Intramolecular Hydroamination with Rhodium(I) and Iridium(I) Complexes Containing a Phosphine−N-Heterocyclic Carbene Ligand

Leslie D. Field,[†] Barbara A. Messerle,*[,‡] Khuong Q. Vuong,[‡] and Peter Turner[†]

School of Chemistry, University of Sydney, New South Wales 2006, Australia, and School of Chemistry, University of New South Wales, New South Wales 2052, Australia

Received March 29, 2005

Cationic Rh(I) and Ir(I) complexes of the form $[M(PC)(COD)]BPh_4$ (M = Rh (**4**), Ir (**5**); PC = 3-[2-(diphenylphosphino)ethyl]-1-methylimidazol-2-ylidene) were synthesized by the addition of 3-[2-(diphenylphosphino)ethyl]-1-methylimidazolium (**3**) to $[M(\mu\text{-OEt})(COD)]_2$ (M = Rh, Ir; COD = 1,5-cyclooctadiene) in the presence of base. COD was successfully displaced from $[Rh(PC)(COD)]BPh_4$ (**4**) by addition of carbon monoxide to a methanol/hexane suspension to form $[Rh(PC)(CO)_2]BPh_4$ (**6**). The analogous addition of CO to the iridium compound **5** resulted in the formation of the five-coordinate Ir(I) complex [Ir(PC)(COD)-(CO)]BPh_4 (**7**). The single-crystal X-ray structures of **4**, **5**, and **7** were determined. The metal centers of **4** and **5** are square planar, and the metal center of **7** is a distorted trigonal bipyramid. Complexes **4**−**7** are effective as catalysts for the intramolecular hydroamination of 4-pentyn-1-amine to 2-methyl-1-pyrroline. Complete conversion (>97%) of 4-pentyn-1-amine was observed using complexes **4**−**7** as catalysts, in both chloroform-*d* and tetrahydrofuran-d_8. Reactions in chloroform-*d* in general exhibited higher turnover rates than reactions in tetrahydrofuran-d_8.

Introduction

Metal complexes with N-heterocyclic carbene (NHC) ligands, originally isolated by Arduengo and co-workers,[1] are in many cases more robust than analogous complexes containing phosphine or nitrogen donor ligands, due to the significantly increased donor capacity of the carbene. Whereas NHC ligands have higher donor capability and basicity than phosphine and nitrogen donor ligands, they tend to be less labile than phosphine and N-donor ligands.[2,3] While ligand lability is an important feature of many efficient catalysts which rely on ligand dissociation during the catalytic cycle, this lability can also provide a route for catalyst decomposition. In certain cases strong coordination of ligands may be desirable in catalysts, especially if other labile coligands are present.

Metal complexes containing mono- or polydentate NHC ligands are known to be active catalysts for a number of organic transformations, including ruthenium-catalyzed olefin metathesis[2,4] and palladium-catalyzed Heck type reactions:[2,5] hydroformylation,[6] hydrogenation,[7] and transfer hydrogenation reactions.[8] There are also examples of mixed polydentate donor ligands containing NHC donors as well as phosphorus and nitrogen donors: in particular, metal complexes containing NHC−imine,[9] NHC−hydroxy/alkoxy/phenoxy,[10] NHC−amine/amido,[11] NHC−sulfide,[12] and NHC−phosphine[12−14] ligands. Applications of these metal complexes with mixed donors in catalysis have, as yet, been quite limited, but examples of asymmetric hydrogen-

* To whom correspondence should be addressed. E-mail: b.messerle@unsw.edu.au.

[†] University of Sydney.

[‡] University of New South Wales.

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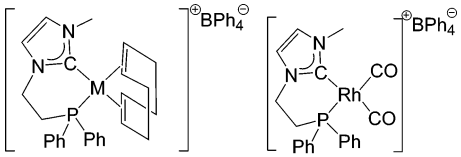
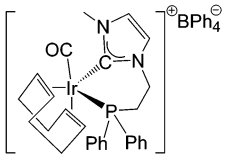
10.1021/om050235p CCC: $30.25
Publication on Web 07/19/2005

ation,[9g] transfer hydrogenation,[9h,10b] Heck type reactions,[9c,e,f,14d] and olefin metathesis[10d] have been reported.

We recently reported a series of rhodium and iridium metal complexes with bidentate sp^2 N-donor ligands which are effective catalysts for hydroamination and, more generally, the addition of X−H (X = N, O, S) to alkynes, an efficient approach to the formation of C−X bonds.[15−17] While these rhodium(I) and iridium(I) complexes with bidentate sp^2 N-donor ligands are effective as catalysts for intramolecular hydroamination, the ligands tend to be labile, and this leads to a decrease in the stability of the catalyst. In developing more robust metal catalysts with more strongly binding ligands, we recently demonstrated that rhodium complexes with a bidentate NHC ligand, [Rh(mdd)$(CO)_2$]X (X = BPh_4 (**1a**), PF_6 (**1b**); mdd = 1,1′-methylene-3,3′-dimethylimidazoline-2,2′-diylidene), are also effective as catalysts for hydroamination.[18]

A number of late-transition-metal complexes catalyze the hydroamination reaction,[19−22] and most of the mechanisms that have been proposed for the reaction involve ligand dissociation as a key step in the reaction process. Optimizing the constitution of the catalyst requires a balance between the stability of the organometallic complexes and the need to incorporate dissociable ligands. Bidentate mixed donor phosphine−NHC ligands are effectively hemilabile and combine the advantages of both the strongly binding NHC donors as well as the more labile phosphine donors. There are, however, no previous reports of Ir complexes with mixed-donor phosphine−NHC ligands and only one report of a Rh complex with ligand of this type.[12] In this paper we report the synthesis and characterization of several rhodium(I) and iridium(I) metal complexes with the bidentate phosphine−NHC donor ligand derived from the imidazolium salt 3-[2-(diphenylphosphino)ethyl]-1-methylimidazolium tetraphenylborate (**3**), [M(PC)(COD)]BPh_4 (M = Rh (**4**); M = Ir (**5**)), [Rh(PC)$(CO)_2$]BPh_4 (**6**), and [Ir(PC)(COD)(CO)]BPh_4 (**7**), where PC = 3-[2-(diphenylphosphino)ethyl]-1-methylimidazol-2-ylidene, and their application as catalysts for the intramolecular hydroamination of alkynes.

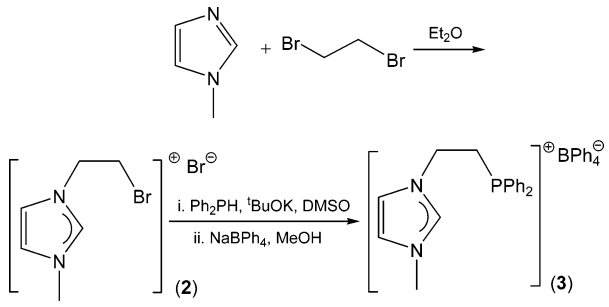




Results and Discussion

Synthesis of Ligand Precursors and Metal Complexes. The ligand precursor 3-[2-(diphenylphosphino)ethyl]-1-methylimidazolium tetraphenylborate (**3**) was synthesized using a two-step reaction sequence (Scheme 1).[14d] The reaction of 1-methylimidazole with an excess of 1,2-dibromoethane in diethyl ether gave the imidazolium salt 3-(2-bromoethyl)-1-methylimidazolium bromide (**2**) in good yield. Nucleophilic substitution of the alkyl bromide with potassium diphenylphosphide in dimethyl sulfoxide[14d] was used to introduce the tertiary phosphine donor. The bromide salt proved to be extremely hygroscopic, and counterion exchange with tetraphenylborate was carried out in situ to assist the isolation of the imidazolium salt. The ^1H NMR spectra of **2** and **3** in DMSO-d_6 exhibit distinct resonances at 9.29 and 9.09 ppm, respectively, and these chemical

Scheme 1



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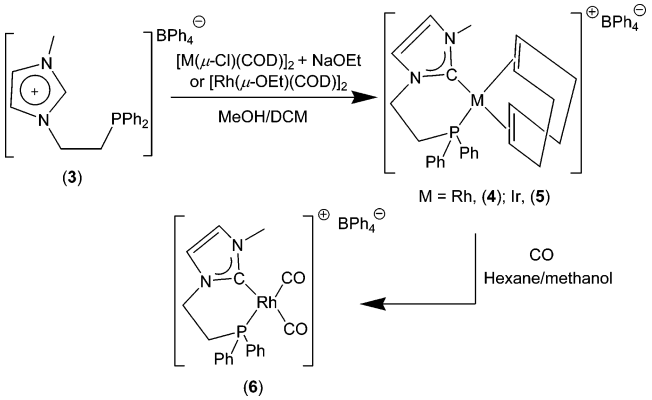
Scheme 2



shifts are typical of H2 on the imidazolium ring.[23] The chemical shifts for H4 and H5 are 7.89 and 7.80 ppm in **2** and 7.77 and 7.58 ppm in **3**, respectively, and are also typical of imidazolium H4/H5 resonances in DMSO-d_6.[23] The $^{31}P\{^1H\}$ NMR spectrum exhibits a singlet resonance at −22.1 ppm, as expected for an alkyldiarylphosphine.

Synthesis of the Rhodium(I) and Iridium(I) Complexes [M(PC)(COD)]BPh$_4$ (M = Rh (4), Ir (5)). The syntheses of the cationic rhodium(I) and iridium(I) metal complexes [M(PC)(COD)]BPh$_4$ (M = Rh (**4**), Ir (**5**)) with the bidentate phosphine−NHC ligand derived from **3** were carried out as indicated in Scheme 2. Suitable metal precursors were generated in situ by the reaction of [M(μ-Cl)(COD)]$_2$ (M = Rh, Ir) with alkoxide base in alcohol solvent. The metal precursors were reacted with the phosphine−carbene generated in situ by the reaction of the imidazolium salt with base. This general approach has been widely used to synthesize complexes of NHCs with a variety of metals.[2] Slow addition of a suspension of the ligand precursor to a solution of the metal precursor was required to obtain mononuclear bidentate P−NHC complexes.

The ^{1}H NMR spectra of both complexes **4** and **5** showed the disappearance of the H2 protons, as expected on deprotonation of the imidazolium nucleus in **3**. The $^{31}P\{^1H\}$ NMR spectra exhibit phosphorus resonances as a singlet at 17.6 ppm for **5** and doublet at 18.3 ppm ($^1J_{Rh-P}$ = 153.5 Hz) for **4**. The ^{13}C resonances due to the carbene carbon in both **4** (175.8 ppm; dd, $^1J_{Rh-C}$ = 48.4 Hz, $^2J_{P-C}$ = 19.4 Hz) and **5** (171.0 ppm; d, $^2J_{P-C}$ = 13.6 Hz) spectroscopically confirm the coordination of carbene to the metal centers. The $^2J_{P-C}$ coupling constants for C2 in both **4** and **5** are consistent with the expected cis relationship between the phosphine and the carbene around the metal centers.

Both complexes **4** and **5** are fluxional in solution, and at room temperature only averaged spectra are observed for the six-membered metallacyclic ring. At low temperature (ca. 200 K) the ring flipping of the metallacycles is frozen, and four different resonances are observed for the protons in N−CH_2 and P−CH_2 of the ethyl bridge. As the ring flip of the metallacyclic rings slows, the two phenyl rings of PPh$_2$ also became inequivalent in both complexes **4** and **5**. The fluxionality of the COD is also significantly reduced at around 200 K, and the four alkenyl protons of the coordinated 1,5-COD appear as four distinct resonances.

Table 1. Crystallographic Data for [Rh(PC)(COD)]BPh$_4$ (4) and [Ir(PC)(COD)]BPh$_4$ (5)

	[Rh(PC)(COD)]BPh$_4$·CH_2Cl_2	[Rh(PC)(COD)]BPh$_4$·CH_2Cl_2
empirical formula	$C_{51}H_{53}BCl_2N_2PRh$	$C_{51}H_{53}BCl_2IrN_2P$
M_r	909.54	998.83
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
a (Å)	9.4557(18)	9.456(2)
b (Å)	15.478(3)	15.486(3)
c (Å)	29.805(6)	29.798(6)
β (deg)	95.351(3)	95.295(4)
V (Å^3)	4343.1(14)	4344.7(16)
D_c (g cm^{-3})	1.391	1.527
Z	4	4
T (K)	150(2)	150(2)
λ(Mo Kα) (Å)	0.71073	0.71073
μ(Mo Kα) (mm^{-1})	0.591	3.271
cryst size (mm)	0.179 × 0.156 × 0.094	0.570 × 0.178 × 0.101
cryst color	orange	red
cryst habit	prism	blade
T(Gaussian)$_{min,max}$	0.910, 0.963	0.305, 0.738
$2\theta_{max}$ (deg)	56.70	56.60
hkl ranges	−12 to +12, −20 to +20, −39 to +39	−12 to +12, −20 to +20, −38 to +39
N	45 601	42 282
N_{ind}	10 598 (R_{merge} = 0.0531)	10 477 (R_{merge} = 0.0609)
$N_{obs}(I > 2\sigma(I))$	7507	8958
GOF(all data)	1.193	1.291
R1(F, $I > 2\sigma(I)$)[a]	0.0358	0.0256
wR2(F^2, all data)[a]	0.0715	0.0633

[a] R1 = $\sum||F_o| - |F||/\sum|F_o|$ for $F_o > 2\sigma(F_o)$; wR2 = $(\sum w(F_o^2 - F_c^2)^2/\sum(wF_c^2)^2)^{1/2}$ for all reflections. $w = 1/[\sigma^2(F_o^2) + (0.020P)^2]$, where $P = (F_o + 2F_c^2)/3$.

Solid-State Structures of 4 and 5. Single crystals of **4** and **5** suitable for X-ray diffraction analysis were obtained by the careful layering of concentrated dichloromethane solutions of **4** and **5** with n-hexane. Crystallographic data are presented in Table 1. The two complexes are isostructural and isomorphous; each asymmetric unit of **4** and **5** contains four crystallographically independent complex molecules, their counteranions, and four molecules of dichloromethane. ORTEP depictions, including atom-numbering schemes of the cations of **4** and **5**, are shown in Figure 1; selected bond lengths and angles are listed in Table 2.

Both complexes crystallized in the space group $P2_1/c$ (No. 14). The metal coordination spheres are square planar, with the rhodium and iridium atoms located only 0.0786 and 0.0878 Å from the coordination planes defined by P(1), C(9), and the midpoints of the alkenyl pairs C(1)−C(2) and C(5)−C(6), respectively. The six-membered metallacycles of **4** and **5** defined by M(1) (M = Rh, Ir), P(1), C(13), C(12), N(2), and C(9) adopt pseudo-boat conformations. Similar conformations have been observed for bidentate NHC−phosphine palladium(II) complexes.[13a] The ligand bite angles are 84.29(6) and 84.91(7)° for **4** and **5**, respectively. The deviations from the ideal angles of 90° may reflect close contact between the methyl group and the COD ligand, with intramolecular distances between C(2) (COD) and C(14) (methyl) of 3.5106(0.0035) and 3.4872(0.0033) Å in **4** and **5**, respectively. This same distortion has been observed for the P−Rh−N bite angle of 82.68° in [Rh(Me$_2$PyP)(COD)]BF$_4$ (Me$_2$PyP = 1-[2-(diphenylphosphino)ethyl]-3,5-dimethylpyrazole) reported by Mathieu et al.[24] in comparison to the significantly larger bite angles

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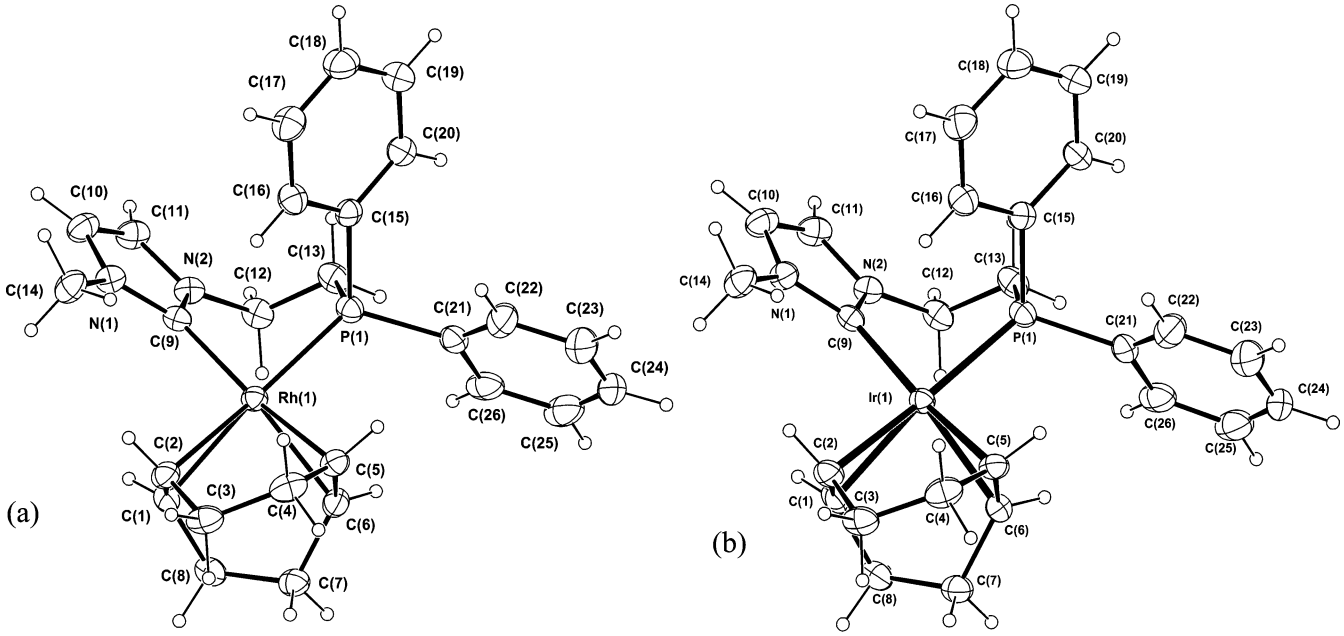

Figure 1. ORTEP depictions of (a) $[Rh(PC)(COD)]^+$ (**4**) and (b) $[Ir(PC)(COD)]^+$ (**5**) as viewed from the top of the coordination plane, showing the pseudo-boat conformations of the $[MCNCH_2CH_2P]$ metallacycles with 50% thermal ellipsoids for the non-hydrogen atoms.

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg)[a] for the Inner Coordination Sphere of $[Rh(PC)(COD)]BPh_4$ (4) and $[Ir(PC)(COD)]BPh_4$ (5)

$[Rh(PC)(COD)]BPh_4$ (**4**)		$[Ir(PC)(COD)]BPh_4$ (**5**)	
Bond Lengths			
Rh(1)−P(1)	2.2811(7)	Ir(1)−P(1)	2.2873(8)
Rh(1)−C(9)	2.064(2)	Ir(1)−C(9)	2.059(2)
Rh(1)−C(1)	2.224(2)	Ir(1)−C(1)	2.208(2)
Rh(1)−C(2)	2.256(2)	Ir(1)−C(2)	2.227(3)
Rh(1)−C(5)	2.198(2)	Ir(1)−C(5)	2.185(2)
Rh(1)−C(6)	2.203(2)	Ir(1)−C(6)	2.187(3)
Bond Angles			
P(1)−Rh(1)−C(9)	84.29(6)	P(1)−Ir(1)−C(9)	84.91(7)
P(1)−Rh(1)−C(5)	93.45(7)	P(1)−Ir(1)−C(5)	93.32(8)
P(1)−Rh(1)−C(6)	95.21(7)	P(1)−Ir(1)−C(6)	94.66(7)
C(9)−Rh(1)−C(1)	91.40(9)	C(9)−Ir(1)−C(1)	91.01(9)
C(9)−Rh(1)−C(2)	99.16(9)	C(9)−Ir(1)−C(2)	98.92(10)
C(1)−Rh(1)−C(5)	95.64(9)	C(1)−Ir(1)−C(5)	96.02(10)
C(1)−Rh(1)−C(6)	80.83(9)	C(1)−Ir(1)−C(6)	80.55(10)
C(2)−Rh(1)−C(5)	80.03(9)	C(2)−Ir(1)−C(5)	79.71(11)
C(2)−Rh(1)−C(6)	86.45(9)	C(2)−Ir(1)−C(6)	86.80(10)

[a] Estimated standard deviations in the least significant figure are given in parentheses.

(88.86(4)°) (M = Rh) and 89.47° (M = Ir) for $[M(PyP)(COD)]BPh_4$[17] (PyP = 1-[2-(diphenylphosphino)ethyl]-pyrazole) in the absence of the interaction between the methyl group and the COD. The M−carbene (M = Rh (**4**), Ir (**5**)) bonds are within the range reported in the literature for M(I)−carbene (M = Rh, Ir).[6a,c,d,8c,9g,12,18,25] The M−C (COD) bonds that are trans to the P are slightly longer than the M−C bonds that are trans to NHC (Table 2). This observation suggests that the phosphine has a slightly stronger trans influence than the NHC ligand. Similar observations have also been made by Danopoulos et al.[13a] for a palladium(II) complex with a related bidentate phosphine NHC−phosphine ligand and Buriak et al.[26] for an iridium(I) complex.

Synthesis of the Rhodium(I) Dicarbonyl Complex $[Rh(PC)(CO)_2]BPh_4$ (6). The cationic rhodium(I) dicarbonyl complex $[Rh(PC)(CO)_2]BPh_4$ (**6**) was synthesized by the displacement of COD from $[Rh(PC)(COD)]BPh_4$ (**4**) under an atmosphere of carbon monoxide in a methanol/*n*-hexane solvent mixture (Scheme 2). Two strong absorption bands at 2083 and 2023 cm^{-1} in the IR spectrum of the resulting bright yellow solid suggest the presence of two inequivalent metal-bound carbonyls. The complex showed signs of decomposition in CD_2Cl_2 solution after about 20 h at room temperature under an atmosphere of nitrogen; however, under an atmosphere of CO, the decomposition of the complex was significantly slowed. $[Rh(PC)(^{13}CO)_2]BPh_4$ (**6b**) was synthesized using the same method as for **6**. The $^{13}C\{^1H\}$ spectrum at room temperature (125 MHz) shows two broad resonances due to ^{13}CO ligands at 187.3 and 183.8 ppm (Figure 2a), whereas all other ^{13}C resonances in the ^{13}C spectrum display no broadening, indicating that the two carbonyls exchange rapidly at this temperature. The phase-sensitive $^{13}C-^{13}C$ NOESY spectrum of **6b** at 275 K[27] exhibits exchange peaks, and this confirms that the two ^{13}COs are exchanging with each other at this temperature. At 200 K, the exchange is slowed significantly and two ^{13}CO resonances for **6b** appear at 186.9 ppm (d of d of d, $^1J_{Rh-C} = 56.4$ Hz, $^2J_{P-C} = 14.5$ Hz, $^2J_{C-C} = 5.0$ Hz, cis to P ^{13}CO), and 183.2 ppm (d of d of d, $^1J_{Rh-C} = 62.4$ Hz, $^2J_{P-C} = 95.2$ Hz, $^2J_{C-C} = 5.0$ Hz, trans to P ^{13}CO) (Figure 2b). When the spectrum was acquired under an atmosphere of ^{13}CO, only a single averaged resonance was observed at 185.6 ppm (Figure 2c). The spectrum of the same sample at

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(27) The spectrum was recorded at 275 K in order to slow the decomposition of the complex.

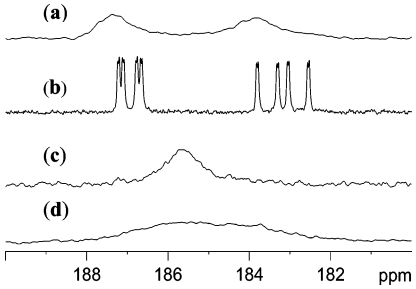
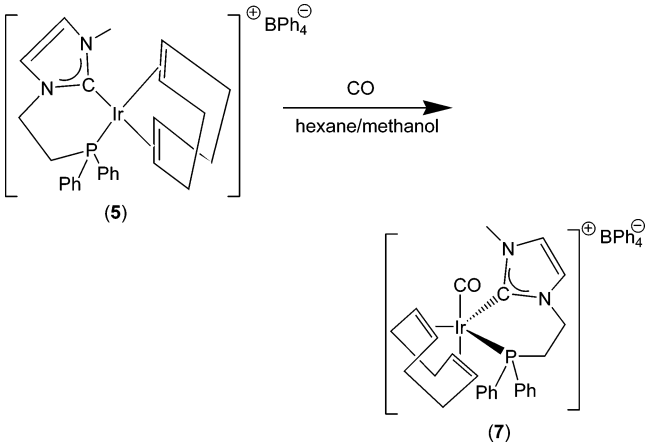


Figure 2. Carbonyl regions of $^{13}C\{^1H\}$ NMR spectra of $[Rh(PC)(^{13}CO)_2]BPh_4$ (**6b**) in CD_2Cl_2: (a) at 298 K under a nitrogen atmosphere; (b) at 200 K under a nitrogen atmosphere; (c) at 298 K under a ^{13}CO atmosphere; (d) at 200 K under a ^{13}CO atmosphere.

Scheme 3



200 K shows only a very broad resonance centered at 185.1 ppm (Figure 2d). These observations clearly show that the two metal-bound CO ligands are in exchange with each other and also with free CO even at 200 K. The exchange mechanism probably involves the formation of the transient, five-coordinate tricarbonyl species $[Rh(PC)(^{13}CO)_3]^+$.

Synthesis of the Iridium(I) Carbonyl Complex [Ir(PC)(COD)(CO)]BPh$_4$ (7). In contrast to the reaction of its rhodium analogue with carbon monoxide, [Ir(PC)(COD)]BPh_4 (**5**) reacts as a suspension in methanol/*n*-hexane under an atmosphere of carbon monoxide to form the stable five-coordinate iridium(I) complex [Ir(PC)(COD)(CO)]BPh_4 (**7**) (Scheme 3). The IR spectrum (KBr disk) of the product shows a single CO absorption band at 1998 cm^{-1}. The $^{31}P\{^1H\}$ NMR shows a single resonance at −26.7 ppm, which is significantly upfield of the phosphorus peak observed at 17.6 ppm in **5**. In the $^{13}C\{^1H\}$ spectra two quaternary carbon peaks at 177.3 (d, $^2J_{P-C}$ = 6.8 Hz) and 139.2 ppm (d, $^2J_{P-C}$ = 10.0 Hz) were assigned to CO and to C2, respectively, by synthesis of the ^{13}C-enriched complex containing ^{13}C-labeled CO and also by long-range $^1H-^{13}C$ correlation experiments. The ^{13}C shift of the metal-bound carbene carbon of the imidazolyl ring appears at 139.2 ppm, which is to significantly higher field than is typical (170−185 ppm) for the iridium(I)-bound carbenes reported so far.[8c,9g,25a,b,28] Octahedral iridium(III) complexes of NH−carbenes normally have metal-bound carbene ^{13}C chemical shifts in the range 127−145 ppm.[8b,29] The shift to higher field of the resonance due to the metal-bound carbene of **7** is most likely because of the unusual trigonal-pyramidal geometry of this iridium(I) complex. As with complexes **4** and **5**, the complex is fluxional at room temperature; however, the ring flip of the six-membered metallacycle is frozen at ca. 200 K.

Table 3. Crystallographic Data for [Ir(PC)(COD)(CO)]BPh$_4$ (7)

empirical formula	$C_{51}H_{51}BIrN_2OP$
M_r	941.92
cryst syst	monoclinic
space group	$P2_1/c$ (No. 14)
a (Å)	16.559(3)
b (Å)	14.696(3)
c (Å)	17.164(3)
β (deg)	99.314(3)
V (Å^3)	4121.9(13)
D_c (g cm^{-3})	1.518
Z	4
T (K)	150(2)
λ(Mo Kα) (Å)	0.710 73
μ(Mo Kα) (mm^{-1})	3.320
cryst size (mm)	0.444 × 0.429 × 0.356
cryst color	colorless
cryst habit	prism
T(SADABS)$_{min,max}$	0.784, 1.000
$2\theta_{max}$ (deg)	56.64
hkl ranges	−22 to +22, −19 to +19, −22 to +22
N	40 164
N_{ind}	9859 (R_{merge} = 0.0206)
$N_{obs}(I > 2\sigma(I))$	8851
GOF(all data)	1.147
R1(F, $I > 2\sigma(I)$)[a]	0.0172
wR2(F^2, all data)[a]	0.0499

[a] $R1 = \sum||F_o| - |F||/\sum|F_o|$ for $F_o > 2\sigma(F_o)$; $wR2 = (\sum w(F_o^2 - F_c^2)^2/\sum(wF_c^2)^2)^{1/2}$ for all reflections. $w = 1/[\sigma^2(F_o^2) + (0.0300P)^2 + 0.0000P]$, where $P = (F_o + 2F_c^2)/3$.

Solid-State Structure of 7. Crystals of **7** suitable for X-ray analysis were obtained by layering a dichloromethane solution of **7** with *n*-hexane at room temperature. Crystallographic data are presented in Table 3. Each unit cell contains four complex molecules and their counterions. ORTEP depictions, including the atom-numbering scheme of the cation of **7**, are shown in Figure 3. Selected bond lengths and angles are listed in Table 4. The complex crystallized in the same space group as that of **4** and **5**. Each unit cell contains four complex molecules and their counterions. The structure of the complex is best described as a distorted-trigonal-bipyramidal geometry about the iridium center with the carbene C and one arm of the COD occupying the two apexes of the bipyramid. The six-membered iridacycle formed by Ir(1), C(9), N(2), C(12), C(13), and P(1) is puckered, and the ligand bite angle is 91.37(5)°. The Ir−carbene bond length (2.0477(18) Å) is slightly shorter than that in complex **5** (2.059(2) Å). The iridium−phosphorus bond length, 2.3613(5) Å, of **7** is significantly longer than the Ir−P bond, 2.2873(8) Å, of complex **5** but is within the range for Ir−P bonds in other five-

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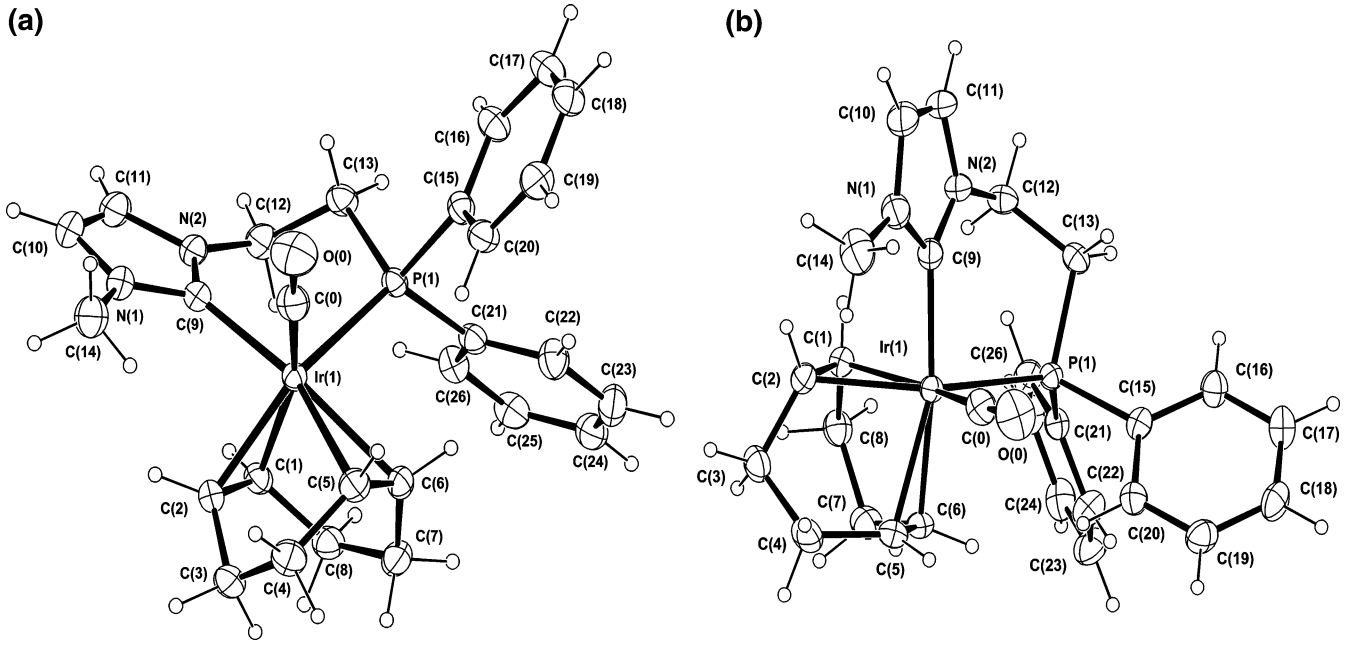

Figure 3. ORTEP depictions of $[Ir(PC)(COD)(CO)]^+$ (**7**) with 50% thermal ellipsoids for the non-hydrogen atoms in two different views (a and b). View b clearly shows the triangular-bipyramidal coordination mode around the Ir(I) center.

Table 4. Selected Bond Lengths (Å) and Bond Angles (deg)[a] for the Inner Coordination Sphere of $[Ir(PC)(COD)(CO)]BPh_4$ (7)

Bond Lengths			
Ir(1)−C(9)	2.0477(18)	Ir(1)−C(5)	2.2775(18)
Ir(1)−P(1)	2.3613(5)	Ir(1)−C(6)	2.2665(17)
Ir(1)−C(0)	1.9119(19)	C(0)−O(0)	1.140(2)
Ir(1)−C(1)	2.1487(17)	C(1)−C(2)	1.436(2)
Ir(1)−C(2)	2.1689(19)	C(5)−C(6)	1.389(3)
Bond Angles			
Ir(1)−C(0)−O(0)	175.35(17)	C(9)−Ir(1)−C(6)	163.57(7)
P(1)−Ir(1)−C(9)	91.37(5)	C(0)−Ir(1)−C(1)	160.49(7)
P(1)−Ir(1)−C(0)	95.50(6)	C(0)−Ir(1)−C(2)	122.02(7)
P(1)−Ir(1)−C(5)	112.90(5)	C(0)−Ir(1)−C(5)	82.42(8)
P(1)−Ir(1)−C(6)	85.34(5)	C(0)−Ir(1)−C(6)	107.46(8)
P(1)−Ir(1)−C(1)	103.47(5)	C(1)−Ir(1)−C(2)	38.84(7)
P(1)−Ir(1)−C(2)	142.31(5)	C(1)−Ir(1)−C(5)	94.17(7)
C(9)−Ir(1)−C(0)	88.87(8)	C(1)−Ir(1)−C(6)	78.97(7)
C(9)−Ir(1)−C(1)	86.19(7)	C(2)−Ir(1)−C(5)	78.58(7)
C(9)−Ir(1)−C(2)	86.27(7)	C(2)−Ir(1)−C(6)	86.54(7)
C(9)−Ir(1)−C(5)	154.80(7)	C(5)−Ir(1)−C(6)	35.59(6)

[a] Estimated standard deviations in the least significant figure are given in parentheses.

coordinate iridium(I) complexes.[30] The Ir−P bond in **7** being longer than the bond in **5** could be attributed to the fact that CO significantly withdraws electrons from the iridium center and, hence, the level of π back-bonding to phosphine is decreased. The Ir−C bond lengths to the equatorial arm COD are Ir(1)−C(1) = 2.1487(17) Å and Ir(1)−C(2) = 2.1689(19) Å, and these are much shorter than the bonds from the metal to the axial arm: Ir(1)−C(5) = 2.2775(18) Å and Ir(1)−C(6) = 2.2665(17) Å. These observations may be explained by the fact that the axial arm is reasonably trans to NHC, C(9)−Ir(1)−C(5) = 154.80(7)° and C(9)−Ir(1)−C(6) = 163.57(7)°, and therefore experiences the rather strong trans influence of the NHC. Hence, the bond length from the alkenyl carbons, C(5) and C(6) of COD, to iridium is longer than the bond lengths to the equatorial alkenyl carbons of COD, C(1) and C(2). Since the equatorial arm is not strictly trans to either CO or P, it does not experience a trans influence from either of these two ligands to any significant extent. The bond length C(1)−C(2) (1.436(2) Å) is also longer than the C(5)−C(6) distance (1.389(3) Å), and this could indicate a significant π back-donation from the metal d orbital into the C−C double bond as well as a σ donation from the alkene π orbital to the metal d orbital.

Catalytic Intramolecular Hydroamination. Complexes of late transition metals[19−22] catalyze both intramolecular and intermolecular hydroamination reactions. Lanthanide catalysts[19,31] and recently reported group IV metal complexes, especially alkyltitanocenes and titanium amido complexes,[32,33] are also effective hydroamination catalysts, particularly in promoting the intermolecular hydroamination of carbon−carbon double and triple bonds. We have shown previously that cationic rhodium(I) complexes with a bidentate chelating NHC ligand, $[Rh(mdd)(CO)_2]X$ (mdd = 1,1′-methylene-3,3′-dimethyldimidazoline-2,2′-diylene, X = BPh_4, PF_6), are known to catalyze the intramolecular hy-

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Scheme 4

Table 5. Relative Efficiency of Complexes 4−7 as Catalysts for the Cyclization of 4-Pentyn-1-amine to 2-Methyl-1-pyrroline[a]

complex	cat. loading (mol %)	N_t [b]	time (h) 50% conversn	time (h) >97% conversn	solvent
[Rh(PC)(COD)]BPh_4 (**4**)	1.1	12	3.8	45	THF-d_8
	1.2	19	2.1	31	$CDCl_3$
[Ir(PC)(COD)]BPh_4 (**5**)	1.4	12	2.9	56	THF-d_8
	1.3	15	2.4	46	$CDCl_3$
[Rh(PC)$(CO)_2$]BPh_4 (**6**)	1.5	51	0.7	14	THF-d_8
	1.3	35	1.2	18	$CDCl_3$
Ir(PC)(COD)(CO)]BPh_4 (**7**)	0.9	19	2.9	40	THF-d_8
	1.4	28	1.3	30	$CDCl_3$
[Rh(mdd)$(CO)_2$]BPh_4 (**1a**)[18]	1.5	6	6	n/a[c]	THF-d_8

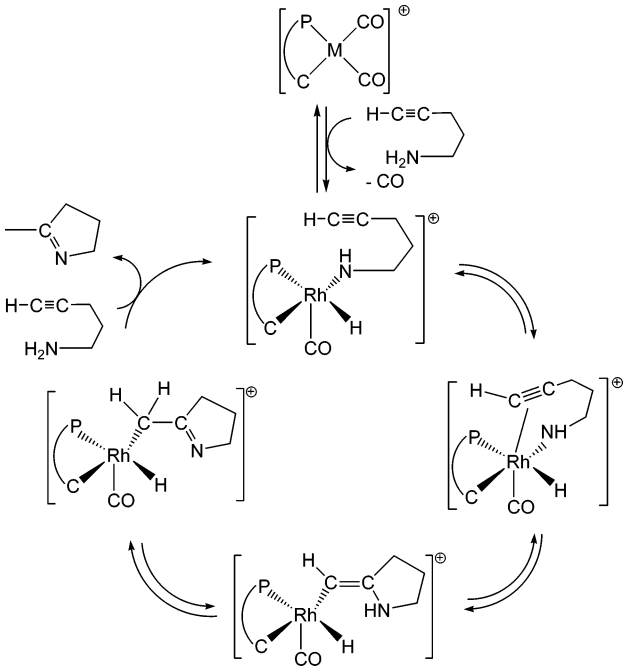
[a] Conditions: reaction at 60 °C. [b] Turnover number = (mol of product produced)/((mol of catalyst used)/h), calculated at 50% conversion. [c] Reaction reached 95% conversion after 61 h.

droamination of aminoalkynes.[18] Likewise, the complexes **4**−**7**, with the mixed-donor phosphine−NHC ligand, are effective catalysts for this reaction. All of the complexes **4**−**7** regioselectively catalyze the intramolecular cyclization of 4-pentyn-1-amine to 2-methyl-1-pyrroline (Scheme 4). The complexes **4**−**7** catalyzed the complete conversion (>97%) of 4-pentyn-1-amine, with 2-methyl-1-pyrroline as the only product in both THF-d_8 and $CDCl_3$ solution at 60 °C. A comparison of the relative efficiencies of the catalysts is given in Table 5. The rhodium dicarbonyl complex **6** is the most effective catalyst, giving turnover rates at 50% conversion of 51 and 35 h^{-1} in THF-d_8 and $CDCl_3$ solutions, respectively. The catalyst efficiency is solvent dependent, and with the exception of compound **6** the hydroamination is faster in $CDCl_3$ than in THF-d_8. The turnover rate for **6** in THF-d_8 is significantly higher than the reaction rate obtained when using the analogous complex with the bidentate bis-carbene ligand [Rh(mdd)$(CO)_2$]BPh_4 (**1a**) as a catalyst for the same transformation under the same reaction conditions.

A working mechanism for the [Rh(PC)$(CO)_2$]BPh_4 (**6**) catalyzed intramolecular hydroamination is given in Scheme 5, on the basis of mechanisms proposed previously for hydroamination using late transition metals.[19,34] In this cycle, the initial step involves loss of a ligand with concomitant oxidative addition of the amine to form the active catalyst. Insertion of the tethered alkyne into the metal−nitrogen bond leads to an enamine which probably tautomerizes to the more stable metal-bound imine before reductive elimination of the product and addition of another substrate molecule to the active catalyst.

There are many places in such a cycle where differences in the coordination environment of the metal could influence the reaction rate. In particular, the mechanism relies on ligand dissociation. The superior catalytic

Scheme 5. Proposed Mechanism for the Intramolecular Cyclization of 4-Pentyn-1-amine to 2-Methyl-1-pyrroline using [Rh(PC)$(CO)_2$]BPh_4 (6)



activity of [Rh(PC)$(CO)_2$]BPh_4 (**6**) in comparison to [Rh(mdd)$(CO)_2$]BPh_4 (**1a**) could result from the fact that the PC ligand in complex **6** is a more labile ligand, with a phosphine donor in place of a strongly binding NHC carbene. Alternatively, increased catalytic activity relative to the symmetric complex [Rh(mdd)$(CO)_2$]BPh_4 (**1a**) could be due to the differences in the trans effects of the carbene and phosphine ligands. This could lead to increased lability of the CO ligands in the presence of the P−NHC donor set. The CO stretching frequencies of compound **6** (2083 and 2023 cm^{-1}) are higher than those observed in **1a** (2071 and 2014 cm^{-1}), and this would be consistent with CO ligands being less strongly bound in complex **6**. Further studies are underway to more fully elucidate the mechanism of the metal-catalyzed cyclization of aminoalkynes.

Conclusions

The syntheses of a series of four complexes of rhodium and iridium incorporating a bidentate phosphine−NHC ligand include the first report of iridium complexes with a chelating mixed phosphine−carbene donor ligand. The solid-state X-ray structures of the complexes [Rh(PC)(COD)]BPh_4 (**4**) and [Ir(PC)(COD)]BPh_4 (**5**) showed that these four-coordinate complexes are square planar about the metal center. The complex [Rh(PC)(CO_2)]BPh_4 (**6**) is also a four-coordinate species and, by analogy with other Rh complexes of this type, is expected to have a square-planar conformation. In contrast, addition of CO to **5** forms the five-coordinate iridium(I) complex [Ir(PC)(COD)(CO)]BPh_4 (**7**), and the crystal structure exhibits effectively a distorted-trigonal-bipyramidal geometry at the metal center.

The complexes [Rh(PC)(COD)]BPh_4 (**4**), [Ir(PC)(COD)]BPh_4 (**5**), [Rh(PC)$(CO)_2$]BPh_4 (**6**), and [Ir(PC)(COD)(CO)]BPh_4 (**7**) are all active as catalysts for the intramolecular cyclization of aminoalkynes. The success of the

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complexes **4**−**7** as hydroamination catalysts relies on the ligands enabling catalysis while also restricting decomposition or deactivation. The complexes with the COD coligands are consistently less active as catalysts than those with CO coligands, and this can probably be attributed to the bulkiness of the COD and the relative strength of binding of the bidentate COD ligand.

Under the conditions investigated, the rhodium dicarbonyl complex **6** was the most efficient catalyst of the four and exhibited a turnover number significantly greater than that for the analogous bis-carbene complex $[Rh(mdd)(CO)_2]BPh_4$ (**1a**). Factors that could give rise to the increased catalyst performance for **6** could be the higher lability of the phosphine ligand or the fact that the mixed PC donor set increases the lability of the carbonyl coligands.

Experimental Section

General Procedures. All manipulations of metal complexes and air-sensitive reagents were carried out using standard Schlenk techniques[35] or in a nitrogen-filled drybox. All solvents were distilled under an atmosphere of nitrogen. Diethyl ether, THF, THF-d_8, *n*-hexane, and *n*-pentane were distilled from sodium benzophenone ketyl. Dichloromethane was distilled from calcium hydride. Methanol was distilled from dimethoxymagnesium. Dimethyl sulfoxide was dried over molecular sieves (4 Å) and degassed via three freeze−thaw−pump cycles prior to use. $CDCl_3$ and CD_2Cl_2 were dried over calcium hydride and vacuum-distilled before use; DMSO-d_6 was used without further purification from freshly opened ampules.

All compressed gases were obtained from British Oxygen Co. (BOC gases) and Linde Gas Pty. Ltd. Nitrogen (>99.5%) and carbon monoxide (>99.5%) were used as supplied without purification. 1-Methylimidazole, 1,2-dibromoethane, potassium *tert*-butoxide, 1,5-cyclooctadiene (COD), sodium tetraphenylborate, and sodium ethoxide were obtained from Aldrich or Lancaster and used without further purification. Iridium(III) chloride hydrate and rhodium(III) chloride hydrate were obtained from Precious Metals Online PMO P/L and were used without further purification. $[Ir(COD)(\mu\text{-}Cl)]_2$,[36] $[Rh(COD)(\mu\text{-}Cl)]_2$,[37] diphenylphosphine,[38] and 4-pentyn-1-amine[39] were prepared by literature methods.

^1H, ^{31}P, and ^{13}C NMR spectra were recorded on Bruker DPX300, DMX500, and DMX600 spectrometers, operating at 300, 500, and 600 MHz (^1H), 121 and 202 MHz (^{31}P), and 75, 125, and 150 MHz (^{13}C). All spectra were recorded at 298 K unless otherwise specified. ^1H NMR and ^{13}C NMR chemical shifts were referenced internally to residual solvent resonances. ^{31}P NMR was referenced externally using H_3PO_4 (85% in D_2O) in a capillary. Electrospray mass spectra were recorded on a Finnigan LQC mass spectrometer.

Melting points were recorded using a Mel-Temp apparatus and are uncorrected. IR spectra were recorded using an ATI Mattson Genesis Series FT-IR spectrometer. Elemental analyses were performed by the Campbell Microanalytical Laboratory at the University of Otago, Otago, New Zealand. Single-crystal X-ray structure analyses were done at the X-ray Crystallography Centre at the University of Sydney, Sydney, Australia.

Synthesis of 3-(2-Bromoethyl)-1-methylimidazolium Bromide (2). 1,2-Dibromoethane (50 mL, 580 mmol) was added to a solution of 1-methylimidazole (8.0 mL, 100 mmol) in diethyl ether (50 mL), and the resulting mixture was stirred at room temperature for 4 days, during which time a white precipitate formed. The precipitate was isolated by filtration and washed with diethyl ether. The filtrate was stirred at room temperature for a further 24 h to give a second crop of crystals, and a third crop was obtained similarly. 3-(2-Bromoethyl)-1-methylimidazolium bromide was collected as a white solid in a total yield of 17.3 g (64%). Mp: 136−138 °C. Anal. Found: C, 26.7; H, 3.8; N, 10.4. Calcd for $C_6H_{10}Br_2N_2$: C, 26.69; H, 3.73; N, 10.38. ES-MS (*m/z*; ES^+): 189.0 ($[C_6H_{10}{}^{79}BrN_2]^+$, 100), 190.9 ($[C_6H_{10}{}^{81}BrN_2]^+$, 95). ^1H NMR (300 MHz, DMSO-d_6): δ 9.29 (s, 1H), 7.89 (d, $^3J_{H4-H5}$ = 1.9 Hz, 1H, *H*4), 7.80 (d, $^3J_{H5-H4}$ = 1.9 Hz, 1H, *H*5), 4.67 (t, $^3J_{CH_2Br-NCH_2}$ = 6.0 Hz, NCH_2), 4.00 (t, 2H, $^3J_{NCH_2-CH_2Br}$ = 6.0 Hz, CH_2Br), 3.93 (s, 3H, NCH_3) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, DMSO-d_6): δ 138.0 (*C*2), 124.7 (*C*5), 123.4 (*C*4), 51.1 (NCH_2), 36.9 (CH_2Br), 32.5 (CH_3) ppm. IR (KBr disk): ν 2984, 1563, 1449, 1360, 1302, 1277, 1234, 1179, 1090, 954, 890, 865, 782, 755, 698, 649, 625 cm^{-1}.

Synthesis of 3-[2-(Diphenylphosphino)ethyl]-1-methylimidazolium Tetraphenylborate (3). Diphenylphosphine (1.92 mL, 11.0 mmol) was added to a solution of potassium *tert*-butoxide (95%, 1.18 g, 10.0 mmol) in dimethyl sulfoxide (16.0 mL) to generate a red solution of potassium diphenylphosphide. After the mixture was stirred for 10 min at room temperature, 3-(2-bromoethyl)-1-methylimidazolium bromide (**2**; fine powder, 2.70 g, 10.0 mmol) was added all at once. The reaction was exothermic, and the diphenylphosphide solution decolorized immediately. The reaction mixture was stirred for 1 h at room temperature, and dimethyl sulfoxide was removed by distillation under vacuum. A solution of sodium tetraphenylborate (3.42 g, 10.0 mmol) in methanol (40 mL) was added, and a white precipitate formed. The reaction mixture was stirred for 30 min, and approximately 25% of the solvent was removed under vacuum. The precipitate was collected by filtration, washed with deoxygenated water (2 × 10 mL), methanol (4 × 15 mL), and diethyl ether (3 × 15 mL) and dried under vacuum. 3-[2-(Diphenylphosphino)ethyl]-1-methylimidazolium tetraphenylborate was obtained as a white solid. Yield: 4.53 g (74%). Mp: 194−195.5 °C. Anal. Found: C, 82.1; H, 6.5; N, 4.1. Calcd for $C_{42}H_{40}BN_2P$: C, 82.08, H, 6.56, N, 4.56. ES-MS (MeOH; *m/z*): ES^+, 295.0 ($C_{18}H_{20}N_2P$, 100%); ES^-, 319.7 (BPh_4, 100%). ^1H NMR (300 MHz, DMSO-d_6): δ 9.09 (s,1H, *H*2), 7.77 (s, 1H, *H*4), 7.58 (s, 1H, *H*5), 7.47−7.40 (m, 10H, C*H*s of PPh_2), 7.18 (br s, 8H, *o*-C*H*s of BPh_4), 6.93 (t, 8H, ^3J = 7.2 Hz, *m*-C*H*s of BPh_4), 6.79 (t, 4H, ^3J = 7.2 Hz, *p*-C*H*s of BPh_4), 4.32 (m, 2H, NCH_2), 3.80 (s, 3H, CH_3), 2.78 (apparent t, ^3J = 7.5 Hz, PCH_2) ppm. $^{31}P\{^1H\}$ NMR (121 MHz, DMSO-d_6): δ −22.1 ppm. $^{13}C\{^1H\}$ NMR (75 MHz, DMSO-d_6): δ 164.3 (q, $^1J_{B-C}$ = 49.4 Hz, *ipso*-*C* of BPh_4), 137.7 (d, $^1J_{P-C}$ = 12.4 Hz, *ipso*-C of PPh_2), 137.5 (s, *C*2), 136.5 (q, $^2J_{B-C}$ = 1.5 Hz, *o*-*C* of BPh_4), 133.4 (d, J_{P-C} = 19.6 Hz, *o*- or *m*-*C* of PPh_2); 130.1 (s, *p*-*C* of PPh_2), 129.7 (d, J_{P-C} = 7.3 Hz, *m*- or *o*-*C* of PPh_2), 126.3 (*q*, $^3J_{B-C}$ = 2.9 Hz, *m*-*C* of BPh_4), 124.4 (s, *C*5), 123.2 (s, *C*4), 122.5 (s, *p*-BPh_4), 47.5 (d, $^2J_{P-C}$ = 26.2 Hz, NCH_2), 36.6 (s, NCH_3), 28.3 (d, $^1J_{P-C}$ = 13.8 Hz, P-CH_2) ppm. IR (KBr disk): ν 3055, 1578, 1550, 1478, 1428, 1267, 1156, 1066, 1029, 834, 741, 708, 626, 610, 601 cm^{-1}.

Synthesis of [Rh(PC)(COD)]BPh_4 (4). A suspension of 3-[2-(diphenylphoshino)ethyl]-1-methylimidazolium tetraphenylborate (**3**; 0.307 g, 0.50 mmol) in methanol (35 mL) was added dropwise to a solution of $[Rh(\mu\text{-}Cl)(COD)]_2$ (0.131 g, 0.265 mmol) and sodium ethoxide (0.055 g. 0.810 mmol) in methanol (15 mL) over 45 min. The reaction mixture was stirred for 30 min, and most of the solvent was removed under vacuum until approximately 4 mL of methanol remained. The yellow-orange precipitate which formed was collected by filtration, washed with methanol (3 × 2 mL) and *n*-pentane (3 × 4 mL), and dried under vacuum. The product **4** was recrystallized by layering hexane (ca. 40 mL) on top of the dichloromethane (ca. 15 mL) solution of the complex overnight

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at 4 °C. Yield: 0.352 g (85.4%). Mp: 166−168 °C dec. ES-MS (MeOH/DCM; *m/z*): ES^+, 505.0 ($[M]^+$, 88%), 428.5 ($[M]^+ - Ph$, 100%); ES^-, 319.6 (BPh_4^-, 100%). Anal. Found: C, 70.3; H, 6.1;, N, 3.5. Calcd for $C_{50}H_{51}BN_2PRh\cdot0.5CH_2Cl_2$: C, 69.95; H, 6.04, N, 3.23. ^1H NMR (300 MHz, CD_2Cl_2): δ 7.49−7.29 (m, 18H, 10H from PPh_2 and 8H from *o*-C*H*s of BPh_4), 7.03 (t, J = 7.5 Hz, 8H, *m*-C*H*s of BPh_4), 6.89 (t, J = 7.2 Hz, 4H, *p*-C*H*s of BPh_4), 6.69 (d, $^3J_{H4-H5}$ = 1.9 Hz, 1H, *H*5), 6.56 (d, $^3J_{H5-H4}$ = 1.9 Hz, 1H, *H*4), 5.23 (br s, 2H, C*H*s of COD), 4.70 (br s, 1H, C*H* of COD), 4.37 (m, 2H, N−CH_2), 4.23 (br s, 1H, C*H*s of COD), 2.48 (m, 2H, P−CH_2), 2.38 (br s, 8H, CH_2 of COD) ppm. $^{31}P\{^1H\}$ NMR (121 MHz, CD_2Cl_2): δ 28.3 (d, ^1J(Rh−P) = 153.5 Hz) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2): δ 175.8 (dd, $^1J_{Rh-C}$ = 48.4 Hz, $^2J_{P-C}$ = 19.4 Hz, *C*2), 163.9 (q, $^1J_{B-C}$ = 49.1 Hz, *ipso-C* of BPh_4), 135.8 (m, *o-C* of BPh_4), 132.4 (br, *C* of PPh_2), 130.9 (*C* of PPh_2), 128.9 (d, J = 10.4 Hz, *C* of PPh_2), 125.5 (q, $^3J_{B-C}$ = 2.1 Hz, *m-C* of BPh_4), 123.0 (C4/C5), 122.0 (C5/C4), 121.7 (*p-C* of BPh_4), 98.0 (br, *C*H of COD), 92.5 (br, *C*H of COD), 49.8 (NCH_2), 38.0 (N−CH_3), 30.6 (br, CH_2 of COD), 27.1 (d, ^1J = 32.5 Hz, P−CH_2) ppm.[40] ^1H NMR (500 MHz, CD_2Cl_2, 200 K): δ 7.57 (m, 2H, C*H*s of PPh_2), 7.46 (m, 1H, C*H* of PPh_2), 7.42−7.36 (m, 5H, C*H*s of PPh_2), 7.27 (br, 8H, *o*-C*H*s of BPh_4), 7.06−7.01 (m, 10H, *m*-C*H*s of BPh_4 and 2H from C*H*s of PPh_2), 6.87 (m, 4H, *p*-C*H*s of BPh_4), 6.70 (s, 1H, *H*5), 6.58 (s, 1H, *H*4), 5.34 (m, 1H, C*H* of COD (trans to P)), 5.04 (m, 1H, C*H* of COD (trans to P)), 4.54 (m 1H, NCH*H*), 4.50 (m, 1H, C*H* of COD (cis to P)), 4.10 (m, 1H, NC*H*H), 3.72 (s, 3H, N−CH_3), 3.53 (m, 1H, C*H* of COD (cis to P)), 2.67−2.59 (m, 5H, P−CH*H* and 2 × CH_2) of COD), 2.27 (m, 1H, P−C*H*H), 2.16 (m, 1H, CH*H* of COD), 2.05 (m, 1H, C*H*H of COD), 1.87 (m, 2H, CH_2 of COD) ppm. IR (KBr disk): ν 3053, 2998, 2982, 2943, 2918, 2878, 2652, 1580, 1556, 1505, 1479, 1455, 1434, 1412, 1395, 1224, 1100, 844, 745, 732, 708, 672, 612, 526 cm^{-1}.

Synthesis of [Ir(PC)(COD)]BPh_4 (5). [Ir(PC)(COD)]BPh_4 (**5**) was prepared using a method similar to that employed for the synthesis of the rhodium analogue **4**. Methanol (30 mL) was added into a solid mixture of [Ir(μ-Cl)(COD)]$_2$ (0.260 g, 0.381 mmol) and sodium ethoxide (0.175 g, 2.572 mmol). The suspension was stirred for 45 min at room temperature, during which time the color of the solid changed from orange-red to yellow. A suspension of 3-[2-(diphenylphosphino)ethyl]-1-methylimidazolium tetraphenylborate (**3**; 0.465 g, 7.567 mmol) in a mixture of methanol (20 mL) and dichloromethane (20 mL) was added dropwise over 40 min. During the addition, the color changed from yellow to dark red, and after the addition was complete, the reaction mixture was stirred for a further 30 min. The solution was filtered, and the flask was rinsed with dichloromethane (2 × 7 mL), leaving a small amount of white solid behind. The red filtrate obtained was stirred for 1 h, and most of the solvent was removed under vacuum until about 25 mL of solvent remained. The solid which precipitated was collected by filtration, washed with ethanol (3 × 5 mL), methanol (3 × 10 mL), and *n*-pentane (3 × 10 mL) and dried under vacuum. The red solid was recrystallized by layering a dichloromethane solution (15 mL) of the solid with hexanes (40 mL) at 4 °C overnight. The red crystals of **5** were collected by filtration, washed with methanol (3 × 3 mL) and *n*-pentane (3 × 5 mL), and dried under vacuum. Yield: 0.562 g (81%). Mp: 146−149 °C (melted then dec). Anal. Found: C, 62.9; H, 5.4; N, 3.0. Calcd for $C_{50}H_{51}BIrN_2P\cdot0.5CH_2Cl_2$: C, 63.42; H, 5.48; N, 2.93. ESI-MS (CH_3CN; *m/z*): ES^+, 595.3 ($[M]^+$, 19%), 591.3 (100%); ES^-, 319.7 ($[BPh_4]^-$, 100%). ^1H NMR (500 MHz, CD_2Cl_2, 205 K): δ 7.50−7.46 (m, 3H, C*H*s of PPh_2), 7.41−7.36 (m, 5H, C*H*s of PPh_2), 7.26 (br s, 8H, *o*-C*H*s of BPh_4), 7.06−7.01 (m, 2H, C*H*s of PPh_2), 6.99 (t, J = 7.3 Hz, 8H, *m*-C*H*s of BPh_4), 6.84 (t, J = 7.3 Hz, 4H, *p*-C*H*s of BPh_4), 6.66 (d, $^3J_{H4-H5}$ = 1.8 Hz, 1H, *H*4), 6.62 (d, $^3J_{H5-H4}$ = 1.8 Hz, 1H, *H*5), 5.09 (m, 1H, C*H* of COD (trans to P)), 4.55 (m, 1H, C*H* of COD trans to P), 4.45 (m, 1H, NC*H*H), 4.35 (m, 1H, C*H* of COD (cis to P)), 3.99 (m, 1H, NCH*H*), 3.70 (s, 3H, NCH_3), 2.91 (m, 1H, C*H* of COD (cis to P)), 2.64−2.43 (m, 3H, CH_2 of COD and P−CH*H*), 2.30−2.11 (m, 3H, C*H* and C*H*H of COD), 2.05 (m, 1H, P−C*H*H), 1.71 (m, 2H, CH_2 of COD), 1.48 (m, 1H, CH*H* of COD) ppm. $^{31}P\{^1H\}$ (202 MHz, CD_2Cl_2, 298 K): δ 17.6 ppm. $^{13}C\{^1H\}$ NMR (150 MHz, CD_2Cl_2, 205 K): δ 171.0 (d, $^2J_{P-C}$ = 13.6 Hz, *C*2), 163.4 (q, $^1J_{B-C}$ = 48.9 Hz, *ipso C* of BPh_4), 135.3 (s, *o-C* of BPh_4), 135.2 (d, J = 11.4 Hz, *o-* or *m-C* of PPh_2), 134.2 (d, $^1J_{P-C}$ = 54.1 Hz, *ipso C* of PPh_2), 131.7 (s, *p-C* of PPh_2), 130.9 (d, J = 9.6 Hz, *m* or *o-C* of PPh_2), 130.5 (s, *p-C* of PPh_2), 128.9 (d, J = 10.8, *m-* or *o-C* of PPh_2), 128.5 (d, J = 9.6 Hz, *m-* or *o-C* of PPh_2), 127.1 (d, J = 40.1 Hz, *ipso-C* of PPh_2), 125.8 (s, *m-C* of BPh_4), 122.3 (s, *C*4), 122.84 (s, *p-C* of BPh_4), 122.81 (s, *C*5), 90.3 (d, $^2J_{P-C}$ = 8.4 Hz, *C*H of COD (trans to P)), 83.1 (d, $^2J_{P-C}$ = 16.2 Hz, *C*H of COD (trans to P)), 79.6 (s, *C*H of COD (cis to P)), 78.7 (s, *C*H of COD (cis to P)), 49.4 (s, NCH_2), 30.1 (s, NCH_3), 35.9 (s, CH_2 of COD), 35.7 (s, CH_2 of COD), 26.7 (s, CH_2 of COD), 26.3 (s, CH_2 of COD), 25.0 (d, ^1J = 37.7 Hz, PCH_2) ppm. IR (KBr disk): ν 3053, 1579, 1435, 1100, 846, 733, 704, 611 cm^{-1}.

Synthesis of [Rh(PC)(CO)$_2$]BPh_4 (6). A suspension of [Rh(PC)(COD)]BPh_4 (**4**; 0.202 g, 0.245 mmol) in a mixture of *n*-hexane (16 mL) and methanol (2 mL) was degassed via three freeze−pump−thaw cycles. The suspension was stirred under an atmosphere of carbon monoxide at room temperature for 2 h, during which time the color of the solid changed from orange to bright yellow. The solid was collected by filtration, washed with methanol (3 × 1.5 mL) and *n*-pentane (3 × 4 mL), and dried under vacuum. [Rh(PC)(CO)$_2$]BPh_4 (**6**) was collected as a bright yellow solid. Yield: 0.176 g (92%). Mp: 130−132 °C dec. Anal. Found: C, 68.6; H, 5.1; N, 3.9. Calcd for $C_{44}H_{39}BN_2O_2PRh$: C, 68.41; H, 5.09; N, 3.63. ES-MS (MeOH/DCM; *m/z*): ES^+, 452.7 ($[M]^+$, 8%), 428.5 ([M − 2 CO + MeOH], 100%), 424.7 ($[M - CO]^+$, 18%); ES^-, 319.5 (100%, BPh_4). ^1H NMR (300 MHz, DCM-d_2): δ 7.60−7.38 (m, 10H, C*H*s of PPh_2), 7.35 (m, 8H, *o*-C*H* of BPh_4), 7.01 (t, ^3J = 7.2 Hz, 8H, *m*-C*H* of BPh_4), 6.87 (t, ^3J = 7.2 Hz, 4H, *p*-C*H* of BPh_4), 6.72 (d, $^3J_{H4-H5}$ = 1.8 Hz, 1H, *H*5), 6.66 (d, $^3J_{H5-H4}$ = 1.8 Hz, 1H, *H*4), 3.98 (m, 2H, NCH_2), 2.31 (m, 2H, PCH_2) ppm. $^{31}P\{^1H\}$ NMR (121 MHz, DCM-d_2): δ 22.1 (d, $^1J_{Rh-P}$ = 124.8 Hz) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2 under CO): δ 185.1 (COs in equilibrium), 167.5 (dd, $^1J_{Rh-C}$ = 42.0, $^2J_{P-C}$ = 19.6 Hz, N*C*N), 163.9 (q, $^1J_{B-C}$ = 49.4 Hz, *ipso*-BPh_4), 135.9 (q, $^2J_{B-C}$ = 1.1 Hz, *o-C*H of BPh_4), 132.4 (d, J_{P-C} = 13.2 Hz, *m*-or *o-C* of PPh_2)132.0 (d, $^4J_{P-C}$ = 2.3 Hz, *p-C* of PPh_2), 130.3 (d, $^1J_{P-C}$ = 51.7 Hz, *ipso-C* of PPh_2), 129.5 (d, J_{P-C} = 10.9 Hz, *o-* or *m- C* of PPh_2), 125.6 (q, $^4J_{B-C}$ = 2.9 Hz, *p-C* of BPh_4), 123.6 (d, $^3J_{Rh-C}$ = 1.1 Hz, *C*5), 123.5 (s, *C*4), 121.8 (s, *p-C* of BPh_4), 48.4 (dd apparent t, $^2J_{P-C}$ = 2.9 Hz, $^3J_{Rh-C}$ = 2.9 Hz, N−CH_2), 38.6 (d, $^3J_{Rh-C}$ = 1.1 Hz, CH_3), 26.4 (d, $^1J_{P-C}$ = 33.3 Hz, PCH_2) ppm. IR (KBr disk): ν 2083 (s, CO), 2023 (s, CO) cm^{-1}.

Synthesis of [Rh(PC)(^{13}CO)$_2$]BPh_4 (6b). The complex was synthesized using the same method as for the synthesis of **6**, except that ^{13}CO was used in place of unlabeled CO. $^{13}C\{^1H\}$ NMR (125 MHz, 200 K): δ 186.9 (d of d of d, $^1J_{Rh-C}$ = 56.4 Hz, $^2J_{P-C}$ = 14.5 Hz, $^2J_{C-C}$ = 5.0 Hz, cis to P ^{13}CO), and 183.2 (d of d of d, $^1J_{Rh-C}$ = 62.4 Hz, $^2J_{P-C}$ = 95.2 Hz, $^2J_{C-C}$ = 5.0 Hz, trans to P ^{13}CO) (enhanced signals) ppm. $^{13}C\{^1H,^{31}P\}$ NMR (125 MHz, 200 K): δ 186.9 (d of d, $^1J_{Rh-C}$ = 56.4 Hz, $^2J_{C-C}$ = 5.0 Hz, cis to P ^{13}CO), 183.2 (d of d, $^1J_{Rh-C}$ = 62.4 Hz, $^2J_{C-C}$= 5.0 Hz, trans to P ^{13}CO) (enhanced signals) ppm. $^{31}P\{^1H\}$ NMR (202 MHz, 200 K): δ 20.8 (d of d of d, $^1J_{Rh-P}$ = 125.3 Hz, $^2J_{C-P}$ = 14.5 Hz, $^2J_{C-P}$ = 95.2 Hz) ppm. IR (KBr disk): ν 2035 (^{13}-CO), 1977 (^{13}CO) cm^{-1}.

Synthesis of [Ir(η^2-PC)(COD)(CO)]BPh_4 (7). A suspension of [Ir(PC)(COD)]BPh_4 (**5**; 0.127 g, 0.139 mmol) in a mixture of *n*-hexane (12 mL) and methanol (1 mL) was degassed via three freeze−pump−thaw cycles. The reaction mixture was stirred under an atmosphere of carbon monoxide for 4 h, during which time the red solid changed to a pale

(40) Only three of the expected four signals for carbons of PPh_2 are reported here. This is possibly due to signal overlapping and/or the fluxionality of the complex at room temperature.

cream color. The solid was collected by filtration, washed with methanol (3 × 0.7 mL) and *n*-pentane (3 × 3 mL), and dried under vacuum. [Ir(PC)(COD)(CO)]BPh_4 (**7**) was collected as a pale cream colored solid. Yield: 0.112 g (92%). Mp: 170 (darkened)−176 (black) °C. Anal. Found: C, 62.7; H, 5.4; N, 3.2. Calcd for $C_{51}H_{51}BIrN_2OP\cdot0.5CH_2Cl_2$: C, 62.83; H, 5.32; N, 2.85. ES-MS (MeOH; *m/z*): ES^+, 595.3 ($[M - CO]^+$, 35%), 591.3 (100%), 483.3 ($[M - CO - COD]^+$, 83%); ES^-, 319.7 ($[BPh_4]^-$, 100%). ES-MS (CH_3CN/DCM; *m/z*): ES^+, 623.5 ($[M]^+$, 6%), 595.3 ($[M - CO]^+$, 30%), 591.3 (100%), 523.9 ($[M - CO - COD + CH_3CN]^+$, 47%), 483.2 ($[M - CO - COD]^+$, 16%); ES^-, 319.5 ($[BPh_4]^-$, 100%). ^{1}H NMR (500 MHz, CD_2Cl_2, 205 K): δ 7.50−7.46 (m, 3H, C*H*s of PPh_2), 7.45−7.40 (m, 1H, C*H* of PPh_2), 7.39−7.35 (m, 2H, C*H*s of PPh_2), 7.29 (br s, 8H, *o*-C*H*s of BPh_4), 7.24−7.20 (m, 2H, C*H*s of PPh_2), 7.15−7.11 (m, 2H, C*H*s of PPh_2), 6.98 (t, J = 7.3 Hz, 8H, *m*-C*H*s of BPh_4), 6.82 (t, J = 7.3 Hz, 4H, *p*-C*H*s of BPh_4), 6.79 (d, ^3J = 1.83 Hz, 1H, *H*5), 6.49 (d, ^3J = 1.83 Hz, 1H, *H*4), 5.26 (m, 1H, C*H* of COD), 4.39 (m, 1H, C*H* of COD), 3.83 (m, 1H, N−CH*H*), 3.81 (s, 3H, N−C*H*$_3$), 3.72 (m, 1H, N−C*H*H), 3.00 (m, 1H, P−CH*H*), 2.69 (m, 1H, C*H* of COD), 2.65−2.54 (m, 3H, C*H*$_2$ and CH*H* of COD), 2.50 (m, 1H, C*H* of COD), 2.12 (m, 1H, C*H*H of COD), 2.04 (m, 1H, CH*H* of COD), 1.96 (m, 1H, P−CH*H* of COD), 1.86 (m, 1H, C*H*H of COD), 1.19 (m, 1H, CH*H* of COD), 0.56 (m, 1H, C*H*H of COD) ppm. ^{31}P{^{1}H} NMR (202 MHZ, CD_2Cl_2, 298 K): δ −26.7 ppm. ^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2, 205 K): δ −27.2 ppm. ^{13}C{^{1}H} NMR (150 MHz, CD_2Cl_2, 205 K): δ 177.3 (d, $^2J_{P-C}$ = 6.8 Hz, *C*O), 163.5 (q, $^1J_{B-C}$ = 49.7 Hz, *ipso-C* of BPh_4), 139.2 (d, $^2J_{P-C}$ = 10.01 Hz, *C*2), 137.5 (d, $^1J_{P-C}$ = 40.9 Hz, *ipso-C* of PPh_2), 135.3 (s, *o-C* of BPh_4), 132.9 (d, J = 11.2 Hz, *o*- or *m-C* of PPh_2), 131.8 (d, $^1J_{P-C}$ = 45.7 Hz, *ipso*-C of PPh_2), 131.5 (s, *p-C* of PPh_2), 130.0 (s, *p-C* of PPh_2), 129.7 (d, J = 8.8 Hz, *m*- or *o-C* of PPh_2), 129.2 (d, J = 10.8 Hz, *o*- or *m-C* of PPh_2), 128.8 (d, J = 9.61, *m*- or *o-C* of PPh_2), 125.8 (s, *m-C* of BPh_4), 123.0 (s, *C*5), 122.0 (s, *C*4), 121.9 (s, *p*-C*H* of BPh_4), 92.6 (s, *C*H of COD), 84.6 (s, *C*H of COD), 61.1 (d, J = 22.8 Hz, *C*H of COD), 50.6 (d, J = 6.4 Hz), 48.8 (s, N*C*H$_2$), 39.2 (s, N*C*H$_3$), 35.4 (d, J = 6.4 Hz, C*H*$_2$ of COD), 34.8 (d, J = 3.6 Hz, C*H*$_2$ of COD), 34.1 (s, *C*H$_2$ of COD), 26.6 (d, $^1J_{P-C}$ = 31.2 Hz, P-*C*H$_2$), 25.8 (s, *C*H$_2$ of COD) ppm. IR (KBr disk): ν 1998 (s, ν(CO)) cm^{-1}. IR (DCM-d_2 solution): ν 1997 (s, ν(CO)) cm^{-1}.

Synthesis of [Ir(η^2-PC)(COD)(^{13}CO)]BPh_4 (7b). The complex was synthesized using the same method as for the synthesis of **7**, except that ^{13}CO was used in place of unlabeled CO. ^{13}C{^{1}H} NMR (125 MHz, CD_2Cl_2): δ 177.02 enhanced signal (d, $^1J_{P-C}$ = 7.4 Hz, ^{13}CO) ppm. IR (KBr disk): ν 1952 (^{13}CO) cm^{-1}.

Crystallographic Studies. Single-crystal diffraction data were collected using a Bruker SMART 1000 CCD diffractometer employing graphite-monochromated Mo Kα radiation generated from a sealed tube. Crystals were attached with Exxon Paratone N to a short length of fiber supported on a thin piece of copper wire inserted in a copper mounting pin and quenched in a cold nitrogen gas stream from an Oxford Cryosystems Cryostream. The data integration and reduction were undertaken with SAINT and XPREP,[41] and subsequent computations were carried out with the WinGX[42] and XTAL[43] graphical user interfaces. A Gaussian absorption correction[41,44] was applied to the data for [Rh(PC)(COD)]BPh_4 (**4**) and [Ir(PC)(COD)]BPh_4 (**5**), and a multiscan correction determined with SADABS[45] was applied to the data for [Ir(PC)(COD)(CO)]BPh_4 (**7**).

The structures were solved by direct methods with SIR97[46] and extended and refined with SHELXL-97.[47] The nonhydrogen atoms were modeled with anisotropic displacement parameters, and in general a riding atom model was used for the hydrogen atoms. The alkene hydrogen sites were located and modeled with isotropic displacement parameters. ORTEP[48] depictions of the molecules with 50% displacement ellipsoids are provided in Figures 1 and 3.

General Procedure for Catalytic Hydroamination. Metal complex catalyzed intramolecular hydroamination reactions of 4-pentyn-1-amine to give 2-methyl-1-pyrroline were performed on a small scale in NMR tubes fitted with Youngs concentric Teflon valves. The substrate was added to a solution of the catalyst in deuterated solvent in a NMR tube at room temperature. All reactions were performed with approximately 1.1−1.5 mol % of catalyst loading at 60 °C by heating the sample in an oil bath maintained at 60 °C or heating within the probe of the NMR spectrometer. The temperature within the magnet was calibrated using an Omega Microprocessor Thermometer (Model HH23) or using ethylene glycol. ^{1}H NMR spectra were recorded with a relaxation delay of 5 s, and the conversion of 4-pentyn-1-amine to 2-methyl-1-pyrroline was determined by integration of the product resonances relative to the substrate resonances. Complete conversion was taken to be the time where no remaining substrate resonances were evident. The turnover rate (N_t, h^{-1}) was calculated as the (mol of product)/((mol of catalyst) h) and was calculated at the point of 50% conversion.

Acknowledgment. We gratefully acknowledge financial support from the University of New South Wales and the Australian Research Council. K.Q.V. thanks the Australian Government for an International Postgraduate Research Scholarship (IPRS). Discussions with Dr. HsiuLin Li (University of Sydney) are warmly acknowledged. We also thank Dr. Keith Fisher for obtaining ESI-MS spectra.

Supporting Information Available: X-ray crystallographic data are available in electronic format as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

OM050235P

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