Weakly coordinating counter-ions for highly efficient catalysis of intramolecular hydroamination†

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A series of cationic rhodium(I) and iridium(I) complexes of the type $[M(L^{\frown}L)(C_2)]BAr^{F}{}_{24}$ (where M = Rh or Ir, L^L = *bis*(pyrazol-1-yl)methane (bpm), *bis*(*N*-methylimidazol-2-yl)methane (bim) or 1-(2-(diphenylphosphino)ethyl)-3,5-diphenylpyrazole (Ph_2PyP), C_2 = 1,5-cyclooctadiene (COD) or $(CO)_2$ and $BAr^{F}{}_{24}$ = *tetrakis*[3,5-*bis*(trifluoromethyl)phenyl]borate) were synthesised in good yields. The solid-state structure of a number of complexes, including $[Ir(Ph_2PyP)(COD)]BAr^{F}{}_{24}$, $[Ir(bpm)(COD)]BAr^{F}{}_{24}$ and $[Ir(bim)(COD)]BAr^{F}{}_{24}$ was determined using X-ray crystallography. The efficiency of the complexes as catalysts for the intramolecular hydroamination of 4-phenyl-3-butyn-1-amine, 4-pentyn-1-amine and 2-(2-phenylethynyl)aniline was established. The incorporation of the $BAr^{F}{}_{24}^{-}$ counter-ion in the Rh(I) and Ir(I) complexes was found to significantly improve the catalytic activity of the complexes, compared to the analogous Rh(I) and Ir(I) complexes containing BPh_4^{-} as the counter-ion. Excellent conversions were achieved for the cyclisation of 2-(2-phenylethynyl)aniline to 2-phenylindole using $[Rh(bpm)(CO)_2]BAr^{F}{}_{24}$ as a catalyst. The use of a microwave reactor for enhancing the catalysed reactions was also investigated.

Introduction

Nitrogen containing heterocycles are sub-units in biologically active compounds which are important in the pharmaceutical and agrochemical industries. Their synthesis *via* convenient and direct approaches is highly desirable. The hydroamination reaction, which involves the direct addition of an N–H bond to a carbon–carbon multiple bond, is an atom-efficient pathway for the formation of N–C bonds.[1,2] Although thermodynamically favorable, the high activation barrier for the hydroamination reaction under normal conditions means a catalyst is required to make the reaction practical.[1–3] Catalysed cyclisation of alkynyl- and alkenylamines *via* intramolecular hydroamination has shown great potential in the energy and atom efficient synthesis of *N*-heterocycles.[1,2] Catalytic systems employed for the intramolecular hydroamination reaction include calcium,[4] lanthanides,[5,6] actinides[7] and both early[8] and late[9–13] transition metals. Late transition metal complexes have an advantage over lanthanides and early transition metal complexes due to their lower oxophilicity, which means they are less sensitive to moisture and air and have a greater functional group tolerance.

A number of rhodium and iridium complexes have been reported to effectively catalyse intramolecular hydroamination.[14–23] In particular, Rh(I) and Ir(I) catalysts have been used to promote the formation of synthetically useful *N*-heterocycles *via* the cyclisation of alkynylamines.[17–23] The efficiency of the catalysis was found to be significantly affected by substitution of the alkyne moiety. Work within our research group has centered on the intramolecular hydroamination of a range of different alkynylamines, such as 4-pentyn-1-amine (**1**), which yields 2-methyl-1-pyrroline (**2**), using rhodium(I) and iridium(I) catalysts with the general formula $[M(L^{\frown}L)(C_2)]BPh_4$ where L^L is a bidentate *N,N*-, *P,C*-, *C,C*- or *P,N*-donor ligand (N^N,[17,20,21,23] P^C,[19] C^C[22] or P^N[18]) and C_2 is either two carbon monoxide (CO) co-ligands or a chelating 1,5-cyclooctadiene (COD) ligand. Of this group of complexes the most efficient catalysts for the formation of **2** were found to be iridium(I) complexes containing either a combination of P^N and COD ligands,[18] or N^N and CO ligands,[17] with conversions of 98% in less than 1.5 hours at 60 °C. Catalysts containing a mixed *P,N*-donor ligand, such as **3b**, promoted turnover frequencies ranging from 1200 to 3100 h^{-1} for the cyclisation of **1** to **2** (Fig. 1).[18] These turnover frequencies are among the highest of any rates reported to date for the catalysed cyclisation of **1** by a late transition metal catalyst.[9,13]

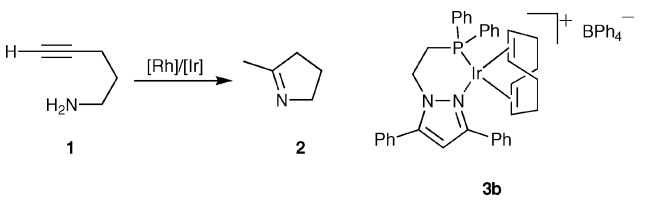

Fig. 1 Intramolecular hydroamination with Rh(I) and Ir(I) catalysts.

The nature of the counter-ion is known to strongly influence the efficiency of ionic metal complexes as catalysts.[24] Tetraphenylborate (BPh_4^{-}) is larger and more weakly co-ordinating than other

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anions, such as PF_6^- and BF_4^-, and has been commonly utilised as a counter-ion for charged metal catalysts as weak coordination is highly desirable for catalytic systems.[25] We have previously demonstrated that Rh(I) complexes incorporating the BPh_4^- counter-ion are more efficient catalysts for intramolecular hydroamination than those incorporating PF_6^- or BF_4^-.[21] The $BAr^F{}_{24}^-$ (*tetrakis*[3,5-*bis*(trifluoromethyl)phenyl]borate) anion, and other fluorinated analogues of BPh_4^-, have properties such as low nucleophilicity, chemical inertness, high solubility and weak co-ordinating strength,[26] all of which can improve catalyst efficiency. For example, studies of iridium phosphino–oxazole (*P,N*-donor ligands) complexes as enantioselective hydrogenation catalysts have shown that charged complexes with the $BAr^F{}_{24}^-$ counter-ion (and other fluorinated analogues of BPh_4^-) are more efficient catalysts than complexes containing the PF_6^-, BF_4^- and BPh_4^- anions.[27–31] Complexes containing $BAr^F{}_{24}^-$ as a counter-ion also appear to be more moisture tolerant[27–29] and, in general, exhibit a longer lifetime and higher catalytic activity.[30,31]

Here we present the synthesis of a range of rhodium(I) and iridium(I) complexes containing the $BAr^F{}_{24}^-$ counter-ion. The activity of these complexes as catalysts for the intramolecular hydroamination reaction was tested, and compared to the catalytic activity of previously studied BPh_4^- analogues.

Results and discussion

Synthesis of metal complexes

Rhodium(I) and iridium(I) complexes bearing COD and the bidentate ligands *bis*(pyrazol-1-yl)methane (bpm), *bis*(*N*-methylimidazol-2-yl)methane (bim) or 1-(2-(diphenylphosphino)ethyl)-3,5-diphenylpyrazole (Ph_2PyP) were prepared using either $[MCl(COD)]_2$ or $[M(COD)_2]BAr^F{}_{24}$ (M = Rh or Ir) as starting materials (Fig. 2). The addition of a solution of both the bidentate ligand and $NaBAr^F{}_{24}$ to a solution of the metal precursor $[MCl(COD)]_2$ (M = Rh or Ir) in tetrahydrofuran yielded $[M(N^{\frown}Y)(COD)]BAr^F{}_{24}$ (where N^Y = Ph_2PyP, M = Ir (**3a**); N^Y = bpm, M = Ir (**4a**), M = Rh (**5a**); or N^N = bim, M = Ir (**6a**), M = Rh (**7a**)) as yellow or orange crystalline solids in moderate to high yields (54–82%). Complexes **4a–7a** were also synthesised by stirring a tetrahydrofuran solution of the *N,N*-donor ligand and $[M(COD)_2]BAr^F{}_{24}$ (M = Rh or Ir) for 1 hour. The overall yields of the Ir complexes **4a** and **6a** were somewhat improved using this second method (76% and 58% from $[IrCl(COD)]_2$, respectively) when compared to the synthesis directly from $[IrCl(COD)]_2$ (66% and to 54%, respectively).

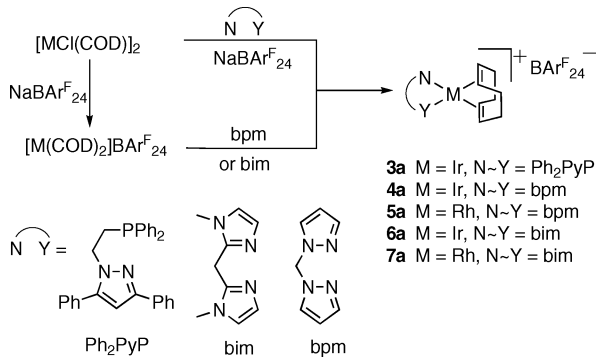
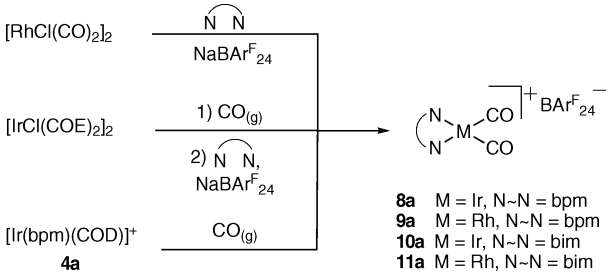


Fig. 2 Synthesis of Ir(I) and Rh(I) complexes containing COD and the bidentate ligands Ph_2PyP, bpm and bim (**3a–7a**).

Rhodium(I) and iridium(I) complexes bearing two carbon monoxide ligands and the *N,N*-donor ligands bpm and bim were prepared *via* the addition of a solution containing both the ligand and $NaBAr^F{}_{24}$ to a solution containing either the metal precursor $[RhCl(CO)_2]_2$, or the *in situ* generated metal complex "$[IrCl(CO)_2]_n$" (prepared by stirring a solution of $[IrCl(COE)_2]_2$ (COE = cyclooctene) under an atmosphere of $CO_{(g)}$) (Scheme 1). The complexes $[M(N^{\frown}N)(CO)_2]BAr^F{}_{24}$ (N^N = bpm, M = Ir (**8a**), M = Rh (**9a**); or N^N = bim, M = Ir (**10a**), M = Rh (**11a**)) were isolated as yellow crystalline solids in good yields (62–76%). The BPh_4^- analogues of Ir complexes **8a** and **10a**, $[Ir(bpm)(CO)_2]BPh_4$ (**8b**) and $[Ir(bim)(CO)_2]BPh_4$ (**10b**), have previously been synthesised by the displacement of the COD ligand of $[Ir(N^{\frown}N)(COD)]BPh_4$ (N^N = bpm or bim) with carbon monoxide.[21,32] Complex **8a** was also synthesised from **4a** *via* this method with a lower yield than that obtained for the synthesis of **8a** from $[IrCl(COE)_2]_2$ (Scheme 1).



Scheme 1

Single crystals of $[Ir(Ph_2PyP)(COD)]BAr^F{}_{24}$ (**3a**), $[Ir(bpm)(COD)]BAr^F{}_{24}$ (**4a**), $[Rh(bpm)(COD)]BAr^F{}_{24}$ (**5a**), $[Ir(bim)(COD)]BAr^F{}_{24}$ (**6a**), $[Ir(bim)(CO)_2]BAr^F{}_{24}$ (**10a**), and $[Rh(bim)(CO)_2]BAr^F{}_{24}$ (**11a**) suitable for X-ray diffraction analysis were obtained by the slow diffusion of *n*-hexane into a concentrated solution of the respective complex in dichloromethane.† The ORTEP diagrams of the cations of **3a**, **4a** and **6a** are shown in Fig. 3. The cations of the solid-state structures of the $BAr^F{}_{24}^-$ complexes **5a**, **10a** and **11a** exhibit the same molecular shape found previously for complexes which contain the identical cations, $[Rh(bpm)(COD)]ClO_4$,[33] $[Ir(bim)(CO)_2]BPh_4$[21] (**10b**) and $[Rh(bim)(CO)_2]BPh_4$[34] (**11b**), respectively.

The crystals of **4a** and **6a** consisted of two crystallographically independent but almost identical sets of ions. Selected bond lengths and bond angles for the solid-state structures of the cation of **3a** and one of the cations of each **4a** and **6a** are given in Table 1. The Ir coordination spheres of **3a**, **4a** and **6a** are essentially square planar (regarding COD as a bidentate chelator). The six-membered metallocycle of **3a**, **4a** and **6a**, formed from the chelate *N,N*-donor ligand or *P,N*-donor ligand, adopts a distorted boat conformation in all three complexes. The Ir-N, Ir-P and Ir-C bond lengths are comparable to those observed in the structures of rhodium(I) and iridium(I) complexes containing bpm, bim or phosphino-pyrazole ligands previously reported.[18,21,22,32-37]

The Ir–C bond lengths of the carbon atoms *trans* to P in **3a** (see Fig. 3) are significantly longer than the Ir–C bond lengths of the carbon atoms *trans* to N (~2.23 Å compared to ~2.13 Å, respectively) which can be explained by the high

Table 1 Selected bond angles and bond lengths for the solid state structures of the cations of **3a**, **4a** and **6a**

Bond Lengths (Å)	3a	4a	6a	Bond Angles (°)	3a	4a	6a
Ir(1)–N(1)[a]	2.1160(13)	2.083(3)	2.087(4)	P(1)–Ir(1)–N(1)	86.72(4)	—	—
Ir(1)–N(4)[b]	—	2.093(4)	2.076(4)	N(1)–Ir(1)–N(4)		87.56(13)	87.28(16)
Ir(1)–P(1)	2.2886(4)	—	—	N(1)[a]–Ir(1)–C(1)	88.73(6)	90.19(17)	91.70(18)
Ir(1)–C(1)	2.2241(16)	2.117(4)	2.123(5)	N(1)[a]–Ir(1)–C(2)	96.58(5)	93.7(2)	97.6(2)
Ir(1)–C(2)	2.2364(15)	2.125(5)	2.135(5)	P(1)–Ir(1)–C(5)	92.68(4)	—	—
Ir(1)–C(5)	2.1291(15)	2.118(4)	2.141(5)	P(1)–Ir(1)–C(6)	95.31(4)	—	—
Ir(1)–C(6)	2.1449(16)	2.139(5)	2.106(5)	N(4)[b]–Ir(1)–C(5)	—	92.45(16)	94.60(18)
C(1)–C(2)	1.392(2)	1.394(8)	1.412(7)	N(4)[b]–Ir(1)–C(6)	—	92.85(15)	89.01(18)
C(5)–C(6)	1.414(2)	1.407(7)	1.409(7)	C(1)–Ir(1)–C(6)	80.24(6)	81.46(19)	80.24(6)
				C(2)–Ir(1)–C(5)	80.72(6)	81.9(2)	80.9(2)

[a] N(1) = N(4) for **4a**, [b] N(4) = N(1) for **4a**.

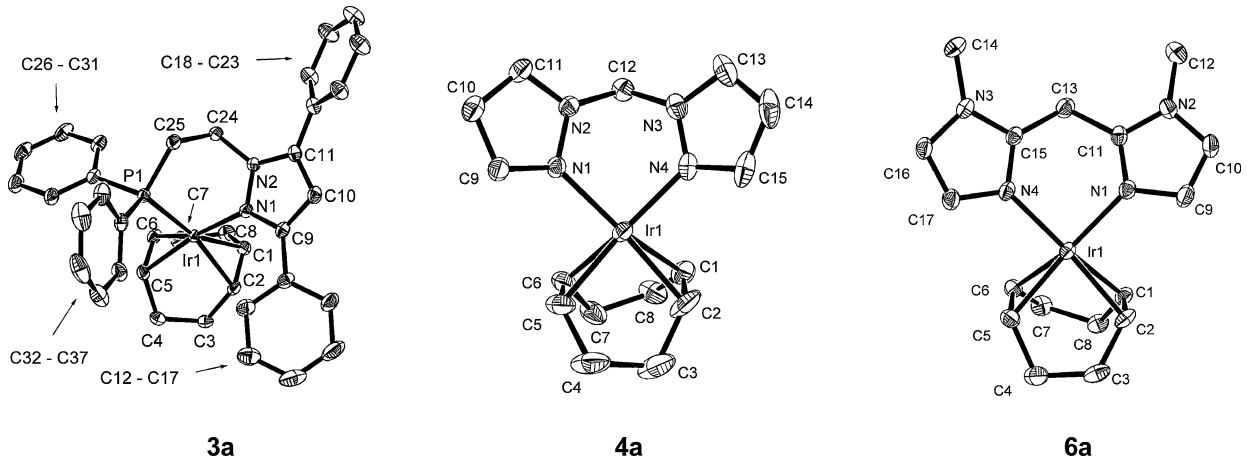


Fig. 3 ORTEP depictions and atom numbering schemes of the cations of **3a**, **4a** and **6a** with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity.

trans-influence of phosphorus compared to that of nitrogen. The N–Ir–P bond angle of **3a** followed the trend previously observed for P^N ligand bite angles of complexes with the general formula [Ir(R_2PyP)(COD)]BPh_4, where R = H (PyP = 1-(2-(diphenylphosphino)ethyl)pyrazole)[36] or Me (Me_2PyP = 1-(2-(diphenylphosphino)ethyl)-3,5-dimethylpyrazole).[18] The R_2PyP ligand bite angle of the complexes decreases with increasing steric bulk of the R substituents, H < Ph < Me, (89.47,[36] 86.72(4) and 84.31(5) °,[18] respectively), which is most likely due to interaction of the substituents at the 3 position of the pyrazole group with the COD ligand.

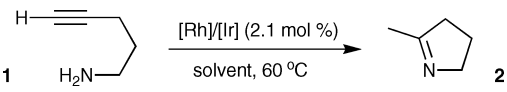
The coordination spheres of the COD complexes **4a** and **6a** are almost identical, with similar Ir–N and Ir–C bond lengths, and similar bond angles about the metal centre. The Ir–C bond lengths of the COD ligands are longer than those of the carbon monoxide ligands in complexes [Ir(bpm)$(CO)_2$]BPh_4 (**8b**)[32] and [Ir(bim)$(CO)_2$]BPh_4 (**10b**),[21] which is expected as carbon monoxide is a more strongly binding ligand than 1,5-cyclooctadiene. The bond lengths and angles of the structure of Ir complex **4a** are almost identical to those of Rh analogue **5a** (see Table 1).

Catalysis

The efficiency of Rh(I) and Ir(I) complexes containing the $BAr^F{}_{24}{}^-$ counter-ion as catalysts for the intramolecular hydroamination of the alkynylamines 4-pentyn-1-amine (**1**), 4-phenyl-3-butyn-1-amine (**12**) and 2-(2-phenylethynyl)aniline (**13**) (Tables 2–4) to yield the synthetically useful *N*-heterocycles 2-methyl-1-pyrroline (**2**), 2-phenyl-1-pyrroline (**14**) and 2-phenylindole (**15**), respectively, was tested. All the reactions were carried out at 60 °C with a catalyst loading of 2.1–2.3 mol%. The effect of solvent on the efficiency of the complexes as catalysts was also investigated. The use of $NaBAr^F{}_{24}$ as a catalyst was tested as a control experiment and it did not promote any conversion of **1** to **2** (Table 2).

Cyclisation of 4-pentyn-1-amine (1). To allow direct comparison of the activity of the $BAr^F{}_{24}{}^-$ complexes as catalysts with two of the most catalytically active analogous $BPh_4{}^-$ complexes reported previously, [Ir(bpm)$(CO)_2$]BPh_4[17] (**8b**) and [Ir(Ph_2PyP)(COD)]BPh_4[18] (**3b**), the catalysed cyclisation of **1** was tested using [Ir(bpm)$(CO)_2$]$BAr^F{}_{24}$ (**8a**) and [Ir(Ph_2PyP)(COD)]$BAr^F{}_{24}$ (**3a**) (Table 2). When the catalysis was performed in benzene the catalytic efficiency of **8a** was very high, reaching 97% conversion after only 0.7 hours with a turnover frequency (TOF) of 387 h^{-1}. Complex **8a**, however, showed similar catalytic activity to the $BPh_4{}^-$ analogue **8b**, in tetrahydrofuran-d_8, with 97% conversion in 1.12 hours and a turnover frequency of 86 h^{-1}, in comparison to **8b** (1.5 mol%) which promoted a conversion of 100% of **1** after 1.5 hours, TOF = 89 h^{-1}.[17] Complex **3a** promoted 97% conversion of **1** to **2** in 2.87 hours (TOF = 384 h^{-1}) which is less efficient than the $BPh_4{}^-$ analogue **3b**, which reached 97% conversion after only 0.2 hours, with a TOF of

Table 2 Catalysed hydroamination of 4-pentyn-1-amine (**1**) to produce 2-methyl-1-pyrroline (**2**)

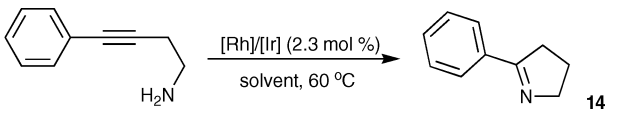


1 2

Catalyst	Solvent	*t* [h][a]	TOF [h^{-1}][b]
$[Ir(bpm)(CO)_2]BAr^F{}_{24}$ (**8a**)	C_6D_6	0.70	387
	THF-d_8	1.12	86
$[Ir(bpm)(CO)_2]BPh_4$ (**8b**)[17,c]	THF-d_8	1.50 (100%)	89
$[Ir(Ph_2PyP)(COD)]BAr^F{}_{24}$ (**3a**)	$CDCl_3$	2.87	384
	THF-d_8	9.55 (96%)	44
$[Ir(Ph_2PyP)(COD)]BPh_4$ (**3b**)[18,c]	$CDCl_3$	0.20	1800
$[Rh(bpm)(CO)_2BAr^F{}_{24}$ (**9a**)	THF-d_8	5.27 (88%)	34
$NaBAr^F{}_{24}$	C_6D_6	—	—

[a] Time to > 97% conversion, unless otherwise stated, [b] Turnover frequency = moles of product per moles of catalyst used per hour; calculated at time of 50% conversion, [c] 1.5 mol%.

Table 3 Catalysed hydroamination of 4-phenyl-3-butyn-1-amine (**12**) to produce 2-phenyl-1-pyrroline (**14**)

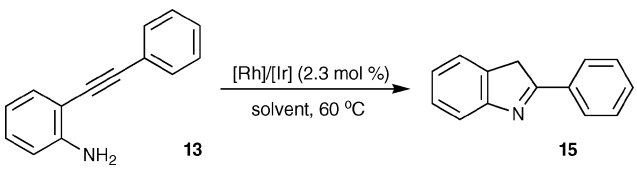


12 14

Catalyst	Solvent	*t* [h][a]	TOF [h^{-1}][b]
$[Rh(bpm)(CO)_2]BAr^F{}_{24}$ (**9a**)	C_6D_6	0.40	201
$[Ir(bpm)(COD)]BAr^F{}_{24}$ (**4a**)	C_6D_6	1.73	119
$[Rh(bim)(CO)_2]BAr^F{}_{24}$ (**11a**)	THF-d_8	2.00	108
$[Ir(bpm)(CO)_2]BAr^F{}_{24}$ (**8a**)	C_6D_6	3.67	22
$[Rh(bpm)(COD)]BAr^F{}_{24}$ (**5a**)	$CDCl_3$	9.15	30
$[Ir(Ph_2PyP)(COD)]BAr^F{}_{24}$ (**3a**)	C_6D_6	9.15	29
$[Ir(bim)(CO)_2]BAr^F{}_{24}$ (**10a**)	$CDCl_3$	12.0 (71%)	3
$[Ir(bim)(COD)]BAr^F{}_{24}$ (**6a**)	C_6D_6	12.0 (39%)	—
$[Rh(bim)(COD)]BAr^F{}_{24}$ (**7a**)	$CDCl_3$	12.0 (13%)	—
$[Rh(bpm)(CO)_2]BAr^F{}_{24}$ (**9a**)	THF-d_8	0.45	50
	Toluene-d_8	0.50	188
	CD_3CN	2.77 (95%)	15
	$CDCl_3$	17.3	12
	CD_3OD	41.5	1

[a] Where catalysis was tested in more than one solvent, only the best result is presented here (except for **9a**), [b] Time to > 97% conversion, unless otherwise stated, [c] Turnover frequency = moles of product per moles of catalyst used per hour; calculated at time of 50% conversion.

Table 4 Catalysed hydroamination of 2-(2-phenylethynyl)aniline (**13**) to produce 2-phenylindole (**15**)



13 15

Catalyst	Solvent	*t* [h][a]	TOF [h^{-1}][b]
$[Rh(bpm)(CO)_2]BAr^F{}_{24}$ (**9a**)	C_6D_6	0.67	87
	$CDCl_3$	1.97	50
$[Ir(bpm)(CO)_2]BAr^F{}_{24}$ (**4a**)	C_6D_6	10.70	6
$[Rh(bim)(CO)_2]BAr^F{}_{24}$ (**11a**)	C_6D_6	27.52	2

[a] Time to > 97% conversion, unless otherwise stated, [b] Turnover frequency = moles of product per mole of catalyst used per hour; calculated at time of 50% conversion.

1800 h^{-1}.[18] The $BAr^F{}_{24}^-$ complexes **3a** and **8a** exhibited similar TOF for the hydroamination reaction; however a significant reduction in activity was observed towards the end of the reaction using **3a**. The catalytic activity of rhodium(I) complex $[Rh(bpm)(CO)_2]BAr^F{}_{24}$ (**9a**) was also tested, but showed lower catalytic efficiency than the iridium(I) analogue **8a**.

The catalytic efficiency of **8a**, containing the $BAr^F{}_{24}^-$ anion, is much improved over that of the BPh_4^- analogue **8b**, where both catalysts contain a *N,N*-donor ligand and carbonyl co-ligands. In contrast, the catalytic efficiency of **3a** (with the $BAr^F{}_{24}^-$ anion) is much less than that of **3b** (with the BPh_4^- anion), where both catalysts contain a *P,N*-donor ligand and a COD coligand. This suggests that the mechanism of catalysed intramolecular hydroamination varies for the two different catalyst systems, and that the effect of the weakly coordinating counter-ion $BAr^F{}_{24}^-$ is not necessarily beneficial for all catalytic systems.

Cyclisation of 4-phenyl-3-butyn-1-amine (12). The rate of cyclisation of alkynylamines is affected by the terminal substituents on the alkyne, with a decrease in substrate reactivity in the order H > Me > Ph observed previously for 5-substituted 4-pentynyl-1-amines,[5,9,17,23] and Ph > *n*-alkyl > H for 4-substituted 3-butynyl-1-amines.[11,17] The efficiency of all the complexes containing $BAr^F{}_{24}^-$ (**3a–11a**) as catalysts for the intramolecular hydroamination of 4-phenyl-3-butyn-1-amine (**12**) to yield 2-phenyl-1-pyrroline (**14**) was tested (Table 3). The most effective catalysts for the hydroamination of **12** were $[Rh(bpm)(CO)_2]BAr^F{}_{24}$ (**9a**), $[Ir(bpm)(COD)]BAr^F{}_{24}$ (**4a**) and $[Rh(bim)(CO)_2]BAr^F{}_{24}$ (**11a**) which reached 97% conversion after 0.40, 1.73 and 2.00 hours, respectively (TOF = 201, 119 and 108 h^{-1}, respectively). The catalytic efficiency of the Rh(I) complexes is significantly improved over the efficiency of the BPh_4^- analogues $[Rh(bpm)(CO)_2]BPh_4$ (**9b**) and $[Rh(bim)(CO)_2]BPh_4$ (**11b**), which led to 100% conversion of **12** after 2.5 and 6 hours (in tetrahydrofuran-d_8), respectively.[17] The turnover frequencies reported here are the highest of any rates reported to date for the catalysed cyclisation of **12**.[11,17] The largest increase in catalytic efficiency of the $BArF_{24}^-$ complexes compared to that of the BPh_4^- complexes was observed for the Ir complex, $[Ir(bpm)(CO)_2]BAr^F{}_{24}$ (**8a**), which promoted 97% conversion of **12** after 3.67 hours whereas $[Ir(bpm)(CO)_2]BPh_4$ (**8b**) promoted the conversion of **12** to only 30% after 20 hours. Complex **4a**, with a COD co-ligand, promoted a 97% conversion of **12** in 1.73 hours, whereas the dicarbonyl analogue **8a** took 3.67 hours, with a TOF of 119 and 22 h^{-1}, respectively. The other complexes incorporating a *N,N*-donor ligand and COD, **5a–7a**, were less efficient catalysts than the analogous dicarbonyl complexes, **9a–11a**, for the cyclisation of **12**.

Overall the rhodium(I) complexes containing $BAr^F{}_{24}^-$ were more efficient catalysts for the intramolecular hydroamination of **12** than the Ir(I) complexes with $BAr^F{}_{24}^-$, which is consistent with the trend previously observed for the reactivity of analogous complexes containing BPh_4^- towards substrates containing internal *versus* terminal alkyne substituents.[17] Kinetic studies are currently underway to determine the mechanism of the catalysed hydroamination reaction, and the possible reasons for differences in substrate preference of the Rh(I) and Ir(I) catalysts. Complexes containing the *bis*pyrazolyl *N,N*-donor ligand bpm showed much greater catalytic efficiency than those incorporating

the *bis*imidazolyl *N,N*-donor ligand bim or the *P,N*-donor ligand Ph_2PyP, which are both more strongly binding ligands.

Of the solvents tested for the cyclisation of **12** using Rh complex **9a** benzene-d_6, toluene-d_8 and tetrahydrofuran-d_8 allowed the highest rate of conversion, with 97% conversion of **12** in under 0.5 hours in each case (Table 3). The catalytic efficiency of **9a** was significantly lower in methanol-d_4 than in any other solvent tested, with 97% conversion of **12** to **14** taking over 40 hours.

Cyclisation of 2-(2-phenylethynyl)aniline (13). The catalysed intramolecular hydroamination of 2-(2-phenylethynyl)aniline (**13**) to yield 2-phenylindole (**15**) has previously been shown to be less facile than the catalysed cyclisation of **1** or **12**,[12,15,16,23,38] with the catalysed hydroamination of **13** using $[Rh(bim)(CO)_2]BPh_4$ (**11b**) (1 mol%, acetone-d_6, 55 °C) reaching 50% conversion after 3 hours, and not reaching 100% conversion until 40 hours (TOF = 17 h^{-1}).[23] The iridium BPh_4^- complexes **8b** and **10b** both failed to catalyse the cyclisation of **13**.[38] Here the use of $[Rh(bpm)(CO)_2]BAr^F{}_{24}$ (**9a**) as the catalyst improved the hydroamination reaction dramatically compared to the BPh_4^- complexes previously tested,[23,38] with 97% conversion reached in 0.67 hours. These results are comparable to the best previously reported catalyst for the cyclisation of **13**, which is an iridium(III) complex which achieved 93% conversion after 1 hour (35 °C, 1 mol%).[15] The rhodium and iridium complexes containing $BAr^F{}_{24}^-$, **4a** and **11a**, also successfully catalysed the hydroamination of **13** with 97% conversion reached in under 30 hours for both complexes (Table 4).

Weakly coordinating anions, such as $BAr^F{}_{24}^-$, allow greater separation of the ions of the catalyst, which in turn allows greater availability of the metal centre to bind to the substrate. This effect is significant when comparing the improvement of catalytic efficiency of complexes containing the $BAr^F{}_{24}^-$ counter-ion, to the analogous complexes containing BPh_4^-, with different substrates. Improvements in catalytic activity of the $BAr^F{}_{24}^-$ complexes were most significant with the much bulkier substrate **13** compared to those observed for the smaller aliphatic substrate **1**. These results indicate that binding of bulkier substrates to the metal centre of the catalyst is more hampered by the close proximity of the BPh_4^- anion than binding of smaller substrates to the metal centre. Intermolecular proton–proton cross-peaks due to through-space interactions between the BPh_4^- counter-ion and the ligands have been previously observed in the ^1H–^1H NOESY spectra of $[Rh(bpm)(CO)_2]BPh_4$ (**9b**), $[Ir(bpm)(CO)_2]BPh_4$ (**4b**) and $[Rh(bim)(CO)_2]BPh_4$ (**11b**), indicating there is a long-lived association between the cations and BPh_4^- anion in the reaction mixture.[21]

Catalysis undertaken with microwave heating. Microwave heating, as against conventional thermal heating, can dramatically improve the efficiency of both standard synthetic, as well as catalysed, reactions.[39,40] Microwave irradiation provides a much more energy efficient heating technique due to its ability to directly heat the reaction mixture. The level of power input, and therefore degree of heating, can also be better controlled.[39,40] Recent investigations into the microwave-assisted hydroamination of alkynes have shown there is a marked improvement in reaction times of the microwave assisted reactions, when compared to those undertaken using conventional heating methods.[41]

The intramolecular hydroamination of **13** to yield **15** was investigated using $[Rh(bpm)(CO)_2]BAr^F{}_{24}$ (**9a**) as a catalyst in a microwave reactor at 60 and 100 °C. The rate of conversion of **13** to **15** was only slightly improved when the reaction was performed at 60 °C by employing microwave irradiation as the heating source. Conversion of **13** to **15** reached 99% after 0.5 hours using microwave irradiation compared to conventional heating when a conversion of 97% took 0.67 hours. Increasing the temperature of the catalytic reaction to 100 °C in the microwave reactor significantly improved the rate of conversion, with 99% conversion of **13** to **15** occurring in only 0.08 hours.

Conclusions

A method was developed for the synthesis of a series of cationic rhodium(I) and iridium(I) complexes of the type $[M(L^{\frown}L)(C_2)]BAr^F{}_{24}$ where M = Rh or Ir, $L^{\frown}L$ = *bis*(pyrazol-1-yl)methane (bpm), *bis*(*N*-methylimidazol-2-yl)methane (bim) or 1-(2-(diphenylphosphino)ethyl)-3,5-diphenylpyrazole (Ph_2PyP) and C_2 = cyclooctadiene (COD) or $(CO)_2$ and $BAr^F{}_{24}$ = *tetrakis*[3,5-*bis*(trifluoromethyl)phenyl]borate) **4a–11a**. The solid-state structures of the complexes containing a COD ligand, $[Ir(Ph_2PyP)(COD)]BAr^F{}_{24}$ (**3a**), $[Ir(bpm)(COD)]BAr^F{}_{24}$ (**4a**) and $[Ir(bim)(COD)]BAr^F{}_{24}$ (**6a**), were determined using X-ray diffraction analysis.

The highest rate of conversion for the cyclisation of the alkynylamine 4-pentyn-1-amine (**1**) was achieved using the iridium catalyst $[Ir(bpm)(CO)_2]BAr^F{}_{24}$ (**8a**), whereas the alkynylamines 4-phenyl-3-butyn-1-amine (**12**) and 2-(2-phenylethynyl)aniline (**13**) were most efficiently cyclised using the rhodium catalyst $[Rh(bpm)(CO)_2]BAr^F{}_{24}$ (**9a**), confirming that the Rh(I) complexes are more reactive toward internal alkynes than the iridium complexes. The use of Rh(I) and Ir(I) complexes which incorporate the $BAr^F{}_{24}^-$ counter-ion exhibited a marked improvement in rates of conversion for the intramolecular hydroamination reaction, compared to analogous metal complexes which contained the BPh_4^- counter-ion. The most significant improvement in the rate of the catalysed intramolecular hydroamination reaction was for the alkynylamine 2-(2-phenylethynyl)aniline (**13**), which reached a conversion of 97% conversion after 0.67 hours. $Rh(bpm)(CO)_2]BAr^F{}_{24}$ (**9a**) promoted comparable, if not higher, rates of cyclisation of **12** and **13** to the most efficient late transition metal catalysts reported previously.[11,15,17]

The substrate dependence of the improvement of catalytic efficiency of complexes containing the $BAr^F{}_{24}^-$ counter-ion, compared to that of the analogous complexes containing BPh_4^-, indicates that the ability of bulkier substrates to bind to the metal centre is more dependent on the coordinating ability of the anion than that of smaller substrates. As a result the catalysts containing the weakly coordinating $BAr^F{}_{24}^-$ counter-ion have a broader substrate scope than those containing the BPh_4^- counter-ion.

In most cases the solvent leading to best conversions for the intramolecular hydroamination reactions was benzene. The use of microwave irradiation as a heating source compared to conventional thermal heating only slightly increased the rate of conversion of **13** at 60 °C. The increase in rate of cyclisation of **13** when microwave irradiation was employed at 100 °C is more likely due to the increase in temperature (from 60 °C) than the use of microwave heating over thermal heating.

Experimental

All manipulations of metal complexes and air sensitive reagents were performed using Schlenk techniques under a dinitrogen atmosphere or in a dinitrogen filled dry box. All solvents were distilled under argon from a drying agent prior to use: sodium benzophenone ketyl (benzene, diethyl ether, tetrahydrofuran, hexane and pentane), calcium hydride (dichloromethane), or magnesium turnings (methanol). Deuterated solvents for NMR were distilled under vacuum from a drying agent prior to use: sodium benzophenone ketyl (benzene-d_6, THF-d_8 and toluene-d_8) or calcium hydride (methanol-d_4, acetonitrile-d_3, dichloromethane-d_2 and chloroform-d_3).

4-Pentyn-1-amine,[42] 4-phenyl-3-butyn-1-amine,[11] 2-(2-phenylethynyl)aniline,[43] *bis*(1-pyrazolyl)methane (bpm),[44] *bis*(*N*-methylimidazolyl)methane (bim),[23] Ph_2PyP,[18] $[Ir(COE)_2Cl]_2$,[45] $[Rh(COD)Cl]_2$,[45] $[Rh(CO)_2Cl]_2$,[46] $[Ir(COD)Cl]_2$,[45] $[Rh(COD)_2]BAr^F{}_{24}$,[47] $[Ir(COD)_2]BAr^F{}_{24}$[47] and $NaBAr^F{}_{24}$[48] were prepared according to literature procedures.

^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$ NMR spectra were recorded on Bruker DPX300, DMX500 or DPX600 spectrometers. All spectra were recorded at 298 K, unless otherwise stated. ^1H and ^{13}C NMR chemical shifts are referenced to internal solvent shifts. ^{31}P NMR chemical shifts were referenced externally to phosphoric acid (85%) in D_2O at 0.0 ppm. *J* values are given in Hz.

Infra-red spectra were obtained using an Avatar 370 FT-IR (Thermo Nicolet) spectrometer. ESI-MS and MALDI-MS were carried out by the Biological Mass Spectrometry Facility (BMSF), University of NSW, the Mass Spectrometry Unit, UNSW School of Chemistry and the Mass Spectrometry Unit, School of Chemistry, University of Sydney. Microanalyses were carried out at the Campbell Analytical Laboratory, University of Otago, New Zealand. Single Crystal X-ray analysis was performed by Dr Jörg Wagler at the Research School of Chemistry, Australian National University, Canberra. X-ray diffraction data was collected in phi and omega scans on a Nonius KappaCCD diffractometer using Mo–K_α radiation. The structures were solved with direct methods (SHELXS97) and refined by full-matrix least-squares refinement of F^2 using SHELXL97.[49] Crystals of **3a–6a**, **10a** and **11a** suitable for X-ray crystallography were grown from layering hexane over a concentrated CH_2Cl_2 solution of the respective compound. Crystallographic data for **3a–6a**, **10a** and **11a** is given in Table 5.

[Ir(Ph$_2$PyP)(COD)]BAr$^F{}_{24}$ (3a)

To a solution of $[Ir(COD)Cl]_2$ (100 mg, 0.14 mmol) in MeOH (10 mL) was added dropwise a solution of Ph_2PyP (130 mg, 0.30 mmol) and $NaBAr^F{}_{24}$ (284 mg, 0.32 mmol) in THF (5 mL). The orange solution was stirred at room temperature for 2 hours, during which time it became cloudy. The suspension was filtered, the filtrate reduced to approximately 1 mL and hexane (10 mL) added. Collection of the subsequent precipitate by filtration followed by recrystallisation from diethyl ether and hexane gave **3a** as an orange solid (278 mg. 62%). Mp 144–147 °C (from CH_2Cl_2/*n*-hexane). Anal. found: C, 51.94; H, 3.00; N, 1.57%. $C_{69}H_{49}BF_{24}IrN_2P$ requires C, 51.92; H, 3.09, N, 1.76%. δ_H (500 MHz; CD_2Cl_2; 200 K) 7.88–7.77 (4H, m, C*H* of Ph), 7.74 (8H, br s, *o*-C*H* of $BAr^F{}_{24}$), 7.60–7.50 (8H, m, C*H* of Ph), 7.53 (4H, br s, *p*-C*H* of $BAr^F{}_{24}$), 7.46–7.36 (6H, m, C*H* of Ph), 7.10 (2H, m, C*H* of Ph), 6.63 (1H, s, *H*4), 5.23–5.01 (2H, m, NCH_2), 4.87

Table 5 Summary of crystallographic data for **3a**, **4a**, **6a**, **5a**, **10a** and **11a**

	3a	**4a**	**6a**	**5a**	**10a**	**11a**
Empirical formula	$C_{69}H_{49}BF_{24}IrN_2P$	$C_{47}H_{32}BF_{24}IrN_4$	$C_{49}H_{36}BF_{24}IrN_4$	$C_{47}H_{32}BF_{24}N_4Rh$	$C_{43}H_{24}BF_{24}IrN_4O_2$	$C_{43}H_{24}BF_{24}N_4O_2Rh.0.5(CH_2Cl_2)$
M (g mol^{-1})	1596.10	1311.78	1339.85	1222.49	1287.67	1240.84
Crystal system	Monoclinic	Triclinic	Triclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$P2_1/n$
a (Å)	12.5044(3)	14.9389(3)	17.0661(2)	13.0057(2)	12.40560(10)	13.1291(3)
b (Å)	35.3357(9)	15.8085(2)	18.5517(2)	13.6112(2)	24.5181(3)	25.6224(6)
c (Å)	14.8836(4)	20.8606(4)	19.3024(2)	15.8258(3)	16.1804(2)	15.3207(4)
α (°)		107.512(1)	65.834(1)	68.912(1)		
β (°)	100.956(1)	92.128(1)	64.306(1)	69.271(1)	111.584(1)	113.072(1)
γ (°)		91.166(1)	75.404(1	68.368(1)		
V (Å ^{3})	6456.5(3)	4692.34(14)	5003.69(10)	2349.38(7)	4576.36(9)	4741.6(2)
D_c (g.cm^{-3})	1.642	1.843	1.779	1.728	1.869	1.738
Z	4	4	4	2	4	4
T (K)	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)
Crystal size (mm)	$0.31 \times 0.29 \times 0.25$	$0.45 \times 0.42 \times 0.28$	$0.30 \times 0.27 \times 0.21$	$0.49 \times 0.44 \times 0.18$	$0.39 \times 0.24 \times 0.15$	$0.39 \times 0.32 \times 0.24$
θ range (°)	2.61–33.00	2.59–30.00	2.57–30.00	2.73–30.00	2.71–30.00	2.73–30.00
Completeness (%)	99.7	99.7	99.9	99.7	99.9	99.6
Index ranges	$-19 \geq h \geq 18$	$-21 \geq h \geq 21$	$-24 \geq h \geq 24$	$-18 \geq h \geq 18$	$-17 \geq h \geq 17$	$-18 \geq h \geq 18$
	$-54 \geq k \geq 54$	$-22 \geq k \geq 21$	$-26 \geq k \geq 26$	$-19 \geq k \geq 19$	$-34 \geq k \geq 34$	$-33 \geq k \geq 36$
	$-22 \geq l \geq 20$	$-29 \geq l \geq 29$	$-27 \geq l \geq 27$	$-22 \geq l \geq 22$	$-22 \geq l \geq 22$	$-21 \geq l \geq 21$
Reflns measured	130673	90419	135754	55288	74647	75612
Unique reflns	24270	27296	29145	13658	13330	13785
R_{int}	0.0393	0.0619	0.0445	0.0383	0.0664	0.0649
GoF(all)	1.046	1.105	1.251	1.068	1.055	1.052
R_1 ($I > 2\sigma(I)$)	0.0254	0.0491	0.0516	0.0478	0.0470	0.0424
wR_2 ($I > 2\sigma(I)$)	0.0552	0.1305	0.1192	0.1267	0.1225	0.1030
R_1 (all data)	0.0346	0.0718	0.0624	0.0589	0.0650	0.0608
wR_2 (all data)	0.0574	0.1399	0.1218	0.1323	0.1306	0.1102

(1H, br s, C*H* of COD), 4.10 (1H, br s, C*H* of COD), 3.32 (1H, m, C*H* of COD), 3.15 (1H, m, C*H* of COD), 2.50 (4H, m, CH_2 of COD), 2.36 (m, 1H, PCH_2), 2.26 (m, 1H, PCH_2), 1.74 (m, 1H, CH_2 of COD), 1.42–1.18 (3H, m, CH_2 of COD) ppm. $\delta_{P\{H\}}$ (121 MHz; CD_2Cl_2) 14.8 (s) ppm. δ_C (75 MHz; CD_2Cl_2; 218 K) 163.0 (q, $^1J_{B\text{-}C}$ 49.8, *ipso*-*C* to B), 153.8 (Ph*C*N), 149.2 (Ph*C*N), 135.9 (s, *o*-*C*H to B), 134.0 (d, $^2J_{P\text{-}C}$ 10.9, *o*-*C* to P), 132.4 (s, *ipso*-*C* of Ph), 132.0 (s, *ipso*-*C* of Ph), 131.5 (d, $^1J_{P\text{-}C}$ 52.4, *ipso*-*C* to P), 130.8 (d, $^2J_{P\text{-}C}$ 10.3, *o*-*C* to P), 130.4 (s, *C* of Ph), 130.2 (qq, $^2J_{F\text{-}C}$ 31.5, $^3J_{B\text{-}C}$ 2.9, *C*CF_3), 130.1 (s, *C* of Ph), 129.8 (s, *C* of Ph), 129.4 (s, *C* of Ph), 129.1 (s, *C* of Ph), 128.9 (s, *C* of Ph), 128.8 (s, *C* of Ph), 128.6 (d, $^1J_{P\text{-}C}$ 50.2, *ipso*-*C* to P), 128.5 (s, *C* of Ph), 128.3 (s, *C* of Ph), 128.0 (s, *C* of Ph), 125.7 (q, $^1J_{F\text{-}C}$ 272.3, *C*F_3), 118.5 (sept, $^3J_{F\text{-}C}$ 4.0, *p*-*C*H to B), 107.8 (s, *C*4), 98.8 (d, $^2J_{P\text{-}C}$ 8.4, *C*H of COD), 91.0 (d, $^2J_{P\text{-}C}$ 13.9, *C*H of COD), 66.7 (s, *C*H of COD), 62.9 (s, *C*H of COD), 47.9 (s, N*C*H_2), 37.1 (s, *C*H_2 of COD), 32.0 (s, *C*H_2 of COD), 27.8 (d, $^2J_{P\text{-}C}$ 36.4, *C*H of COD), 27.1 (s, *C*H_2 of COD), 26.1 (s, *C*H_2 of COD). MALDI-MS *m*/*z* 733 ([M]$^+$, 100%).

Complexes **4a–7a** were synthesised by two different methods, (a) and (b):

Method (a): To a solution of [M(COD)Cl]$_2$ (M = Rh or Ir) (0.14 mmol) in THF (10 mL) was added dropwise a solution of either bim or bpm (0.30 mmol) and $NaBAr^F_{24}$ (0.32 mmol) in THF (5 mL). The solution was stirred at room temperature for 2 hours, resulting in a yellow, cloudy suspension. The suspension was filtered, the filtrate reduced to approximately 1 mL and hexane (10 mL) added. Collection of the subsequent precipitate by filtration followed by washing with hexane (3 × 10 mL) or recrystallization from diethyl ether and hexane gave the product as a yellow or orange solid.

Method (b): A solution of bpm or bim (0.16 mmol) and [M(COD)$_2$]BAr^F_4 (M = Rh or Ir) (~0.17 mmol) in THF (5 mL) were stirred for 1 hour. The solution was reduced to 2 mL and hexane added slowly. Collection of the resulting solid by filtration followed by washing with hexane (3 × 10 mL) gave the product as a yellow or orange solid.

[Ir(bpm)(COD)]BAr^F_{24} (4a)

Obtained as a yellow crystalline solid. Yield: 66% (Method (a)), 97% (Method (b)). Mp: 162–165 °C (from CH_2Cl_2/*n*-hexane). Anal. found: C, 43.32; H, 2.76; N, 4.49%. $C_{47}H_{32}BF_{24}IrN_4$ requires C, 43.03; H, 2.46; N, 4.27%. δ_H (300 MHz; THF-d_8) 8.08 (2H, d, ^3J 2.6, C*H*), 7.98 (2H, br s, C*H*), 7.83 (8H, br s, *o*-C*H* of BAr^F_{24}), 7.61 (4H, br s, *p*-C*H* of BAr^F_{24}), 6.74 (2H, s, CH_2), 6.60 (2H, apparent t, ^3J 2.4, C*H*), 4.33 (4H, br s, C*H* of COD), 2.37 (4H, m, CH_2 of COD), 1.90 (4H, m, CH_2 of COD) ppm. δ_C (75 MHz, THF-d_8) 163.0 (q, $^1J_{B\text{-}C}$ 49.9, *ipso*-*C* to B), 144.0 (s, CH), 135.8 (s, *o*-*C*H to B), 135.4 (br s, *C*H), 130.2 (qq, $^2J_{F\text{-}C}$ 31.6, $^3J_{B\text{-}C}$ 2.9, *ipso*-*C* to *C*F_3), 125.7 (q, $^1J_{F\text{-}C}$ 272.2, *C*F_3), 118.4 (sept, $^3J_{F\text{-}C}$ 4.0, p-*C*H to B), 109.1 (s, *C*H), 70.1 (s, *C*H of COD), 64.5 (s, *C*H_2), 32.0 (s, *C*H_2 of COD) ppm. MALDI-MS *m*/*z* 449 ([M]$^+$, 100%).

[Rh(bpm)(COD)]BAr^F_{24} (5a)

Obtained as a bright yellow crystalline solid. Yield: 82% (Method (a)), 72% (Method (b)). Mp: 158–160 °C (from CH_2Cl_2/*n*-hexane). Anal. found: C, 46.17; H, 2.95; N, 4.49%. $C_{47}H_{32}BF_{24}RhN_4$ requires C, 46.18; H, 2.64; N, 4.58%. δ_H (300 MHz; THF-d_8) 7.99 (2H, d, ^3J 2.7, C*H*), 7.82 (8H, br s, *o*-C*H* of BAr^F_{24}), 7.76 (2H, d, ^3J 2.3, C*H*), 7.60 (4H, br s, *p*-C*H* of BAr^F_{24}), 6.81 (2H, s, CH_2), 6.49 (2H, apparent t, ^3J 2.5, C*H*), 4.57 (4H, br s, C*H* of COD), 2.56 (4H, m, CH_2 of COD), 2.08 (4H, m, CH_2 of COD) ppm. δ_C (75 MHz; THF-d_8) 163.0 (q, $^1J_{B\text{-}C}$ 49.8, *ipso*-C to B), 143.8 (s, *C*H), 135.8 (s, *o*-*C*H to B), 134.8 (s, *C*H), 130.3 (qq, $^2J_{F\text{-}C}$ 31.5, $^3J_{B\text{-}C}$ 2.9, *C*CF_3), 125.7 (q, $^1J_{F\text{-}C}$ 272.3, *C*F_3), 118.4 (sept, $^3J_{F\text{-}C}$ 4.0, *p*-CH to B), 108.9 (s, *C*H), 85.5 (d, $^1J_{Rh\text{-}C}$ 12.5, *C*H of COD), 64.6 (s, *C*H_2), 31.4 (s, *C*H_2 of COD) ppm. MALDI-MS *m*/*z* 359 ([M]$^+$, 100%).

[Ir(bim)(COD)]BAr^F_{24} (6a)

Obtained as an orange solid. Yield: 54% (Method (a)), 74% (Method (b)). Mp: 124–128 °C (from CH_2Cl_2/*n*-hexane). Anal. found: C, 43.92; H, 3.08; N, 4.12%. $C_{49}H_{36}BF_{24}IrN_4$ requires C, 43.93; H, 2.71; N, 4.18%. δ_H (300 MHz; THF-d_8) 7.79 (8H, br s, *o*-C*H* of BAr^F_{24}), 7.57 (4H, br s, *p*-C*H* of BAr^F_{24}), 7.35 (2H, d, ^3J 1.8, C*H*), 7.11 (2H, d, ^3J 1.8, C*H*), 4.48 (2H, s, CH_2), 4.10 (4H, br s, C*H* of COD), 3.81 (6H, s, CH_3), 2.28 (4H, m, CH_2 of COD), 1.80 (4H, m, CH_2 of COD) ppm. δ_C (75 MHz; THF-d_8) 163.0 (q, $^1J_{B\text{-}C}$ 49.9, *ipso*-C to B), 142.4 (s, N*C*(CH_2-)N), 135.8 (s, *o*-*C*H to B), 130.2 (qq, $^2J_{F\text{-}C}$ 31.65, $^3J_{B\text{-}C}$ 2.9, *C*CF_3), 125.7 (q, $^1J_{F\text{-}C}$ 272.2, *C*F_3), 125.4 (s, *C*H), 124.2 (s, *C*H), 118.4 (sept, $^3J_{F\text{-}C}$ 4.0, *p*-*C*H to B), 66.7 (s, *C*H of COD), 34.3 (s, N*C*H_3), 32.0 (s, *C*H_2 of COD), 24.5 (s, *C*H_2) ppm. MALDI-MS *m*/*z* 477 ([M]$^+$, 100%).

[Rh(bim)(COD)]BAr^F_{24} (7a)

Obtained as a yellow crystalline solid. Yield: 80% (Method (a)), 79% (Method (b)). Mp: 146–148 °C (from CH_2Cl_2/*n*-hexane). Anal. found: C, 47.15 ; H, 3.16; N, 4.49%. $C_{49}H_{36}BF_{24}RhN_4$requires C, 47.06; H, 2.90; N, 4.48%. δ_H (300 MHz; THF-d_8) 7.83 (8H, br s, *o*-C*H* of BAr^F_{24}), 7.61 (4H, br s, *p*-C*H* of BAr^F_{24}), 7.20 (2H, d, ^3J 1.6, C*H*), 6.82 (2H, d, ^3J 1.6, C*H*), 4.39 (2H, s, CH_2), 4.35 (4H, br s, C*H* of COD), 3.77 (6H, s, CH_3), 2.47 (4H, m, CH_2 of COD), 2.01 (4H, m, CH_2 of COD) ppm. δ_C (75 MHz; THF-d_8) 163.0 (q, $^1J_{B\text{-}C}$ 49.9, *ipso*-C to B), 142.6 (s, N*C*(CH_2-)N), 135.8 (s, *o*-*C*H to B), 130.3 (qq, $^2J_{F\text{-}C}$ 31.6, $^3J_{B\text{-}C}$ 2.9, *C*CF_3), 125.7 (q, $^1J_{F\text{-}C}$ 272.3, *C*F_3), 125.7 (s, *C*H), 123.7 (s, *C*H), 118.4 (sept, $^3J_{F\text{-}C}$ 4.0, *p*-*C*H to B), 82.9 (d, $^1J_{Rh\text{-}C}$ 12.6, C*H* of COD), 34.0 (s, N*C*H_3), 31.4 (s, *C*H_2 of COD), 24.4 (s, CH_2) ppm. MALDI-MS *m*/*z* 387 ([M]$^+$, 100%).

[Ir(bpm)(CO)$_2$]BAr^F_{24} (8a)

Method (a): A solution of [Ir(COE)$_2$Cl]$_2$ (134 mg, 0.15 mmol) in THF (20 mL) was degassed *via* 3 cycles of freeze–vac–thaw and stirred under an atmosphere of $CO_{(g)}$ for 5 minutes. To the resulting blue–black suspension was added a solution of bpm (46 mg, 0.30 mmol) and $NaBAr^F_{24}$ (284 mg, 0.32 mmol) in THF (5 mL). Within 1 hour formation of a yellow solution containing a small quantity of colourless solid was observed. This suspension was stirred for a further hour at room temperature and filtered. The filtrate was reduced to approximately 1 mL and hexane (10 mL) added. Collection of the subsequent precipitate by filtration followed by washing with hexane (3 × 10 mL) and recrystallization from diethyl ether and hexane gave **8a** as a yellow solid (269 mg, 71%).

Method (b): A solution of **4a** (150 mg) in CH_2Cl_2 (5 mL) was stirred under an atmosphere of $CO_{(g)}$ at room temperature for

30 min. After completion of the reaction, the solution was reduced to 1 mL and hexane was added slowly. Collection of the resulting solid by filtration followed by washing with hexane (3 × 10 mL) gave **8a** as a pale yellow crystalline solid (105 mg, 66%).

Mp 113–116 °C (from CH_2Cl_2/*n*-hexane). Anal. found: C, 39.42; H, 1.88; N, 4.46%. $C_{41}H_{20}BF_{24}IrN_4O$ requires C, 39.09; H, 1.60; N, 4.45%. υ_{max}/cm^{-1} 2100 m (CO), 2035 m (CO). δ_H (300 MHz; THF-d_8) 8.23 (2H, br s, C*H*), 8.18 (2H, d, *J* 2.7, C*H*), 7.83 (8H, br s, *o*-C*H* of $BAr^F{}_{24}$), 7.60 (4H, br s, *p*-CH of $BAr^F{}_{24}$), 6.78 (2H, s, CH_2), 6.64 (2H, apparent t, $^3J = 2.6$, C*H*) ppm. δ_C (75 MHz; THF-d_8) 171.2 (s, *C*O), 163.1 (q, $^1J_{B\text{-}C}$ 50.0, *ipso*-C to B), 148.5 (s, *C*H), 136.5 (s, *C*H), 135.9 (s, *o*-CH to B), 130.3 (qq, $^2J_{F\text{-}C}$ 31.9, $^3J_{B\text{-}C}$ 2.9, *C*CF_3), 125.8 (q, $^1J_{F\text{-}C}$ 272.4, *C*F_3), 118.5 (sept, $^3J_{F\text{-}C}$ 3.9, *p*-CH to B), 109.9 (s, *C*H), 64.4 (s, *C*H_2) ppm. MALDI-MS *m*/*z* (%): 397 ([M]$^+$, 100). MALDI-MS *m*/*z* 397 ([M]$^+$, 100%).

[Rh(bpm)(CO)$_2$]BAr$^F{}_{24}$ (9a)

Method (a): To a solution of $[Rh(CO)_2Cl]_2$ (54.4 mg, 0.14 mmol) in diethyl ether (5 mL) was added dropwise a solution of bpm (46 mg, 0.30 mmol) and $NaBAr^F{}_{24}$ (284 mg, 0.32 mmol) in diethyl ether (10 mL). The solution was stirred at room temperature for 2 hours, resulting in a pale yellow, cloudy suspension. The suspension was filtered, the filtrate reduced to approximately 1 mL and hexane (10 mL) added. Collection of the subsequent precipitate by filtration followed by washing with hexane (3 × 10 mL) and recrystallisation from diethyl ether and hexane gave **9a** as a pale yellow solid (216 mg, 62%).

Mp 124–127 °C (from CH_2Cl_2/*n*-hexane). υ_{max}/cm^{-1} 2110 m (CO), 2052 m (CO). δ_H (300 MHz; THF-d_8) 8.12 (4H, m, C*H*), 7.82 (8H, br s, *o*-C*H* of $BAr^F{}_{24}$), 7.61 (4H, br s, *p*-C*H* of $BAr^F{}_{24}$), 6.71 (2H, s, CH_2), 6.62 (2H, apparent t, ^3J 2.5, C*H*) ppm. δ_C (75 MHz; THF-d_8) 183.4 (d, $^1J_{Rh\text{-}C}$ 69.5, *C*O), 163.0 (q, $^1J_{B\text{-}C}$ 49.8, *ipso*-C to B), 147.6 (s, *C*H), 135.8 (s, *o*-*C*H to B), 135.7 (s, *C*H), 130.3 (qq, $^2J_{F\text{-}C}$ 31.6, $^3J_{B\text{-}C}$ 2.9, *C*CF_3), 125.7 (q, $^1J_{F\text{-}C}$ 272.5, *C*F_3), 118.4 (sept, $^3J_{F\text{-}C} = 4.0$, *p*-*C*H to B), 109.4 (s, *C*H), 64.4 (s, *C*H_2) ppm. MALDI-MS *m*/*z* 307 ([M]$^+$, 82%).

[Ir(bim)(CO)$_2$]BAr$^F{}_{24}$ (10a)

A solution of $[Ir(COE)_2Cl]_2$ (134 mg, 0.15 mmol) in THF (20 mL) was degassed *via* 3 cycles of freeze-vac-thaw and stirred under an atmosphere of $CO_{(g)}$ for 5 minutes. To the resulting blue–black suspension was added a solution of bim (54 mg, 0.30 mmol) and $NaBAr^F{}_{24}$ (284 mg, 0.32 mmol) in THF (5 mL). Within 1 hour formation of a yellow suspension containing a small quantity of colourless solid was observed. This suspension was stirred for a further hour at room temperature and filtered. The filtrate was reduced to approximately 1 mL and hexane (10 mL) added. Collection of the subsequent precipitate by filtration followed by washing with hexane (3 × 10 mL) and recrystallisation from diethyl ether and hexane gave **10a** as a red crystalline solid (290 mg, 75%). Mp 144–147 °C (from CH_2Cl_2/*n*-hexane). Anal. found: C, 40.49; H, 2.22; N 4.39%. $C_{43}H_{24}BF_{24}IrN_4O_2$ requires C, 40.11; H, 1.88; N, 4.35%. υ_{max}/cm^{-1} 2067 m (CO), 2005 m (CO). δ_H (300 MHz; THF-d_8) 7.90 (8H, br s, *o*-C*H* of $BAr^F{}_{24}$), 7.67 (4H, br s, *p*-C*H* of $BAr^F{}_{24}$), 7.43 (2H, d_{AB}, ^3J 1.8, C*H*), 7.40 (2H, d_{AB}, ^3J 1.8, C*H*), 4.57 (2H, s, CH_2), 3.88 (6H, s, CH_3) ppm. δ_C (75 MHz; THF-d_8) 173.8 (s, *C*O), 162.6 (q, $^1J_{B\text{-}C}$ 49.9, *ipso*-C to B), 144.0 (s, N*C*(CH_2-)N), 135.9 (s, *o*-*C*H to B), 131.8 (s, *C*H), 130.3 (qq, $^2J_{F\text{-}C}$ 31.5, $^3J_{B\text{-}C}$ 2.9, *C*CF_3), 125.8 (q, $^1J_{F\text{-}C}$ 272.4, *C*F_3), 124.8 (s, *C*H), 118.5 (sept, $^3J_{F\text{-}C}$ 3.9, *p*-*C*H to B), 34.5 (s, N*C*H_3), 24.3 (s, *C*H_2) ppm. MALDI-MS *m*/*z* 425 ([M]$^+$, 100%).

[Rh(bim)(CO)$_2$]BAr$^F{}_{24}$ (11a)

To a solution of $[Rh(CO)_2Cl]_2$ (54.4 mg, 0.14 mmol) in diethyl ether (5 mL) was added dropwise a solution of bim (54 mg, 0.30 mmol) and $NaBAr^F{}_{24}$ (284 mg, 0.32 mmol) in diethyl ether (10 mL). The solution was stirred at room temperature for 2 hours, resulting in a yellow, cloudy suspension. The suspension was filtered, the filtrate reduced to approximately 1 mL and hexane (10 mL) added. Collection of the subsequent precipitate by filtration followed by washing with hexane (3 × 10 mL) gave **11a** as a yellow crystalline solid (256 mg, 76%). Mp 116–118 °C (from CH_2Cl_2/*n*-hexane). Anal. found: C, 42.97; H, 2.33; N, 4.63%. $C_{43}H_{24}BF_{24}RhN_4O_2$ requires C, 43.10; H, 2.02; N, 4.68%. υ_{max}/cm^{-1} 2097 m (CO), 2030 m (CO). δ_H (300 MHz; THF-d_8) 7.79 (8H, br s, *o*-C*H* of $BAr^F{}_{24}$), 7.58 (4H, br s, *p*-C*H* of $BAr^F{}_{24}$), 7.36 (2H, d_{AB}, ^3J 1.6, C*H*), 7.29 (2H, d_{AB}, ^3J 1.6, C*H*), 4.43 (2H, s, CH_2), 3.83 (6H, s, CH_3) ppm. δ_C (75 MHz; THF-d_8) 185.3 (d, $^1J_{Rh\text{-}C}$ 67.6, *C*O), 163.0 (q, $^1J_{B\text{-}C}$ 49.8, *ipso*-C to B), 143.8 (s, N*C*(CH_2-)N), 135.8 (s, *o*-CH to B), 131.6 (d, $^2J_{Rh\text{-}C}$ 1.2, *C*H), 130.2 (qq, $^2J_{F\text{-}C}$ 31.5, $^3J_{B\text{-}C}$ 2.9, *C*CF_3), 125.7 (q, $^1J_{F\text{-}C}$ 272.3 Hz, *C*F_3), 124.3 (d, $^3J_{Rh\text{-}C}$ 0.8, *C*H), 118.4 (sept, $^3J_{F\text{-}C}$ 4.0, *p*-*C*H to B), 34.4 (s, N*C*H_3), 24.3 (s, *C*H_2) ppm. MALDI-MS *m*/*z* 335 ([M]$^+$, 100%).

General procedure for catalysis

Thermal catalysed hydroamination reactions were conducted in NMR tubes fitted with a concentric Teflon valve. The catalyst complex (4.8 μmol, 2.30 mol%) was dissolved in dry, degassed deuterated solvent (0.6 mL) in the NMR tube, and the substrate (0.21 mmol) added by injection. All catalytic reactions were conducted under a nitrogen atmosphere at 60 °C in the NMR spectrometer. The temperature in the NMR magnet was calibrated using neat ethylene glycol. Characterisation of products was confirmed by comparison to literature data or an authentic sample, only one product was formed in each reaction.[11,17]

Conversion rates and yields were determined by integration of the product resonances relative to the substrate resonances in the ^{1}H NMR spectra acquired at given time intervals. All yields refer to the NMR yield. The turnover frequency (TOF) was calculated as the number of moles of product/moles catalyst/hour and was calculated at the point of 50% conversion of substrate.

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