Improving intramolecular hydroamination Rh(I) and Ir(I) catalysts through targeted ligand modification†

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A series of complexes containing the phosphino-pyrazolyl ligand 1-(2-(diphenylphosphino)phenyl)pyrazole (PyPhP) and 1-(2-(diphenylphosphino)ethyl)pyrazole (PyP) were synthesized: [Ir(PyPhP)(COD)]BPh_4, [Ir(PyPhP)$(CO)_2$]BPh_4, Rh(PyPhP)(CO)Cl and Ir(PyPhP)(CO)Cl. The complexes Rh(PyP)(CO)OSO_2CF_3 and Rh(PyPhP)(CO)OSO_2CF_3 were also synthesized, using the parent complexes Rh(PyP)(CO)Cl and Rh(PyPhP)(CO)Cl. The solid-state structures of the new complexes were determined by X-ray diffraction analysis. The cationic Ir(I) complex [Ir(PyPhP)(COD)]BPh_4 was found to be a highly efficient catalyst for the intramolecular hydroamination of 4-pentyn-1-amine, achieving a turnover rate of 1500 h^{-1}, with >98% conversion in 6 minutes. The efficiency of the catalyzed hydroamination of 4-pentyn-1-amine using the neutral Ir(I) and Rh(I) complexes as catalysts was significantly improved by generating active catalysts *in situ* through abstraction of a chloride ligand by reaction with $AgOSO_2CF_3$, $TMSOSO_2CF_3$ or $NaBPh_4$. The catalytic efficiency of the catalysts generated from Ir(PyP)(CO)Cl and a sodium salt were found to be inversely proportional to the coordinating strength of the counter-ion of the sodium salt. Rh(PyP)(CO)OSO_2CF_3 is a more efficient catalyst for the cyclization of 4-pentyn-1-amine than the complex generated *in situ* from $AgOSO_2CF_3$ and chloride complex Rh(PyP)(CO)Cl indicating that the higher lability of the triflate co-ligand of Rh(PyP)(CO)OSO_2CF_3, compared to the chloride co-ligand of Rh(PyP)(CO)Cl, enhances the catalytic activity of the Rh(I) complexes.

Introduction

Hydroamination is the addition of amine N–H bonds across carbon–carbon multiple bonds and provides an atom efficient route for the synthesis of amines, enamines and imines.[1–3] The importance of these molecules as feedstocks for the synthesis of bulk or fine chemicals and as intermediates in organic chemistry is illustrated by the yearly production of amines worldwide, which reaches several millions of tons.[2] *N*-Heterocycles, which can be formed by catalyzed intramolecular hydroamination, are particularly important because they are commonly key components of biologically significant organic compounds and their synthesis is therefore important to the pharmaceutical, agrochemical and dye industries. Catalytic systems employed for the intramolecular hydroamination reaction include Group 2 metals,[4] lanthanides,[5] actinides,[6] early[7] and late[8–14] 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 catalyze intramolecular hydroamination very effectively.[15–26] We have developed Rh(I) and Ir(I) catalysts which promote the formation of synthetically useful *N*-heterocycles *via* the cyclization of alkynylamines.[18–24,26] In particular the alkynylamine 4-pentyn-1-amine (**1**) has been cyclized to form 2-methylpyrroline (**2**) using a series of rhodium(I) and iridium(I) catalysts with general formula [M(L⌒L)(C_2)][BPh_4] where L⌒L is either a bidentate N⌒N-,[18,21,22,24] P⌒C-,[20] C⌒C-,[23] or P⌒N-[19] donor ligand 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,[19] or N⌒N and CO ligands,[18] with conversions of 98% in less than 1.5 hours at 60 °C. Catalysts containing a mixed P⌒N-donor ligand, such as **3**, promoted turnover frequencies ranging from 1200 to 3100 h^{-1} for the cyclization of **1** to **2** (Fig. 1).[19] These turnover frequencies are among the highest of any rates reported to date for the catalyzed cyclization of **1** by a late transition metal catalyst.[10,12,14] Reported here are investigations into the effect that replacing the PyP ligand with a more rigid P,N-donor ligand in complexes of general formula [M(P⌒N)(C_2)][BPh_4] has on catalyst efficiency.

The first step of the majority of mechanisms previously proposed for the late-transition metal catalyzed intramolecular hydroamination reaction involves the binding of the substrate

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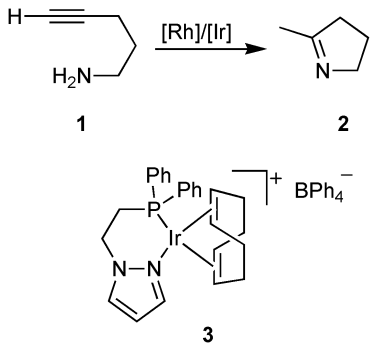


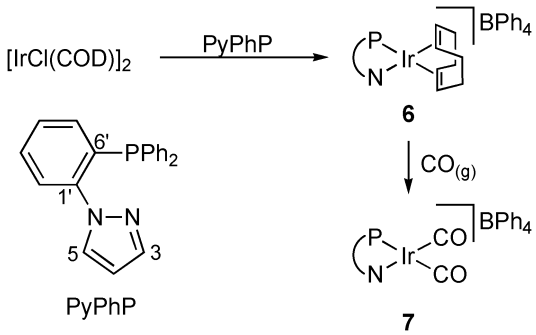
Fig. 1 Intramolecular hydroamination of **1** to form **2** using Rh(I) and Ir(I) catalysts.

to a coordinatively unsaturated metal center. The unsaturated metal center can be formed through either dissociation of a labile ligand[9,12,17] or the irreversible abstraction of a bound ligand to create an activated metal catalyst *in situ*.[11,16] For example, when using Cu(II) based catalysts, dissociation of one labile ligand from CuX_2 (where $[X]^-$ = $[OCOCF_3]^-$, $[OSO_2CF_3]^-$ or $[OAc]^-$) was found to promote binding of the alkynylamine substrate to the metal center and the subsequent cyclization of the alkynylamine.[9] Alternatively, an active catalyst can be generated *in situ* by the abstraction of a chloride ligand using a sodium or silver salt. A combination of NaBArF (BArF = tetrakis[3,5-bis(trifluoromethyl)phenyl]-borate) and a neutral iridium chloride complex (containing a P,N,C-donor ligand) has been shown to catalyze the complete cyclization of *o*-(2-phenylethynyl)aniline, whereas there was no reaction observed when the complex was used with no NaBArF present.[16] Here we report alternative approaches for promoting the formation of charged catalytic species by abstracting the chloride co-ligand from the neutral complexes Rh(PyP)(CO)Cl (**4**) and Ir(PyP)(CO)Cl (**5**)[27] *in situ* or by substitution of the Cl^- ligand with the more labile $OSO_2CF_3^-$ ligand forming new reactive complexes.

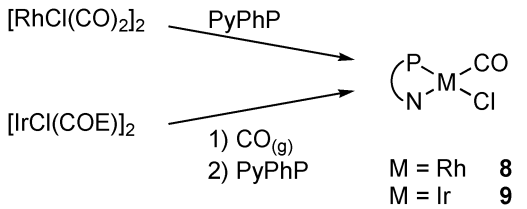
Results and discussion

Synthesis of metal complexes

A set of Ir(I) and Rh(I) complexes containing the ligand 1-(2-(diphenylphosphino)phenyl)pyrazole (PyPhP)[13] were synthesized following modifications of the methods developed for the syntheses of the corresponding complexes that contain the PyP ligand (Schemes 1 and 2).[27] In PyPhP a planar phenyl bridge has been introduced in place of the flexible ethylene linkage of PyP. By thus expanding the range of phosphino-pyrazole ligands incorporated into metal catalysts we can consider the importance of the relative flexibility of the ligand backbone in catalysis. The cationic Ir(I) complexes $[Ir(PyPhP)(COD)]BPh_4$ (**6**) and $[Ir(PyPhP)(CO)_2]BPh_4$ (**7**) were synthesized from $[IrCl(COD)]_2$ (COD = cyclooctadiene) and isolated as air stable complexes in moderate yields, 47% and 65%, respectively, (Scheme 1). The neutral complexes Rh(PyPhP)(CO)Cl (**8**) and Ir(PyPhP)(CO)Cl (**9**) were synthesized from $[RhCl(CO)_2]_2$ or $[IrCl(CO)_2]_n$ (generated *in situ* from stirring a solution of $[IrCl(COE)]_2$ (COE = cyclooctene) under



Scheme 1 COD = cyclooctadiene.

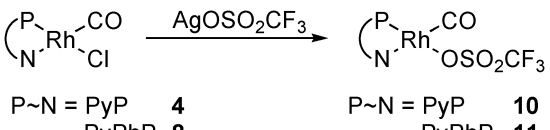


Scheme 2 COE = cyclooctene.

carbon monoxide) in yields of 34% and 39%, respectively (Scheme 2).

Rhodium triflate complexes were synthesized *via* the abstraction of chloride from the complexes **4** or **8** (Scheme 3), followed by the binding of a triflate anion. Dichloromethane was chosen as the solvent, as coordinating solvents such as tetrahydrofuran are known to compete with the triflate group for binding to the metal center.[28] Addition of silver triflate to a solution of either **4** or **8** in dichloromethane, to remove Cl^- in the presence of $OSO_2CF_3^-$, and subsequent removal of AgCl through filtration, yielded the rhodium triflate complexes $Rh(PyP)(CO)(OSO_2CF_3)$ (**10**) and $Rh(PyPhP)(CO)(OSO_2CF_3)$ (**11**) in good yields (77% and 94%, respectively). Attempted synthesis of the Ir(I) analogues of **10** and **11**, $Ir(PyP)(CO)(OSO_2CF_3)$ and $Ir(PyPhP)(CO)(OSO_2CF_3)$, led to the formation of mixtures of products, which could not be separated or purified. The use of thallium triflate in place of silver triflate, or performing the reactions at lower temperatures, did not improve the outcome of these reactions.

The iridium complexes **6**, **7** and **9** all exhibit a singlet in the $^{31}P\{^1H\}$ NMR spectra in the range 11.5–15.6 ppm, which is a similar range to the chemical shifts reported for the analogous complexes containing PyP (Table 1).[27] On substitution of the chloride co-ligand of **4** and **8** with the triflate anion the resonances due to the phosphorus atom in the $^{31}P\{^1H\}$ NMR spectrum shifted significantly downfield. The $^{31}P\{^1H\}$ NMR spectrum for **4**[27] exhibited a doublet at 38.7 ppm compared to the doublet observed at 46.8 ppm for the triflate analogue **10**. Likewise, the phosphorus resonances appeared at 41.7 and



Scheme 3

Table 1 $^{31}P\{^{1}H\}$ NMR spectroscopic data for complexes **6–11**

Complex	δ ^{31}P (ppm)	$^{1}J_{Rh-P}$/Hz
[Ir(PyPhP)(COD)]BPh_4 (**6**)	11.5	—
[Ir(PyPhP)$(CO)_2$]BPh_4 (**7**)	15.6	—
Ir(PyPhP)(CO)Cl (**9**)	12.0	—
Rh(PyP)(CO)Cl (**4**)[27]	38.7	165.5
Rh(PyPhP)(CO)Cl (**8**)	41.7	161.7
Rh(PyP)(CO)(OSO_2CF_3) (**10**)	46.8	182.7
Rh(PyPhP)(CO)(OSO_2CF_3) (**11**)	50.1	176.0

50.1 ppm in the $^{31}P\{^{1}H\}$ NMR spectra of **8** and **11**, respectively. The $^{1}J_{Rh-P}$ coupling constants were larger for the triflate complexes **10** and **11** (182.7 and 176.0 Hz, respectively) compared to the equivalent coupling constants of their chloride analogues **4** and **8** (165.5 and 161.7 Hz, respectively) (Table 1), which suggests that the triflate co-ligand has a lower *trans*-influence compared to that of the chloride co-ligand. The IR spectra of the triflate complexes **10** and **11** exhibit higher frequencies for the carbonyl bands than the analogous chloride complexes, **4** and **8** (2015/2003 and 2010/2002 compared to 1995/1951[27] and 1991 cm^{-1}, respectively, with the two frequencies observed for the carbonyl complexes due to splitting of the carbonyl peak caused by solid-state effects), which reflects the weaker π-donor ability of triflate compared to chloride.[29]

Solid state structures of the Rh(I) and Ir(I) complexes

Crystals suitable for X-ray crystallographic analysis were obtained for [Ir(PyPhP)(COD)]BPh_4 (**6**), Rh(PyPhP)(CO)Cl (**8**), Ir(PyPhP)(CO)Cl (**9**), Rh(PyP)(CO)(OSO_2CF_3) (**10**) and Rh(PyPhP)(CO)(OSO_2CF_3) (**11**) by the slow diffusion of diethyl ether or *n*-hexane into concentrated solutions of the complexes in dichloromethane. ORTEP plots of the structures of the complexes are shown in Fig. 2 and 3. Selected bond lengths and bond angles for the inner coordination sphere are listed in Tables 2 and 3.

The Rh and Ir coordination spheres of Rh(PyPhP)(CO)Cl (**8**), Ir(PyPhP)(CO)Cl (**9**), [Ir(PyPhP)(COD)]BPh_4 (**6**), Rh(PyP)-(CO)(OSO_2CF_3) (**10**) and Rh(PyPhP)(CO)(OSO_2CF_3) (**11**) are essentially all distorted square planar and the six-membered metallocycle, formed from the chelate P,N-donor ligand, adopts a pseudo-boat conformation that is similar to the conformation of the metallocycles found in other Group 9 metal complexes with pyrazolyl-phosphine ligands.[19,27]

The P(1)–M(1)–N(11) bite angles for complexes containing PyPhP (85.55(1)°, 83.65(8)° and 83.94(9)° and for **6**, **8**, and **9**, respectively) are each significantly smaller than 90°, in comparison to the complexes containing PyP, **3–5**, which have P(1)–M(1)–N(1) bite angles of 93.93(5)°, 92.21(5)° and

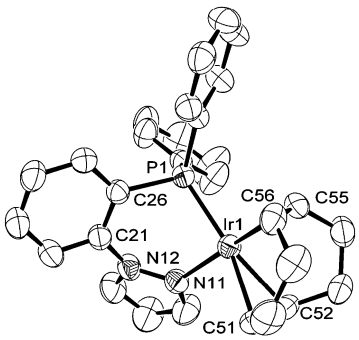


Fig. 3 ORTEP depiction of the cation of **6** with thermal ellipsoids at the 50% probability level. Hydrogen atoms have been omitted for clarity.

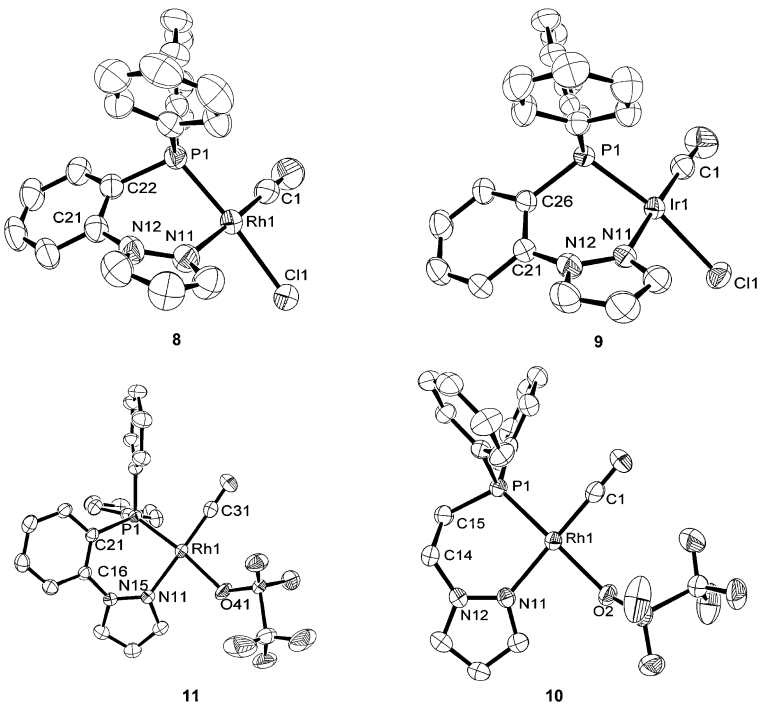


Fig. 2 ORTEP depictions of **8–11** with thermal ellipsoids at the 50% probability level. Hydrogen atoms have been omitted for clarity.

Table 2 Bond lengths (Å) and angles (°) for the inner coordination sphere of Ir(PyPhP)(CO)Cl (**9**), Rh(PyPhP)(CO)Cl (**8**), Rh(PyP)(CO)-(OSO_2CF_3) (**10**) and Rh(PyPhP)(CO)(OSO_2CF_3) (**11**)

	9	8	10	11
Bond lengths/Å				
M(1)–P(1)	2.217(1)	2.2064(9)	2.198(1)	2.1785(7)
M(1)–N(11)	2.098(3)	2.109(3)	2.108(3)	2.088(3)
M(1)–C(1)[a]	1.821(4)	1.800(4)	1.820(4)	1.824(4)
M(1)–Cl(1)	2.368(1)	2.3887(9)		
Rh(1)–O(2)[b]			2.174(2)	2.147(2)
Bond angles/°				
P(1)–M(1)–N(11)	83.94(9)	83.65(8)	94.03(7)	88.52(7)
N(11)–M(1)–Cl(1)	87.29(9)	90.54(8)		
N(11)–Rh(1)–O(2)[a]			84.65(9)	84.31(10)
Cl(1)–M(1)–C(1)	92.49(13)	90.95(11)		
C(1)[a]–Rh(1)–O(2)[b]			94.43(12)	98.00(13)

[a] C(31) for **11**. [b] O(41) for **11**.

Table 3 Bond lengths (Å) and angles (°) of the inner coordination sphere of [Ir(PyPhP)(COD)]BPh_4 (**6**)

Bond lengths/Å			
Ir(1)–P(1)	2.280(1)	Ir(1)–C(52)	2.227(4)
Ir(1)–N(11)	2.083(3)	Ir(1)–C(55)	2.124(4)
Ir(1)–C(51)	2.222(4)	Ir(1)–C(56)	2.143(4)
Bond angles/°			
P(1)–Ir(1)–N(11)	85.55(10)	C(51)–Ir(1)–C(56)	80.87(19)
P(1)–Ir(1)–C(55)	93.97(12)	C(52)–Ir(1)–C(55)	80.31(17)
P(1)–Ir(1)–C(56)	97.60(13)	C(51)–Ir(1)–C(55)	96.46(18)
N(11)–Ir(1)–C(51)	90.11(16)	C(52)–Ir(1)–C(56)	87.82(17)
N(11)–Ir(1)–C(52)	94.42(16)		

89.47(6)°, respectively.[27] It is clear that the rigid phenyl ring of PyPhP induces significant ring strain in the metallocycles of complexes **6**, **8** and **9**, in comparison to the more flexible ethylene bridge of PyP. The Rh–O bond lengths for Rh–OSO_2CF_3 in **10** and **11** are at the lower end of the Rh–O bond distances that are reported in the literature for rhodium triflate complexes.[30–36] The Rh–P bonds *trans* to the chloride anion in **4** and **8** (2.22(7) and 2.21(9) Å, respectively) are similar, within error, to the Rh–P bonds of **10** and **11** (2.20(1) and 2.18(7) Å, respectively) which are *trans* to $OSO_2CF_3^-$.

Rh(PyPhP)(CO)(OSO_2CF_3) (**11**) exhibits the greatest distortion from the ideal square planar geometry, compared to **4**, **8** or **10**, with the N(11)–Rh(1)–O(2), C(1)–Rh(1)–O(2), N(11)–Rh(1)–C(1), and P(1)–Rh(1)–O(2) bond angles falling further than 5° from the ideal 90° or 180°, (84.31(10)°, 98.00(13)°, 174.60(14)° and 172.65(8)°, respectively).

Catalysis

4-Pentyn-1-amine (**1**) was chosen as the test substrate for the investigations into the catalyzed cyclization of alkynylamines for consistency with previously reported hydroamination results.[19,20] In all cases the reactions were performed in THF-d_8 at 60 °C, with 2 mol% catalyst loading.

Catalysis using complexes containing PyPhP

The series of complexes containing PyPhP, [Ir(PyPhP)-(COD)]BPh_4 (**6**), [Ir(PyPhP)$(CO)_2$]BPh_4 (**7**), Rh(PyPhP)(CO)Cl (**8**) and Ir(PyPhP)(CO)Cl (**9**) (Table 4, entries 1, 2, 3 and 5) were all tested as catalysts for the hydroamination of **1**. The cationic complex **6** was found to be a highly efficient catalyst for this reaction, promoting the complete conversion of the substrate in 6.5 minutes with a turnover rate of 1500 h^{-1}. This result is comparable to the best previously reported late-transition metal hydroamination catalysts for the cyclization of **1**.[10,12,14,19] The cationic dicarbonyl complex **7** was also an effective catalyst (N_T = 48 h^{-1}) but the neutral complexes **8** and **9** proved to be poor catalysts with neither reaching 70% conversion after 90 hours. This trend in the catalyst efficiency of **6–9** for the cyclization of **1** parallels that observed for analogous Ir(I) and Rh(I) complexes containing pyrazolyl-phosphine ligands based on the PyP ligand. Previous studies have suggested that in analogous complexes, the loss of COD is necessary for formation of the catalytically active species.[19] Substitution of PyP with the more rigid PyPhP ligand of Ir(I) complexes containing the COD co-ligand has significantly improved the conversion of **1** to **2**, with a conversion time of 6.5 minutes using **6** (Table 4), compared to a conversion time of 90 minutes for [Ir(PyP)(COD)]BPh_4 (**3**).[19]

Table 4 Hydroamination of 4-pentyn-1-amine (**1**) with Ir(I) and Rh(I) catalysts

Entry	Complex[a]	Chloride abstractor[b]	N_T/h^{-1}[c]	Time/h[d]
1	[Ir(PyPhP)(COD)]BPh_4 (**6**)	—	1500	0.1
2	[Ir(PyPhP)$(CO)_2$]BPh_4 (**7**)	—	48	1.9
3	Rh(PyPhP)(CO)Cl (**8**)	None	—	106 (64%)
4		$NaBPh_4$	68	4.8
5	Ir(PyPhP)(CO)Cl (**9**)	None	—	95 (41%)
6		$NaBPh_4$	25	6
7	Ir(PyP)(CO)Cl (**5**)	None	—	91 (33%)
8		NaBArF	24	5.8
9		$NaBPh_4$	13	9.8
10		$NaBF_4$	5.7	15.8 (96%)
11		$TMSOSO_2CF_3$	5.1	41
12		$NaOSO_2CF_3$	3.0	30.8 (92%)
13		$AgOSO_2CF_3$	2.6	34 (96%)
14[13]	$AgOSO_2CF_3$	—	62	41(86%)
15	Rh(PyP)(CO)Cl (**4**)	None	2.7	96 (88%)
16		$NaBPh_4$	36	7.5
17	Rh(PyP)(CO)(OSO_2CF_3) (**10**)	—	3.5	15 (75%)

[a] Reactions were carried out using 2 mol% of complex in THF-d_8 at 60 °C. [b] 2 mol%. [c] N_T is calculated as (moles of product at 50% conversion)/(moles of catalyst)/(time to reach 50% conversion). [d] Time at 98% conversion unless otherwise stated.

Improving the efficiency of the neutral Ir and Rh catalysts by *in situ* chloride abstraction

The abstraction of a chloride co-ligand from neutral Ir(I) and Rh(I) carbonyl chloride complexes that contain pyrazolylphosphine ligands, allows us to generate coordinatively unsaturated complexes *in situ*, with weakly associated counter-ions. Silver and sodium salts can be used to abstract a chloride ligand from a metal complex to yield AgCl or NaCl, which can in some cases be removed easily from the reaction mixture by filtration. Here we have used $AgOSO_2CF_3$ and trimethylsilyltriflate ($TMSOSO_2CF_3$) in addition to a series of sodium salts to exchange the chloride ligand of Rh(PyP)(CO)Cl (**4**), Ir(PyP)(CO)Cl (**5**), Rh(PyPhP)(CO)Cl (**8**) and Ir(PyPhP)(CO)Cl (**9**) with a series of less coordinating ligands and form more active hydroamination catalysts.

The hydroamination of 4-pentyn-1-amine (**1**) was catalyzed using Ir(PyP)(CO)Cl (**5**) (2 mol%) in the presence of a series of sodium salts (2 mol%) with counter-ions of varying coordinating ability ($OSO_2CF_3^- > BF_4^- > BPh_4^- > BArF^-$)[37] (Table 4, entries 12, 10, 9 and 8, respectively). In all cases an improvement in the rate of hydroamination was observed in comparison to catalysis using **5** alone, which reached only 33% conversion of **1** to **2** after 91 hours. Although there are reported instances of acid catalysed hydroamination,[38] any acid contamination of the reaction mixture due to the sodium salts would be at too low a concentration to have a notable effect on the catalytic results presented here. A significant improvement was observed for the *in situ* generated catalysts formed from the addition of either $NaBPh_4$ or NaBArF to **5**, with cyclization of (**1**) in 9.8 and 5.8 hours, respectively. The efficiency of the catalysts generated from (**5**) and a sodium salt was inversely proportional to the coordinating strength of the counter-ion of the sodium salt, with catalytic efficiency in the order of $NaBArF > NaBPh_4 > NaBF_4 > NaOSO_2CF_3$ (24, 13, 5.7, 3.0 h^{-1}, respectively). The counter-ions BPh_4^- and $BArF^-$ are the more weakly coordinating and allow the formation of a coordinatively unsaturated active catalyst, which enhances substrate binding.

The hydroamination of 4-pentyn-1-amine (**1**) was also carried out in the presence of 2 mol% $NaBPh_4$ and Rh(PyP)-(CO)Cl (**4**), Rh(PyPhP)(CO)Cl (**8**) and Ir(PyPhP)(CO)Cl (**9**) (Table 4 entries 16, 4 and 6). In all cases, the efficiency of catalysis was significantly improved by exchange of chloride for BPh_4^-. The catalysts generated *in situ* from the Rh complexes **4** and **8** (N_T = 36 h^{-1} and N_T = 68 h^{-1}, respectively) were more active than their Ir counterparts **5** and **9** with $NaBPh_4$ (N_T = 13 h^{-1} and N_T = 25 h^{-1}, respectively). The complexes **8** and **9** containing the ligand PyPhP were more active catalysts in the presence of $NaBPh_4$ than complexes **4** and **5**, which contain the PyP ligand, further confirming the potential of PyPhP for use in catalysis compared to PyP. The two ligands differ both in backbone flexibility and donor basicity. The PyPhP ligand has a sterically more rigid structure. The IR stretches of the CO substituents of the pairs of complexes with these two ligands are also different, suggesting that the difference in catalytic efficiency may result from both electronic and structural effects.

The trimethylsilyl and silver salts, $AgOSO_2CF_3$ and $TMSOSO_2CF_3$, also have the potential to abstract chloride co-ligands from metal complexes, and the efficiency of the neutral Ir(PyP)(CO)Cl (**5**) as a catalyst in the presence of each of these chloride abstractors (Table 4, entries 13 and 11) was established. The addition of one equivalent of either $TMSOSO_2CF_3$ or $AgOSO_2CF_3$ to **5** enhanced the activity of **5**, decreasing the catalyzed reaction time for >96% conversion to 41 and 34 hours, respectively, compared to **5** alone, which only reached a conversion of 33% after 91 hours. The more rapid initial reaction rate did not in all cases provide the best final reaction outcome. The catalyst generated *in situ* from **5** and $AgOSO_2CF_3$ promoted a significantly lower *initial* conversion rate of **1** to **2** in comparison with the turnover rate achieved using $AgOSO_2CF_3$ alone (N_T = 62 h^{-1}) (Table 4, entries 13 and 14[13]). However, where the reaction in the presence of **5** and $AgOSO_2CF_3$ reached 96% conversion after 34 hours, the catalyzed reaction using $AgOSO_2CF_3$ alone failed to reach >95% conversion even after 7 days. The apparent decomposition of the catalytic Ag^+ species when $AgOSO_2CF_3$ is used alone has been noted previously, and in this case the addition of P,N-donor ligands to the reaction mixture was shown to stabilise the reactive catalytic species.[13] It is worth noting that the catalytic system incorporating $NaOSO_3CF_3$ is a potentially more useful catalyst than the system incorporating $AgOSO_3CF_3$, as sodium salts are, in general, easier to handle and less expensive than silver salts.

Synthesis of the triflate complex Rh(PyP)(CO)(OSO_2CF_3) (**10**) allowed direct comparison between the efficiencies of isolated catalysts as opposed to those generated *in situ*. The efficiency of Rh(PyP)(CO)Cl (**4**) as a catalyst for the cyclization of **1** was tested alone, as well as in the presence of chloride abstractors $AgOSO_2CF_3$ and $TMSOSO_2CF_3$, and these results were then compared to the efficiency of the isolated triflate complex **10** (Fig. 4) as a catalyst for the same cyclization. Rh(PyP)(CO)(OSO_2CF_3) (**10**), is a slightly more efficient catalyst for the cyclization of **1**, with a turnover number of 3.5 h^{-1}, compared to the chloride complex **4** (N_T = 2.7 h^{-1}). Rh(PyP)(CO)(OSO_2CF_3) (**10**) is also a more efficient catalyst than the *in situ* generated catalysts formed from **4** together with either $AgOSO_2CF_3$ or $TMSOSO_2CF_3$, as can be seen

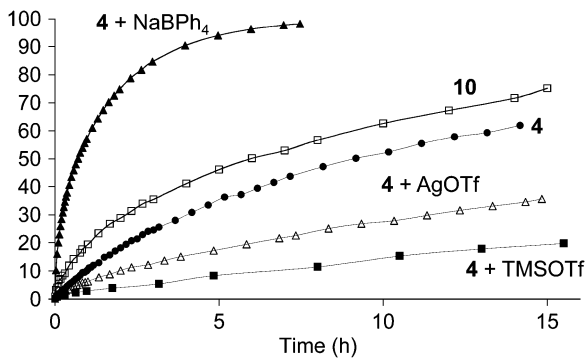


Fig. 4 Reaction profile for the cyclization of 4-pentyn-1-amine (**1**) catalyzed by 2 mol% of Rh(PyP)(CO)Cl (**4**) with 2 mol% $NaBPh_4$ (▲), 2 mol% of Rh(PyP)(CO)(OSO_2CF_3) (**10**) (□), 2 mol% of **4** (●), 2 mol% of **4** with 2 mol% $AgOSO_2CF_3$ (△), 2 mol% of **4** with 2 mol% of $TMSOSO_2CF_3$ (■).

from the reaction profiles in Fig. 4. These results indicate that the higher lability of the triflate co-ligand of **10**, compared to that of the chloride co-ligand of **4**, has the potential to enhance the catalytic activity of Rh(I) complexes. The poor catalytic activity of the catalyst generated *in situ* from **4** and $AgOSO_2CF_3$, compared to the Ir(I) reaction, may be due to formation of inactive complexes containing a Rh–Cl–Ag motif. Complexes such as these have been observed previously upon reaction of Ag salts with Rh(I) complexes containing Cl^- ligands.[39]

Conclusions

A series of complexes containing the phosphino-pyrazolyl ligand 1-(2-(diphenylphosphino)phenyl)pyrazole (PyPhP) were synthesized, [Ir(PyPhP)(COD)]BPh_4 (**6**), [Ir(PyPhP)$(CO)_2$]-BPh_4 (**7**), Rh(PyPhP)(CO)Cl (**8**) and Ir(PyPhP)(CO)Cl (**9**), in addition to two complexes Rh(PyP)(CO)(OSO_2CF_3) (**10**) and Rh(PyPhP)(CO)(OSO_2CF_3) (**11**) which were synthesized from the parent complexes Rh(PyP)(CO)Cl (**4**) and **8** *via* chloride abstraction with silver triflate. The solid-state structures of **6**, **8–11** were determined using X-ray diffraction analysis (Table 5).

The cationic Ir(I) complex **6** was found to be the best catalyst for the intramolecular hydroamination cyclization of 4-pentyn-1-amine (**1**), promoting a turnover rate of 1500 h^{-1}, which is comparable to the best previously reported late-transition metal hydroamination catalysts for the cyclization of **1**.[10,27] Substitution of PyP with the PhPyP ligand in the Ir(I) complexes with the COD co-ligand significantly improved the catalyzed cyclization of 4-pentyn-1-amine **1**, with a conversion time of 6 minutes for [Ir(PhPyP)(COD)]BPh_4 **6**, compared to 90 minutes for [Ir(PyP)(COD)]BPh_4 (**3**). This was attributed to changes in the basicity of the ligand, and the ligand flexibility.

The efficiency of the catalyzed hydroamination of 4-pentyn-1-amine (**1**) by the neutral complexes Ir(PyP)(CO)Cl (**5**), **4**, **8** and **9** was significantly improved by generating active catalysts *in situ* through abstraction of a chloride ligand by reaction with $NaBPh_4$. In the case of complex **5**, chloride abstraction by addition of $AgOSO_2CF_3$ or $TMSOSO_2CF_3$ also generated an effective *in situ* catalyst with a loosely bound triflate anion in the place of Cl^-. The catalytic efficiency of the catalysts generated from **5** and a sodium salt was inversely proportional to the coordinating strength of the counter-ion of the sodium salt, with catalytic efficiency in the order of $NaBArF > NaBPh_4 > NaBF_4 > NaOSO_2CF_3$. The catalytic system incorporating silver triflate was less efficient than those incorporating $TMSOSO_3CF_3$ or $NaOSO_3CF_3$.

The isolated complex formed from the reaction of **4** and $AgOSO_2CF_3$, Rh(PyP)(CO)OSO_2CF_3 (**10**), is a more efficient catalyst for the cyclization of **1** than the chloride complex **4** indicating that the higher lability of the triflate co-ligand of **10**, compared to the chloride co-ligand of **4** in fact enhances the catalytic activity of the Rh(I) complexes. The poor catalytic activity of the *in situ* generated, and isolated Rh(I) complexes containing a triflate anion compared to the catalyst formed from $NaBPh_4$ and **4** is most likely due to the fact that the triflate is a more strongly binding anion than the BPh_4^- anion.

Experimental section

The manipulations of metal complexes and air sensitive reagents were carried out using standard Schlenk techniques

Table 5 Crystallographic data for **6**, **8–11**

	6[a]	**8**[b]	**9**	**10**	**11**
Empirical formula	$C_{53}H_{49}BIrN_2P$	$C_{22}H_{17}ClN_2OPRh$	$C_{22}H_{17}ClIrN_2OP$	$C_{19}H_{17}F_3N_2O_4PRhS$	$C_{23}H_{17}F_3N_2O_4PRhS{\cdot}0.5(CH_2Cl_2)$
M/g mol^{-1}	947.92	494.71	584.00	560.29	650.80
Crystal system	Triclinic	Orthorhombic	Monoclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_12_12_1$	$P2_1/n$	$P2_1/c$	$P2_1/c$
a/Å	10.780(2)	9.6570(19)	8.7900(18)	12.002(2)	10.5808(1)
b/Å	14.674(3)	10.144(2)	22.900(5)	11.376(2)	20.0102(3)
c/Å	14.848(3)	21.513(4)	10.496(2)	15.535(3)	12.2975(2)
β/°	73.30(3)[a]	90	100.13(3)	94.51(3)	100.3725(10)
V/Å^3	2176.0(8)	2107.4(7)	2079.8(7)	2114.5(7)	2561.13(6)
D_c/g cm^{-3}	1.447	1.559	1.865	1.760	1.688
Z	2	4	4	4	4
T/K	290(2)	290(2)	200(2)	200(2)	200
λ (Mo-Kα)/Å	0.71073	0.71073	0.71073	0.71073	0.71073
μ(Mo-Kα)/mm^{-1}	3.143	1.027	6.640	1.038	0.97
Crystal size/mm	0.31 × 0.17 × 0.11	0.50 × 0.24 × 0.16	0.68 × 0.15 × 0.13	0.24 × 0.19 × 0.14	0.27 × 0.06 × 0.04
$2\theta_{max}$	54.96	54.94	55.22	55.06	55.00
Index ranges	$-13 \geq h \geq 13$ $-19 \geq k \geq 17$ $-19 \geq l \geq 19$	$-12 \geq h \geq 12$ $-13 \geq k \geq 13$ $-27 \geq l \geq 27$	$-11 \geq h \geq 11$ $-29 \geq k \geq 29$ $-13 \geq l \geq 13$	$-15 \geq h \geq 15$ $-14 \geq k \geq 13$ $-20 \geq l \geq 20$	$-13 \geq h \geq 13$ $-25 \geq k \geq 25$ $-15 \geq l \geq 15$
N	36 500	30 380	39 741	46 655	52 493
N_{ind} (R_{merge})	9936	4822	4799(0.1068)	4871	5855
R_{int}	0.0705	0.0554	0.1068	0.0810	0.086
GoF (all data)	1.026	0.987	0.993	1.005	0.977
R_1 ($I > 2\sigma(I)$)	0.0368	0.0288	0.0256	0.0371	0.028
wR_2 ($I > 2\sigma(I)$)	0.0757	0.0588	0.0600	0.0862	0.0665
R_1 (all data)	0.0611	0.0458	0.0359	0.0600	0.0495
wR_2 (all data)	0.0862	0.0660	0.0651	0.0985	0.0887

[a] α (°) = 81.77(3), γ (°) = 76.00(3). [b] Flack parameter = −0.04(2).

or in a nitrogen-filled dry box. For use in the synthesis of air sensitive materials, solvents were dried and degassed prior to use. Tetrahydrofuran (THF), diethyl ether, *n*-hexane, *n*-pentane and benzene were pre-dried over sodium wire then distilled from benzophenone over sodium shavings under nitrogen. Dichloromethane and acetonitrile were distilled from calcium hydride and methanol was dried over and distilled from magnesium turnings. Most chemicals were purchased from Aldrich Chemical Inc., with a few exceptions; THF-d_8, benzene-d_6, and CD_2Cl_2, were purchased from Cambridge Isotopes, $AgOSO_3CF_3$ was purchased from Lancaster, $IrCl_3{\cdot}xH_2O$ and $RhCl_3{\cdot}xH_2O$ were obtained from Precious Metals Online PMO P/L and were used without further purification. All bulk compressed gases were obtained from British Oxygen Company (BOC gases) and Linde Gas Pty. Ltd.

$[Ir(COD)(\mu\text{-}Cl)]_2$,[40] $[Rh(CO)_2(\mu\text{-}Cl)]_2$,[41] $[Ir(COE)_2(\mu\text{-}Cl)]_2$ [37] and NaBArF[42] were prepared according to literature methods. We have previously reported the synthesis of ligand PyPhP[13] and the metal complexes Ir(PyP)(CO)Cl (**5**)[27] and Rh(PyP)(CO)Cl (**4**).[27] 4-Pentyn-1-amine (**1**) was synthesized by the Organic Synthesis Center, School of Chemistry, University of Sydney and dried over calcium hydride prior to use. ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker DPX300 or DMX500 spectrometer. All spectra were obtained at 298 K unless otherwise reported and ^1H and ^{13}C spectra are referenced to internal solvent references. ^{31}P NMR chemical shifts were externally referenced to H_3PO_4 (85% in D_2O) at 0 ppm. Infra-red spectroscopy was performed using an ATI Mattson *Genesis Series* F.T.I.R. spectrometer. Melting points were determined using a Reichert melting point apparatus and are uncorrected. ESI-MS was performed by Dr Russell Pickford at the Bioanalytical Mass Spectroscopy Facility, University of New South Wales. Microanalyses were carried out at the Campbell Analytical Laboratory, University of Otago. The X-ray crystal structures were determined by Dr Matthew Smith and Dr Anthony Willis at the Research School of Chemistry, Australian National University. X-Ray diffraction data were measured on a Nonius KappaCCD diffractometer using Mo-Kα radiation. Intensity data were collected with phi and omega scans and corrected for absorption analytically. The structures were solved with the use of SIR92 and refined using the SHELXL-97 or CRYSTALS software packages.

Synthesis of [Ir(PyPhP)(COD)]BPh_4 (6)

A solution of PyPhP (209 mg, 0.621 mmol) in methanol (10 mL) was added dropwise over 15 min to a red suspension of $[Ir(\mu\text{-}Cl)(COD)]_2$ (209 mg, 0.311 mmol) in methanol (10 mL). The red solid dissolved to form an orange solution which was stirred for 1 hour. $NaBPh_4$ (213 mg, 0.622 mmol) was added as a solid, resulting in the formation of an orange precipitate. This mixture was stirred for 3 hours. The volatiles were reduced to approximately 10 mL *in vacuo*, and diethyl ether (5 mL) was added. The orange solid was collected by filtration, washed with methanol (2 × 1 mL) and diethyl ether (2 × 2 mL) and dried *in vacuo* to yield (**6**) (275 mg, 47%), mp 219–222 °C (decomp.).

δ_H(500 MHz; CD_2Cl_2; Me_4Si) 7.71 (1H, d, $^3J_{H3-H4}$ 1.9, H3), 7.66 (1H, m, H5′), 7.57 (1H, d, $^3J_{H5-H4}$ 2.5, H5), 7.55–7.51 (4H, m, *p*-CH of PPh_2, H3′ and H4′), 7.44 (4H, m, *m*-CH of PPh_2), 7.35–7.28 (13H, m, *o*-CH of PPh_2, *o*-CH of BPh_4 and H6′), 6.99 (8H, dd apparent t, ^3J 7.3, *m*-CH of BPh_4), 6.84 (4H, dd apparent t, ^3J 7.3, *p*-CH of BPh_4), 6.39 (1H, dd apparent t, ^3J 2.7, H4), 5.14 (2H, br s, C*H*CH_2 of COD), 3.40 (2H, br s, C*H*CH_2 of COD), 2.33 (4H, d, CHCH_2 of COD), 2.10 (4H, d, CHCH_2 of COD) ppm.

$\delta_{P\{H\}}$(121 MHz; CD_2Cl_2) 11.5 ppm.

$\delta_{C\{H\}}$(75 MHz; CD_2Cl_2; Me_4Si) 164.3 (q, $^1J_{C-B}$ 49.4, *i*-C of BPh_4), 144.9 (C3), 141.7 (d, $^1J_{C1'-P}$ 9.4, C1′), 136.2 (q, $^2J_{C-B}$ 1.5, *o*-C of BPh_4), 135.4 (C5), 135.4 (d, $^2J_{C-P}$ 11.6, *o*-C of PPh_2), 133.2 (d, $^4J_{C5'-P}$ 2.2, C5′), 132.7 (d, $^4J_{C-P}$ 2.9, *p*-C of PPh_2), 132.4 (d, $^2J_{C3'-P}$ 2.9, C3′), 130.1 (d, $^3J_{C4'-P}$ 6.5, C4′), 129.5 (d, $^3J_{C-P}$ 10.9, *m*-C of PPh_2), 125.9 (q, $^3J_{C-B}$ 2.9, *m*-C of BPh_4), 125.70 (d, $^3J_{C6'-P}$ 6.5, C6′), 124.4 (d, $^1J_{C-P}$ 55.9, *i*-C of PPh_2), 122.0 (*p*-C of BPh_4), 121.2 (d, $^1J_{C2'-P}$ 48.0, C2′), 111.1 (C4), 96.0 (d, $^2J_{C-P}$ 14.5, *C*HCH_2 of COD), 63.5 (*C*HCH_2 of COD), 33.0 (CH*C*H_2 of COD), 29.5 (CH*C*H_2 of COD) ppm.

ESI-MS (MeOH): *m*/*z* 630 ($[M + H]^+$, 100%), 629 ($[M]^+$, 77).

Synthesis of [Ir(PyPhP)$(CO)_2$][BPh_4] (7)

An orange suspension of [Ir(PyPhP)(COD)][BPh_4] (**6**) (176 mg, 0.185 mmol) in *n*-pentane (15 mL) and methanol (3 mL) was degassed *via* three cycles of *freeze*/*pump*/*thaw*. Carbon monoxide was introduced *via* a balloon and the suspension turned yellow after 10 min. The mixture was stirred for a further 1 h, and the atmosphere was replaced with nitrogen. The yellow solid was collected by filtration, washed with *n*-pentane (2 × 3 mL) and dried *in vacuo* to yield **7** (108 mg, 65%), mp 150–155 °C (decomp.).

Found C, 62.7; H, 4.25; N, 3.18%. $C_{47}H_{37}BIrN_2O_2P$ requires C, 63.0; H, 4.15; N, 3.15%.

δ_H(500 MHz; THF-d_8; Me_4Si) 8.11 (1H, d, $^3J_{H3-H4}$ 2.7, H3), 7.66 (1H, d, $^3J_{H5-H4}$ 2.4, H5), 7.65–7.60 (3H, m, *p*-CH of PPh_2 and H5′), 7.54–7.44 (9H, m, *o*-CH and *m*-CH of PPh_2 and H4′), 7.27 (8H, m, *o*-CH of BPh_4), 7.22 (1H, dd, $^3J_{H6'-H5'}$ 8.2, $^3J_{H6'-P}$ 4.8, H6′), 7.08 (1H, ddd, $^3J_{H3'-H4'}$ 7.7, $^4J_{H3'-H5'}$ 1.3, $^2J_{H3'-P}$ 11.9, H3′), 6.80 (8H, dd apparent t, ^3J = 7.4 Hz, *m*-CH of BPh_4), 6.67 (4H, t, ^3J 7.0, *p*-CH of BPh_4), 6.38 (1H, dd apparent t, ^3J 2.4, H4) ppm.

$\delta_{P\{H\}}$(121 MHz; CD_2Cl_2) 15.56 ppm.

$\delta_{C\{H\}}$(75 MHz; THF-d_8; Me_4Si) 165.2 (q, $^1J_{C-B}$ 49.4, *i*-C of BPh_4), 150.9 (C3), 141.2 (d, $^1J_{C1'-P}$ 8.0, C1′), 137.7 (C5), 137.2 (q, $^2J_{C-B}$ 1.5, *o*-BPh_4), 135.3 (C5′), 135.1 (d, $^2J_{C-P}$ 12.4, *o*-PPh_2), 134.7 (C4′), 134.4 (d, $^4J_{C-P}$ 2.9, *p*-C of PPh_2), 133.8 (d, $^2J_{C3'-P}$ 4.4, C3′), 131.4 (d, $^2J_{C2'-P}$ 8.0, C2′), 130.8 (d, $^3J_{C-P}$ 12.4 Hz, *m*-PPh_2), 126.9 (d, $^3J_{C6'-P}$ 6.5 Hz, C6′), 125.8 (q, $^3J_{C-B}$ 2.9, *m*-C of BPh_4), 121.9 (*p*-C of BPh_4), 112.38 (C4) ppm.

ES-ESI-MS (MeOH): *m*/*z* 549 ($[M - CO]^+$, 40%).

ν_{max}/cm^{-1} 2088 (CO), 2023 (CO).

Synthesis of Rh(PyPhP)(CO)Cl (8)

A solution of PyPhP (291 mg, 0.886 mmol) in methanol (20 mL) was added dropwise to a red suspension of

$[Rh(\mu\text{-}Cl)(CO)_2]_2$ (174 mg, 0.448 mmol) in methanol (10 mL). The red solid dissolved to form a yellow solution and then a yellow precipitate. After stirring for 30 min, 80% of the solvent was removed *in vacuo* and diethyl ether (10 mL) was added. The product was collected by filtration, washed with methanol (2 × 1 mL) and diethyl ether (2 × 2 mL) to yield complex **8** (172 mg, 39%), mp 285–290 °C (decomp.).

δ_H(500 MHz; CD_2Cl_2; Me_4Si) 8.31 (1H, d, $^3J_{H3-H4}$ 1.8, H3), 7.77 (1H, d, $^3J_{H5-H4}$ 2.2, H5), 7.61 (1H, dd apparent t, ^3J 7.7, H5′), 7.55–7.46 (6H, m, *o*-CH and *p*-CH of PPh_2), 7.42–7.38 (6H, m, *m*-CH of PPh_2, H4′ and H6′), 6.96 (1H, dd apparent t, ^3J 8.8, H3′), 6.40 (1H, dd apparent t, ^3J 2.4, H4) ppm.

$\delta_{P\{H\}}$(121 MHz; $CDCl_3$) 41.7 (d, $^1J_{Rh-P}$ 161.7 Hz) ppm.

$\delta_{C\{H\}}$(75 MHz; $CDCl_3$; Me_4Si) 189.6 (dd, $^1J_{C-Rh}$ 74.8, $^2J_{C-P}$ 16.0, CO), 146.7 (C3), 141.4 (d, $^2J_{C1'-P}$ 8.7, C1′), 134.1 (d, $^2J_{C-P}$ 13.1, *o*-C of PPh_2), 132.3 (C5), 132.0 (d, $^2J_{C3'-P}$ 2.2, C3′), 131.9 (d, $^4J_{C5'-P}$ 2.2, C5′), 131.6 (d, $^4J_{C-P}$ 2.2 Hz, *p*-C of PPh_2), 129.6 (d, $^1J_{C-P}$ 55.2 Hz, C2′ or *i*-C of PPh_2), 128.9 (d, $^3J_{C-P}$ 11.6 Hz, *m*-C of PPh_2), 128.7 (d, $^3J_{C-P}$ 7.3, C4′ or C6′), 124.6 (d, $^1J_{C2'-P}$ 41.4, C2′), 124.1 (d, $^3J_{C-P}$ 5.8, C4′ or C6′), 109.5 (C4) ppm.

ESI-MS (MeOH): *m*/*z* 459.0 ($[M - Cl]^+$, 100%), 952 ($[[Rh(PyPhP)(CO)]_2Cl]^+$, 78).

ν_{max}/cm^{-1} 1991 (CO).

Synthesis of Ir(PyPhP)(CO)Cl (9)

An orange suspension of $[Ir(\mu\text{-}Cl)(COE)_2]_2$ (160 mg, 0.179 mmol) in acetonitrile (40 mL) was degassed *via* three cycles of *freeze*/*pump*/*thaw* and carbon monoxide was introduced *via* a balloon. The suspension was stirred under a carbon monoxide atmosphere for 15 min, during which time the orange solid dissolved to form a yellow solution. A solution of PyPhP (117 mg, 0.356 mmol) in acetonitrile (9 mL) was added dropwise to the reaction mixture. After stirring for 1 h, 75% of the solvent was removed *in vacuo* and a yellow solid precipitated. The solid was collected by filtration, washed with methanol (3 × 1 mL) and diethyl ether (3 × 3 mL) and dried *in vacuo* to yield **9** (71 mg, 34%), mp 278–282 °C (decomp.).

Found: C, 45.25; H, 2.95; N, 4.92%. $C_{22}H_{18}ClIrN_2OP$ requires C, 45.25; H, 2.95; N, 4.8%.

δ_H(500 MHz; CD_2Cl_2; Me_4Si) 8.40 (1H, d, $^3J_{H3-H4}$ 1.8, H3), 7.84 (1H, d, $^3J_{H5-H4}$ 2.7, H5), 7.60 (1H, dd apparent t, ^3J 7.7, H5′), 7.53 (4H, dd, $^3J_{o\text{-}H-P}$ 12.3, $^3J_{o\text{-}H-m\text{-}H}$ = 7.5 Hz, *o*-CH of PPh_2), 7.46 (2H, m, *p*-CH of PPh_2), 7.42–7.38 (6H, m, *m*-CH of PPh_2, H4′ and H6′), 6.99 (1H, dd apparent t, ^3J 8.7, H3′), 6.45 (1H, dd apparent t, ^3J 2.8, H4) ppm.

$\delta_{P\{H\}}$(121 MHz; $CDCl_3$) 12.0 ppm.

$\delta_{C\{H\}}$(125 MHz; CD_2Cl_2; Me_4Si) 176.3 (d, $^3J_{C-P}$ 13.0, CO), 146.4 (C3), 141.3 (C1′), 134.3 (d, $^2J_{C-P}$ 12.0, *o*-C of PPh_2), 133.5 (C5), 131.9 (d, $^4J_{C-P}$ 2.0, C5′), 131.8 (m, C3′ and *p*-C of PPh_2), 129.2 (C4′ or C6′), 129.1 (d, $^2J_{C-P}$ 7.0, C2′), 128.8 (d, $^3J_{C-P}$ 12.0, *m*-C of PPh_2), 124.5 (d, $^3J_{C-P}$ 6.0, C4′ or C6′), 109.4 (C4) ppm.

ESI-MS (MeOH): *m*/*z* 549 ($[M - Cl]^+$, 100%).

ν_{max}/cm^{-1} 1978 (CO).

Synthesis of Rh(PyP)(CO)(OSO_2CF_3) (10)

$AgOSO_2CF_3$ (124 mg, 0.482 mmol) was added to a solution of Rh(PyP)(CO)Cl (**4**) (214 mg, 0.479 mmol) in dichloromethane (30 mL). The solution was stirred for 3 h, during which time it became cloudy. The reaction mixture was filtered through Celite™ and the filtrate concentrated *in vacuo*. *n*-Hexane was added to give the product as a dark yellow precipitate which was collected by filtration, washed with *n*-hexane (3 × 3 mL) and dried *in vacuo* to yield **10** (206 mg, 77%).

Found C, 40.68; H, 3.18; N, 5.05%. $C_{19}H_{17}F_3N_2O_4PRhS$ requires C, 40.73; H, 3.06; N, 5.00%.

δ_H(300 MHz; $CDCl_3$; Me_4Si) 8.02 (1H, s, H3), 7.84–7.77 (4H, m, *o*-CH of PPh_2), 7.54–7.46 (7H, m, *m*-CH, *p*-CH of PPh_2 and H5), 6.30 (1H, apparent t, $^3J_{H3-H4,H5-H4}$ 2.3, H4), 4.51–4.40 (2H, m, NCH_2), 2.65 (2H, m, PCH_2) ppm.

$\delta_{P\{H\}}$(121 MHz, CD_2Cl_2) 46.8 (d, $^1J_{Rh-P}$ 182.7) ppm.

$\delta_{C\{H\}}$(125 MHz, CD_2Cl_2) 186.2 (dd, $^1J_{Rh-C}$ 72.7, $^2J_{P-C}$ 22.0, CO), 143.4 (s, C3), 133.7 (s, C5), 132.9 (dd, $^2J_{P-C}$ 11.6, $^3J_{Rh-C}$ 1.5, *o*-C of PPh_2), 132.3 (br d, $^2J_{Rh-C}$ 1.5, *i*-C of PPh_2), 131.5 (d, $^4J_{P-C}$ 2.2, *p*-C of PPh_2), 128.9 (d, $^3J_{P-C}$ 10.9, *m*-C of PPh_2), 106.2 (s, C4), 47.5 (s, NCH_2), 28.0 (d, $^1J_{P-C}$ 32.0, PCH_2) ppm.

δ_F(282 MHz, CD_2Cl_2) −78.6 ppm.

ESI-MS (DCM): *m*/*z* 383.7 ($[Rh(PyP)]^+$, 60%), 411.8 ($[M - OSO_2CF_3]^+$, 55).

ν_{max}/cm^{-1} 2015 (CO), 2003 (CO) cm^{-1}.

Synthesis of Rh(PyPhP)(CO)(OSO_2CF_3) (11)

$AgOSO_2CF_3$ (128 mg, 0.496 mmol) was added to a solution of Rh(PyPhP)(CO)Cl (**8**) (202 mg, 0.406 mmol) in dichloromethane (25 mL). The solution was stirred for 3 h, during which time it became cloudy. The reaction mixture was filtered through Celite™ and the filtrate concentrated *in vacuo*. *n*-Hexane was added to give the product as a dark yellow precipitate which was collected by filtration, washed with *n*-hexane (3 × 3 mL) and dried *in vacuo* to yield **11** (223 mg, 94%).

δ_H(500 MHz; CD_2Cl_2; Me_4Si) 7.97 (1H, s, H3), 7.86 (1H, s, H5), 7.67 (1H, dd apparent t, ^3J 7.6, H3′), 7.54–7.43 (12H, m, PPh_2, H4′ and H6′), 7.00 (1H, dd apparent t, ^3J 9.3, H5′), 6.47 (1H, s, H4) ppm.

$\delta_{P\{H\}}$(121 MHz, CD_2Cl_2) 50.1 (d, $^1J_{Rh-P}$ 176.0) ppm.

δ_F(282 MHz, CD_2Cl_2) −78.5 ppm.

ESI-MS (DCM): *m*/*z* 459.02 ($[M - OSO_2CF_3]^+$, 100%).

ν_{max}/cm^{-1} 2010 (CO), 2002 (CO).

General procedures for catalytic reactions

All metal catalyzed hydroamination reactions were performed on a small scale in an NMR tube fitted with a Young's concentric Teflon valve. All samples were prepared and reactions carried out under a nitrogen atmosphere using freshly distilled, dry degassed THF-d_8. Either 4-pentyn-1-amine (**1**) was injected into a solution of the catalyst, or a solution of **1** in THF-d_8 was reacted with the solid catalyst. The reactions were performed at 60 °C by heating in an oil bath or within the spectrometer. The temperature within the magnet was calibrated using ethylene glycol.[38,43]

The progress of the hydroamination reaction was monitored by acquiring ^1H NMR spectra at regular intervals. In the preparation of each sample, when all reactants had been added to the NMR tube, it was frozen in liquid nitrogen. The first spectrum was measured as soon as the sample had been

thawed to room temperature and inserted into the spectrometer. The moment of this first acquisition was taken to be time zero. Conversion of starting material to product was determined by integration of the product resonances relative to the substrate resonances. The turnover rate (N_T (h^{-1})) was calculated as the number of moles of product/moles of catalyst/hour and was determined at the point of 50% conversion.

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