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New Rhodium(I) and Iridium(I) Complexes Containing Mixed Pyrazolyl−1,2,3-Triazolyl Ligands As Catalysts for Hydroamination

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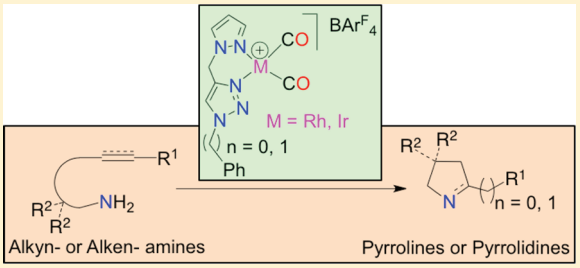
Supporting Information

ABSTRACT: Two new bidentate pyrazolyl−triazolyl donor ligands, 4-((1*H*-pyrazol-1-yl)methyl)-1-benzyl-1*H*-1,2,3-triazole, PyT (**1a**), and 4-((1*H*-pyrazol-1-yl)methyl)-1-phenyl-1*H*-1,2,3-triazole, PyS (**1b**), were synthesized using the copper(I)-catalyzed "click" reaction between 1-propargylpyrazole and benzyl azide or phenyl azide, respectively. Cationic rhodium(I) and iridium(I) complexes containing the new N−N′ ligands of the general formulas [M(N−N′)(COD)]X (M = Rh or Ir, N−N′ = PyT or PyS, and X = BPh_4^- or $BAr^F{}_4^-$ (tetrakis[3,5-bis(trifluoromethyl)phenyl]borate) **2a−c** for Rh and **3a−c** for Ir) and [M(N−N′)$(CO)_2$]X (M = Rh or Ir, N−N′ = PyT or PyS, and X = BPh_4^- or $BAr^F{}_4^-$ **4a−d** for Rh and **5a−d** for Ir) were successfully prepared and fully characterized. The solid-state structures of eight of these complexes were determined using single-crystal X-ray diffraction and show that the triazolyl moiety coordinates to the metal center via the N3′ atom, forming six-membered metallacycles. These metallacycles adopted a distorted boat conformation in all of the structures determined. The M−N(triazole) bonds were found to be slightly shorter than the M−N(pyrazole) bonds, illustrating the stronger donating capacity of the triazolyl donor in comparison to that of the pyrazolyl donor. All of the cationic rhodium and iridium complexes reported here are catalytically active for the intramolecular hydroamination of 4-pentyn-1-amine (**6**) to 2-methyl-1-pyrroline (**7**) at 60 °C, with TOFs > 400 h^{-1} in many cases. The dicarbonyl complexes [M(N−N′)$(CO)_2$]$BAr^F{}_4$ (M = Rh or Ir) **4c,d** and **5c,d** were efficient as catalysts for the intramolecular cyclization of nonterminal alkynamines (**8a,b**) to cyclic imines (**9a,b**) via the hydroamination reaction and the cyclization of alkenamines (**10a−c**) to their corresponding cyclic amines (**11a−c**) also via the hydroamination reaction.



INTRODUCTION

The N-containing heterocycle 1,2,3-triazole has great potential in coordination chemistry as an N-donor ligand due to its ease of synthesis and the wide functional group tolerance of the "click" reaction. Ligands containing sp^2-hybridized nitrogen donor atoms have been widely used in the synthesis of metal complexes, where the strength of the metal−N bond depends upon the degree of σ-covalency in the bond as well as any π-back-bonding effects, particularly in the case of aromatic nitrogen donor ligands.[1] As N-donors are typically labile, multidentate nitrogen donor ligands have been most widely used.[1] Poly(pyrazol-1-yl)borate[2] and poly(pyrazol-1-yl)-methane[3] are two of the most studied classes of multidentate nitrogen donor ligands, and complexes of these ligands have found wide application in a variety of catalytic reactions including C−H activation chemistry. The use of the 1,2,3-triazole as a ligand has been much less explored, even though the copper(I)-catalyzed azide−alkyne Huisgen cycloaddition reaction ("click" reaction) has been widely used as a linker for biological applications and in the modification of surfaces and nanoparticles.[4−6] The "click" reaction is a convenient approach to anchoring homogeneous transition metal catalysts on surfaces, and the anchoring of pincer ligands, N-heterocyclic carbene ligands, and their metal complexes has been recently reported.[7] The coordinative properties of the 1,2,3-triazole as part of monodentate, bidentate, and tridentate ligands have been recently explored (Figure 1) in complexes of transition

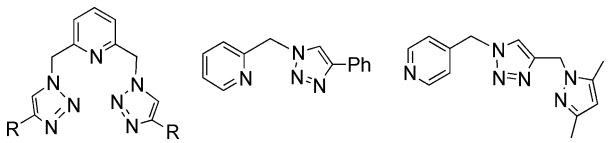


Figure 1. Examples of multidentate ligands containing the 1,2,3-triazolyl moiety with R = Ph or *n*-Bu.

metals including Fe, Cu, Ru, Ir, Pd, and Pt.[8−11] The 1,2,3-triazolyl moiety provides three potential metal binding sites, N3, N2, and C5 (as triazolylidene).[4]

The hydroamination of alkynes and alkenes involves the addition of an N−H bond to an unsaturated C−C bond. It is a highly atom-efficient approach to the synthesis of amines and imines, widely occurring functional groups in fine chemicals such as pharmaceuticals, fragrances, and agrochemicals.[12,13] Lanthanide and actinide complexes[14,15] and both early[16] and

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late[17] transition metal complexes can be effective catalysts for promoting the hydroamination of alkynes and alkenes. In 1989 Marks and co-workers demonstrated that lanthanoid metallocenes such as $(Cp^*LaH)_2$, $(Cp^*LuH)_2$, and $[Me_2Si(Me_4C_5)_2LuH]_2$ ($Cp^* = Me_5C_5$) are highly active catalysts for the cyclization of alkenamines to form a number of five- and six-membered cyclic amines.[18] Since this initial report, a large number of metallocenes and, more recently, nonmetallocenes of lanthanides and actinides including chiral complexes have been developed as catalysts for the hydroamination of alkenes, alkynes, and allenes.[19,13] Almost parallel to the discovery of lanthanide-based catalysts for hydroamination, early transition metal complexes were first demonstrated in the early 1990s by Bergman[20] and Livinghouse[21] to be efficient as catalysts for the hydroamination reaction. Although a significant number of early transition metal hydroamination catalytic systems, particularly titanium- and zirconium-based systems, have since been developed,[13,16,22] the high oxophility of lanthanide, actinide, and early transition metal complexes has restricted their general application.

Hydroamination catalysts based on late transition metals offer the advantage of being generally more functional group tolerant and less sensitive toward oxygen and moisture. Late transition metal complexes are known to be effective catalysts for the hydroamination reaction, and Ru, Rh, Ir, Pd, Pt, and Cu complexes all display good catalytic activity.[12,13] There are only a limited number of reports of the catalyzed intramolecular hydroamination of alkenamines involving late transition metal catalysts,[12,13,23,24] including Pt(II), Rh(I), and Ir(I) complexes with strongly donating donors such as phosphines or carbenes.[25] Greater success has been shown for the alkynamine substrates over the alkenamine substrates as a result of the higher reactivity of alkynes when compared to alkenes. We have previously shown that rhodium and iridium complexes containing bidentate N–N or N–P donor ligands, bis(pyrazol-1-yl)methane,[26] bis(1-methylimidazolyl)methane,[26] pyrazolyl-phosphine,[27,49] and imidazolyl-phosphine,[28] are highly efficient as catalysts for C–X (X = N, O or S) bond formation via the addition of X–H across C–C multiple bonds. We found that subtle changes in the donating ability of the N-donor through steric and/or electronic modifications greatly influence the catalytic efficiency of the resulting metal complexes.[26−28,49] We have now designed and synthesized two new bidentate N–N′ donor ligands with mixed N–N′ pyrazolyl–triazolyl donors using the highly versatile "click" chemistry. These bidentate ligands have great potential for immobilization on solid supports, using "click" chemistry as the key step for immobilization. We have also synthesized a series of cationic rhodium and iridium complexes with these ligands (Figure 2a) and established the efficiency of the new metal complexes as catalysts for the intramolecular hydroamination of a series of alkynamines and alkenamines (Figure 2b).

RESULTS AND DISCUSSION

Synthesis of the Pyrazolyl–Triazolyl Ligands PyT (1a) and PyS (1b). The two novel pyrazolyl–triazolyl bidentate ligands PyT (**1a**) and PyS (**1b**) were synthesized in moderate to good yields via the Cu(I)-catalyzed Huisgen "click" reaction between 1-propargylpyrazole and benzyl azide and phenyl azide, respectively (Scheme 1).[6,29]

Synthesis of Cationic Rh(I) and Ir(I) Complexes with PyT (1a) or PyS (1b) Ligands and COD (1,5-cyclooctadiene) as the Co-ligand. Cationic rhodium(I) and iridium(I) complexes of PyT (**1a**) and PyS (**1b**) $[M(N–N')(COD)]X$ (M = Rh or Ir, N–N′ = PyT or PyS, and X = BPh_4^- or $BAr^F{}_4^-$; **2a–c** and **3a–c**) were synthesized in excellent yields by the reaction of each of the N–N′ donor ligands with $[M(\mu\text{-Cl})(COD)]_2$ (M = Rh or Ir) and $NaBPh_4$ in methanol for **2a,b** and **3a,b** or by the reaction of PyT (**1a**) or PyS (**1b**) with $[M(COD)_2]BAr^F{}_4$ (M = Rh or Ir) in tetrahydrofuran (Scheme 2) for **2c** and **3c**. All complexes **2a–c** and **3a–c** are yellow or bright yellow in the solid state.

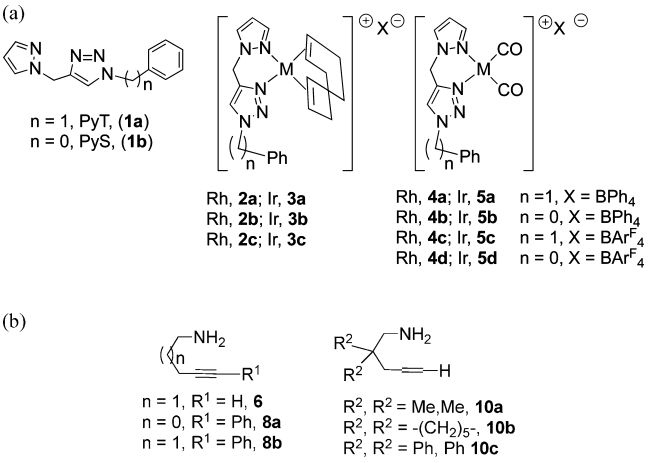
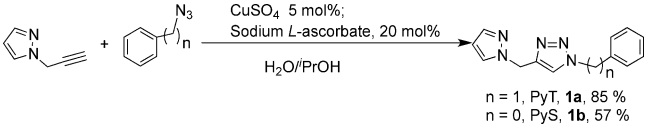
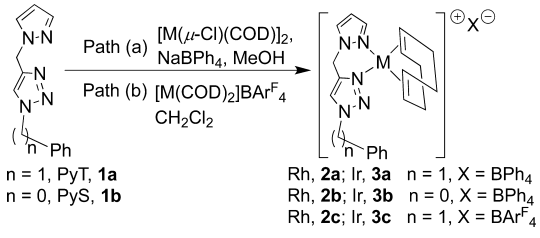


Figure 2. (a) Pyrazolyl–triazolyl bidentate ligands and their rhodium(I) and iridium(I) complexes, $BAr^F{}_4^-$ = tetrakis[(3,5-trifluoromethyl)phenyl]borate; (b) alkyn- and alkenamines for the hydroamination reaction.

Scheme 1. Synthesis of the Pyrazolyl–Triazolyl Bidentate Ligands PyT (1a) and PyS (1b)



Scheme 2. Synthesis of $[M(N–N')(COD)]X$[a]



[a]M = Rh or Ir; N–N′ = PyT or PyS, and X = BPh_4^- or $BAr^F{}_4^-$.

The structures of complexes **2a–c** and **3a–c** were fluxional on the NMR time scale at room temperature. Analogous structural fluxionality has been previously observed and explained for similar rhodium(I) and iridium(I) complexes containing the bidentate pyrazolyl or imidazolyl ligands, bis(pyrazol-1-yl)methane and bis(1-methylimidazol-2-yl)-methane.[26b,c]

Synthesis of Cationic Rh(I) and Ir(I) Complexes Containing PyT (1b) or PyS (1a) Ligands and CO as Co-ligands. The cationic rhodium(I) and iridium(I) complexes containing dicarbonyls as co-ligands, **4a–d** and **5a–d**, were prepared either by (i) displacing the COD co-ligand from

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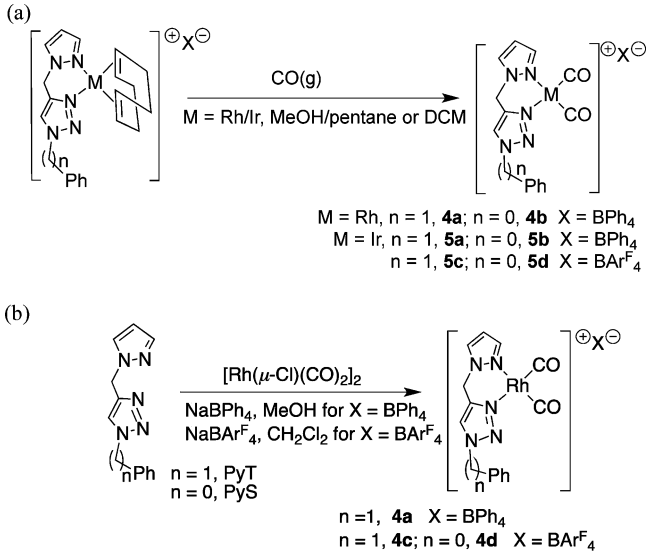
[M(N-N′)(COD)]X (**2a**–**c** and **3a**–**c**) by placing a suspension or solution of the COD complex under an atmosphere of carbon monoxide or (ii) using the rhodium carbonyl dimer, $[Rh(\mu\text{-}Cl)(CO)_2]_2$, as the starting material (Scheme 3).

Scheme 3. Synthesis of $[Rh(N{-}N')(CO)_2]X$ (4a–d) and $[Ir(N{-}N')(CO)_2]X$ (5a–d) with N–N′ = PyT or PyS and X = BPh_4 or $BAr^F{}_4$



The displacement of COD by carbon monoxide proceeded smoothly for the iridium complexes [Ir(N–N′)(COD)]X (N–N′ = PyT or PyS; X = BPh_4^- or $BArF_4^-$ **3a**–**c**), leading to the formation of the corresponding dicarbonyl complexes [Ir(N–N′)$(CO)_2$]X (N–N′ = PyT or PyS; X = BPh_4^- or $BAr^F{}_4^-$ **5a**–**c**) as bright orange or red solids in excellent yields (Scheme 3a). The iridium complex $[Ir(PyS)(CO)_2]BAr^F{}_4$ (**5d**) was synthesized by carbonylation of the complex $[Ir(PyS)(COD)]BAr^F{}_4$ without isolation of this intermediate. The preferred route for the preparation of [Rh(N–N′)$(CO)_2$]X (N–N′ = PyT or PyS, X = BPh_4^- and $BAr^F{}_4^-$ **4a**–**d**) complexes was reaction of either the PyT (**1a**) or PyS (**1b**) ligand with $[Rh(\mu\text{-}Cl)(CO)_2]_2$ followed by the addition of $NaBPh_4$ or $NaBAr^F{}_4$ for salt metathesis (Scheme 3b). This approach led to the formation of the desired complexes in very good yields.

The infrared spectrum of each of the complexes with CO co-ligands **4a**–**d** and **5a**–**d** (Table 1) shows the presence of two strong CO vibrational stretches as expected for four-coordinate *cis*-dicarbonyl complexes. The $^{13}C\{^1H\}$ NMR spectra of these complexes show the presence of two resonances in the low-field region of the spectrum characteristic of two nonequivalent metal-bound carbonyls. In the case of the [Rh(N–N′)$(CO)_2$]X (N–N′ = PyT or PyS and X = BPh_4 or $BAr^F{}_4$ **4a**–**d**) complexes, heteronuclear couplings of the ^{13}CO resonances to Rh, $^1J_{Rh\text{-}13C} \approx 70$ Hz, confirmed the coordination of CO to the rhodium metal center.

Solid-State Structures of [Rh(PyT)(COD)]X (X = BPh_4^- (2a), $BAr^F{}_4^-$ (2c)), $[Ir(PyT)(COD)]BPh_4$ (3a), $Rh(PyT)(CO)_2]BPh_4$ (4a), $[Rh(PyS)(CO)_2]BAr^F{}_4$ (4d), $[Ir(PyT)(CO)_2]X$ (X = BPh_4^- (5a), $BAr^F{}_4^-$ (5c)), and $[Ir(PyS)(CO)_2]BAr^F{}_4$ (5d). Crystals suitable for X-ray diffraction studies of complexes **2a**, **2c**, **3a**, **4a**, **4d**, **5a**, **5c**, and **5d** were obtained by layering a concentrated dichloromethane (or dichloromethane-d_2) solution of each of the complexes with *n*-pentane. X-ray

Table 1. νCO and ^{13}C NMR Resonances of the Dicarbonyls of [M(N–N′)$(CO)_2$]X (M = Rh or Ir, N–N′ = PyT or PyS, and X = BPh_4 or $BAr^F{}_4$)

complex	νCO (cm^{-1})[a]	^{13}C resonances for CO[b] (ppm)
$[Rh(PyT)(CO)_2]BPh_4$ (**4a**)	2105, 2045	183.1 (d, $^1J_{Rh-C}$ = 69.4 Hz), 182.4 (d, $^1J_{Rh-C}$ = 69.8 Hz)[c]
$[Rh(PyS)(CO)_2]BPh_4$ (**4b**)	2105, 2046	184.1, 183.3[d,e] (d, $^1J_{Rh-C} \approx$ 70 Hz)
$[Rh(PyT)(CO)_2]BAr^F{}_4$ (**4c**)	2108, 2050	182.8 (d, $^1J_{Rh-C}$ = 68.9 Hz), 182.0 (d, $^1J_{Rh-C}$ = 71.5 Hz)
$[Rh(PyS)(CO)_2]BAr^F{}_4$ (**4d**)	2108, 2051	182.6 (d, $^1J_{Rh-C}$ = 67.5 Hz), 181.9 (d, $^1J_{Rh-C}$ = 69.0 Hz)
$[Ir(PyT)(CO)_2]BPh_4$ (**5a**)	2095, 2028	171.5, 169.8
$[Ir(PyS)(CO)_2]BPh_4$ (**5b**)	2094, 2029	172.1, 171.3[d]
$[Ir(PyT)(CO)_2]BAr^F{}_4$ (**5c**)	2097, 2033	170.7, 169.2
$[Ir(PyS)(CO)_2]BAr^F{}_4$ (**5d**)	2098, 2034	170.5, 169.1

[a]IR spectra were acquired as solutions in dichloromethane. [b]NMR spectra were acquired in CD_2Cl_2 unless otherwise noted. [c]At −30 °C (243 K). [d]In acetone-d_6. [e]The two ^{13}CO resonances overlap.

crystallographic data are shown in Table S1 (**2a**, **2c**, and **3a**) and Table S2 (**4a**, **4d**, **5a**, **5c**, and **5d**), Supporting Information. The solid-state structures (Figure 3 (**2a** and **3a**) and Figure 4 (**4d**, **5a**, and **5d**), Figure S1 (**2c**) and Figure S2 (**4a** and **5c**)) of the eight complexes show that the triazolyl ligand coordinates to the rhodium or iridium metal center via the N3′ nitrogen atom. In the solid state, all of the eight complexes display a square-planar coordination around the metal center. The six-membered metallacycles formed upon chelation of the PyT or PyS ligand adopt pseudo-boat conformations in all structures. This metallacyclic conformation is similar to that found for the solid-state structures of analogous rhodium(I) and iridium(I) complexes containing the bis(1-pyrazolyl)methane ligand.[26b,30]

Selected bond lengths and bond angles of the inner coordination sphere of complexes **2a**, **2c**, **3a**, **4a**, **4d**, **5a** **5c**, and **5d** are listed in Table 2. The M–N(triazole) bond lengths are slightly shorter than those of the M–N(pyrazole) bond lengths, indicating that the triazolyl sp^2 N3′-donor binds more strongly to the metal center than the sp^2 N-donor of the pyrazolyl ring. The triazolyl sp^2 N-donor has previously been reported to possess similar donor strength to that of the imidazolyl sp^2 N-donor,[4] and the imidazolyl sp^2 N-donor was shown to be a stronger N-donor than the pyrazolyl donor in competitive NMR binding experiments.[26d] The N–M–N bite angles (85.8–88.1°) are slightly smaller (2–4°) than the ideal 90° angles expected for square-planar complexes. The N–M–N bite angles in the complexes with dicarbonyls as co-ligands were found to be 1–2° smaller than those measured for analogous complexes with the COD co-ligand. Although the reasons for this observation are not clear, it cannot be accounted for on steric grounds given that the COD co-ligand imposes significantly more steric hindrance than the dicarbonyl co-ligands. The M–N bonds in complexes **4a**, **4d**, **5a**, **5c**, and **5d** with dicarbonyl co-ligands are generally shorter than the M–N bonds in analogous complexes **2a**, **2c**, and **3a** with COD as co-ligands (Table 2). This is likely due to the better electron-withdrawing ability of the dicarbonyl ligands in comparison with the 1,5-cyclooctadiene donor. The M–N bond lengths and the N–M–N (M = Rh/Ir) bite angles of complexes **2a**, **2c**, **3a**, **4a**, **4d**, **5a**, **5c**, and **5d** are similar to those reported in the

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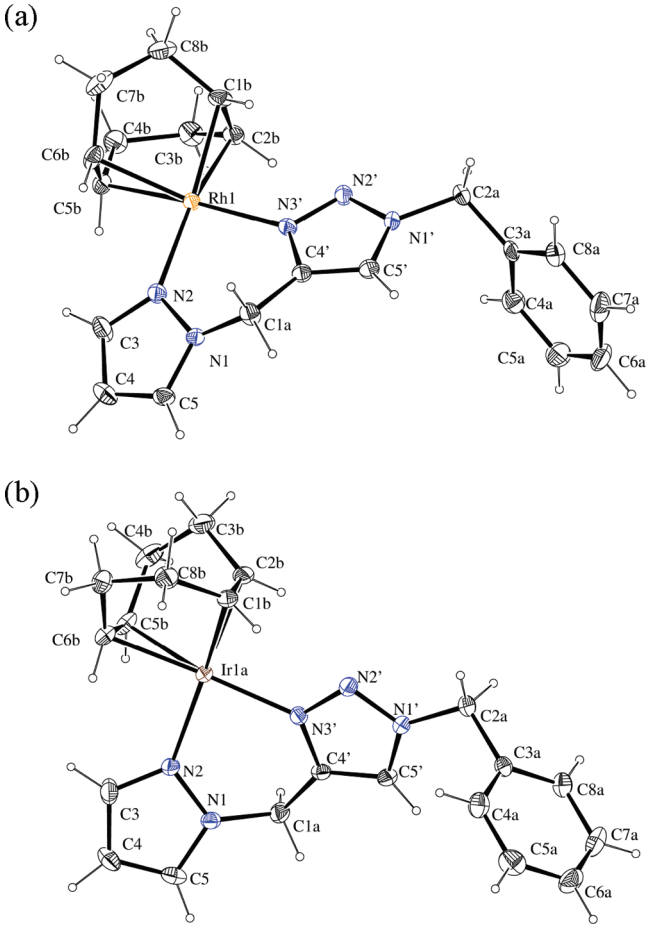

Figure 3. ORTEP depictions of the cationic fragments of the solid-state structures of (a) [Rh(PyT)(COD)]BPh_4 (**2a**) and (b) [Ir(PyT)(COD)]BPh_4 (**3a**) at 40% thermal ellipsoids for the non-hydrogen atoms.

literature for analogous Rh(I)/Ir(I) complexes bearing the pyrazolyl or triazolyl donor ligands.[26b,15d,31]

Catalyzed Intramolecular Hydroamination. We have previously reported that rhodium(I) and iridium(I) complexes containing bidentate sp^2 N−N′ (pyrazolyl and imidazolyl) or N-heterocyclic carbene (NHC) donors or mixed phosphine-NHC, phosphine-sp^2 N (pyrazolyl or imidazolyl) ligands are effective as catalysts for the intramolecular hydroamination of alkynes and alkenes.[26−28,32,49] We have also shown that the efficiency of the catalyst varies significantly even with subtle changes to the ligand donor set. In this work, the efficiency of the rhodium and iridium complexes **2**−**5** containing the PyT (**1a**) or PyS (**1b**) ligands as catalysts for the hydroamination of a number of alkyn- and alkenamines was established.

*a. Cyclization of 4-Pentyn-1-amine (**6**) to 2-Methyl-1-pyrroline (**7**).* Rhodium and iridium complexes (**2**−**5**) exclusively promoted the *exo*-cyclization of 4-pentyn-1-amine (**6**) to form 2-methyl-1-pyrroline (**7**) (Table 3 and Table S3 (Supporting Information)).

The iridium complexes [Ir(N−N′)$(CO)_2$]$BAr^F{}_4$ (**5c**,**d**; N−N′ = PyT or PyS) were the most active catalysts, with TOFs >400 h^{-1} obtained (Table 3). In most cases, it took only ca. 2 h for the reaction to reach completion at 60 °C. A slightly higher TOF of 491 h^{-1} was obtained using the complex [Rh(PyS)-$(CO)_2$]$BAr^F{}_4$ (**4d**) in $CDCl_3$; however, complete conversion was not achieved even after 5 h, possibly due to the low stability of this rhodium complex under the reaction conditions used. The complex **4d** was observed to slowly decompose in CD_2Cl_2 at room temperature, under argon overnight. The TOFs obtained using iridium complexes **5c**,**d** were higher than the reported TOF (387 h^{-1} in C_6D_6) for the same reaction catalyzed by the analogous complex with the bidentate pyrazolyl donor ligand [Ir(bpm)$(CO)_2$]$BAr^F{}_4$, bpm = bis(1-pyrazolyl)methane.[26c] In comparison with other catalysts reported to date for the intramolecular hydroamination of 4-pentyn-1-amine (**6**), the iridium complexes [Ir(N−N′)$(CO)_2$]-$BAr^F{}_4$ (**5c**,**d**) are among the most highly active.[12,14,49]

Generally, the iridium complexes (**5**) assessed here were more active as catalysts for the intramolecular hydroamination reaction of 4-pentyn-1-amine (**6**) than their rhodium analogues. These results are in agreement with previous findings from our studies of a number of cationic rhodium(I) and iridium(I) catalysts with bidentate N−N-donor ligands as catalysts for the hydroamination reaction of 4-pentyn-1-amine (**6**).[26]

The solvent used had a significant effect on the efficiency of these catalyzed reactions, with the efficiency of cyclization following the trend $C_6D_6 \approx CDCl_3$ > THF-d_8. The enhanced reactivity of cationic metal complexes with the $BAr^F{}_4^-$ counteranion in aromatic solvents such as benzene and toluene has been previously observed in our studies of both hydroamination and hydroalkoxylation reactions using similar complexes.[26b,c]

The complexes **4** and **5** with dicarbonyls as co-ligands were, in most cases, significantly better at facilitating the cyclization of 4-pentyn-1-amine (**6**) than the analogous complexes (**2**, **3**) with COD co-ligands (the full catalytic data for the hydroamination of 4-pentyn-1-amine (**6**) are shown in Table S3, Supporting Information). It was also found that complexes **2**−**5** (**c** and **d**) with $BAr^F{}_4^-$ as the counteranion were much more effective as catalysts for the hydroamination reaction than complexes with the BPh_4^- counteranion, **2**−**5** (**a** and **b**) (Table 3).

*b. Catalyzed Hydroamination of Nonterminal Alkynamines 4-Phenyl-3-butyn-1-amine (**8a**) and 5-Phenyl-4-pentyn-1-amine (**8b**) in Toluene-d_8 at 110 °C.* The efficiency of a number of the Rh(I) and Ir(I) complexes **2**−**5** as catalysts for the cyclization of the nonterminal alkynamines 4-phenyl-3-butyn-1-amine (**8a**) and 5-phenyl-4-pentyn-1-amine (**8b**) (Scheme 4 and Table 4) was also determined.

As can be seen in Table 4, all of the complexes used were highly efficient as catalysts, promoting the complete conversion of **8a** and **8b** to the corresponding five-membered cyclic imine products, 2-phenyl-1-pyrroline (**9a**) and 2-benzyl-1-pyrroline (**9b**), at 110 °C in less than 2.4 h. Under the reaction conditions used, the cyclization of 4-phenyl-3-butyn-1-amine (**8a**) reached complete conversion when the first spectrum was acquired after 0.5 h heating in an oil bath at 110 °C. The Ir complexes **5c**,**d** were better than their Rh analogues in promoting the hydroamination of **8a** and **8b**.

The catalyzed hydroamination of **8a** and **8b** was also carried out at 60 °C in benzene-d_6 (Tables S4 and S5, Supporting Information) in order to provide a better comparison with the catalyzed cyclization of 4-pentyn-1-amine (**6**) using cationic rhodium and iridium complexes **2**−**5**. Similar trends to those observed in the cyclization of 4-pentyn-1-amine (**6**) were seen for the cyclization of **8a** and **8b**, namely, that the cationic rhodium and iridium complexes with dicarbonyl co-ligands (**4a**−**d** and **5a**−**d**) were significantly better at promoting this transformation than their analogous complexes with the COD

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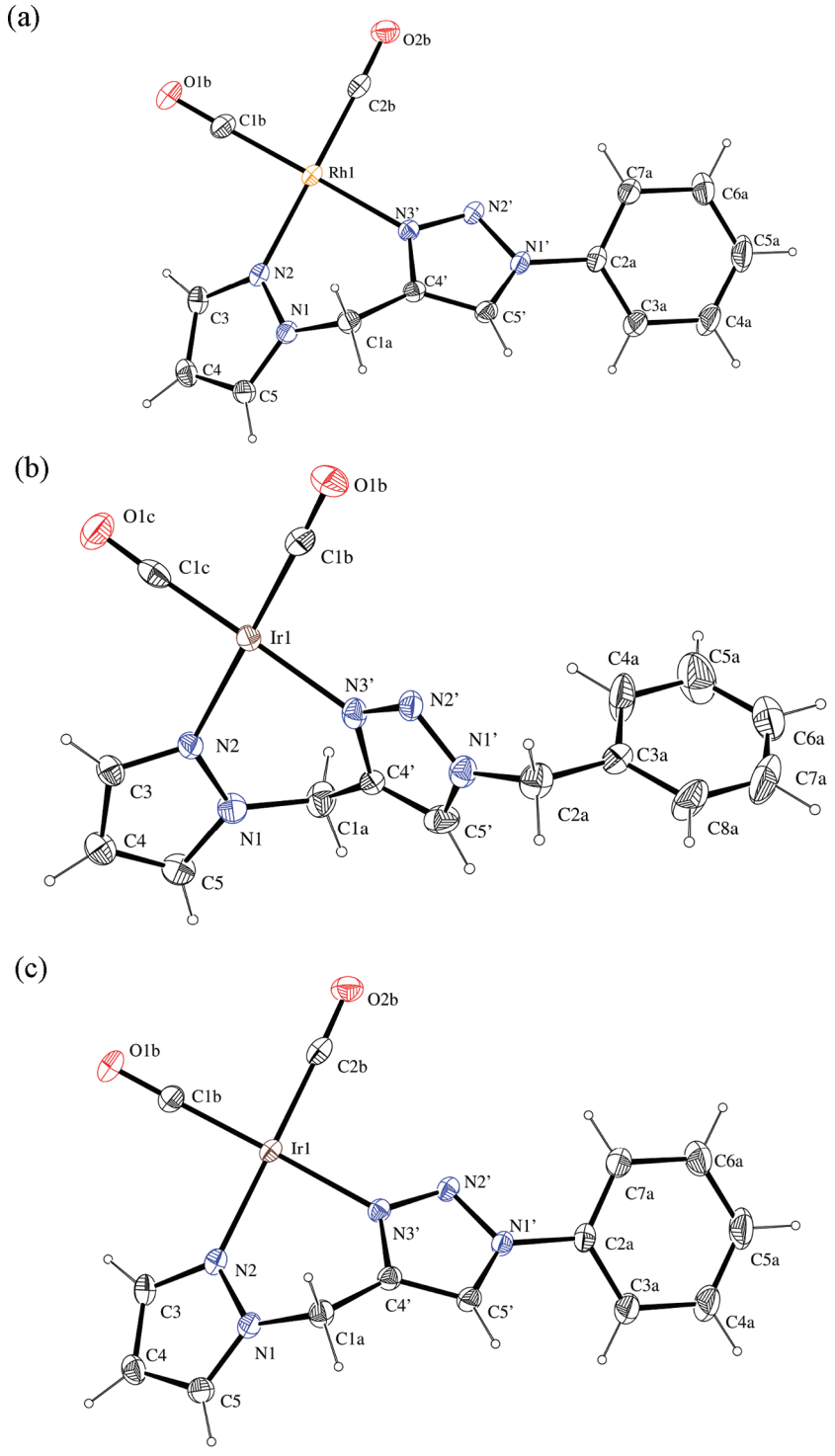

Figure 4. ORTEP depictions of the cationic fragments of (a) $[Rh(PyS)(CO)_2]BAr^F{}_4$ (**4d**); (b) $[Ir(PyT)(CO)_2]BPh_4$ (**5a**); and (c) $[Ir(PyS)(CO)_2]BAr^F{}_4$ (**5d**) at 40% thermal ellipsoids for the non-hydrogen atoms.

co-ligand (**2a–d** and **3a–d**), and cationic complexes with the $BAr^F{}_4^-$ counteranion were again significantly more active than complexes with the BPh_4^- counteranion.

*c. Catalyzed Cyclization of Substituted 4-Penten-1-amines (**10a–c**) to Pyrrolidines (**11a–c**).* Despite significant effort in the area, only a small number of late transition metal catalysts have been reported to promote the intramolecular cyclization of alkenamines.[13,23,25,24] Recently we have shown that cationic rhodium(I) and iridium(I) complexes containing bis(1-pyrazolyl)methane (bpm), $[M(bpm)(CO)_2]BAr^F{}_4$ (M = Rh or Ir), efficiently promoted the cyclization of alkenamines **10a–c** to the corresponding cyclic amines, **11a–c** (Scheme 5).[26e]

Several of the catalysts with the pyrazolyl–triazolyl bidentate ligands PyT (**1a**) or PyS (**1b**) tested here were found to be more effective in catalyzing the cyclization of alkynamines (**6**, **8a**, and **8b**) than the analogous $[M(bpm)(CO)_2]BAr^F{}_4$ complexes with bis(1-pyrazolyl)methane ligands.[26] Encouraged by these results, we utilized the rhodium and iridium complexes

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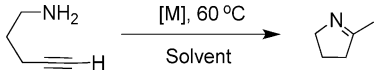
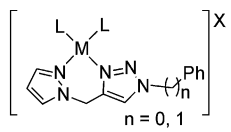
Table 2. Selected Bond Lengths (Å) and Bond Angles (deg)[a] of the Inner Coordination Sphere of $[Rh(PyT)(COD)]BPh_4$ (2a), $[Rh(PyT)(COD)]BAr^F{}_4$ (2c), $[Ir(PyT)(COD)]BPh_4$ (3a) $[Rh(PyT)(CO)_2]BPh_4$ (4a), $[Rh(PyS)(CO)_2]BAr^F{}_4$ (4d), $[Ir(PyT)(CO)_2]BPh_4$ (5a), $[Ir(PyT)(CO)_2]BAr^F{}_4$ (5c), and $[Ir(PyS)(CO)_2]BAr^F{}_4$ (5d)

	2a	2c	3a	4a	4d	5a	5c	5d
				Bond Lengths (Å)				
M–N2 (pyrazole)	2.107(2)	2.084(3)	2.086(2)	2.079(2)	2.074(2)	2.086(4)	2.086(7)	2.073(4)
M–N3′ (triazole)	2.091(2)	2.071(2)	2.081(2)	2.073(2)	2.064(3)	2.064(4)	2.052(4)	2.068(3)
M–C[b] (*trans* N3′)	2.035(2)	2.021(2)	2.026(5)	1.864(3)	1.865(4)	1.838(5)	1.860(7)	1.858(4)
M–C[b] (*trans* N2)	2.021(3)	2.022(2)	2.012(4)	1.862(3)	1.871(3)	1.852(5)	1.844(7)	1.868(4)
				Bond Angles (deg)				
N2–M1–N3′ (M = Rh/Ir)	87.76(8)	86.8(1)	88.11(8)	86.48(8)	86.7(1)	86.3(2)	86.4(1)	85.8(1)

[a]Standard deviations in the least significant figures are given in parentheses. [b]C is the midpoint of the alkene bond for complexes with COD co-ligand or the C atom of the CO co-ligand.

Table 3. Catalyzed Cyclization of 4-Pentyn-1-amine (6) to 2-Methyl-1-pyrroline (7)[a]

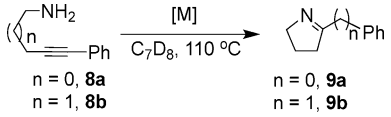


[M] = 

					n =1, PyT (1a)		n = 0, PyS (1b)	
M	**L, L**	**X**	**Complex**	**Solvent**	**TOF[d] (h^{-1})**	**% Conv. at 5 h**	**TOF[d] (h^{-1})**	**% Conv. at 5 h**
Rh	CO, CO	$BAr^F{}_4$	**4c,d** (n=1,0)	THF-d_8	41[b]	79[e]	80[b]	84[e]
				$CDCl_3$	28	67[f]	491	85[e]
				C_6D_6	232	91[g]	270	84[e]
		BPh_4	**4a,b** (n=1,0)	THF-d_8	22	70[h]	2.3	29[e]
Ir	CO, CO	$BAr^F{}_4$	**5c,d** (n=1,0)	THF-d_8	125[c]	>98 (2.0 h)	149	>98 (2.2 h)
				$CDCl_3$	453	>98 (2.6 h)	345	>98 (2.1 h)
				C_6D_6	430	>98 (2.0 h)	428	>98 (1.9 h)
		BPh_4	**5a,b** (n=1,0)	THF-d_8	71[d]	>98 (2.5 h)	121	>98 (2.7 h)

[a]All reactions were carried out under an atmosphere of nitrogen or argon in Young's NMR tubes with 0.6 mL of solvent at 60 °C with 1.7–2.3 mol % of catalyst loading and [substrate] between 0.45 and 0.49 M. [b][Substrate] = 0.50 M. [c][Substrate] = 0.51 M. [d]Calculated at 50% conversion of **6** to **7**. [e]All of these reactions reached complete conversion (>98%) when the last spectra were acquired after 20–23 h. [f]94% conversion reached after 29 h. [g]Completed in 8 h. [h]Reached 88% conversion after 22 h.

Scheme 4. Catalyzed Cyclization of Nonterminal Alkynamines 8a and 8b



containing the PyT (**1a**) or PyS (**1b**) ligands as catalysts for the cyclization of substituted 4-penten-1-amines, **10a–c**, to pyrrolidines, **11a–c** (Scheme 5 and Table 5).

As can be seen in Table 5, the complexes $[M(N–N')(CO)_2]BAr^F{}_4$, **4** and **5** (**c** and **d**), were efficient in promoting the intramolecular *exo*-cyclization of alkenamines **10a–c**, leading exclusively to the formation of the five-membered cyclic amine. Complete conversion of the alkenamines **10a–c** to cyclic amines **11a–c** was observed in most cases after less than 40 h. The rhodium complexes $[Rh(N–N')(CO)_2]BAr^F{}_4$ (**4c** and **4d**) were more active catalysts than their iridium counterparts for the cyclization of substrates **10a–c**. In the case where the catalyzed cyclization of **10c** was performed using the rhodium catalyst $[Rh(PyS)(CO)_2]BAr^F{}_4$ (**4d**) a small amount of side product was observed (ca. 5%). This side product resulted from isomerization of terminal alkene 2,2-diphenyl-4-penten-1-amine (**10c**) to the corresponding internal alkene 2,2-diphenyl-3-penten-1-amine. This has previously been observed with similar catalyzed cyclization reactions using **10c** as reported by us[26e] and others in the catalyzed cyclization of alkene amines.[33]

Increasing steric bulk of the R substituents at the 2 position of the alkenamines **10a–c** led to a significant improvement of the TOFs obtained for the cyclization of **10a–c** to **11a–c**, with the TOFs corresponding to the series R = Ph_2 > $(CH_2)_5$ > $(CH_3)_2$. This trend is clearer and more profound for the rhodium complex catalyzed reactions than in the case of the iridium complexes. The correlation of reaction efficiency with the steric bulk of the substituents on the substrates has also been observed in similar studies and can be attributed to the Thorpe–Ingold effect.[26e,34]

The TOFs obtained here for the Rh(I) and Ir(I) complexes **4c,d** and **5c,d** were similar to those we reported recently using

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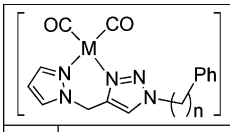
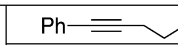
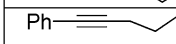
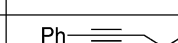
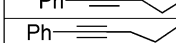
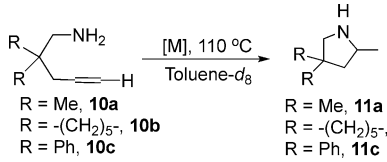
Table 4. Catalyzed Cyclization of 4-Phenyl-3-butyn-1-amine (8a) to 2-Phenyl-1-pyrroline (9a) and 5-Phenyl-4-pentyn-1-amine (8b) to 2-Benzyl-1-pyrroline (9b) in Toluene-d_8 at 110 °C[a]

		n = 1, PyT (1a)		n = 0, PyS (1b)	
		TOF[b] (h^{-1})	Time (h) at >98% Conv.	TOF[b] (h^{-1})	Time (h) at >98% Conv.
Rh	 **8a**	>172[c]	0.5	>182[c]	0.5
	 **8b**	144	2.4	113	1.6
Ir	 **8a**	>186[c]	0.5	>225[c]	<0.4
	 **8b**	202	2.4	>260[c]	0.9

[a]All reactions were carried out under an atmosphere of nitrogen or argon in Young's NMR tubes with 0.6 mL of toluene-d_8 at 110 °C with 1.7−2.3 mol % of catalyst loading and [substrate] between 0.41 and 0.44 M. [b]Calculated at 50% conversion of substrate to product. [c]TOF was estimated from the first two data points at 0 and 0.5 h .

Scheme 5. Catalyzed Cyclization of Alkenamines 10a−c

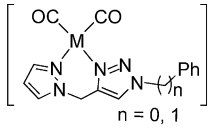
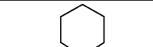
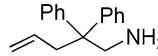
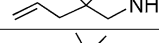


$[M(bpm)(CO)_2]BAr^F_4$ (M = Rh or Ir and bpm = bis(1-pyrazolyl)methane).[26e] The Rh(I) and Ir(I) complexes with pyrazolyl−triazolyl donor ligands investigated here, **4c,d** and **5c,d**, show higher reactivity than a number of catalysts with phosphine-based ligands reported by Hartwig and co-workers for the same substrates.[25b] Our catalysts promote exclusively the cyclization of alkenamines **10a−c** to pyrrolidines **11a−c** with almost no isomerization of the starting materials, unlike the recently reported catalysts by the Hartwig group, for which significant amounts of byproduct were observed for the hydroamination of similar substrates.[25f] This outcome highlights the potential that these rhodium and iridium complexes with pyrazolyl−triazolyl ligands have for wider applications in organic synthesis.

CONCLUSIONS

A series of rhodium(I) and iridium(I) complexes containing the two new pyrazolyl−triazolyl bidentate ligands PyT (**1a**) and PyS (**1b**), [M(N−N′)(COD)]X (**2**, **3**) and $[M(N-N')(CO)_2]$-X (**4**, **5**) (M = Rh or Ir; N−N′ = PyT or PyS, X = BPh_4 or BAr^F_4), Figure 1, were prepared and fully characterized. The solid-state structures of **2a**, **2c**, **3a**, **4a**, **4d**, **5a**, **5c**, and **5d** were determined using single-crystal X-ray diffraction studies, and all complexes have a square-planar coordination around the metal center, as normally expected for Rh(I) and Ir(I) complexes. The N(pyrazole)−M−N(triazole) bite angles deviate slightly (2−4° smaller) from the ideal 90° values. The M−N(triazole) bond lengths are slightly shorter than the M−-N(pyrazole) bond lengths in all the solid-state structures determined, indicating that the 1,2,3-triazolyl sp^2-N3′ donor is a slightly stronger N-donor ligand than the pyrazolyl sp^2 N-donor. The six-membered metallacycles formed upon coordination of the N−N′-donor ligands to the Rh(I) and Ir(I) metal centers adopt slightly distorted boat conformations in all of the solid-state structures determined.

Table 5. Catalyzed Hydroamination of Alkenamines 10a−c to Cyclic Amines 11a−c in Toluene-d_8 at 110 °C[a]

		n = 1, PyT (1a)			n = 0, PyS (1b)		
		TOF[e] (h^{-1})	% Conv. at 5 h	% Conv. at 40 h	TOF[e] (h^{-1})	% Conv. at 5 h	% Conv. at 40 h
Rh	 **10a**	1.6[b]	40	74	8.9	65	96 (21 h)
	 **10b**	4.6[b]	72	93 (22 h)	19	75	>98 (21 h)
	 **10c**	9.5[c]	75	>98 (22 h)	43	89[f]	>93[f]
Ir	 **10a**	6.3	69	96	5.5	56	78
	 **10b**	16	71	92	13	71	97
	 **10c**	7.5	75	98	6.7	64	94

[a]All reactions were carried out under an atmosphere of nitrogen or argon in Young's NMR tubes with 0.6 mL of toluene-d_8 at 110 °C; 4.2 −5.8 mol % of catalyst loading, and [substrate] between 0.30 and 0.35 M. [b][Substrate] = 0.27 M. [c][Substrate] = 0.36 M. [d][Substrate] = 0.40 M. [e]Calculated at 50% conversion of substrate to product. [f]Isomerization to internal alkene was observed (ca. 5%).

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All of the complexes were found to be active as catalysts for the cyclization of 4-pentyn-1-amine (**6**) to 2-methyl-1-pyrroline (**7**) at 60 °C, with TOFs > 400 h^{-1} in many cases. The iridium complexes **3** and **5** were more active in the cyclization of **6** than the analogous rhodium complexes **2** and **4**. Complexes containing the $BAr^F{}_4^-$ counteranion are better catalysts than the analogous complexes with the BPh_4^- counteranion. The cationic Rh(I) and Ir(I) complexes with dicarbonyl co-ligands were generally more active catalysts than those containing the COD co-ligand. Solvent played a significant role in the catalyst efficiency, with C_6D_6 found to be the most suitable solvent of C_6D_6, $CDCl_3$, and THF-d_8.

The cationic dicarbonyl complexes **4c,d** and **5c,d** were efficient in catalyzing the intramolecular cyclization of nonterminal alkynamines (**8a,b**) to cyclic imines (**9a,b**) and cyclization of alkenamines (**10a−c**) to their corresponding cyclic amines (**11a−c**) with minimal formation of byproduct. This highlights the potential application of these catalysts in organic synthesis. The iridium complexes **5c,d** were more efficient than their rhodium **4c,d** analogues for the hydroamination of nonterminal alkynamines **8a,b** while the opposite trend was observed in the hydroamination of alkenamines **10a−c**. The more reactive rhodium and iridium complexes with pyrazolyl−triazolyl donor ligands reported in this work are more efficient and selective than previously reported late transition metal catalysts for the same reactions.

EXPERIMENTAL SECTION

General Considerations. All manipulations of metal complexes and air-sensitive reagents were performed either using standard Schlenk techniques or in a nitrogen- or argon-filled Braun glovebox. Reagents were purchased from Aldrich Chemical Co. Inc. or Alfa Aesar Inc. and were used without further purification unless otherwise stated. Iridium(III) chloride hydrate and rhodium(III) chloride hydrate were obtained from Precious Metals Online, PMO P/L. $[Rh(\mu\text{-Cl})(COD)]_2$,[35] $[Ir(\mu\text{-Cl})(COD)]_2$,[36] $[Rh(\mu\text{-Cl})(CO)_2]_2$,[37] $NaBAr^F{}_4$,[38] $[Rh(COD)_2]BAr^F{}_4$,[39] $[Ir(COD)_2]BAr^F{}_4$,[39] 1-propargylpyrazole,[40] benzyl azide,[41] phenyl azide,[42] 4-pentyn-1-amine (**6**),[43] 4-phenyl-3-butyn-1-amine (**8a**),[26c,44] 5-phenyl-4-pentyn-1-amine (**8b**),[26c,44] and alkenamines (**10a−c**)[26e,45] were prepared using literature methods.

For the purposes of air-sensitive manipulations and in the preparation of air-sensitive complexes, *n*-pentane, tetrahydrofuran, dichloromethane, and methanol were dispensed from a PuraSolv solvent purification system. Tetrahydrofuran and methanol were also distilled from sodium benzophenone ketyl or dimethoxymagnesium, respectively, under an atmosphere of nitrogen or argon. The bulk compressed gases argon (>99.999%) and carbon monoxide (>99.5%) were obtained from Air Liquide and used as received. Nitrogen gas for Schlenk line operation comes from in-house liquid nitrogen boil-off.

^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on Bruker DPX300, DMX400, DMX500, and DMX600 spectrometers operating at 300, 400, 500, and 600 MHz (^1H), respectively, and 75, 100, 125, and 150 MHz (^{13}C), respectively. Unless otherwise stated, spectra were recorded at 25 °C and chemical shifts (δ) are quoted in ppm. Coupling constants (J) are quoted in Hz and have uncertainties of ±0.05 Hz for ^1H and ±0.5 Hz for ^{13}C. ^1H and ^{13}C NMR chemical shifts were referenced internally to residual solvent resonances. Deuterated solvents were purchased from Cambridge Stable Isotopes and used as received. Air-sensitive NMR samples were prepared in an inert gas glovebox or by vacuum transfer of deuterated solvents into NMR tubes fitted with a Young's Teflon valve. For air-sensitive NMR samples CD_2Cl_2 and $CDCl_3$ were distilled over calcium hydride. THF-d_8, C_6D_6, and toluene-d_8 were distilled over sodium benzophenone ketyl.

Infrared spectra were measured using a Nicolet 380 Avatar FTIR spectrometer as solutions in dichloromethane. Melting points were measured using a Stanford Research Systems Optimelt melting point apparatus in glass capillaries and are uncorrected. Microanalyses were carried out at the Campbell Microanalytical Laboratory, University of Otago, New Zealand. Mass spectra were acquired using a Micromass ZQ (ESI-MS) mass spectrometer located in the School of Chemistry, UNSW, or as service samples with the UNSW-Bioanalytical Mass Spectrometry Facility-BMSF (using the Thermo LTQ Orbitrap XL). M is defined as the molecular weight of the compound of interest or cationic fragment for cationic metal complexes.

Synthesis of Ligands 1a and 1b. *Synthesis of 4-((1H-Pyrazol-1-yl)methyl)-1-benzyl-1H-1,2,3-triazole, PyT (**1a**).* 1-Propargylpyrazole (1.06 g, 10.0 mmol) and benzyl azide (1.33 g, 10.0 mmol) were added to a deoxygenated water/2-propanol solvent mixture (20 mL, water/2-propanol = 3:1 (v/v)). Sodium L-ascorbate (0.400 g, 2.00 mmol, 20 mol %) and copper(II) sulfate (0.080 g, 0.500 mmol, 5.00 mol %) were added to the reaction mixture. The mixture was stirred under nitrogen at room temperature overnight, during which the reaction mixture changed from clear to cloudy and precipitation was observed. 2-Propanol was removed *in vacuo*, and the solid product collected by filtration and washed with a saturated solution of disodium ethylenediamine tetraacetic acid (Na_2EDTA) until the filtrate became colorless (8 × 15 mL) and then water (6 × 10 mL). The white solid product was dried in a vacuum desiccator containing potassium hydroxide pellets for several days. Yield: 2.03 g, 85%; mp 99−100 °C. *Note:* if desired, the product can be recrystallized from boiling methanol/water. Anal. Found: C, 65.36; H, 5.38; and N, 29.53. Calcd for $C_{13}H_{13}N_5$: C, 65.25; H, 5.48; and N, 29.27. ESI-MS (ESI$^+$, MeOH), m/z (%, assignment): 262.09 (100, $[M + Na]^+$) amu. ^1H NMR ($CDCl_3$, 500 MHz): δ 7.50 (d, $^3J_{H4-H5}$ = 2.0 Hz, 1H, **H5**), 7.49 (d, $^3J_{H4-H3}$ = 1.9 Hz, 1H, **H3**), 7.41 (s, 1H, triaz-**H5′**), 7.36−7.34 (m, 3H, *p- and m*-C**H** of *Ph*), 7.26−7.24 (m, 2H, *o*-C**H** of *Ph*), 6.24 (apparent t, ^3J = 1.9 Hz, 1H, **H4**), 5.48 (s, 2H, PhC$\mathbf{H}_2$), 5.41 (s, 2H, Pz-C$\mathbf{H}_2$) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 144.4 (triaz-**C4′**), 139.9 (**C3**), 134.5 (*ipso*-**C** of *Ph*), 129.5 (**C5**), 129.3 (*m*-**C** of *Ph*), 129.0 (*p*-**C** of *Ph*), 128.3 (*o*-**C** of *Ph*), 122.6 (triaz-**C**H), 106.2 (**C4**), 54.4 (Ph$\mathbf{C}H_2$) 47.6 (Pz$\mathbf{C}H_2$) ppm.

*Synthesis of 4-((1H-Pyrazol-1-yl)methyl)-1-phenyl-1H-1,2,3-triazole, PyS (**1b**).* 1-Propargylpyrazole (1.00 g, 9.40 mmol) and phenyl azide (1.16 g, 9.35 mmol) were added to a deoxygenated solution of 2-propanol and water (2:1 (v/v), 7.5 mL). Sodium L-ascorbate (0.373 g, 1.88 mmol, 20 mol %) was then added, and the reaction was allowed to stir for 5 min prior to the addition of copper(II) sulfate (0.075 g, 0.47 mmol, 5.0 mol %). The reaction was stirred over 3 days at room temperature under nitrogen. The solvent was removed, and the solid residue washed with a saturated solution of disodium ethylenediamine tetraacetic acid (Na_2EDTA) until the filtrate lost any tinge of blue. This was followed by washing the residue with cold water (3 × 1 mL). *Note*: compound can be recrystallized from water if required. Yield: 1.20 g, 57%; mp 97−99 °C. Anal. Found: C, 63.20; H, 5.17; and N, 31.32. Calcd for $C_{12}H_{11}N_5{\cdot}0.1H_2O$: C, 63.48; H, 4.97; and N, 30.84. ESI-HRMS (ESI$^+$, MeOH), m/z (%, assignment): 226.1084 (100%, $[M + H]^+$). Calcd for $[M + H]^+$ = 226.1014 amu. ^1H NMR ($CDCl_3$, 600 MHz): δ 7.96 (s, 1H, triaz-**H5′**), 7.70 (d, $^3J_{H-H}$ = 7.8 Hz, 2H, *o*-C**H** of **Ph**), 7.59 (br s, 1H, **H3**), 7.56 (br s, 1H, **H5**), 7.43 (t, $^3J_{H-H}$ = 7.8 Hz, 2H, *m*-C**H** of **Ph**), 7.43 (t, $^3J_{H-H}$ = 7.8 Hz, 1H, *p*-C**H** of **Ph**), 6.30 (br s, 1H, **H4**), 5.55 (s, 2H, C$\mathbf{H}_2$) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ 144.5 (triazole-**C4′**), 140.0 (**C5**), 137.1 (**C**$_q$ of **Ph**), 129.9 (*m*-**C**H of **Ph**), 129.8 (**C3**), 129.1 (*p*-**C**H of **Ph**), 121.0 (**C5′**), 120.7 (*o*-**C**H of **Ph**), 106.4 (**C4**), 47.6 (**C**H_2) ppm.

Synthesis of Rhodium and Iridium Complexes. Only representative synthetic procedures are provided here. The synthesis and characterization data for other complexes are supplied as Supporting Information.

*Synthesis of [Rh(PyT)(COD)]BPh$_4$ (**2a**).* A solution of PyT (**1a**, 0.120 g, 0.500 mmol) in methanol (20 mL) was added slowly to a Schlenk flask containing a suspension of $[Rh(\mu\text{-Cl})(COD)]_2$ (0.123 g, 0.250 mmol) in methanol (15 mL) over 15 min. A bright yellow solution was obtained, and the solution was stirred at room

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temperature for 30 min before sodium tetraphenylborate (0.172 g, 0.500 mmol) was added to the solution. A yellow precipitate formed, and the reaction mixture was stirred at room temperature for 1 h. The yellow precipitate was collected by filtration, washed with methanol (3 × 3 mL), and dried under vacuum. Yield: 0.333 g, 87%; mp 134−136 °C (dec). Anal. Found: C, 70.04; H, 5.86; and N, 9.21. Calcd for $C_{45}H_{45}BN_5Rh$: C, 70.23; H, 5.89; and N, 9.21. ESI-MS (ESI^+, MeOH), *m*/*z* (%, assignment): 450.09 (100%, $[M]^+$) amu. ^1H NMR (CD_2Cl_2, 600 MHz): δ 7.40−7.37 (m, 3H, *m- and p*-C**H** of CH_2Ph), 7.38 (br m, 8H, *o*-C**H** of BPh_4), 7.29 (d, $^3J_{H4-H3}$ = 2.5 Hz, 1H, Pz-**H**3), 7.17 (m (dd), ^3J = 7.5 Hz, ^4J = 1.8 Hz, 2H, *o*-C**H** of CH_2Ph), 7.15 (d, ^3J = 2.5 Hz, 1H, **H**5), 6.99 (t, ^3J = 7.5 Hz, 8H, *m*-C**H** of BPh_4), 6.86 (t, ^3J = 7.4 Hz, 4H, *p*-C**H** of B*Ph*$_4$), 6.40 (s, 1H, triaz-C**H**), 6.28 (apparent t (dd), $^3J_{H3-H4,\ H5-H4}$ = 2.5 Hz, 1H, Pz-**H**4), 5.18 (s, 2H, PhC$\mathbf{H}_2$), 4.69 (br s, 2H, C**H** of COD (*trans* to Pz)), 4.47 (s, 2H, Pz-C$\mathbf{H}_2$), 4.44 (br s, 2H, C**H** of COD (*trans* to triaz), 2.56 (m, 4H, C$\mathbf{H}_a\mathbf{H}_b$ of COD), 2.07 (m, 4H, C$\mathbf{H}_a\mathbf{H}_b$ of COD) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 150 MHz): δ 164.6 (q, $^1J_{B-C}$ = 49.4 Hz, *ipso*-**C** of BPh_4), 141.7 (Pz- **C**3), 139.3 (triaz *ipso*-**C**), 136.4 (*o*-**C**H of BPh_4), 134.4 (Pz-**C**5), 133.3 (*ipso*-**C** of CH_2Ph), 129.8 (*p*-**C**H of CH_2Ph), 129.7 (*m*-**C**H of CH_2Ph), 128.8 (*o*-**C**H of CH_2Ph), 126.3 (*m*-**C**H of BPh_4), 124.5 (triaz **C**H), 122.4 (*p*-**C**H of BPh_4), 107.5 (s, Pz-**C**4), 85.8 (d, $^1J_{Rh-C}$ = 11.9 Hz, **C**H of COD (*trans* to Pz)), 84.7 (d, $^1J_{Rh-C}$ = 11.3 Hz, **C**H of COD (*trans* to triaz), 55.8 (s, Ph**C**H_2), 45.3 (Pz-**C**H_2), 30.9 (**C**H_2 of COD, same resonances for all four **C**H_2) ppm.

Synthesis of [Rh(PyS)(COD)]BPh$_4$ ***(2b)***. The synthesis was performed in an analogous fashion to the synthesis of **2a**; see Supporting Information.

Synthesis of [Rh(PyT)(COD)]BAr$^F_4$ ***(2c)***. $[Rh(COD)_2][BAr^F_4]$ (0.090 mg, 0.076 mmol) and PyT (**1a**, 0.018 g, 0.076 mmol) were placed under vacuum for 5 min before being backfilled with argon in a Schlenk flask. Tetrahydrofuran (10 mL) was added, resulting in the formation of a dark yellow solution, which was allowed to stir for an hour. The solvent was then removed *in vacuo*, and dichloromethane (5 mL) added to dissolve the residue. *n*-Pentane (20 mL) was added with vigorous stirring. The reaction mixture was then filtered, and the solid residue was washed with pentane (2 × 20 mL) and dried under vacuum to yield the product as a dark yellow solid. Yield: 0.090 g, 90%; mp 130−132 °C. Anal. Found: C, 48.97; H, 3.23; and N, 4.93. Calcd for $C_{53}H_{37}BF_{24}N_5Rh$: C, 48.46; H, 2.84; and N, 5.33. ESI-MS (ESI^+, MeOH): 449.97 ($[M]^+$, 100%) amu. ^1H NMR ($CDCl_3$, 500 MHz): δ 7.70 (br s, 8H, *o*-C**H** of BAr^F_4), 7.51 (br s, 4H, *p*-C**H** of BAr^F_4), 7.43 (s, 1H, **H5′**), 7.39−7.37 (m, 3H, *p- and m*-C**H** of **Ph**), 7.33 (d, $^3J_{H4-H5}$ = 2.0 Hz, 1H, **H5**), 7.29 (d, $^3J_{H4-H3}$ = 2.0 Hz, 1H, **H3**), 7.21 (d, $^3J_{H-H}$ = 6.5 Hz, 2H, *o*-C**H** of **Ph**), 6.28 (t, $^3J_{H-H}$ = 2.5 Hz, 1H, **H4**), 5.43 (s, 2H, $\mathbf{CH}_2^b$), 5.24 (s, 2H, $\mathbf{CH}_2^a$), 4.77 (br s, 2H, C**H** of COD), 4.48 (br s, 2H, C**H** of COD), 2.56−2.54 (m, 4H, C$\mathbf{H}_2$ of COD), 2.09−2.08 (m, 4H, C$\mathbf{H}_2$ of COD) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 161.7 (q, $^1J_{B-C}$ = 49.0 Hz, *ipso*-**C** to B, BAr^F_4), 142.2 (**C**5), 139.0 ($\mathbf{C}_q$ of triaz), 134.9 (*o*-**C**H to B, BAr^F_4 and $\mathbf{C}_q$ of **Ph**), 133.6 (**C**3), 131.6 (*p*-**C**H of **Ph**), 130.5 (*m*-**C**H of **Ph**), 129.1 (qq, $^2J_{F-C}$ = 30.0 Hz, $^3J_{B-C}$ = 3.0 Hz, CCF_3), 128.7 (*o*-**C**H of **Ph**), 124.7 (q, $^1J_{F-C}$ = 272.3 Hz, $\mathbf{CF}_3$), 122.8 (**C**5′), 117.7 (sept, $^3J_{F-C}$ = 4.0 Hz, *p*-**C**H to B, BAr^F_4), 108.0 (**C**4), 86.2 (d, $^1J_{Rh-C}$ = 13.0 Hz, **C**H of COD), 85.1 (d, $^1J_{Rh-C}$ = 13.0 Hz, **C**H of COD), 56.3 ($\mathbf{CH}_2^b$), 45.5 ($\mathbf{CH}_2^a$), 30.6 (C$\mathbf{H}_2$ of COD), 30.5 (C$\mathbf{H}_2$ of COD) ppm.

Syntheses of [Ir(PyT)(COD)]BPh$_4$ ***(3a)*** *and [Ir(PyS)(COD)]BPh*$_4$ ***(3b)***. The syntheses of **3a** and **3b** were performed in an analogous fashion to the synthesis of [Rh(PyT)(COD)]BPh_4, **2a**; see Supporting Information.

Synthesis of [Ir(PyT)(COD)]BAr$^F_4$ ***(3c)***. The synthesis of **3c** was performed in an analogous fashion to the synthesis of [Rh(PyT)-(COD)]BAr^F_4, **2c**; see Supporting Information.

Synthesis of [Rh(PyT)(CO)$_2$*]BPh*$_4$ ***(4a)***. *Method A (preferred method for the synthesis of* ***4a****)*. A solution of PyT (**1a**, 0.120 g, 0.500 mmol) in methanol (15 mL) was added slowly to a solution of $[Rh(\mu\text{-}Cl)(CO)_2]_2$ (0.097 g, 0.25 mmol) in methanol (15 mL) using a cannula over 15 min. The resulting yellow solution was stirred for 20 min at room temperature. Sodium tetraphenylborate (0.172 g, 0.500 mmol) was added to the reaction, leading to the formation of a yellow precipitate; the reaction mixture was then stirred for a further 15 min. The yellow product was collected by filtration, washed with methanol (3 × 4 mL) and *n*-pentane (3 × 4 mL), and dried *in vacuo*. The desired complex, [Rh(PyT)$(CO)_2$]BPh_4, was collected as a yellow solid. Yield: 0.312 g, 87%; mp 128−130 °C (dec).

Method B. Methanol (3 mL) and pentane (20 mL) were added to a Schlenk containing [Rh(PyT)(COD)]BPh_4 (**2a**, 0.170 g, 0.221 mmol) under an atmosphere of argon. The reaction mixture was degassed via three freeze−pump−thaw cycles and left under vacuum. The reaction mixture was then placed under an atmosphere of carbon monoxide using a balloon for 1 h. The carbon monoxide balloon was removed, and the pale yellow solid was collected by filtration, washed with methanol (2 × 2 mL) and pentane (3 × 5 mL), and dried *in vacuo*. The ^1H NMR spectrum of the solid showed that approximately 40% of the starting material had converted to the desired dicarbonyl product. The carbonylation process had to be repeated twice to obtain complete conversion. Yield: 0.107 g, 72%.

Note: the complex is not very stable in solution (in CD_2Cl_2) at room temperature. NMR spectra were therefore acquired at −30 °C for characterization purposes.

Anal. Found: C, 64.68; H, 4.70; and N, 9.66. Calcd for $C_{39}H_{33}BN_5O_2Rh$: C, 65.29; H, 4.64; and N, 9.76. ESI-MS (ESI^+, MeOH), *m*/*z* (%, assignment): 397.98 (100, $[M]^+$) amu. FTIR (CH_2Cl_2): 2105 (s, νCO) and 2045 (s, νCO) cm^{-1}. ^1H NMR (CD_2Cl_2, 600 MHz): δ 7.68 (d, $^3J_{H4-H3}$ = 2.5 Hz, 1H, Pz-**H**3), 7.42−7.36 (m, 3H, *m*- and *p*-C**H** of CH_2Ph), 7.37 (br m, 8H, *o*-C**H** of BPh_4), 7.24 (m (dd), ^3J = 7.8 Hz, ^4J = 2.6 Hz, 2H, *o*-C**H** of CH_2Ph), 7.20 (d, $^3J_{H4-H5}$ = 2.5 Hz, 1H, Pz-**H**5), 6.97 (t, ^3J = 7.5 Hz, 8H, *m*-C**H** of BPh_4), 6.83 (t, ^3J = 7.4 Hz, 4H, *p*-C**H** of BPh_4), 6.40 (apparent t (dd), $^3J_{H3-H4,\ H5-H4}$ = 2.5 Hz, 1H, Pz- **H**4), 6.33 (s, 1H, triaz-C**H**), 5.29 (s, 2H, PhC$\mathbf{H}_2$), 4.22 (s, 2H, Pz-C$\mathbf{H}_2$) ppm. ^1H NMR (−30 °C, CD_2Cl_2, 600 MHz): δ 7.66 (d, $^3J_{H4-H3}$ = 2.5 Hz, 1H, Pz-**H**3), 7.40−7.36 (br m, 11H, *o*-C**H** of BPh_4 (8H) and *m*- and *p*-C**H** (3H) of CH_2Ph), 7.22−7.19 (m, 3H, *o*-C**H** of CH_2Ph and Pz-**H**5), 6.95 (t, ^3J = 7.5 Hz, 8H, *m*-C**H** of BPh_4), 6.80 (t, ^3J = 7.5 Hz, 4H, *p*-C**H** of BPh_4), 6.38 (apparent t (dd), $^3J_{H3-H4,H5-H4}$ = 2.5 Hz, 1H, **H**4), 5.98 (s, 1H, triaz-C**H**), 5.23 (s, 2H, PhC$\mathbf{H}_2$), 4.03 (s, 2H, Pz-C$\mathbf{H}_2$) ppm. $^{13}C\{^1H\}$ NMR (−30 °C, CD_2Cl_2, 150 MHz): δ 183.1 (d, $^1J_{Rh-C}$ = 69.4 Hz, **C**O), 182.4 (d, $^1J_{Rh-C}$ = 69.8 Hz, **C**O), 164.0 (d, $^1J_{B-C}$ = 49.0 Hz, *ipso*-**C** of BPh_4), 145.8 (Pz-**C**3), 139.3 (*ipso*-**C** of triazole), 135.7 (*o*-**C**H of BPh_4), 134.92 (**C**5), 132.4 (*ipso*-**C** of CH_2Ph), 129.7 (*p*-**C**H of CH_2Ph), 129.4 (*m*-**C**H of CH_2Ph), 128.66 (*o*-**C**H of CH_2Ph), 126.2 (*m*-**C**H of BPh_4) 124.3 (triazole-**C**H), 122.3 (*p*-**C**H of BPh_4), 107.9 (**C**4), 55.7 (Ph$\mathbf{CH}_2$), 44.3 (Pz$\mathbf{CH}_2$) ppm.

Syntheses of [Rh(PyS)(CO)$_2$*]BPh*$_4$ ***(4b)***, *[Ir(PyT)(CO)*$_2$*]BPh*$_4$ ***(5a)***, *[Ir(PyS)(CO)*$_2$*]BPh*$_4$ ***(5b)***, *and [Ir(PyT)(CO)*$_2$*]BAr*$^F_4$ ***(5c)***. The syntheses of **4b** and **5a−c** were performed in an analogous fashion to the synthesis of [Rh(PyT)$(CO)_2$]BPh_4 (**4a**), method B. See Supporting Information.

Synthesis of [Rh(PyT)(CO)$_2$*]BAr*$^F_4$ ***(4c)*** *and [Rh(PyS)(CO)*$_2$*]BAr*$^F_4$ ***(4d)***. The syntheses of **4c** and **4d** were performed in an analogous fashion to the synthesis of [Rh(PyT)$(CO)_2$]BPh_4 (**4a**), method A, with dichloromethane as the solvent; see Supporting Information.

Synthesis of [Ir(PyS)(CO)$_2$*]BAr*$^F_4$ ***(5d)***. $[Ir(COD)_2]BAr^F_4$ (0.150 g, 0.012 mmol) was dissolved in dichloromethane (10 mL), and a solution of PyS (**1b**, 0.027 mg, 0.012 mmol) in dichloromethane (2 mL) was added dropwise, resulting in a color change from purple to bright yellow. This solution was allowed to stir for 3 h before three freeze−pump−thaw cycles were performed. The reaction mixture was then exposed to an atmosphere of carbon monoxide from a balloon and stirred for 2 h, resulting in a very pale yellow solution. The balloon was then removed, and the flask backfilled with nitrogen. The volume was reduced (∼2 mL), and pentane (∼20 mL) added, yielding a bright orange solid upon stirring. This was washed with pentane (2 × ∼20 mL) to yield a bright orange-yellow solid, which was dried *in vacuo* to yield the product. Yield: 0.130 g, 82%. Anal. Found: C, 41.20; H, 2.06; and N, 5.36. Calcd for $C_{46}H_{23}BF_{24}IrN_5O_2$: C, 41.33; H, 1.73; and N, 5.24. FTIR (CH_2Cl_2) ν: 2098 (s, νCO) and 2034 (s, νCO) cm^{-1}. HR-

MS (ESI$^+$, MeOH): $[M]^+$ = 474.0542 (calcd $[M]^+$ = 474.0542) amu. ^{1}H NMR (CD_2Cl_2, 600 MHz): δ 8.32 (s, 1H, **H5′**), 8.05 (br s, 1H, **H5**), 7.86 (br s, 1H, **H3**), 7.74−7.72 (m, 2H, *o*-**CH** of **Ph**), 7.72 (br s, 8H, *o*-**CH** of BAr^F_4), 7.68−7.67 (m, 3H, *p- and m*-**CH** of **Ph**), 7.55 (br s, 4H, *p*-**CH** of BAr^F_4), 6.69 (br s, 1H, **H4**), 5.60 (s, 2H, CH_2) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 150 MHz): δ 170.5 (**CO**), 169.1 (**CO**), 162.2 (q, $^1J_{B-C}$ = 49.5 Hz, *ipso*-**C** to B, BAr^F_4), 148.3 (**C5**), 140.2 (C_q of triaz), 135.8 (**C3**), 135.2 (*o*-**CH** to B, BAr^F_4), 132.5 (*p*-**CH** of **Ph**), 131.1 (*m*-**CH** of **Ph**), 130.8 (C_q of **Ph**), 129.3 (q, $^2J_{F-C}$ = 30.0 Hz, CCF_3, BAr^F_4), 125.0 (q, $^1J_{F-C}$ = 270.0 Hz, CF_3, BAr^F_4), 122.8 (**C5′**), 121.7 (*o*-**CH** of **Ph**), 117.9 (br s, *p*-**CH** to B, BAr^F_4), 109.9 (**C4**), 46.0 (CH_2) ppm.

Single X-ray Crystallographic Studies. X-ray crystallography: A suitable single crystal of **2a**, **2c**, **3b**, **4a**, **4d**, **5a**, **5c**, and **5d** selected under the polarizing microscope (Leica M165Z) was picked up on a MicroMount (MiTeGen, USA) consisting of a thin polymer tip with a wicking aperture. The X-ray diffraction measurements were carried out on a Bruker kappa-II CCD diffractometer at 150 K (**2a**), 151 K (**4d**, **5a**, and **5d**), 155 K (**2c**, **4a**, and **5a**), and 293 K (**3a**) by using graphite-monochromated Mo Kα radiation (λ = 0.710723 Å). The single crystal, mounted on the goniometer using cryo loops for intensity measurements, was coated with paraffin oil and then quickly transferred to the cold stream using an Oxford Cryostream attachment. Symmetry-related absorption corrections using the program SADABS[46] were applied, and the data were corrected for Lorentz and polarization effects using Bruker APEX2 software.[47] The structure was solved by direct methods, and the full-matrix least-squares refinement was carried out using SHELXL. The non-hydrogen atoms were refined anisotropically. Crystallographic data (without structure factors) for the structure[48] reported in this paper have been deposited with the Cambridge Crystallographic Data Centre (CCDC) as supplementary publication numbers 855012−855019. Copies of the data can be obtained free of charge from the CCDC (12 Union Road, Cambridge CB21EZ, UK; tel: +44-1223-336408; fax: +44-1223-336003; e-mail: deposit@ccdc.cam.ac.uk).

Procedure for Catalytic Hydroamination. Procedures for catalytic hydroamination on NMR scales have been reported previously.[49] For reactions carried out at 60 °C, the reaction samples were heated inside the NMR probe in Young's NMR tubes. For the reactions conducted at 110 °C, the reaction samples were heated outside the NMR machine in an oil bath and spectra were acquired periodically at 25 °C.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Synthesis and characterization data for compounds **2b**, **3a−c**, **4b−d**, and **5a−c**; X-ray crystallographic data and a combined CIF file for **2a**, **2c**, **3a**, **4a**, **4d**, **5a**, **5c**, and **5d**. Full results for the catalyzed hydroamination of **6** and the results for the hydroamination of **8a**,**b** at 60 °C and representative ([product] versus time) plots for the catalyzed hydroamination reaction. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Togni, A.; Venanzi, L. M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 497.

(2) (a) Trofimenko, S. *Polyhedron* **2004**, *23*, 197. (b) Edelmann, F. T. *Angew. Chem., Int. Ed.* **2001**, *40*, 1656. (c) Slugovc, C.; Padilla-Martinez, I.; Sirol, S.; Carmona, E. *Coord. Chem. Rev.* **2001**, *213*, 129.

(3) (a) Pettinari, C.; Pettinari, R. *Coord. Chem. Rev.* **2005**, *249*, 663. (b) Bigmore, H. R.; Lawrence, S. L.; Mountford, P.; Tredget, C. S. *Dalton Trans.* **2005**, 635. (c) Pettinari, C.; Pettinari, R. *Coord. Chem. Rev.* **2005**, *249*, 525. (d) Reger, D. L. *Comments Inorg. Chem.* **1999**, *21*, 1. (e) Otero, A.; Fernánez-Baeza, J.; Antiñolo, A.; Tejeda, J.; Lara-Sánchez, A. *Dalton Trans.* **2004**, 1499.

(4) Struthers, H.; Mindt, T. L.; Schibli, R. *Dalton Trans.* **2010**, *39*, 675.

(5) Bai, S.-Q.; Young, D. J.; Hor, T. S. A. *Chem. Asian J.* **2011**, *6*, 292.

(6) Meldal, M.; Tornøe, C. W. *Chem. Rev.* **2008**, *108*, 2952.

(7) (a) McDonald, A. R.; Dijkstra, H. P.; Suijkerbuijk, B. M. J. M.; van Klink, G. P. M; van Koten, G. *Organometallics* **2009**, *28*, 4689. (b) He, Y.; Cai, C. *Chem. Commun.* **2011**, *47*, 12319. (c) Zeitler, K.; Mager, I. *Adv. Synth. Catal.* **2007**, *349*, 1851.

(8) Brotherton, W. S.; Guha, P. M.; Phan, H.; Clark, R. J.; Shatruk, M.; Zhu, L. *Dalton Trans.* **2011**, 3655.

(9) Kilpin, K. J.; Crowley, J. D. *Polyhedron* **2010**, *29*, 3111.

(10) Bai, S.-Q.; Kwang, J. Y.; Koh, L. L.; Young, D. J.; Hor, T. S. A. *Dalton Trans.* **2010**, *39*, 2631.

(11) Crowley, J. D.; Lee, A.-L.; Kilpin, K. J. *Aust. J. Chem.* **2011**, *64*, 1118.

(12) Alonso, F.; Beletskaya, I. P.; Yus, M. *Chem. Rev.* **2004**, *104*, 3079.

(13) (a) Müller, T. E.; Hultzsch, K. C.; Yus, M.; Foubelo, F.; Tada, M. *Chem. Rev.* **2008**, *108*, 3795. (b) Severin, R.; Doye, S. *Chem. Soc. Rev.* **2007**, *36*, 1407. (c) Brunet, J. J.; Neibecker, D. In *Catalytic Heterofunctionlization*; Togni, A.; Grützmacher, H., Eds.; Wiley-VCH: Weinheim, 2001; p 91.

(14) (a) Hong, S.; Marks, T. J. *Acc. Chem. Res.* **2004**, *37*, 673. (b) Molander, G. A.; Romero, J. A. C. *Chem. Rev.* **2002**, *102*, 2161.

(15) (a) Eisen, M. S. *Top. Organomet. Chem.* **2010**, *31*, 157. (b) Stubbert, B. D.; Marks, T. J. *J. Am. Chem. Soc.* **2007**, *129*, 6149. (c) Barnea, E.; Eisen, M. S. *Coord. Chem. Rev.* **2006**, *250*, 855. (d) Broderick, E. M.; Gutzwiller, N. P.; Diaconescu, P. L. *Organometallics* **2010**, *29*, 3242.

(16) (a) Pohlki, F.; Doye, S. *Chem. Soc. Rev.* **2003**, *32*, 104. (b) Odom, A. L. *Dalton Trans.* **2005**, 225.

(17) (a) Müller, T. E.; Pleier, A.-K. *J. Chem. Soc., Dalton Trans.* **1999**, 583. (b) Hartwig, J. F. *Pure Appl. Chem.* **2004**, *76*, 507. (c) Widenhoefer, R. A.; Han, X. Q. *Eur. J. Org. Chem.* **2006**, 4555. (d) Lutete, M.; Kadota, I.; Yamamoto, Y. *J. Am. Chem. Soc.* **2004**, *126*, 1622. (e) Hartung, C. G.; Tillack, A.; Trauthwein, H.; Beller, M. *J. Org. Chem.* **2001**, *66*, 6339. (f) Kondo, T.; Okada, T.; Suzuki, T.; Mitsudo, T. *J. Organomet. Chem.* **2001**, *622*, 149. (g) Brunet, J. J.; Cadena, M.; Chju, N. C.; Diallo, O.; Jacob, K.; Mothes, E. *Organometallics* **2004**, *23*, 1264.

(18) Gagné, M. R.; Marks, T. J. *J. Am. Chem. Soc.* **1989**, *111*, 4108.

(19) (a) Edelmann, F. T. *Coord. Chem. Rev.* **2006**, *250*, 2511. (b) Yin, P.; Loh, T.-P. *Org. Lett.* **2009**, *11*, 3791. (c) Yuen, H. F.; Marks, T. J. *Organometallics* **2008**, *27*, 155.

(20) Walsh, P. J.; Barranger, A. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1992**, *114*, 5459.

(21) (a) McGrane, P. L.; Jensen, M.; Livinghouse, T. *J. Am. Chem. Soc.* **1992**, *114*, 5459. (b) McGrane, P. L.; Livinghouse, T. *J. Am. Chem. Soc.* **1993**, *115*, 11485.

(22) (a) Ayinla, R. O.; Schafer, L. L. *Dalton Trans.* **2011**, *40*, 7769. (b) Swatz, D. L. II; Staples, R. J.; Odom, A. L. *Dalton Trans.* **2011**, *40*, 7762.

(23) Hesp, K. D.; Stradiotto, M. *ChemCatChem* **2010**, *2*, 1192.

(24) (a) Fadini, L.; Togni, A. *Chem. Commun.* **2003**, *1*, 30. (b) Bender, C. F.; Widenhoefer, R. A. *J. Am. Chem. Soc.* **2005**, *127*, 1070. (c) Zhang, Z.; Lee, S. D; Widenhoefer, R. A. *J. Am. Chem. Soc.* **2009**, *131*, 5372. (d) Seayad, A. M.; Selvakumar, K.; Ahmed, M.; Beller, M. *Tetrahedron Lett.* **2003**, *44*, 1679.
(25) (a) Shen, X.; Buchwald, S. L. *Angew. Chem., Int. Ed.* **2010**, *49*, 564. (b) Liu, Z.; Hartwig, J. F. *J. Am. Chem. Soc.* **2008**, *130*, 1570. (c) Hesp, K. D.; Stradiotto, M. *Org. Lett.* **2009**, *11*, 1449. (d) Hesp, K. D.; Tobisch, S.; Stradiotto, M. *J. Am. Chem. Soc.* **2010**, *132*, 413. (e) Bender, C. F.; Widenhoefer, R. A. *J. Am. Chem. Soc.* **2005**, *127*, 1070. (f) Julian, L. D.; Hartwig, J. F. *J. Am. Chem. Soc.* **2010**, *132*, 13813. (g) Taylor, J. G.; Whittall, N.; Hii, K. K. *Org. Lett.* **2006**, *8*, 3561.
(26) (a) Ho, J. H. H.; Hodgson, R.; Wagler, J.; Messerle, B. A. *Dalton Trans.* **2010**, *39*, 4062. (b) Dabb, S. L.; Ho, J. H. H.; Hodgson, R.; Messerle, B. A.; Wagler, J. *Dalton Trans.* **2009**, 634. (c) Burling, S.; Field, L. D.; Messerle, B. A.; Rumble, S. L. *Organometallics* **2007**, *26*, 4335. (d) Burling, S.; Field, L. D.; Messerle, B. A.; Turner, P. *Organometallics* **2004**, *23*, 1714. (e) Nguyen, T. O.; Man, B. Y.-W.; Hodgson, R.; Messerle, B. A. *Aust. J. Chem.* **2011**, *64*, 741.
(27) Burling, S.; Field, L. D.; Messerle, B. A.; Vuong, K. Q.; Turner, P. *Dalton Trans.* **2003**, 4181.
(28) Field, L. D.; Messerle, B. A.; Vuong, K. Q.; Turner, P. *Dalton Trans.* **2009**, 3599.
(29) Kolb, H. C.; Finn, M. G.; Sharpless, K. B. *Angew. Chem., Int. Ed.* **2001**, *40*, 2004.
(30) Field, L. D.; Messerle, B. A.; Rehr, M.; Soler, L. P.; Hambley, T. W. *Organometallics* **2003**, *22*, 2387.
(31) Duan, H.; Sengupta, S.; Petersen, J. L.; Shi, X. *Organometallics* **2009**, *28*, 2352.
(32) (a) Burling, S.; Field, L. D.; Li, H. L.; Messerle, B. A.; Shasha, A. *Aust. J. Chem.* **2004**, *57*, 677. (b) Burling, S.; Field, L. D.; Li, H. L.; Messerle, B. A.; Turner, P. *Eur. J. Inorg. Chem.* **2003**, 3179.
(33) Kondo, T.; Okada, T.; Mitsudo, T. *J. Am. Chem. Soc.* **2002**, *124*, 186.
(34) Reigert, D.; Collin, J.; Meddour, A.; Schulz, E.; Trifonov, A. *J. Org. Chem.* **2006**, *71*, 2514.
(35) Giordano, G. C.; Crabtree, R. H. *Inorg. Synth.* **1990**, *28*, 88.
(36) Herde, J. L.; Lambert, J. C.; Senoff, C. V. *Inorg. Synth.* **1974**, *14*, 18.
(37) McCleverty, J. A.; Wilkinson, G. *Inorg. Synth.* **1976**, *16*, 84.
(38) Yakelis, N. A.; Bergman, R. G. *Organometallics* **2005**, *24*, 3579.
(39) Guzel, B.; Omary, M. A.; Fackler, J. P.; Akgerman, A. *Inorg. Chim. Acta* **2001**, *325*, 45.
(40) Mohr, F.; Mendía, A.; Laguna, M. *Eur. J. Inorg. Chem.* **2007**, 3115.
(41) Alvarez, S. G.; Alvarez, M. T. *Synthesis* **1997**, 413.
(42) Kwok, S. W.; Fotsing, J. R.; Fraser, R. J.; Rodionov, V. O.; Fokin, V. V. *Org. Lett.* **2010**, *12*, 4217.
(43) Burling, S. Ph.D. Thesis, The University of Sydney, 2001.
(44) Fukuda, Y.; Martsubara, S.; Utimoto. *J. Org. Chem.* **1991**, *56*, 5812.
(45) (a) Horillo-Martínez, P.; Hultzch, K. C. *Tetrahedron Lett.* **2009**, *50*, 2054. (b) Horillo-Martínez, P.; Hultzch, K. C.; Hampel, F. *Chem. Commun.* **2006**, *21*, 2221.
(46) *SADABS*; Bruker AXS Inc.: Madison, WI, USA, 2001.
(47) *APEX2* and *SAINT*; Bruker AXS Inc.: Madison, WI, USA, 2007.
(48) Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112.
(49) Field, L. D.; Messerle, B. A.; Vuong, K. Q.; Turner, P.; Failes, T. *Organometallics* **2007**, *26*, 2058.