C_6H_4[(PyT)Rh(Cp^*)Cl]_2[BAr^F{}_4]_2$ (**4a**) in dcm-d_2 and in acetone-d_6.

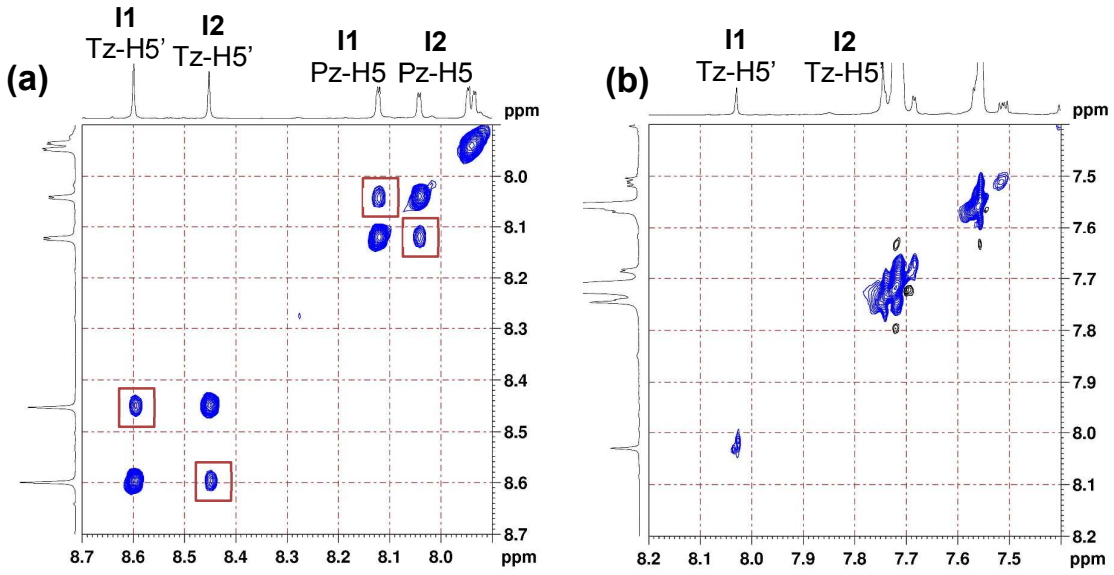


Figure 2: Section of the ^{1}H-^{1}H NOESY spectrum of *o*-$C_6H_4[(PyT)Rh(Cp^*)Cl]_2[BAr^F{}_4]_2$ (**4a**) in (a) acetone-d_6 showing the exchange cross-peaks (in red squares) between resonances due to protons of two magnetically different diastereomers (**I1** and **I2**) and (b) in dcm-d_2 not showing any exchange cross-peaks.

Two possible mechanisms for the epimerization process at the metal centres are proposed (Figure 3 (a) and (b)). In the first case (Figure 3(a)), the epimerization involves intermolecular halogen exchange, with initial de-coordination of the Cl^- donor from the metal centre to form a 16e$^-$ $[(PyT)MCp^*]^{2+}$ intermediate which could be either planar or pyramidal. The re-coordination of the Cl^- to the opposite side of the complex if the $[(PyT)MCp^*]^{2+}$ intermediate is planar, or after inversion if the intermediate is pyramidal, leads to the epimerization of the metal centre. In the second case (Figure 3(b)) the de-coordination-rotation followed by re-coordination of one arm of the PyT donor ligand is invoked. In each case, the vacant coordination site which appears during the de-coordination of either the Cl^- or one arm of the N-N donor is likely to be stabilised by a coordinating solvent such as acetone-d_6. The Cl^- exchange mechanism (Figure 3 (a)) has been

proposed by Carmona and Davies in their studies of similar Cp*M (M = Rh, Ir) complexes.[35, 36] We have previously observed the high lability of N-N donor ligands such as *bis*(pyrazolyl)methane in rhodium and iridium complexes which supports the second case (Figure 3 (b)).[37] In the absence of further studies each of the proposed mechanism is equally valid.

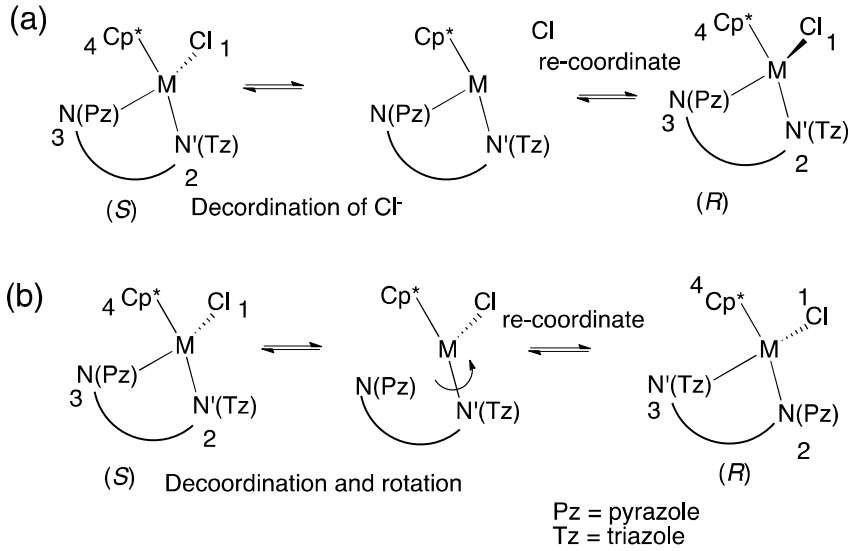


Figure 3: Proposed epimerization processes at the chiral metal centres of **4a-d** and **5a-d** (Cp* is considered as a single donor).

Single crystal solid state structures

X-ray quality crystals of complexes *m*-$C_6H_4[(PyT)Rh(CO)_2]_2[BAr^F{}_4]_2$ (**2b**), *p*-$C_6H_4[(PyT)Rh(CO)_2]_2[BAr^F{}_4]_2$ (**2c**) and *o*-$C_6H_4[(PyT)RhCp^*Cl]_2[BAr^F{}_4]_2$ (**4a**) were obtained by layering a concentrated dichloromethane solution with *n*-pentane. The ORTEP depictions of the solid state structures of the cationic fragments of **2b** and **2c**, and **4a** are shown in Figures 4 and 5 respectively. Table 1 gives the selected bond lengths, bond angles and metal-metal distances of the solid state structures of complexes **2b**, **2c** and **4a**. The crystallographic data for these structures obtained using single crystal X-ray analysis is provided in the ESI (Table S4). During the various attempts to obtain X-ray quality crystals of complexes *1,3,*5-$C_6H_3[(PyT)RhCp^*Cl]_3[BAr^F{}_4]_3$ (**4d**) and *m*-$C_6H_4[(PyT)IrCp^*Cl]_2[BAr^F{}_4]_2$ (**5b**) from pure samples of **4d** and **5b**, we obtained some

additional yellow orange plate and yellow cubic crystals respectively which were found to have the bimetallic bridged structure [Cp*M(μ-Cl)$_3$MCp*][BAr$^F{}_4$] with M = Rh (**6**) or Ir (**7**) respectively. The ORTEP depictions of the solid state structures and crystal data for complexes **6** and **7** are given in Figure S1 and Table S3 (ESI). The pathways leading to the formation of **6** and **7** are not clear.

In the solid state, the pyrazolyl-triazolyl bidentate donor coordinates to the metal centre *via* the pyrazolyl-**N**2 and triazolyl-**N**3' atoms to from 6 membered metallocycles which adopt distorted boat conformations (Figures 4, 5, S1 and S2). The cationic Rh(I) (**2b** and **2c**) complexes adopt the expected square planar coordination around the metal centre. The coordination around the Rh(III) centre in complex **4a** has a piano stool geometry as is normally observed for complexes of this nature. The N-M-N bite-angles in these complexes range from 84.1° to 87.4° which are similar to those observed in analogous monometallic Rh/Ir complexes previously reported by us [9, 10] and literature values for Rh/Ir complexes with N-N donor ligands.[38] The M-N (M = Rh, Ir) bond lengths in complexes **2b**-**c** and **4a** did not show any significant variations from other M-N bond lengths reported in the literature.[9, 10, 38] In the solid state structure of *o*-C$_6$H$_4$[(PyT)RhCp*Cl]$_2$ (**4a**) the absolute stereochemistry at the metal centres is *(R,R)*. The stereochemistry observed here is of course not a reflection of the stereochemistry of the bulk solid as a single crystal only was selected from each of the complexes for X-ray diffraction analysis.

The X-ray structure of **4a** (Figure 5) displays a folded structure where the two metal centres are quite close to each other (8.66 Å). One factor which could contribute to this observed folding is the interaction between the Rh-**Cl**---**H**(triazole) atoms in the structure of **4a (**Rh2, Cl1B and H5A' atoms, Rh-**Cl**---H distance = 2.750(1) Å and Rh-Cl-H angle = 102.93(4)°). This interaction in **4a** can be classified as hydrogen bonding according to the requirements that (i) the H-Cl distance is less than the sum of van der Waals radii for neutral H and Cl atoms (2.95 Å) and that (ii) M-Cl----H angle is in between 90-130°. [39] However it is well accepted that solid state structures can arise from a large number of intra and intermolecular forces. A thorough analysis of these forces is clearly beyond the scope of this paper.

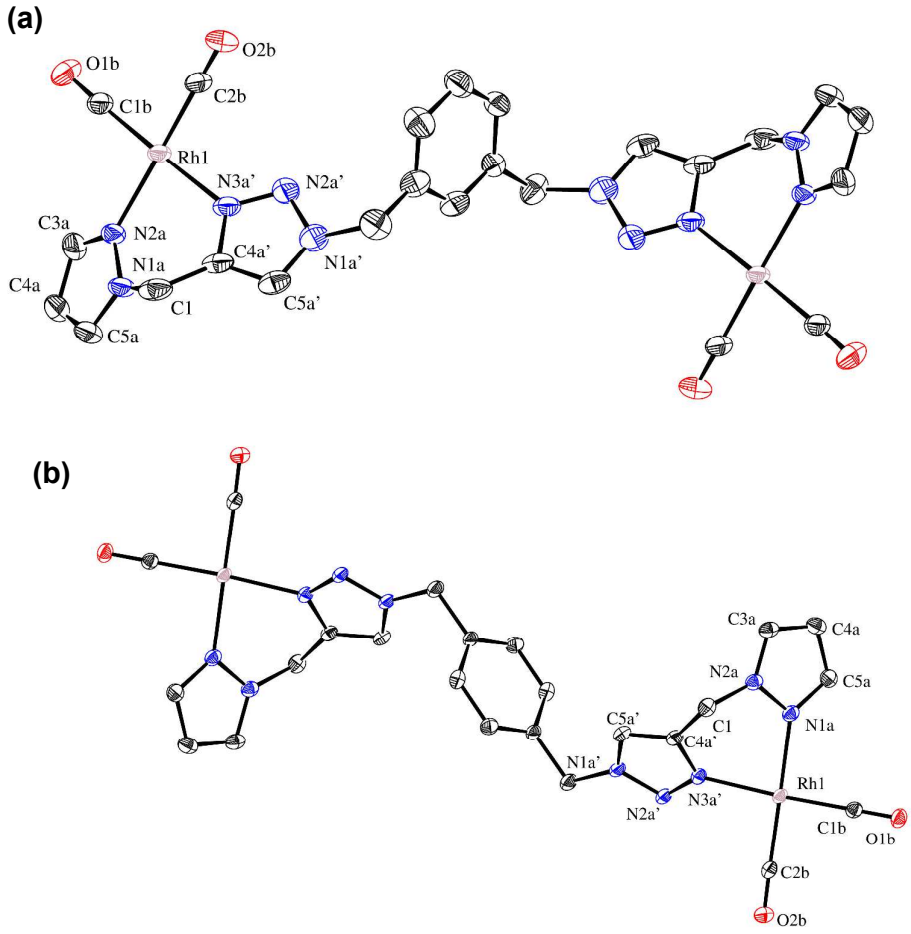


Figure 4: ORTEP depictions of the cationic fragments of the single crystal X-ray structures of *m*-$C_6H_4[(PyT)Rh(CO)_2]_2[BAr^F{}_4]_2$ (**2b**) and *p*-$C_6H_4[(PyT)Rh(CO)_2]_2[BAr^F{}_4]_2$ (**2c**) at 40% thermal ellipsoid for the non-hydrogen atoms.

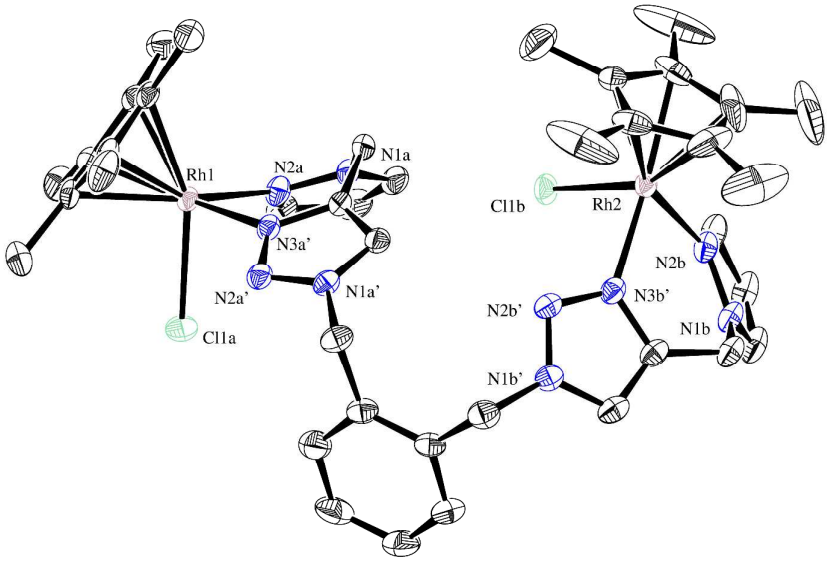


Figure 5: ORTEP depiction of the cationic fragment of the single crystal X-ray structure of *o*-$C_6H_4[(PyT)RhCp^*Cl]_2[BAr^F{}_4]_2$ (**4a**) at 40% thermal ellipsoid for the non-hydrogen atoms.

Table 1: Selected bond lengths (Å), bond angles (°) and intermetallic distances (Å) of the inner coordination spheres of *m*-$C_6H_4[(PyT)Rh(CO)_2]_2[BAr^F{}_4]_2$ (**2b**), *p*-$C_6H_4[(PyT)Rh(CO)_2]_2[BAr^F{}_4]_2$ (**2c**) and *o*-$C_6H_4[(PyT)Rh(Cp^{*)}Cl]_2[BAr^F{}_4]_2$ (**4a**).

Complex	2b	2c	4a
Bond Lengths (Å)			
M-N(Pz)	2.075(3)	2.078(3)	2.109(4)
M-N(Tz)	2.072(4)	2.065(3)	2.097(3)
M-**C**O (*trans* to Pz)	1.856(4)	1.868(4)	-
M-**C**O (*trans* to Tz)	1.869(6)	1.869(4)	-
M-Cl	-	-	2.409(1)
M-C*	-	-	1.770
Bond Angles (°)			
N(Pz)-M-N(Tz)	87.4(1)	84.9(1)	84.7(1)
N(Tz)-M-**C**O (*trans* to Pz)	90.2(2)	94.6(1)	-
CO (*trans* to Pz)-M-**C**O (*trans* to Tz)	89.0(2)	88.5(2)	-
CO (*trans* to Tz)-M-N(Pz)	93.6(2)	92.0(1)	-
N(Tz)-M-Cl	-	-	88.9(1)
Cl-M-N(Pz)	-	-	86.2(1)
M-M Distance (Å)			
M-M	13.275(1)	15.171(4)	8.6641(6)

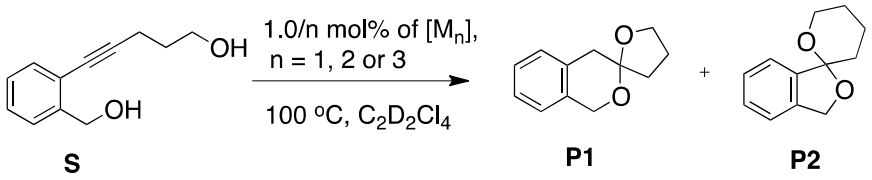
[a] Standard deviations in the least significant figures are given in parentheses. [b] C* is the centroid of the Cp* ring.

Catalysis: catalysed dihydroalkoxylation of alkynes

A selection of the homo bi- and trimetallic Rh or Ir complexes **2-5** were assessed as catalysts for the dihydroalkoxylation of alkynes using 2-(5-hydroxypent-1-ynyl)benzyl alcohol (**S**) as the substrate (Table 2). As has previously been reported with this reaction, when catalysed by Rh(I) and Ir(I) complexes,[27, 28, 29, 34] a mixture of two spiroketal products **P1** and **P2** were formed with **P1** = 2,3,4,5-tetrahydro-spirol[furan-2,3'-isochroman] and **P1** = 3',4',5',6'-tetrahydro-spiro[isobenzofuran-1(3*H*),2'(2*H*)pyran]. During the course of the catalysed reaction, a portion of the **P2** formed isomerised to **P1** so that the molar ratio of **P1** : **P2** increased as the reaction progressed, and after complete conversion of **S** the isomerisation continued until an equilibrium between **P1** and **P2** was reached (Table 2).

Table 2 shows that Rh(I) complexes with dicarbonyl coligands $[Rh(PyT)(CO)_2][BAr^F{}_4]$, $C_6H_{6-n}[Rh(PyT)(CO)_2]_n[BAr^F{}_4]_n$ (n = 2 or 3; **2a-d**) were the most active amongst all the complexes assessed here for the dihyroalkoxylation of **S** to a mixture of **P1** and **P2** (entries 1-5) with a TOF (calculated at the point of 50% conversion of the substrate) of 2052 h^{-1} recorded for the trimetallic complex **2d**. The monometallic complex $[Rh(PyT)(CO)_2][BAr^F]$ (Table 1, TOF = 770 h^{-1}) is slightly less reactive than the similar complex with *bis*(1-pyrazolyl)methane donor, bpm, $[Rh(bpm)(CO)_2][BAr^F{}_4]$ (TOF of 961 h^{-1}).[28a] The bi- and tri-nuclear Rh(I) complexes $C_6H_{6-n}[Rh(PyT)(CO)_2]_n[BAr^F{}_4]_n$ (n = 2 or 3; **2a-d**) did not show any significant cooperativity between metal centres during catalysis, with small cooperativity indices of between -0.3 to 0.4 (calculated using literature methods).[28b, 40]

Table 2: Catalysed cylisation of 2-(5-hydroxypent-1-ynyl)benzyl alcohol (**S**) with mono-, bi- and trimetallic Rh and Ir complexes.[a]



S **P1** **P2**

Entry	Catalyst	TOF[b] (P1:P2 ratio at 50% conv.)	Final Conversion, % (hrs, P1:P2)	Coop. Index
1	$[Rh(PyT)(CO)_2][BAr^F{}_4]$	770 (2.0 : 1.0)	≥ 98 (0.53, 2.7 : 1.0)	-
2	*o*-$C_6H_4[Rh(PyT)(CO)_2]_2[BAr^F{}_4]_2$ (**2a**)	1534 (2.0 : 1.0)	≥ 98 (0.67, 2.1 : 1.0)	0.0
3	*m*-$C_6H_4[Rh(PyT)(CO)_2]_2[BAr^F{}_4]_2$ (**2b**)	1736 (1.9 : 1.0)	≥ 98 (0.72, 2.2 : 1.0)	0.3
4	*p*-$C_6H_4[Rh(PyT)(CO)_2]_2[BAr^F{}_4]_2$ (**2c**)	1840 (1.6 : 1.0)	≥ 98 (0.20, 2.2 : 1.0)	0.4
5	*1,3,5*-$C_6H_3[Rh(PyT)(CO)_2]_3[BAr^F{}_4]_3$ (**2d**)	2052 (1.7 : 1.0)	≥ 98 (0.50, 2.0 : 1.0)	-0.3
6	$[Ir(PyT)(CO)_2][BAr^F{}_4]$	38 (1.5 : 1.0)	97 (8.4, 2.2 : 1.0)	-
7	*o*-$C_6H_4[Ir(PyT)(CO)_2]_2[BAr^F{}_4]_2$ (**3a**)	489 (1.1 : 1.0)	98 (1.5, 3.4 : 1.0)	10.8
8	*m*-$C_6H_4[Ir(PyT)(CO)_2]_2[BAr^F{}_4]_2$ (**3b**)	284 (1.1 : 1.0)	97[c] (2.7, 1.3 : 1.0)	5.5
9	*p*-$C_6H_4[Ir(PyT)(CO)_2]_2[BAr^F{}_4]_2$ (**3c**)	299 (1.0 : 1.5)	≥ 98 (≤4.5, 1.3 : 1.0)	5.9
10	*1,3,5*-$C_6H_3[Ir(PyT)(CO)_2]_3[BAr^F{}_4]_3$ (**3d**)	422 (1.0 : 1.2)	100 (≤19.5, 1.8 : 1.0)	8.1
11	$[Rh(PyT)(Cp^*)Cl][BAr^F{}_4]$	3	51 (17, 25 : 1.0)	-
12	*m*-$C_6H_4[Rh(PyT)(Cp^*)Cl]_2[BAr^F{}_4]_2$ (**4b**)	n/a	34 (16.5, 24 : 1.0)	n/a
13	$[Ir(PyT)(Cp^*)Cl][BAr^F{}_4]$	n/a	2 (20, 16.0 : 1.0)	n/a
14	*m*-$C_6H_4[Ir(PyT)(Cp^*)Cl]_2[BAr^F{}_4]_2$ (**5b**)	n/a	22 (16, 9.0 : 1.0)	n/a

[a] Catalysed reactions were conducted in a Young's NMR tube with 0.6 mL of $C_2D_2Cl_4$ and [**S**] = 0.30 ± 0.01 M. [b] TOF (h^{-1}) = (moles of products/moles of catalyst)/time (h) at the point of 50% conversion of the substrate to products **P1** and **P2**. [c] 100% conversion reached at ≤ 7.0 hrs (**P1** : **P2** =3.0 :1.0).

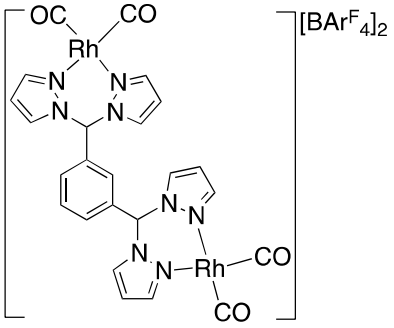
The Ir(I) dicarbonyl complexes $[Ir(PyT)(CO)_2][BAr^F{}_4]$, $C_6H_{6-n}[Ir(PyT)(CO)_2]_n[BAr^F{}_4]_n$ (n = 2 or 3; **3a-d**) were found to be less active catalysts for the cyclisation of **S** to **P1** and **P2** (Table 2, entries 6-10) than their Rh analogues, $[Rh(PyT)(CO)_2][BArF_4]$ and **2a-d** (entries 1-5). The TOF values obtained when using these complexes as catalysts varied significantly, from 38 to 489 h^{-1}. The TOF value determined for the monometallic complex $[Ir(PyT)(CO)_2][BAr^F{}_4]$ is significantly lower than that of the analogous Ir(I) complex containing the *bis*(1-pyrazolyl)methane (bpm) donor $[Ir(bpm)(CO)_2][BAr^F{}_4]$ (TOF = 374 h^{-1}).[28a] In contrast to the catalytic reactivities observed in the Rh series of complexes (Table 2, entries 1-5), significant enhancement in reactivity was observed for the bi- and trimetallic complexes **3a-d**, when compared with their homometallic analogues. The cooperativity indexes were calculated to be greater than 5, with an index as high as 10.8 observed for the ortho-bimetallic Ir complex **3a**, possibly due to the closer arrangement of the two Ir centres in this complex when compared with complexes **3b-d**. The fact that the Ir series of complexes in shows enhancement of catalytic activity when multi-metallic complexes are used whereas the Rh series does not show this enhancement is surprising, and will be a part of our ongoing computational and mechanistic investigations into understanding intermetallic cooperativity for dihydroalkoxylation.

Table 3 lists the efficiencies of some of the most effective catalysts reported to date for the dihydroalkoxylation reaction of 2-(5-hydroxypent-1-ynyl)benzyl alcohol (**S**) as the model substrate. Monobimetallic Rh(I) dicarbonyl complexes with *bis*(1-pyrazolyl)methane donor ligands[28b, 29] (**6-8**) have TOFs for the reaction that are between 2-5 fold greater than those found here for the analogous Rh bimetallic complexes containing the pyrazolyl-triazolyl *N,N'*-donor ligands (**2a-d**) under similar conditions. Additionally, significant intermetallic co-operativities were observed for complexes **6-8**, with calculated cooperativity indexes of between 2.8 and 7.9 and, in contrast, no significant co-operativity between metal centres was seen for the bi- and trimetallic Rh(I) complexes with pyrazolyl-triazolyl *N,N'*- donor ligands (PyT) under investigation here (**2a-d**, Table 2). Similarly, where the analogous Ir(I) complexes based on the *bis*(1-pyrazolyl)methane donor ligands were less

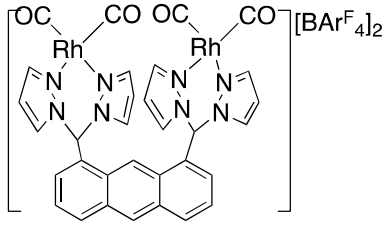
effective catalysts for the dihydroalkoxylation reaction under consideration here than their Rh(I) counterparts, with TOF ranging from 374 h^{-1} to 2468,[28b] the Ir complexes with *bis*(1-pyrazolyl)methane donor ligands[28b] were again much more efficient that the analogous Ir(I) catalysts (**3a-c**) presented here. The intermetallic cooperativity observed previously for the Ir(I) complexes with *bis*(1-pyrazolyl)methane donor ligands were much lower than those observed here for the complexes with the PyT ligands. These differences between the complexes containing the PyT dinitrogen donor ligands and the *bis*(1-pyrazolyl)methane donor ligands can be largely attributed to the difference in the nature of the ligand donors, where the PyT ligand system contains a triazolyl *N*-donor in place of one of the pyrazolyl *N*-donors. The triazolyl-**N**'3 donor is a somewhat stronger donor than the pyrazolyl-**N** donor and this is likely to be the cause of the decrease in catalytic reactivity of the complexes containing the pyrazolyl-triazolyl donor ligand, PyT, when compared with analogous complexes containing *bis*(1-pyrazolyl)methane ligands.[9] A similar effect has been previously observed by us in the case of catalyzed dihydroalkoxylation reactions using Rh(I) and Ir(I) complexes with *bis*(1-methylimidazol-2-yl)methane (bim) and bis(1-pyrazolyl)methane (bpm) donor ligands as catalysts, where the metal complexes with the more strongly donating bim donor ligands were not as effective as catalysts as the metal complexes with bpm donor ligands.[28a]

The Ir(III) hydride complex (**10**) by Crabtree *et al.* was also reported to be an efficient catalyst for the dihydroalkoxylation of **S**, however as the reaction was performed under somewhat different conditions, a direct comparison is difficult. Clearly, as can be seen in Table 3, the Au(I)-carbene complex (**11**) reported by Hashmi and co-workers,[32a] in the presence of $AgSbF_6$ to remove the chloride donor, is by far the most active complex reported for this transformation with the TOF of greater than 400,000 h^{-1}, using an extremely low catalyst loading of only 0.000001 mol% for each of the Au-carbene complex (**10**) and the silver salt $AgSbF_6$.

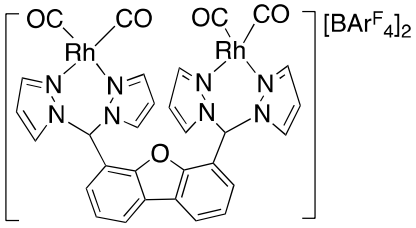
Table 3: Comparison of the efficiency of some representative metal complexes in the catalysed dihydroalkoxylation of alkynediol **S** to form a mixture of spiroketal products **P1** and **P2**.



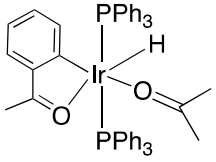
$[Rh_2(CO)_4(L_m)][BAr^F_4]_2$ (**6**)



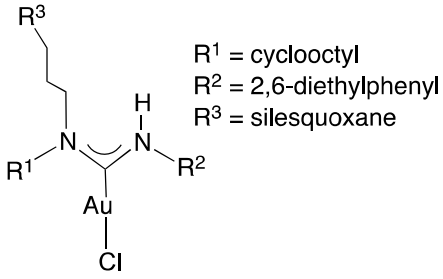
$[Rh_2(CO)_4(L_{Ant})][BAr^F_4]_2$ (**7**)



$[Rh_2(CO)_4(L_{Dib})][BAr^F_4]_2$ (**8**)



Ir(III) hydride (**9**)



Au-carbene (**10**)

Complexes	t, h [a]	TOF, h^{-1} [b]	Coop. Index[c]	Reference
$[Rh(bpm)(CO)_2][BAr^F_4]$	0.22	961	-	28b
$[Rh_2(CO)_4(L_m)][BAr^F_4]_2$ (**6**)	0.06	5988	4.2	28b
$[Rh_2(CO)_4(L_{Ant})][BAr^F_4]_2$ (**7**)	0.08	9522	7.9	28b
$[[Rh_2(CO)_4(L_{Dib})][BAr^F_4]_2$ (**8**)	0.99	4597	2.8	29
Ir(III) hydride (**9**)	5.0 [d]	-	-	30a
Au-carbene (**10**)	72[e]	440000[f]	-	32a

[a] Time at > 98% total conversion, reactions in $C_2D_2Cl_4$ at 100 °C. [b] TOF = (moles of products/moles of catalyst)/time (h) at 50% conversion. [c] Calculated using literature methods.[28b, 40] [d] Reaction at 60 °C in $CDCl_3$, 85% isolated yield. [e] 33% conversion at 72 hrs. [f] Calculated over the reaction time of 72 hours, in CD_2Cl_2 at 40 °C.

The Rh(III) and Ir(III) complexes [Rh(PyT)(Cp*)Cl][BAr_4^F], *m*-C_6H_4[Rh(PyT)(Cp*)Cl]$_2$[BAr^F_4]$_2$ (**4b**), [Ir(PyT)(Cp*)Cl][BAr^F_4] and *m*-C_6H_4[Ir(PyT)(Cp*)Cl]$_2$[BAr^F_4]$_2$ (**5b**) were not active as catalysts for this transformation (Table 2, entries 11-14) and complete conversion of the alkyne diols **S** was not achieved in these reactions. The Rh(III) complexes were more reactive than analogous Ir(III) complexes assessed here (Table 2, entries 11-14). In the cyclisation of 2-(5-hydroxypent-1-ynyl)benzyl alcohol (**S**) using Rh(III) and Ir(III) complexes here, **P1** was formed almost exclusively (with **P1**: **P2** ratios of up to 25 : 1). Recently, Fensterbank and co-workers reported that the Ir dimer [Cp*$IrCl_2$]$_2$ is highly effective as for the cycloisomerisation of homopropargylic diols to *O,O*-acetals at room temperature.[30b] This implies that the N-N' donor ligands used in this work might have a detrimental effect on the catalytic reactivity of the Cp*IrCl fragment for this cyclisation reaction. The decrease in reactivity could be due to the fact that the N-N' donor ligands can compete with the substrate for coordination sites on the metal centre in these Cp*Ir complexes.

Conclusions

A series of bi- and tri-topic bidentate pyrazolyl-triazolyl donor ligands were conveniently prepared in a one-pot approach using the Cu(I) catalysed alkyne-azide 'click' reaction. Homo bi- and trimetallic Rh and Ir complexes of these multi-topic ligands of the general formulae C_6H_{6-n}[(PyT)M(CO)$_2$]$_n$[BAr^F_4]$_n$ (M = Rh/Ir and n =2, 3) and C_6H_{6-n}[(PyT)MCp*Cl]$_n$[BAr^F_4]$_n$ (M = Rh/Ir and n = 2, 3) were also successfully prepared and fully characterised. Each of the complexes C_6H_{6-n}[(PyT)MCp*Cl]$_n$[BAr^F_4]$_n$ (M = Rh/Ir and n = 2, 3) exists as a mixture of two (n =2) and three (n = 3) diastereomers and it appears that the relative position of each bidentate donor arm of the ligands on the phenylene scaffold has some influence on the diastereomeric ratio. In a coordinating solvent (acetone), the disastereomers are in an exchange equilibrium with each other due to the solvent assisted epimerization of the chiral metal centre. This was confirmed by the observation of exchange peaks between resonances of different diastereomers in the ^{1}H-^{1}H NOESY in acetone-d_6.

The epimerization process observed here could have significant implications when using chiral Cp*Rh/Cp*Ir complexes in asymmetric catalysis. The single crystal X-ray structures of complexes **2b-c** and **4a**. show each of the bidentate ligands coordinates to the metal centre to form a distorted boat conformation. The intermetallic distances in these structures vary from 8.66 Å to 15.17 Å.

On testing all of the complexes synthesized here as catalysts for the dihydroalkoxylation of the alkyne diol 2-(5-hydroxypent-1-ynyl)benzyl alcohol (**S**), the Rh(I) dicarbonyl complexes **2a-d** were the most active catalysts, with a TOF of 2052 h^{-1} observed on using the trimetallic complex **2d**. In comparison with some of the most active catalysts that our group and others have developed for the dihydroalkoxylation reaction of alkynes, the catalysts based on pyrazolyl-triazolyl *N-N'* donor ligands have a lower activity for this transformation, and display different trends in terms of intermetallic cooperativity. The activity trend of the complexes with PyT ligands for the cyclisation of **S** can be grouped as Rh(I) > Ir(I) >> Rh(III) > Ir(III). The Ir(I) complexes are moderately active whereas the Rh(III) and Ir(III) complexes are ineffective catalysts for promoting the dihydroalkoxylation reaction under investigation here. Significant enhancement in activity was observed on using the multimetallic Ir complexes **3a-d** as catalysts relative to that of the monometallic complex for the same reaction, leading to high levels of intermetallic cooperativity. In contrast, no significant intermetallic cooperativity in catalyst activity for the dihydroalkoxylation reaction was observed on using the Rh multimetallic complexes **2a-d** when compared with their monometallic counterparts.

Experimental

General consideration

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. [$[RhCl(CO)_2]_2$,[41] $[IrCl_2Cp^*]_2$,[42] $[RhCl_2Cp^*]_2$,[42] $NaBAr^F_4$, [43] 1-propargylpyrazole[44] were prepared using literature methods.

For the purposes of air sensitive manipulations and in the preparation of air sensitive complexes, *n*-pentane and dichloromethane and were dispensed from a PuraSolv solvent purification system. 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. Dimethylsulfoxide was dried and stored over activated 4 Å molecular sieves.

^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 glove-box or by vacuum transfer of deuterated solvents into NMR tubes fitted with a Young's Teflon valve. For air sensitive NMR samples CD_2Cl_2, $CDCl_3$ were distilled over calcium hydride. Acetone-d_6 was distilled from calcium sulfate.

Infrared spectra were measured using a Nicolet 380 Avatar FTIR spectrometer as solutions in

dichloromethane. Melting points were measured using a Stanford Research Systems Optimelt melting point apparatus in glass capillaries and are un-corrected. Microanalyses were carried out at the Campbell Micro-analytical Laboratory, University of Otago, New Zealand or at The Research School of Chemistry, Australian National University, Canberra, Australia . Mass spectra were acquired using a Thermo LTQ Orbitrap XL located in the Bioanalytical Mass Spectrometry Facility (BMSF). M is defined as the molecular weight of the neutral compound of interest or cationic fragment for cationic metal complexes.

Synthesis of Ligands

The synthesis of *o*-$C_6H_4(PyT)_2$ (**1a**) is presented here. The syntheses of *m*-$C_6H_4(PyT)_2$ (**1b**); *p*-$C_6H_4(PyT)_2$ (**1c**) and *1,3,5*-$C_6H_3(PyT)_3$ (**1d**) were conducted in a similar fashion and are provided in the electronic supporting information (ESI).

Synthesis of o-$C_6H_4(PyT)_2$ (1a)

Dimethylsulfoxide (20 mL) was added to a Schlenk flask containing sodium azide (0.715 g, 11.0 mmol) under an atmosphere of nitrogen. The reaction mixture was stirred at room temperature for one hour. 1,2-*Bis*(bromomethyl)benzene (1.32 g, 5.00 mmol) was added to the reaction mixture and the slightly yellow reaction mixture was stirred at room temperature for three days.

1-Propargylpyrazole (1.06 g, 10.0 mmol) was added to the reaction mixture. The reaction mixture was deoxygenated by placing the flask under vacuum (house vacuum ca. 20 mmHg) and back-filling with nitrogen (x3). Sodium L-ascorbate (0.400 g, 2.00 mmol) and $CuSO_4.5H_2O$ (0.125 g, 0.50 mmol, 10 mol%) were added and the yellowish brown reaction mixture was stirred for two days at room temperature.

The reaction mixture was poured into a conical flask containing aqueous Na_2EDTA (0.025 M, 200 mL) and was stirred rigorously for 2 hours. The aqueous solution was extracted with dichloromethane (3 x 80 mL). The combined organic layer was washed with saturated aqueous Na_2EDTA solution (3 x 20 mL), water (2 x 20 mL) and dried over anhydrous sodium sulfate, filtered and the solvent was removed *in vacuo* to yield a thick oil which solidified upon standing.

The crude product was recrystallised from ethanol/water to afford a very pale cream solid. Yield: 1.41 g, 71%.

m.p. 139-142 °C.

Elemental Analysis, Found: C, 59.63, H, 5.14 and N, 34.81; Calculated for $C_{20}H_{20}N_{10}$: C, 59.99; H, 5.03 and N, 34.98%.

HR-MS (ESI^+, MeOH): *m/z* (%): 423.3333 (100%, $[M+Na]^+$) amu.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.51 (d, ^3J = 2.0 Hz, 2H, Pz-**H5**), 7.50 (d, ^3J = 2.0 Hz, 2H, Pz-**H3**), 7.39 (s, 2H, Tz-**H**5'), 7.36 (m, 2H, Ar-**H3** and **H6**), 7.20 (m, 2H Ar-**H**4 and **H**5), 6.25 (apparent t, 2H, Pz-**H4**), 5.56 (s, 4H, Pz-NC**H**$_2$), 5.40 (s, 4H, Pz-NC**H**$_2$) ppm.

^{13}C{1H} NMR (150 MHz, $CDCl_3$): δ 144.21 (Tz-**C4'**), 139.96 (Pz-**C3**), 133.13 (*ipso*-**C** of C_6H_4), 130.56 (**C4** and **C5** of C_6H_4), 130.05 (**C3** and **C6** C_6H_4), 129.64 (Pz-**C**5), 106.25 (**C**4), 51.40 (Tz-N**C**H_2), 47.41 (Pz-N**C**H_2) ppm.

Synthesis of $Rh(CO)_2$ complexes

The synthesis of *o*-$C_6H_4[(PyT)Rh(CO)_2]_2[BAr^F{}_4]_2$ (**2a**) is presented here. The syntheses of *m*-$C_6H_4[(PyT)Rh(CO)_2]_2[BAr^F{}_4]_2$ (**2b**), *p*-$C_6H_4[(PyT)Rh(CO)_2]_2[BAr^F{}_4]_2$ (**2c**) and *1,3,5*-$C_6H_3[(PyT)Rh(CO)_2]_3[BAr^F{}_4]_3$ (**2d**) were conducted in an analogous fashion and are provided in the ESI.

Synthesis of o-$C_6H_4[(PyT)Rh(CO)_2]_2[BAr^F{}_4]_2$ (2a)

Dichloromethane (25 mL) was added to a mixture of $[Rh(Cl)(CO)_2]_2$ (0.039 g, 0.10 mmol) and *o*-$C_6H_4(PyT)_2$ (**1a**) (0.040 g, 0.10 mmol) in a Schlenk flask under an atmosphere of argon. The yellow solution obtained was stirred at room temperature for 30 minutes. $NaBAr^F{}_4$ (0.177 g, 0.20 mmol) was added and the colour of the reaction solution changed to orange with some cloudy white solid. The reaction mixture was filtered through a pad of Celite and the orange yellow filtrate was reduced until about 2-3 mL of solution was left. Pentane (ca. 40 mL) was added to the filtrate with vigorous stirring and the thick oil-solid was collected by filtration and washed with pentane (3 x 5

mL) and dried *in vacuo* to afford a yellow solid. Yield: 0.209 g, 86%; m.p. 67-79 °C (melted and then decomposed).

Elemental Analysis, Found: C, 43.32; H, 1.88 and N, 5.76. Calculated for $C_{88}H_{44}B_2F_{48}N_{10}O_4Rh_2$: C, 43.23; H, 1.81; N, 5.73 %.

HR-MS (ESI, MeOH): *m/z* (%, assignment): 1581.0396 (10, $[M+BAr^F{}_4]^+$), 531.0852 (100, [Ligand + RhCO]$^+$) amu.

FT-IR (dcm): ν 2109 (s, ν CO), 2051 (s, ν CO) cm^{-1}

^{1}H NMR (600 MHz, acetone-d_6): δ 8.62 (s, 2H, Tz-**H**5'), 8.28 (s, 2H, Pz-**H**5), 8.27 (s, 2H, Pz-**H**3), 7.79 (br m, 16H, *ortho*-C**H** of $BAr^F{}_4$), 7.67 (br s, 8H, *para*-C**H** of $BAr^F{}_4$), 7.60 (m, 2H, C_6H_4-**H**3 & **H**6), 7.56 (m, 2H, C_6H_4-**H**4 & **H**5), 6.71 (apparent t, ^3J = 2.5 Hz, 2H, Pz-**H**4), 6.24 (s, 4H, Tz-NC$\mathbf{H}_2$), 5.90 (s, 4H, Pz-NC$\mathbf{H}_2$) ppm.

^{13}C{^{1}H} NMR (150 MHz, acetone-d_6): δ 183.76 (br d, $^1J_{Rh\text{-}C}$ ~ 71 Hz, Rh-**C**O), 162.60 (q, $^1J_{B\text{-}C}$ = 49.4 Hz, *ipso*-**C**-B of $BAr^F{}_4$), 147.88 (Pz-**C**3), 141.96 (Tz-**C**4'), 136.95 (Pz-**C**5), 135.55 (*ortho*-**C** of $BAr^F{}_4$), 133.49 (C_6H_4**C**1 & **C**2), 132.11 (C_6H_4**C**3 & **C**6), 131.44 (C_6H_4**C**4 & **C**5), 130.02 (q, $^2J_{F\text{-}C}$ = 30.0 Hz, *ipso*-**C** of **C**CF_3), 126.50 (Tz-**C**4'), 125.39 (q, ^1J = 272.1, **C**F_3), 118.45 (*para*-**C** of $BAr^F{}_4$), 108.93 (Pz-**C**4), 53.74 (Tz-N**C**H_2), 46.16 (Pz-N**C**H_2) ppm.

Synthesis of Ir(CO)$_2$ complexes

The synthesis of *o*-$C_6H_4[(PyT)Ir(CO)_2]_2[BAr^F{}_4]_2$ (**3a**) is presented here. The syntheses of *m*-$C_6H_4[(PyT)Ir(CO)_2]_2[BAr^F{}_4]_2$ (**3b**), *p*-$C_6H_4[(PyT)Ir(CO)_2]_2[BAr^F{}_4]_2$ (**3c**) and *1,3,5*-$C_6H_3[(PyT)Ir(CO)_2]_3[BAr^F{}_4]_3$ (**3d**) were conducted in an analogous fashion and are provided in the ESI.

Synthesis of o-$C_6H_4[(PyT)Ir(CO)_2]_2[BAr^F{}_4]_2$ (3a)

Dichloromethane (20 mL) was added to a mixture of *o*-$C_6H_4(PyT)_2$ (**1a**) (0.020 g, 0.050 mmol) and $[Ir(Cl)(COD)]_2$ (0.034 g, 0.050 mmol) in a flask under an atmosphere of argon. The bright yellow solution obtain was stirred at RT for 30 minutes and $NaBAr^F{}_4$ (0.090 g, 0.10 mmol)

was added. The slightly cloudy yellow solution was stirred at RT at 1 hour, filtered through a pad of Celite and rinsed with dichloromethane (2 x 15 mL). The combined organic layer was deoxygenated *via* freeze-pump-thaw (x2) and was placed under at atmosphere of carbon monoxide and stirred overnight. The solvent was reduced to approximately 3 mL and pentane (25 mL) was added to the reaction mixture with vigorous stirring. The yellow solid and thick oil residue obtained was collected by filtration, washed with pentane (3 x 5 mL) and dried *in vacuo* to afford **3a** as an orange solid. Yield: 0.098 g, 75%.

m.p. 73-76 °C.

FT-IR (dcm): ν 2099 (s, νCO), 2034 (s, νCO) cm^{-1}.

Elemental Analysis, Found: C, 40.21; H, 1.76; N, 5.41. Calculated for $C_{88}H_{44}B_2F_{48}Ir_2N_{10}O_4$: C, 40.29; H, 1.69; N, 5.34 %.

HR-MS (ESI, MeOH): *m/z* (%, assignment): 1759.1572 (100, $[M+BAr^F{}_4]^+$), 649.1388 (65, $[M – Ir(CO)_2]^+$), 448.0471 (28, $[M]^{2+}$) amu.

^{1}H NMR (600 MHz, acetone-d_6): δ 8.74 (s, 2H, Tz-**H**5'), 8.46 (d, ^3J = 2.3 Hz, 2H, Pz-**H**3), 8.39 (d, ^3J = 2.5 Hz, 2H, Pz-**H**5), 7.79 (br m, 16H, *ortho*-C**H** of $BAr^F{}_4$), 7.70 (m, 2H, C_6H_4-**H**3 & **H**6), 7.67 (br s, 8H, *para*-C**H** of $BAr^F{}_4$), 7.60 (m, 2H, C_6H_4-**H**4 & **H**5), 6.82 (apparent t, ^3J = 2.5 Hz, 2H, Pz-**H**4), 6.29 (s, 4H, Tz-NC**H**$_2$), 6.00 (s, 4H, Pz-NC**H**$_2$) ppm.

^{13}C{^{1}H} NMR (150 MHz, acetone-d_6): δ 171.88 (**C**O), 171.20 (**C**O), 162.62 (q, $^1J_{B\text{-}C}$ = 49.8 Hz, *ipso*-**C**-B of $BAr^F{}_4$), 149.08 (Pz-**C**3), 141.69 (Tz-**C**4'), 137.74 (Pz-**C**5), 135.56 (*ortho*-**C** of $BAr^F{}_4$), 133.31 (C_6H_4 **C**1 & **C**2), 132.64 (C_6H_4 **C**3 & **C**6), 131.66 (C_6H_4 **C**4 & **C**5), 130.04 (q, $^2J_{F\text{-}C}$ = 31.0 Hz, *ipso*-**C** of **C**CF_3), 126.88 (Tz-**C**4'), 125.38 (q, $^1J_{F\text{-}C}$ = 270.3, **C**F_3), 118.47 (*para*-**C** of $BAr^F{}_4$), 108.93 (Pz-**C**4), 54.13 (Tz-N**C**H_2), 46.52 (Pz-N**C**H_2) ppm.

Synthesis of Rh(Cp*) complexes

The synthesis of *o*-$C_6H_4[(PyT)Rh(Cp^*)Cl]_2[BAr^F{}_4]_2$ (**4a**) is presented here. The syntheses of *m*-$C_6H_4[(PyT)Rh(Cp^*)Cl]_2[BAr^F{}_4]_2$ (**4b**), *p*-$C_6H_4[(PyT)Rh(Cp^*)Cl]_2[BAr^F{}_4]_2$ (**4c**) and

1,3,5-C_6H_3[(PyT)Rh(Cp*)Cl]$_3$[BAr^F_4]$_3$ (**4d**) were conducted in an analogous fashion and are provided in the ESI.

Synthesis of o-C$_6$H$_4$[(PyT)Rh(Cp*)Cl]$_2$[BAr$^F_4$]$_2$ (4a)

Dichloromethane (20 mL) was added to a mixture of [Rh(Cp*)Cl_2]$_2$ (0.031 g, 0.05 mmol) and *o*-C_6H_4(PyT)$_2$ (**1a**, 0.020 g, 0.05 mmol) in a flask under argon. The orange solution obtained was stirred for 30 minutes and $NaBAr^F_4$ (0.090 g, 0.10 mmol) was added to the reaction mixture. The slightly orange reaction mixture was stirred under argon at RT overnight. The reaction mixture was filtered through a pad of Celite, rinsed with dichloromethane (2 x 15 mL) and the filtrate was reduced until approximately 2 mL of solvent remained. Pentane (25 mL) was added to the reaction mixture and the orange precipitate formed was collected by filtration and washed with pentane (2 x 5mL). Yield: 0.124 g, 93%; m.p. 98-103 °C (melted and turned red). The product is a mixture of two diastereoisomers, **I1** and **I2** (**I1** : **I2** = 1.16 : 1.00).

Elemental Analysis: Found, C, 45.88; H 2.71 and N, 5.10. Calculated for: $C_{104}H_{74}B_2Cl_2F_{48}N_{10}Rh_2.CH_2Cl_2$: C, 45.71, H, 2.78 and N, 5.08 %.

HR-MS (MeOH): *m/z* (%, assignment): 1809.2349 (100, $[M + BAr^F_4]^+$), 473.0861 (12, $[M]^{2+}$) amu.

^{1}H NMR (acetone-d_6, 600 MHz): δ 8.60 (**I1**, s, 2H, Tz-**H**5'), 8.45 (**I2**, s, 2H, Tz-**H**5'), 8.12 (**I1**, d, ^3J = 2.4 Hz, 2H, Pz-**H**5), 8.04 (**I2**, d, ^3J = 2.4 Hz, 2H, Pz-**H**5), 7.95 (**I1**, d, ^3J = 2.4 Hz, 2H, Pz-**H**3), 7.94 (**I2**, d, ^3J = 2.4 Hz, 2H, Pz-**H**3), 7.79 (**I1** + **I2**, br m, 16H + 16H, *o*-C**H** of BAr^F_4), 7.67 (**I1** + **I2**, br, 8H + 8H, *p*-C**H** of BAr^F_4), 7.46-7.38 (**I1** + **I2**, m, 4H + 4H, C_6H_4-**H**), 6.60 (**I1,** apparent t, ^3J = 2.4 Hz, Pz-**H**4), 6.58 (**I2,** apparent t, ^3J = 2.4 Hz, Pz-**H**4), 6.27 (**I1**, d, ^2J = 15.7 Hz, 1H, Tz-NC**H**H), 6.19 (**I2**, d, ^2J = 15.5 Hz, 1H, NC**H**H), 6.14-6.11 (**I1** + **I2**, m, 3H, Tz-NC**H**H and NC**H**H), 6.04 (**I1**, d, ^2J = 16.3 Hz, 1H, NCH**H**), 5.43 (**I1**, d, ^2J = 16.3 Hz, 1H, Pz-NCH**H**), 5.40 (**I2**, d, ^2J = 16.2 Hz, 1H, Pz-NCH**H**), 1.77 (**I2**, 15H, CC**H**$_3$), 1.74 (**I1**, 15H, CC**H**$_3$) ppm.

^{13}C{^{1}H} NMR (acetone-d_6, 150 MHz): δ 162.60 (**I1 + I2**, q, $^1J_{B\text{-}C}$ = 49.50 Hz, *ipso*-**C**B of BAr^F_4), 146.03 (**I1**, Pz-**C3**), 145.95 (**I2**, Pz-**C3**), 141.80 (**I1**, Pz-**C4'**), 141.71 (**I2**, Pz-**C4'**), 135.91 (**I1** + **I2**, Pz-**C**5), 135.55 (br s, *o*-**C**H of BAr^F_4), 134.30, 134.05 (**I1** + **I2**, *ipso*-**C** of C_6H_4 (last two

resonances), 131.53, 130.89, 130.76 (last three resonances, **C**H of *o*-C_6H_4), 130.02 (q, $^2J_{F\text{-}C}$ = 31.8 Hz, CC**F**$_3$), 126.59 (**I1**, Tz-**C5**'), 126.37 (**I2**, Tz-**C5**'), 125.41 (**I1** + **I2**, q, $^1J_{F\text{-}C}$ = 271.5 Hz, **C**F_3), 118.46 (**I1** + **I2**, *p*-**C**H of BAr^F_4), 108.87 (**I1**, Pz-**C**4), 108.80 (**I2**, Pz-**C**4'), 98.06 (**I1**, **C**CH_3 (Cp*)), 98.00 (**I2**, **C**CH_3 (Cp*)), 53.24 (**I1** + **I2**, Tz-N**C**H_2), 45.82 (**I1**, Pz-N**C**H_2), 45.72 (**I2**, PzN**C**H_2), 9.36 (**I1** + **I2**, **C**H_3) ppm.

Synthesis of Ir(Cp*) Complexes

The synthesis of *o*-C_6H_4[(PyT)Ir(Cp*)Cl]$_2$[BAr^F_4]$_2$ (**5a**) is presented here. The syntheses of *m*-C_6H_4[(PyT)Ir(Cp*)Cl]$_2$[BAr^F_4]$_2$ (**5b**), *p*-C_6H_4[(PyT)Ir(Cp*)Cl]$_2$[BAr^F_4]$_2$ (**5c**) and *1,3,5*-C_6H_3[(PyT)Rh(Cp*)Cl]$_3$[BAr^F_4]$_3$ (**5d**) were conducted in an analogous fashion and are provided in the ESI.

Synthesis of o-C_6H_4[(PyT)Ir(Cp*)Cl]$_2$[BAr^F_4]$_2$ (5a)

Dichloromethane (15 mL) was added to a mixture of *o*-$C_6H_4(PyT)_2$ (**1a**, 0.020 g, 0.050 mmol) and [IrCp*Cl_2]$_2$ (0.040 g, 0.050 mmol) in a flask and the yellow reaction mixture was stirred for 30 minutes at RT. $NaBAr^F_4$ (0.090 g, 0.10 mmol) was added and the cloudy yellow solution was stirred for 1 hour at RT. The reaction mixture was filtered through a pad of Celite and rinsed with dichloromethane (2 x 15 mL). The combined organic layer was reduced to approximately 2 mL and pentane (20 mL) was added with rigorous stirring. The yellow thick oil and solid formed was collected by filtration, washed with pentane (2 x 5mL) and dried *in vacuo*. *o*-C_6H_4[(PyT)Ir(Cp*)Cl]$_2$[BAr^F_4]$_2$ (**5a**) was collected as a light yellow solid. Yield: 0.103 g, 73%; m.p. 102-106 °C. The product is a mixture of two diastereoisomers **I1** and **I2**, **I1** : **I2** = 1.10 : 1.00.

Elemental analysis; found: C, 43.72; H, 2.69 and N, 5.11; calculated for $C_{104}H_{74}B_2Cl_2F_{48}Ir_2N_{10}$: C, 43.79, H, 2.61 and N, 4.91 %.

HR-MS (MeOH): *m/z* (%, assignment): 1989.3486 (47, [M + BAr^F_4]$^+$), 563.1397 (100, [M]$^{2+}$) amu.

^{1}H NMR (acetone-d_6, 600 MHz): δ 8.63 (**I1**, s, 2H, Tz-**H**5'), 8.55 (**I2**, s, 2H, Tz-**H**5'), 8.14 (**I1**, d, ^3J = 2.4 Hz, 2H, Pz-**H**5), 8.09 (**I2**, d, ^3J = 2.4 Hz, 2H, Pz-**H**5), 7.90 (**I1**, d, ^3J = 2.3 Hz, 2H, Pz-**H**3), 7.89 (**I2**, d, ^3J = 2.3 Hz, 2H, Pz-**H**3), 7.79 (**I1** + **I2**, br m, 16H +16H, *o*-C**H** of BAr^F_4), 7.67 (**I1** + **I2**,

br s, 8H + 8H, *p*-C**H** of BAr^F_4), 7.48-7.37 (**I1** + **I2**, m, 4H + 4H, C**H** of C_6H_4), 6.65 (**I1**, apparent t, ^3J = 2.4 Hz, 2H, Pz-**H**4), 6.63 (**I2**, apparent t, ^3J = 2.4 Hz, 2H, Pz-**H**4), 6.28-6.11 (**I1** + **I2**, m, 6H + 6H, CH_2 (AB systems)), 5.29 (**I1**, d, ^2J = 15.8 Hz, 2H, Pz-NC**H**), 5.28 (**I2**, d, ^2J = 16.1 Hz, 2H, Pz-NC**H**), 1.73 (**I1**, s, 15H, CH_3), 1.70 (**I2**, s, 15H, CH_3) ppm.

$^{13}C\{^1H\}$ NMR (acetone-d_6, 150 MHz): δ 162.61 (**I1** + **I2**, q, $^1J_{B\text{-}C}$ = 49.5 Hz, *ipso*-**C**B of BAr^F_4), 145.83 (**I1**, Pz-**C**3), 145.80 (**I2**, Pz-**C**3), 140.91 (**I1**, Tz-**C**4'), 140.86 (**I2**, Tz-**C**4'), 135.64 (**I1** and/or **I2**, Tz-**C**5), 135.55 (*o*-**C**H of BAr^F_4), 134.24 (**I1**/**I2**, *ipso*-**C** of C_6H_4), 134.06 (**I1**/**I2**, *ipso*-**C** of C_6H_4), 131.32 (**I1**/**I2**, **C**H of C_6H_4), 130.95 (**I1**/**I2**, **C**H of C_6H_4), 130.03 (**I1** + **I2**, q, $^2J_{F\text{-}C}$ = 31.9 Hz, **C**CF_3), 126.51 (**I1**, Tz-C5'), 126.36 (**I2**, Tz-C5'), 125.39 (**I1** + **I2**, q, $^1J_{F\text{-}C}$ = 270.7 Hz, **C**F_3) 118.46 (**I1** + **I2**, *p*-C**H** of BAr^F_4), 109.15 (**I1**, Pz-**C**4), 109.10 (**I2**, Pz-**C**4), 89.88 (**I1** + **I2**, **C**CH_3), 53.38 (**I1**, Tz-N**C**H_2), 53.33 (**I2**, Tz-N**C**H_2), 46.23 (**I1**, Pz-N**C**H_2), 46.19 (**I2**, Pz-N**C**H_2), 9.11 (**I1** + **I2**, C**C**H_3) ppm.

X-ray crystallography: experimental details for X-ray crystallographic determination are provided in the electronic supporting information. Crystal data for all of the single crystal X-ray structures are provided in Tables S3 and S4 of the ESI.

Procedure for catalytic reactions: Catalysed dihydroalkoxylation reactions were performed in NMR tubes fitted with concentric Teflon (Youngs) valves under an inert atmosphere as reported previously.[28b] Specifically for the catalytic experiments reported in this paper the procedure is as follows: the substrate (2-(5-hydroxypent-4-ynyl)benzyl alcohol (**S**, 35.0 ± 1.0 mg, 0.184 ± 0.005 mmol)) and the catalyst (1.0, 0.50 or 0.33 mol% for monometallic, bimetallic or trimetallic complexes respectively) were weighted into an NMR tube. $C_2D_2Cl_4$ (0.6 ml) was then added to the NMR tube under an atmosphere of nitrogen or argon. The NMR tube was sealed and cooled in an ethanol/acetone liquid nitrogen slush bath until the reaction was started. The reaction was conducted at 100°C inside the NMR spectrometer or in an oil bath if prolonged heating was required. The reaction progress was monitored by 1H NMR spectroscopy at regular intervals. The characterization of products was confirmed by comparison to literature data.[27b] The conversion of

the substrate to products was determined by integration of the product resonances (at 4.70 (doublet) ppm for **P1**; 5.12 (doublet or broad) and/or 5.19 (doublet or broad) for **P2**) relative to the substrate resonance (singlet at 4.84 ppm) in the ^{1}H NMR spectra. The turnover frequency (TOF) was calculated as the number of moles of product/moles of catalyst/h and was calculated at the point of 50% conversion of the substrate.

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Electronic Supporting Information: Synthetic procedures and characterisation data for compounds **1c-d**; **2c-d**; **3c-d**; **4c-d** and **5c-d**; Table S1 provides the νCO and ^{13}C δ of complexes **2a-d** and **3a-d**; Table S2: the ratios of different stereoisomers of complexes **4a-d**; **5a-d**. Experimental for X-ray crystallography and crystal data for compounds **1b-c**, **2b-c**, **4a**, **6** and **7** (CCDC number 966297-966300, 966302, 966304-966305) are also included here.

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Table of Contents Entry

Bi- and trimetallic Rh and Ir complexes were successfully synthesised from multitopic ‘click derived’ ligands and shown to catalyse the dihydroalkoxylation of alkynes.