Late Transition Metal Catalyzed Intramolecular Hydroamination: The Effect of Ligand and Substrate Structure

Suzanne Burling,[†] Leslie D. Field,*[,‡] Barbara A. Messerle,*[,‡] and Sarah L. Rumble[‡]

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

Received May 2, 2007

A series of cationic rhodium(I) and iridium(I) complexes of the type $[M(N-N)(CO)_2][BPh_4]$ containing the imidazole-based bidentate nitrogen donor ligands (N−N), including bis(*N*-methylimidazol-2-yl)methane (bim) (**1**, **a** M = Rh, **b** M = Ir), bis(*N*-methylimidazol-2-yl)ketone (bik) (**5, a** M = Rh, **b** M = Ir), 1,1-bis(*N*-methylimidazol-2-yl)ethane (bie) (**3**, M = Rh), 2,2-bis(*N*-methylimidazol-2-yl)propane (bip) (**4**, M = Rh), and bis(*N*-methylbenzimidazol-2-yl)methane (bbnzim) (**6a** M = Rh, **6b** M = Ir), were synthesized and characterized. Complexes incorporating the pyrazole analogue bis(1-pyrazolyl)methane (bpm) $[M(bpm)(CO)_2][BPh_4]$ (**2**, **a** M = Rh, **b** M = Ir) were also prepared. The efficiency of each of the complexes as catalysts for the cyclization of 4-pentyn-1-amine to 2-methyl-1-pyrroline is reported. The influence of structural variations of the nitrogen donor ligand on the catalytic efficiency of cationic complexes of the type $[M(N-N)(CO)_2][BPh_4]$ for the hydroamination reaction was found to be much less than the influence of the nature of the counterion. The scope of the substrates for the intramolecular hydroamination of alkynamines was also investigated using Rh and Ir catalysts with the bim and bpm ligands, using 3-butyn-1-amine (**7a**), 3-pentyn-1-amine (**7b**), 4-phenyl-3-butyn-1-amine (**7c**), 4-pentyn-1-amine (**8a**), 4-hexyn-1-amine (**8b**), 5-phenyl-4-pentyn-1-amine (**8c**), 5-hexyn-1-amine (**9**), and 6-heptyn-1-amine (**10**) as substrates. The rhodium and iridium catalysts under investigation preferentially catalyze the formation of five-membered rings and do not catalyze the formation of four- or seven-membered rings. The effect of the substituents on the alkyne on the efficiency of hydroamination differentiates Rh(I) and Ir(I) and suggests the nature of the reactive metal-bound alkynyl intermediate.

Introduction

The hydroamination reaction involves the addition of N−H bonds across carbon−carbon double and triple bonds and offers an atom-efficient pathway to produce new primary, secondary, and tertiary amines as well as imines and enamines.[1,2] While the hydroamination reaction is thermodynamically reasonable, there is a high activation barrier under normal conditions, and the reaction is only practical when it is appropriately catalyzed.[3] Many catalytic systems are known to promote hydroamination, including acids,[4] bases,[5] and alkali earth metals,[1] but the most successful approaches have been the use of transition metal complexes and lanthanide complexes.[1,6,7,10] Recent significant developments have been the use of active group IV metal complexes including alkyltitanocenes and titanium amido complexes.[8] Intermolecular hydroamination reactions have also been achieved using lanthanide,[9,10] actinide,[11] and late transition metal complexes.[12] Catalytic systems employed for the intramolecular hydroamination reaction include calcium,[13] early transition metals,[14] rare earth metals,[15] and lanthanides,[9,16−18] as well as late transition metals,[6,19−23] especially palladium.[24−27] In contrast to both early transition metal and lanthanide complexes, late transition metal complexes have the advantage of a low

* Corresponding author. E-mail: b.messerle@unsw.edu.au.
[†] University of Sydney.
[‡] University of New South Wales.

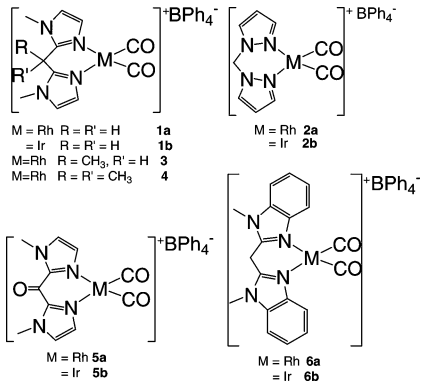
(1) Müller, T. E.; Beller, M. *Chem. Rev.* **1998**, *98*, 675−703, and references therein.
(2) Pohlki, F.; Doye, S. *Chem. Soc. Rev.* **2003**, *32*, 104−114.
(3) Beller, M.; Seayad, J.; Tillack, A.; Jiao, H. *Angew. Chem., Int. Ed.* **2004**, *43*, 3368−3398.
(4) Schlummer, B.; Hartwig, J. F. *Org. Lett.* **2002**, *4*, 1471−1474. Cossy, J.; Belotti, D.; Bellosta, V.; Boggio, C. *Tetrahedron Lett.* **1997**, *38*, 2677−2680.
(5) Seayad, J.; Tillack, A.; Hartung, C. G.; Beller, M. *Adv. Synth. Catal.* **2002**, *344*, 795−813. Ates, A.; Quinet, C. *Eur. J. Org. Chem.* **2003**, 1623−1626.
(6) Alonso, F.; Beletskaya, I. P.; Yus, M. *Chem. Rev.* **2004**, *104*, 3079−3159.
(7) Ryu, J.-S.; Li, G. Y.; Marks, T. J. *J. Am. Chem. Soc.* **2003**, *125*, 12584−12605.
(8) Haak, E.; Bytschkov, I.; Doye, S. *Angew. Chem., Int. Ed.* **1999**, *38*, 3389−3391. Pohlki, F.; Doye, S. *Angew. Chem., Int. Ed.* **2001**, *40*, 2305−2308. Cao, C.; Li, Y.; Shi, Y.; Odom, A. L. *Chem. Commun.* **2004**, 2002−2003. Tillack, A.; Castro, I. G.; Hartung, C. G.; Beller, M. *Angew. Chem., Int. Ed.* **2002**, *41*, 2541−2543. Bytschkov, I.; Doye, S. *Eur. J. Org. Chem.* **2003**, 935−946. Ackermann, L. *Organometallics* **2003**, *22*, 4367−4368. Zhang, Z.; Schafer, L. L. *Org. Lett.* **2003**, *5*, 4733−4736. Doye, S. *Synlett* **2004**, 1653−1672. Odom, A. L. *Dalton Trans.* **2005**, 225−233.
(9) Li, Y.; Marks, T. J. *J. Am. Chem. Soc.* **1998**, *120*, 1757−1771.
(10) Li, Y.; Marks, T. J. *Organometallics* **1996**, *15*, 3770−3772.
(11) Haskel, A.; Straub, T.; Eisen, M. S. *Organometallics* **1996**, *15*, 3773−3775. Straub, T.; Haskel, A.; Neyroud, T. G.; Kapon, M.; Botoshansky, M.; Eisen, M. S. *Organometallics* **2001**, *20*, 5017−5035.
(12) Casalnuovo, A. L.; Calabrese, J. C.; Milstein, D. *J. Am. Chem. Soc.* **1988**, *110*, 6738−6744. Brunet, J. J.; Commenges, G.; Neibecker, D.; Philippot, K. *J. Organomet. Chem.* **1994**, *469*, 221−228. Dorta, R.; Egli, P.; Zurcher, F.; Togni, A. *J. Am. Chem. Soc.* **1997**, *119*, 10857−10858. Tokunaga, M.; Eckert, M.; Wakatsuki, Y. *Angew. Chem., Int. Ed.* **1999**, *38*, 3222−3225. Hartung, C. G.; Tillack, A.; Trauthwein, H.; Beller, M. *J. Org. Chem.* **2001**, *66*, 6339−6343. Kawatsura, M.; Hartwig, J. F. *Organometallics* **2001**, *20*, 1960−1964. Li, K.; Horton, P. N.; Hursthouse, M. B.; Hii, K. K. *J. Organomet. Chem.* **2003**, *665*, 250−257. Yi, C. S.; Yun, S. Y.; Guzei, I. A. *J. Am. Chem. Soc.* **2005**, *127*, 5782−5783. Takaya, J.; Hartwig, J. F. *J. Am. Chem. Soc.* **2005**, *127*, 5756−5757. Brunet, J.-J.; Chu, N. C.; Diallo, O. *Organometallics* **2005**, *24*, 3104−3110. Vasen, D.; Salzer, A.; Gerhards, F.; Gais, H. J.; Sturmer, R.; Bieler, N. H.; Togni, A. *Organometallics* **2000**, *19*, 539−546.
(13) Crimmin, M. R.; Casely, I. J.; Hill, M. S. *J. Am. Chem. Soc.* **2005**, *127*, 2042−2043.

10.1021/om700428q CCC: $37.00
Publication on Web 07/21/2007

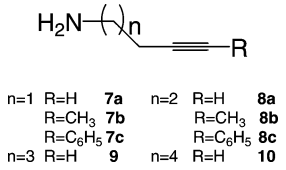
oxophilicity and better functional group tolerance. There are few rhodium or iridium complexes that have been reported to catalyze intramolecular hydroamination.[22,28−30]

The generality of the catalyzed hydroamination reaction is important in developing synthetic approaches to amines and nitrogen-containing heterocycles. The late transition metal catalysts preferentially form five-membered rings.[20,27] Late transition metal complexes have also been shown to efficiently promote the synthesis of six-membered heterocycles from appropriate alkynamine starting materials.[22,26] Where the majority of catalysts reported to date for hydroamination are effective for the addition of amines to terminal alkynes, the efficiency of the catalysis is also significantly affected by the use of substituted alkynes.[18,20,25]

We have previously shown that the cationic Rh(I) and Ir(I) complexes $[M(bim)(CO)_2][BPh_4]$ (**1**, **a** M = Rh, **b** M = Ir) and $[M(bpm)(CO)_2][BPh_4]$ (**2**, **a** M = Rh, **b** M = Ir), containing the bidentate imidazole ligands bis(*N*-methylimidazol-2-yl)-methane (bim) and bis(1-pyrazolyl)methane (bpm), are effective catalysts for the intramolecular hydroamination of 4-pentyn-1-amine.[28,30] With the aim of establishing the key structural features of the ligand system as well as making improvements to the catalyst performance, a series of analogous complexes of the type $[M(N-N)(CO)_2][BPh_4]$ (**3**−**6**) were prepared with modifications to the bidentate nitrogen donor ligands (N−N), including bis(*N*-methylimidazol-2-yl)ketone (bik) (**5**, **a** M = Rh, **b** M = Ir), 1,1-bis(*N*-methylimidazol-2-yl)ethane (bie) (**3**), 2,2-bis(*N*-methylimidazol-2-yl)propane (bip) (**4**), and bis-(*N*-methylbenzimidazol-2-yl)methane (bbnzim) (**6**, **a** M = Rh, **b** M = Ir).



Using the most active catalysts, the dependence of the efficiency of the hydroamination reaction on substrate chain length was investigated using the substrates 3-butyn-1-amine (**7a**), 3-pentyn-1-amine (**7b**), 4-phenyl-3-butyn-1-amine (**7c**), 4-pentyn-1-amine (**8a**), 4-hexyn-1-amine (**8b**), 5-phenyl-4-pentyn-1-amine (**8c**), 5-hexyn-1-amine (**9**), and 6-heptyn-1-amine (**10**).



Results and Discussion

(a) Rhodium-Catalyzed Cyclization of 4-Pentyn-1-Amine (8a) to 2-Methyl-1-pyrroline (11) with Modifications of N-Donor Ligands. The efficiency of each of the rhodium complexes $[Rh(bim)(CO)_2][BPh_4]$ (**1a**), $[Rh(bie)(CO)_2][BPh_4]$ (**3**), $[Rh(bip)(CO)_2][BPh_4]$ (**4**), $[Rh(bik)(CO)_2][BPh_4]$ (**5a**), $[Rh(bbnzim)(CO)_2][BPh_4]$ (**6a**), and $[Rh(bpm)(CO)_2][BPh_4]$ (**2a**) for promoting the hydroamination reaction was tested using 4-pentyn-1-amine (**8a**) as a substrate (Scheme 1, Table 1). Similarly, the efficiency of each of the iridium complexes $[Ir(bim)(CO)_2][BPh_4]$ (**1b**), $[Ir(bik)(CO)_2][BPh_4]$ (**5b**), $[Ir(bbnzim)(CO)_2][BPh_4]$ (**6b**), and $[Ir(bpm)(CO)_2][BPh_4]$ (**2b**) for promoting the hydroamination reaction was tested (Table 1). All metal complexes tested

(14) Bexrud, J. A.; Beard, J. D.; Schafer, L. L. *Org. Lett.* **2005**, *7*, 1959−1962. Gribkov, D. V.; Hultzsch, K. C. *Angew. Chem., Int. Ed.* **2004**, *43*, 5542−5546. Hoover, J. M.; Petersen, J. R.; Pikul, J. H.; Johnson, A. R. *Organometallics* **2004**, *23*, 4614−4620. Knight, P. D.; Munslow, I.; O'Shaughnessy, P. N.; Scott, P. *Chem. Commun.* **2004**, 894−895. Ackermann, L.; Bergman, R. G.; Loy, R. N. *J. Am. Chem. Soc.* **2003**, *125*, 11956−11963. Bytschkov, I.; Doye, S. *Tetrahedron Lett.* **2002**, *43*, 3715−3718. Ackermann, L.; Bergman, R. G. *Org. Lett.* **2002**, *4*, 1475−1478. McGrane, P. L.; Livinghouse, T. *J. Am. Chem. Soc.* **1993**, *115*, 11485−11489.

(15) Gribkov, D. V.; Hultzsch, K. C. *Chem. Commun.* **2004**, 730−731. Kim, Y. K.; Livinghouse, T.; Horino, Y. *J. Am. Chem. Soc.* **2003**, *125*, 9560−9561. Lauterwasser, F.; Hayes, P. G.; Braese, S.; Piers, W. E.; Schafer, L. L. *Organometallics* **2004**, *23*, 2234−2237.

(16) Gagne, M. R.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1992**, *114*, 275−294.

(17) Giardello, M. A.; Conticello, V. P.; Brard, L.; Gagne, M. R.; Marks, T. J. *J. Am. Chem. Soc.* **1994**, *116*, 10241−10254. Douglass, M. R.; Ogasawara, M.; Hong, S.; Metz, M. V.; Marks, T. J. *Organometallics* **2002**, *21*, 283−292. Hong, S.; Tian, S.; Metz, M. V.; Marks, T. J. *J. Am. Chem. Soc.* **2003**, *125*, 14768−14783. Arredondo, V. M.; McDonald, F. E.; Marks, T. J. *Organometallics* **1999**, *18*, 1949−1960. Hong, S.; Kawaoka, A. M.; Marks, T. J. *J. Am. Chem. Soc.* **2003**, *125*, 15878−15892. Collin, J.; Daran, J.-C.; Jacquet, O.; Schulz, E.; Trifonov, A. *Chem.−Eur. J.* **2005**, *11*, 3455−3462. Gagne, M. R.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1992**, *114*, 275−294. O'Shaughnessy, P. N.; Gillespie, K. M.; Knight, P. D.; Munslow, I. J.; Scott, P. *Dalton Trans.* **2004**, 2251−2256. Li, Y.; Marks, T. J. *J. Am. Chem. Soc.* **1996**, *118*, 707−708. Bürgstein, M. R.; Berberich, H.; Roesky, P. W. *Chem.−Eur. J.* **2001**, *7*, 3078−3085. Hultzsch, K. C.; Hampel, F.; Wagner, T. *Organometallics* **2004**, *23*, 2601−2612.

(18) Li, Y.; Marks, T. J. *J. Am. Chem. Soc.* **1996**, *118*, 9295−9306.

(19) Campi, E. M.; Jackson, W. R. *J. Organomet. Chem.* **1996**, *523*, 205−209. Fukuda, Y.; Utimoto, K.; Nozaki, H. *Heterocycles* **1987**, *25*, 297−300. Ouh, L. L.; Müller, T. E.; Yan, Y. K. *J. Organomet. Chem.* **2005**, *690*, 3774−3782. Krogstad, D. A.; Owens, S. B.; Halfen, J. A.; Young, V. G., Jr. *Inorg. Chem. Commun.* **2005**, *8*, 65−69. van Esseveldt, B. C. J.; Vervoort, P. W. H.; van Delft, F. L.; Rutjes, F. P. J. T. *J. Org. Chem.* **2005**, *70*, 1791−1795. Robinson, R. S.; Dovey, M. C.; Gravestock, D. *Eur. J. Org. Chem.* **2005**, 505−511. Su, R. Q.; Nguyen, V. N.; Müller, T. E. *Top. Catal.* **2003**, *22*, 23−29.

(20) Müller, T. E.; Grosche, M.; Herdtweck, E.; Pleier, A.-K.; Walter, E.; Yan, Y.-K. *Organometallics* **2000**, *19*, 170−183.

(21) Müller, T. E. *Tetrahedron Lett.* **1998**, *39*, 5961−5962.

(22) Müller, T. E.; Pleier, A. K. *J. Chem. Soc., Dalton Trans.* **1999**, 583−587.

(23) Kondo, T.; Okada, T.; Suzuki, T.; Mitsudo, T. *J. Organomet. Chem.* **2001**, *622*, 149−154.

(24) Hultzsch, K. C. *Adv. Synth. Catal.* **2005**, *347*, 367−391. Bender, C. F.; Widenhoefer, R. A. *J. Am. Chem. Soc.* **2005**, *127*, 1070−1071. Harrington, P. J.; Hegedus, L. S.; McDaniel, K. F. *J. Am. Chem. Soc.* **1987**, *109*, 4335−4338. Arcadi, A.; Cacchi, S.; Marinelli, F. *Tetrahedron Lett.* **1989**, *30*, 2581−2584. Cacchi, S. *J. Organomet. Chem.* **1999**, *576*, 42−64. Utimoto, K.; Miwa, H.; Nozaki, H. *Tetrahedron Lett.* **1981**, *22*, 4277−4278. Richmond, M. K.; Scott, S. L.; Alper, H. *J. Am. Chem. Soc.* **2001**, *123*, 10521−10525. Wolf, L. B.; Tjen, K. C. M. F.; ten Brink, H. T.; Blaauw, R. H.; Hiemstra, H.; Schoemaker, H. E.; Rutjes, F. P. J. T. *Adv. Synth. Catal.* **2002**, *344*, 70−83.

(25) Fukuda, Y.; Matsubara, S.; Utimoto, K. *J. Org. Chem.* **1991**, *56*, 5812−5816.

(26) Müller, T. E.; Berger, M.; Grosche, M.; Herdtweck, E.; Schmidtchen, F. P. *Organometallics* **2001**, *20*, 4384−4393.

(27) Lutete, L. M.; Kadota, I.; Yamamoto, Y. *J. Am. Chem. Soc.* **2004**, *126*, 1622−1623. Bajracharya, G. B.; Huo, Z.; Yamamoto, Y. *J. Org. Chem.* **2005**, *70*, 4883−4886.

(28) Burling, S.; Field, L. D.; Messerle, B. A. *Organometallics* **2000**, *19*, 87−90.

(29) Burling, S.; Field, L. D.; Li, H. L.; Messerle, B. A.; Turner, P. *Eur. J. Inorg. Chem.* **2003**, 3179−3184. Burling, S.; Field, L. D.; Messerle, B. A.; Vuong, K. Q.; Turner, P. *Dalton Trans.* **2003**, 4181−4191. Field, L. D.; Messerle, B. A.; Vuong, K. Q.; Turner, P. *Organometallics* **2005**, *24*, 4241−4250.

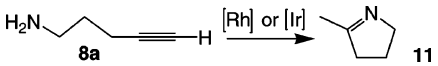
(30) Burling, S.; Field, L. D.; Messerle, B. A.; Turner, P. *Organometallics* **2004**, *23*, 1714−1721.

Table 1. Yield of 2-Methyl-1-pyrroline (11) Obtained from the Rhodium(I)- and Iridium(I)-Catalyzed Cyclization of 4-Pentyn-1-amine (8a) in Tetrahydrofuran-d_8 at 60 °C, with 1.5 mol % Catalyst

complex	time (h)	% conversion	TOF (h^{-1})[a]
$[Ir(bpm)(CO)_2][BPh_4]$, **2b**	1.5	100	89
$[Ir(bim)(CO)_2][BPh_4]$, **1b**	24	92	5
$[Ir(bik)(CO)_2][BPh_4]$, **5b**	12	98	7
$[Ir(bbnzim)(CO)_2][BPh_4]$, **6b**	12	93	10
$[Rh(bim)(CO)_2][BPh_4]$, **1a**	14	100	17
$[Rh(bie)(CO)_2][BPh_4]$,[b] **3**	12	71	6
	24	87	
$[Rh(bip)(CO)_2][BPh_4]$,[c] **4**	12	78	8
	24	84	
$[Rh(bik)(CO)_2][BPh_4]$,[c] **5a**	12	79	10
	24	94	
$[Rh(bbnzim)(CO)_2][BPh_4]$, **6a**	12	86	11
	24	100	
$[Rh(bpm)(CO)_2][BPh_4]$, **2a**	12	90	20

[a] Turnover frequency = moles of product produced per mole of catalyst used per hour; typically calculated at time of 50% conversion. [b] 1.6 mol % catalyst. [c] 1.3 mol % catalyst.

Scheme 1. Catalyzed Cyclization of 4-Pentynamine



catalytically cyclized the substrate **8a** regioselectively to 2-methyl-1-pyrroline (**11**), with varying degrees of efficiency. No six-membered heterocyclic products resulting from the alternative *endo*-cyclization pathway were observed.

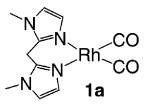
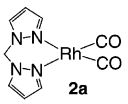
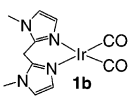
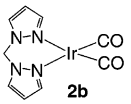
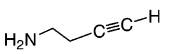
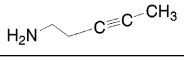
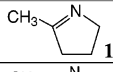
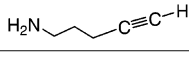
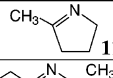
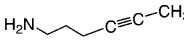
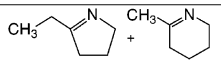
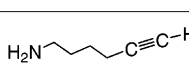
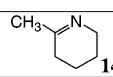
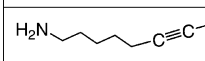
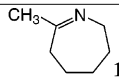
After 24 h, all Rh catalysts had promoted conversion of between 84 and 100%, with small variation in the reaction curve profiles. For the Ir(I) catalysts, greater variation was observed, with the $[Ir(bim)(CO)_2][BPh_4]$ (**1b**) catalyst being significantly less effective in 12 h than the other Ir(I) catalysts. It can be concluded that the exact nature of the substituents on the bis(imidazolyl) ligand is not a critically important feature of the catalyst, with substitution by electron-withdrawing CO, or by alkyl groups, at the bridging carbon having only a minor effect on reactivity. Substitution with very bulky alkyl groups was not considered here, but may well have a more significant effect on the catalytic efficiency.

(b) Rhodium- and Iridium-Catalyzed Intramolecular Cyclization of a Series of Alkyn-1-amines. The catalyzed intramolecular hydroamination of a series of alkynamine substrates of varying chain length and with both terminal and internal acetylene bonds (**7a**−**c**, **8a**−**c**, **9**, **10**) was investigated to assess the selectivity and limitations of the intramolecular hydroamination reaction using cationic Rh(I) and Ir(I) catalysts. In order to compare the metal centers rhodium and iridium, and the two nitrogen donor ligands bis(*N*-methylimidazol-2-yl)methane and bis(1-pyrazolyl)methane, the efficiency of the four catalysts $[Rh(bim)(CO)_2][BPh_4]$ (**1a**), $[Rh(bpm)(CO)_2][BPh_4]$ (**2a**), $[Ir(bim)(CO)_2][BPh_4]$ (**1b**), and $[Ir(bpm)(CO)_2][BPh_4]$ (**2b**) in promoting the cyclization was established. The same reaction procedure as was used above for the metal-catalyzed cyclization of 4-pentyn-1-amine (**8a**) was applied to the catalyzed cyclization of all alkynamine substrates (Table 2).

(i) Cyclization of 3-Butyn-1-amine (7a) to 1-Pyrroline (12). Intramolecular cyclization of 3-butyn-1-amine (**7a**) via hydroamination may give two possible isomers resulting from either 4-*exo* or 5-*endo* ring closure. Heating 3-butyn-1-amine (**7a**) for 24 h with $[Rh(bim)(CO)_2][BPh_4]$ (**1a**) at reflux led to a low level of conversion (20%) to 1-pyrroline (**12**) resulting from 5-*endo* ring closure. The other complexes did not promote the cyclization of this substrate.

(ii) Cyclization of 3-Pentyn-1-amine (7b) to 2-Methyl-1-pyrroline (11). Reaction of 3-pentyn-1-amine (**7b**) using complexes **1a**, **1b**, **2a**, and **2b** as catalysts, at 60 °C, afforded 2-methyl-1-pyrroline (**11**) as the only product, which represents the successful cyclization of a substrate with an internal acetylene functionality (Table 2). The rhodium complexes $[Rh(bim)(CO)_2][BPh_4]$ (**1a**) and $[Rh(bpm)(CO)_2][BPh_4]$ (**1b**) both reached >90% conversion to 2-methyl-1-pyrroline (**11**) after 2

Table 2. Summary of the Rhodium- and Iridium-Catalyzed Intramolecular Hydroamination of Alkynamines Using Catalysts $[Rh(bim)(CO)_2][BPh_4]$ (1a), $[Rh(bpm)(CO)_2][BPh_4]$ (2a), $[Ir(bim)(CO)_2][BPh_4]$ (1b), and $[Ir(bpm)(CO)_2][BPh_4]$ (2b) with between 1.4 and 1.6 mol % Catalyst Loading, in Tetrahydrofuran-d_8

Substrate	**Product**		**Yield (%) (time in h)**			
			 **1a**	 **2a**	 **1b**	 **2b**
 **7a**	 **12**	a	20(24)	×	×	×
 **7b**	 **11**	b	63 (12)	63 (12)	50 (12)	22 (12)
 **8a**	 **11**	b	98 (14)	90 (12)	98 (2.3)	92 (24)
 **8b**	 **13** **14**	a	68/7 (16)	34/3 (16)	6/0 (24)	<10/0 (24)
		b	85/9 (6.5)	84/8(6.5)	79/13 (6)	85/11 (6)
 **9**	 **14**	a	32 (24)	12 (24)	95 (24)	12 (24)
 **10**	 **15**	a	×	×	×	×

[a] At reflux. [b] At 60 °C.

days. The iridium analogues were far less active catalysts, with the reaction catalyzed by $[Ir(bpm)(CO)_2][BPh_4]$ (**2b**) producing only 50% conversion after 2 days. Only minor conversion was achieved using $[Ir(bim)(CO)_2][BPh_4]$ (**1b**) as the catalyst.

For all of the complexes, 5-*endo* cyclization is a considerably less facile process than the 5-*exo* process, which is utilized in the cyclization of 4-pentyn-1-amine (**8a**) to afford the same product, with >90% conversion. The preference for 5 *exo* cyclization is most pronounced for the iridium catalyst $[Ir(bpm)(CO)_2][BPh_4]$ (**2b**).

(iii) Cyclization of 4-Hexyn-1-amine (8b) to 2-Ethyl-1-pyrroline (13). The reaction of 4-hexyn-1-amine (**8b**) was catalyzed by each of the four complexes **1a**,**b** and **2a**,**b** in tetrahydrofuran-d_8 at both 60 °C and reflux. The major product in all cases was 2-ethyl-1-pyrroline (**13**), resulting from *exo* addition of the N−H to the acetylene. A second minor product was also formed and was identified as 2-methyl-3,4,5,6-tetrahydropyridine (**14**), the six-membered heterocycle resulting from the alternative 6-*endo* cyclization.

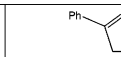
Although all four complexes **1a**, **1b**, **2a**, and **2b** achieved approximately 80% conversion of 4-hexyn-1-amine (**8b**) in 6 h at high temperature, at lower temperatures it was clear that the best conversions to 2-ethyl-1-pyrroline (**13**) were achieved using the rhodium complexes (Table 2). The formation of 2-ethyl-1-pyrroline (**13**) occurs via a 5-*exo* ring closure in the same fashion as the cyclization of 4-pentyn-1-amine (**8a**) to 2-methyl-1-pyrroline (**11**), although at a considerably slower rate.

(iv) Cyclization of 5-Hexyn-1-amine (9) to 2-Methyl-3,4,5,6-tetrahydropyridine (14). The reaction of 5-hexyn-1-amine (**9**) catalyzed by each of the four complexes **1a**,**b** and **2a**,**b** at reflux gave 2-methyl-3,4,5,6-tetrahydropyridine (**12**),[31] resulting from 6-*exo* cyclization of the substrate. Almost quantitative conversion of **9** to 2-methyl-3,4,5,6-tetrahydropyridine (**14**) was achieved using the Ir catalyst, **2a**, after 24 h, whereas after the same time the equivalent Rh catalyst, **1a**, catalyzed the reaction with only moderate conversion (32%). Low conversions (12%) were also achieved after 24 h using both of the rhodium or iridium complexes containing bis(1-pyrazolyl)methane ligands (Table 2). No conversion was observed for any of the catalysts at 60 °C. Müller and co-workers have studied the same cyclization reaction extensively, catalyzed by a series of transition metals.[21,22] Superior results were achieved using 1 mol % of $[Cu(CH_3CN)_4][PF_6]$ in acetonitrile at reflux, with complete conversion in under 9 h.[20]

(v) Attempted Cyclization of 6-Heptyn-1-amine (10). Li and Marks reported the production of a seven-membered heterocycle (92%) via the intramolecular hydroamination of 7-phenyl-6-heptyn-1-amine, although with a very low turnover rate (0.11 h^{-1}).[18] In this work, the catalyzed cyclization of 6-heptyn-1-amine (**10**) was attempted, although the reaction as catalyzed by each of the Rh and Ir complexes **1a**,**b** and **2a**,**b** failed to cleanly produce the seven-membered heterocycle, 3,4,5,6-tetrahydro-7-methyl-azepine (**15**), which would result from 7-*exo* cyclization (Table 2).

(b) Alkynyl Substituent Effects: Comparing Rh(I) and Ir(I). The cyclization of two alkynamines with methyl substituents on the alkyne (**7b** and **8b**) has been demonstrated above. The catalyzed reaction of 4-phenyl-3-butyn-1-amine (**7c**) with all four complexes **1a**, **1b**, **2a**, and **2b** in tetrahydrofuran-d_8 at 60 °C led to the formation of 2-phenyl-1-pyrroline (**16**) as the sole product (Table 3). The cyclization of 5-phenyl-4-pentyn-1-amine (**8c**) to 2-benzyl-1-pyrroline (**17**) catalyzed by all four

Table 3. Yield of 2-Phenyl-1-pyrroline (16) from the Catalyzed Cyclization of 4-Phenyl-3-butyn-1-amine (7c) (thf-d_8 at 60 °C) and Yield of 2-Benzyl-1-pyrroline (17) from the Catalyzed Cyclization of 5-Phenyl-4-pentyn-1-amine (8c) (dioxane-d_8 at 95 °C)

	 **16**		 **17**	
Complex	**Mol% of catalyst**	**% Conversion of 7c (time in h)**	**Mol% of catalyst**	**% Conversion of 8c (time in h)**
$[Rh(bpm)(CO)_2][BPh_4]$	1.8	100 (2.5)	4.6	87 (4.5)
$[Rh(bim)(CO)_2][BPh_4]$	2.0	100 (6)	4.8	96 (2.3)
$[Ir(bpm)(CO)_2][BPh_4]$	1.9	30 (20)	4.9	92 (49)
$[Ir(bim)(CO)_2][BPh_4]$	1.5	54 (16)	3.8	32 (47)

complexes **1a**, **1b**, **2a**, and **2b** required more forcing conditions to be efficient and was therefore conducted in dioxane-d_8 at 95 °C (Table 3). The rhodium complexes **1a** and **2a** were significantly better catalysts for both of these cyclizations than their iridium analogues, confirming that the rhodium complexes are more reactive toward internal alkynes than the iridium complexes.

For the cyclization of 5-phenyl-4-pentyn-1-amine (**8c**), the rhodium complexes **1a** and **2a** promote a rapid initial reaction rate, with a high turnover rate at 45% of 580 h^{-1} for $[Rh(bpm)(CO)_2][BPh_4]$ (**2a**) and lower initial turnover rate of 189 h^{-1} for $[Rh(bim)(CO)_2][BPh_4]$ (**1a**). $[Rh(bpm)(CO)_2][BPh_4]$ (**2a**) appears to be more prone to catalyst deactivation as the reaction rate slows considerably after the first 10 min, reaching only 87% after 4.5 h.

In the case of the cyclization of 4-phenyl-3-butyn-1-amine (**7c**), the best catalyst was $[Rh(bpm)(CO)_2][BPh_4]$ (**2a**), with quantitative conversion being achieved in just 2.5 h. However, $[Rh(bim)(CO)_2][BPh_4]$ (**1a**) had a faster initial rate of reaction, with a turnover rate at 50% conversion of 75 h^{-1} for $[Rh(bim)(CO)_2][BPh_4]$ (**1a**), and for $[Rh(bpm)(CO)_2][BPh_4]$ (**2a**) a lower initial rate of 35 h^{-1}. This indicates that $[Rh(bim)(CO)_2][BPh_4]$ (**2a**) is more susceptible to catalyst deactivation with non-terminal alkynes as substrates. Previous work has shown that the iridium complexes are more robust and continue to act as effective catalysts over several reaction cycles for the cyclization of **8a**, while the performance of the rhodium analogues was reduced on performing addition of new substrate.[30]

The catalytic activity of $[Rh(bim)(CO)_2][BPh_4]$ (**1a**) for the cyclization of 5-phenyl-4-pentyn-1-amine is the highest of all late transition metal complexes reported to date for the cyclization of this substrate (Table 4).[20,23]

Rhodium(I). $[Rh(bim)(CO)_2][BPh_4]$ (**1a**) was the most active catalyst over the range of substrates studied, so to compare the effect of the nature of the substituent on the alkyne moiety on the efficiency of catalyzed cyclization, the cyclization of the terminal alkyne as well as methyl- and phenyl-substituted alkynes were compared using $[Rh(bim)(CO)_2][BPh_4]$ (**1a**) as catalyst.

The efficiency of cyclization by **1a** of the substituted 4-alkynamines 5-phenyl-4-pentyn-1-amine (**8c**), 4-hexyn-1-amine (**8b**), and 4-pentyn-1-amine (**8a**) is shown in Table 5. The rate of cyclization decreases with substrate reactivity in the order H > Me > Ph. Müeller observed a similar rate comparison for the late transition metal (Pd, Zn, and Cu complexes) catalyzed cyclization of 4-alkynamines and suggested that 4-pentyn-1-amine (**8a**) is cyclized more rapidly than the 5-phenyl-4-pentynamine (**8c**) due to steric hindrance in the transition state in the cyclization of **8c**.[20] Marks et al. observed

(31) Hua, D. H.; Miao, S. W.; Bharathi, S. N.; Katsuhira, T.; Bravo, A. A. *J. Org. Chem.* **1990**, *55*, 3682−3684.

Table 4. Comparison of Yields and Turnover Frequencies for the Cyclization of 5-Phenyl-4-pentyn-1-amine (8c) to 2-Benzyl-1-pyrroline (17) Catalyzed by Late Transition Metal Complexes

entry	catalyst (mol %)	solvent and temp	% conversion (time in h)	TOF (h^{-1})
1	$[Rh(bim)(CO)_2][BPh_4]$ (**S7**) (4.8mol%)	dioxane-d_8, 95 °C	96 (2.3)	189
2[20]	$[Cu(CH_3CN)_4]PF_6$ (1 mol %)	CH_3CN, 82 °C	100 (16)	29
3[20]	$Zn(CF_3SO_3)_2$ (1 mol %)	toluene, 111 °C	100 (8.3)	55
4[20]	$[Pd(triphos)](CF_3SO_3)_2$ (1 mol %)	toluene, 111 °C	100 (9)	51
5[23]	$Ru_3(CO)_{12}$ (1.3 mol %)	diglyme, 110 °C	>99 (4)	

Table 5. Hydroamination of 3- and 4-Alkynamines 8a−c and 7a−c Catalyzed by $[Rh(bim)(CO)_2][BPh_4]$, 1a, in thf-d_8 at 60 °C[a]

Substrate	Mol% of catalyst	Time	% Conversion
Ph—≡—NH_2 **8c**	1.9	20 h	2%
Me—≡—NH_2 **8b**	1.5	16 h	68%[a]
H—≡—NH_2 **8a**	1.5	14 h	100%
Ph—≡—NH_2 **7c**	1.8	6 h	100%
Me—≡—NH_2 **7b**	1.5	12 h	63%[a]
H—≡—NH_2 **7a**	1.6	16 h	7%[a]

[a] 7% conversion to the 6-endo product 2-methyl-3,4,5,6-tetrahydropyridine also observed.

[a] 7% conversion to the 6-*endo* product 2-methyl-3,4,5,6-tetrahydropyridine also observed.

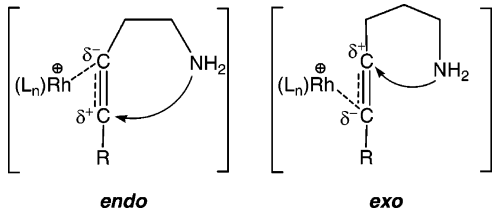
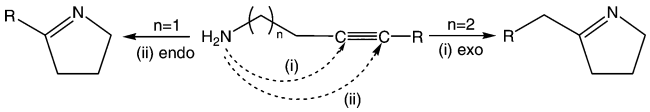


Figure 1. Postulated transition states for the rhodium-catalyzed cyclization of alkynamines proceeding through *endo*- and *exo*-cyclization pathways.

Scheme 2. Cyclization Routes for 3-Alkynamines ($n = 1$) and 4-Alkynamines ($n = 2$)



the same order of reactivity using lanthanide complex catalyzed hydroamination reactions, with H > Me > Ph, and also cited steric effects as the primary reason for the relative activities, although the differences were not as pronounced as those in Table 5.[18]

The efficiency of hydroamination catalyzed by **1a** for the substituted 3-alkynamines 4-phenyl-3-butyn-1-amine (**7c**), 3-pentyn-1-amine (**7b**), and 3-butyn-1-amine (**7a**) is presented in Table 5. In this case, the rate of cyclization is affected by the nature of the substituents on the alkyne with a decrease in substrate reactivity in the order Ph > Me > H. Utimoto et al. have investigated the Pd(II)-catalyzed cyclization of a similar series of 3-alkynamines and found that the rate of cyclization was affected by the nature of the substituents on the alkyne with Ph ≈ *n*-C_4H_9 ≫ H and postulated that the terminal alkyne substrate would form a palladium acetylide, which could not be transformed into a nitrogen heterocycle.[25]

In the case of the Rh(I) catalyst **1a**, the influence of the substituent on the alkyne moiety on the cyclization rate has the opposite effect for 4-alkynamines (H > Me > Ph) than for the 3-alkynamines (Ph > Me > H). Steric effects in the transition state are therefore unlikely to provide the explanation for the order of substrate reactivity as both the 4-alkynamines and the 3-alkynamines should have similar steric constraints with regard to the substituent on the alkyne moiety. The mechanistic pathway for hydroamination includes an activation of the alkyne moiety by metal binding. The major difference between the cyclization of the two classes of substrates here (4-alkynyl- and 3-akynyl-) is the ring-closing pathway, where the cyclization of the 4-alkynamines proceeds through an *exo*-cyclization pathway and the cyclization of the 3-alkynamines proceeds through an *endo*-cyclization pathway (Scheme 2). Postulated structures for key transition states are shown in Figure 1.

The binding of the alkyne moiety to the metal center activates the triple bond, and the amino group is then able to attack one of the carbon atoms. In the *endo*-cyclization pathway, attack occurs on the external carbon. Carbocations are stabilized by increasing substitution on the cationic carbon and by aryl substituents, so that when R = H the carbocation will be least stabilized. Therefore the order of stability of the *endo*-derived transition state would be Ph > Me > H, which correlates with the order of reactivity observed for the 3-alkynamine substrates. In the case of the *exo*-cyclization pathway the internal carbon must have greater carbocation character (Figure 1). In this case, the carbon bearing the R substituent would have some carbanionic character, and this would have the opposite dependence on R for the order of stability of that of the transition state for the *endo* cyclization, as observed (Table 5).

Conclusions

Each of the rhodium and iridium complexes investigated were catalytically active for the cyclization of 4-pentyn-1-amine (**8a**) to 2-methyl-1-pyrroline (**11**). On comparison of the activity of complexes **3**, **4**, **5**, and **6** to that of $[Rh(bim)(CO)_2][BPh_4]$ (**1a**), it was clear that the modifications to the bis(imidazolyl) ligand in complexes **3**, **4**, **5**, and **6** did not produce a significant effect on the rate of the reaction. Introduction of the alternate bidentate nitrogen donor bis(1-pyrazolyl)methane in complex **2a** also produced a catalyst comparable to **1a**. These results indicate that small structural and electronic variations to the bidentate sp^2 nitrogen donor ligand did not significantly affect the reactivity of the catalyst.

The catalyzed formation of a series of N-containing heterocycles demonstrated that these catalysts have a strong preference for the formation of five-membered heterocycles over four- or six-membered rings. 3-Butyn-1-amine (**7a**) and 3-pentyn-1-amine (**7b**) afford pyrroline products by 5-*endo* cyclization, although not as readily as the 5-*exo* cyclization of 4-pentyn-1-amine (**8a**), and 4-hexyn-1-amine (**8b**) afforded pyrroline products. Intramolecular hydroamination to afford the six-membered heterocycle 2-methyl-3,4,5,6-tetrahydropyridine (**14**)

was less facile but still occurred, both as a minor product via 6-*endo* cyclization from **8b** and as the sole product of the 6-*exo* cyclization of 5-hexyn-1-amine (**27**). Attempts to produce a seven-membered ring via hydroamination were unsuccessful.

Comparison of the catalysis results for each of the four complexes $[Rh(bim)(CO)_2][BPh_4]$ (**1a**), $[Rh(bpm)(CO)_2][BPh_4]$ (**2a**), $[Ir(bim)(CO)_2][BPh_4]$ (**1b**), and $[Ir(bpm)(CO)_2][BPh_4]$ (**2b**) over the range of substrates places the rhodium complex **1a** as the most versatile catalyst examined. $[Rh(bim)(CO)_2][BPh_4]$ (**1a**) successfully catalyzed more reactions and usually with higher rates of conversion than the three remaining analogues **1b**, **2a**, and **2b**. There were, however, two anomalous results produced by the iridium catalysts: the superior rate of cyclization achieved by $[Ir(bim)(CO)_2][BPh_4]$ (**1b**) when reacted with 5-hexyn-1-amine (**9**) and the unexpectedly rapid rate with which $[Ir(bpm)(CO)_2][BPh_4]$ (**2b**) cyclized 4-pentyn-1-amine (**8a**).

The Rh(I) catalysts were significantly more efficient catalysts for the cyclization of alkynamines with phenyl- and methyl-substituted alkynyls than the Ir(I) catalysts. Differences were observed between the Rh(I)-catalyzed cyclization rates of butynyl and pentynyl alkynamines with substituents on the alkyne. The dependence of reaction efficiency on the nature of the substituents was consistent with a mechanism where the substituents could stabilize or destabilize the developing charge in the metal-bound intermediate.

Experimental Section

All manipulations of metal complexes and air-sensitive reagents were carried out using standard Schlenk techniques or in a Vacuum Atmospheres nitrogen-filled glovebox. Organic starting materials were obtained from Aldrich Chemical Co. Inc. The metal halide salts $RhCl_3 \cdot xH_2O$ and $IrCl_3 \cdot xH_2O$ were purchased from Strem Inc. and used as received.

Di-μ-chlorotetracarbonyldirhodium,[32] di-μ-chlorobis(1,5-cyclooctadiene)diiridium,[33] bis(*N*-methylimidazol-2-yl)ketone (bik),[28] bis(*N*-methylimidazol-2-yl)methane (bim),[28] bis(pyrazol-1-yl)methane (bpm),[34] bis(*N*-methylbenzimidazol-2-yl)methane (bbnzim),[35] and the complexes $[Rh(bim)(CO)_2][BPh_4]$,[28] $[Rh(bik)(CO)_2][BPh_4]$,[35] $[Rh(bbnzim)(CO)_2][BPh_4]$,[35] and $[Ir(bpm)(CO)_2][BPh_4]$[36] were prepared by literature methods.

The substrates 4-pentyn-1-amine (**8a**)[37] and 4-hexyn-1-amine (**8b**)[18] were prepared by literature methods and gave identical spectroscopic detail to the published data. The alkynamines 3-butyn-1-amine (**7a**), 3-pentyn-1-amine (**7b**), 5-hexyn-1-amine (**9**), 6-heptyn-1-amine (**10**), 4-phenyl-3-butyn-1-amine (**7c**), and 5-phenyl-4-pentyn-1-amine (**8c**) were prepared following literature procedures.[38]

For the purposes of air-sensitive manipulations and in the preparation of metal complexes tetrahydrofuran and hexane were predried over sodium wire and distilled from benzophenone ketyl immediately prior to use. Methanol was dried over and distilled from magnesium methoxide under nitrogen. Deuterated solvents for NMR purposes were obtained from either Merck or Cambridge Isotopes. Chloroform-*d* was used as supplied. Acetone-d_6 and tetrahydrofuran-d_8, for use with air-sensitive compounds, were degassed using three consecutive freeze−pump−thaw cycles and vacuum distilled from suitable drying agents immediately prior to use.

Bulk compressed gases nitrogen (>99.5%) and carbon monoxide (>99.5%) were obtained from British Oxygen Company (BOC Gases) and used as supplied.

Infrared spectra were recorded on a Perkin-Elmer 1600 Series FTIR spectrometer. Microanalyses were carried out at the Campbell Microanalytical Laboratory, University of Otago, New Zealand. Mass spectra of organic compounds were recorded on a Finnigan Polaris Q mass spectrometer using a direct exposure probe (DEP). Electrospray mass spectra of organometallic complexes were recorded on a Finnigan LCQ mass spectrometer by direct infusion of a tetrahydrofuran solution of the complex into the source. Melting points were determined using a Gallenkamp melting point apparatus and are uncorrected.

^1H and ^{13}C NMR spectra were recorded on a Bruker DRX400 spectrometer at 400.13 and 100.62 MHz, respectively, or a Bruker DPX300 operating at 300 and 75 MHz, respectively. Spectra were recorded at 300 K for characterization purposes unless otherwise stated, as determined using a variable-temperature unit. ^1H and ^{13}C NMR chemical shifts (δ) were referenced to internal solvent references.

(a) Synthesis of 1,1-(Bis(*N*-methylimidazol-2-yl))ethane (bie). A solution of *n*-butyllithium (1.3 mL, 2 mmol) in hexanes was added dropwise to a suspension of bis(*N*-methylimidazol-2-yl)-methane (330 mg, 1.9 mmol) in tetrahydrofuran (20 mL) at −78 °C under nitrogen. After stirring for 30 min at −78 °C, iodomethane (0.12 mL, 1.9 mmol) in tetrahydrofuran (5 mL) was added. The mixture was immediately warmed to −40 °C, at which temperature a saturated ammonium chloride solution (10 mL) was added to quench the reaction. The mixture was allowed to warm to room temperature and water (5 mL) was added. Following acidification with 3 M hydrochloric acid, the organic layer was separated and extracted with 3 M hydrochloric acid (3 × 5 mL). The combined aqueous layers were neutralized with sodium carbonate, filtered, and extracted with dichloromethane (3 × 10 mL). The organic extracts were dried over magnesium sulfate and filtered, and the solvent was removed under reduced pressure. 1,1-(Bis(*N*-methylimidazol-2-yl))ethane remained as a cream solid (134 mg, 37%), mp 82−85 °C (lit.[16] 82−83 °C) and was used in subsequent reactions without further purification. ^1H NMR (400 MHz, acetone-d_6): δ 6.91 (d, 2H, $^3J_{H4-H5} = 1.0$ Hz, *H4*), 6.78 (d, 2H, *H5*), 4.52 (q, 1H, $^3J_{H-CH3} = 7.4$ Hz, C-*H*), 3.44 (s, 6H, N-CH_3), 1.68 (d, 3H, C−CH_3) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, acetone-d_6): δ 148.3 (*C2*), 127.1 (*C4*), 122.3 (*C5*), 33.0 (N-*C*H_3), 32.6 (*C*-H), 17.5 (C-*C*H_3) ppm. MS *m*/*z* (%): 190 (M^+, 60), 175 (64), 134 (25), 96 (73), 81 (45), 42 (100).

(b) Synthesis of 2,2-(Bis(*N*-methylimidazol-2-yl))propane (bip). A solution of *n*-butyllithium (1.25 mL, 2 mmol) in hexanes was added dropwise to a suspension of 1,1-(bis(*N*-methylimidazol-2-yl))ethane (370 mg, 1.95 mmol) in tetrahydrofuran (20 mL) at −78 °C under nitrogen. After stirring for 30 min at −78 °C, iodomethane (0.13 mL, 2.1 mmol) in tetrahydrofuran (5 mL) was added. The mixture was stirred for 1 h, followed by warming to −40 °C, at which temperature saturated ammonium chloride solution (20 mL) was added to quench the reaction. The mixture was allowed to warm to room temperature, and water (10 mL) was added. Following acidification with 3 M hydrochloric acid, the organic layer was separated and extracted with 3 M hydrochloric acid (3 × 5 mL). The combined aqueous layers were neutralized with sodium carbonate, filtered, and extracted with chloroform (3 × 10 mL). The organic extracts were dried over magnesium sulfate and filtered, and the solvent was removed under reduced pressure. 2,2-(Bis(*N*-methylimidazol-2-yl))propane remained as small cream crystals (158 mg, 40%), mp 110−112 °C, and was used in subsequent reactions without further purification. High-resolution

(32) McCleverty, J. A.; Wilkinson, G. *Inorg. Synth.* **1991**, *28*, 84−86.
(33) Herde, J. L.; Lambert, J. C.; Senoff, C. V. *Inorg. Synth.* **1974**, *15*, 18−19.
(34) Elguero, J.; Julia, S.; Mazo, J. M. d.; Avila, L. *Org. Prep. Proc. Int.* **1984**, *16*, 299−307.
(35) Elgafi, S.; Field, L. D.; Messerle, B. A.; Turner, P.; Hambley, T. W. *J. Organomet. Chem.* **1999**, *588*, 69−77.
(36) Soler, L. P. Ph.D. Thesis; University of Sydney, 1999.
(37) Dumont, J.-L.; Chodkiewicz, W.; Cadiot, P. *Bull. Soc. Chim. Fr.* **1967**, *2*, 588−596.
(38) Morgan, J.; Field, L. D. Manuscript in preparation.

mass spectrum: calculated for $C_{11}H_{16}N_4$ (M^+) 204.1375; found 204.1377. ^{1}H NMR (400 MHz, chloroform-*d*): δ 7.02 (d, 2H, $^3J_{H4-H5}$ = 1.0 Hz, *H4*), 6.81 (d, 2H, *H5*), 3.10 (s, 6H, N−CH_3), 1.86 (s, 6H, C-CH_3) ppm. ^{13}C{^{1}H} NMR (100 MHz, chloroform-*d*): δ 150.7 (*C2*), 126.5 (*C4*), 123.5 (*C5*), 38.2 (*C*-$(CH_3)_2$) 33.8 (N-*C*H_3), 27.5 (C-(CH_3)$_2$) ppm. MS *m/z* (%): 204 (M^+, 83), 189 (100), 123 (99), 109 (96), 96 (99) 83 (49), 42 (36).

(c) Synthesis of [Rh(bie)(CO)$_2$][BPh$_4$]. 1,1-(Bis(*N*-methylimidazol-2-yl))ethane (43 mg, 0.23 mmol) in methanol (5 mL) was added to a solution of $[Rh(CO)_2Cl]_2$ (44 mg, 0.11 mmol) in methanol (3 mL) at room temperature. The mixture was stirred for 30 min before adding excess sodium tetraphenylborate (50 mg) in methanol (2 mL). A white-yellow gelatinous precipitate formed immediately and this was isolated by filtration and washed with methanol. The precipitate was recrystallized from acetone, affording (1,1-(bis(*N*-methylimidazol-2-yl)ethane))dicarbonylrhodium(I) tetraphenylborate as a fine yellow-green crystalline solid (40 mg, 27%), mp 211−213 °C (dec). Anal. Found: C, 64.8; H, 5.2; N, 8.4. $C_{36}H_{34}BN_4O_2Rh$ requires: C, 64.7; H, 5.1; N, 8.4. ^{1}H NMR (400 MHz, tetrahydrofuran-d_8): δ 7.30 (m, 8H, *o-H*), 7.19 (d, 2H, $^3J_{H4-H5}$ = 1.5 Hz, *H4*), 7.04 (d, 2H, *H5*), 6.81 (m, 8H, *m-H*), 6.65 (m, 4H, *p-H*), 4.30 (q, 1H, $^3J_{H-CH3}$ = 7.2 Hz, C-*H*), 3.35 (s, 6H, N-CH_3), 1.48 (d, 3H, C-CH_3) ppm. ^{13}C{^{1}H} NMR (100 MHz, tetrahydrofuran-d_8): δ 185.2 (d, $^1J_{Rh-CO}$ = 68 Hz, Rh-*C*O), 165.7−164.3 (m, B-*C*), 147.6 (*C2*), 137.0 (*o-C*), 130.5 (*C4*), 125.6 (*m-C*) 124.1 (*C5*), 121.8 (*p-C*), 34.0 (N-*C*H_3), 29.6 (*C*-H), 22.6 (C-*C*H_3) ppm. ν (KBr): 2090 (Rh−CO), 2028 (Rh−CO) cm^{-1}. MS *m/z*: (ES^+) 349 (100%, $[Rh(bie)(CO)_2]^+$).

(d) Synthesis of [Rh(bip)(CO)$_2$][BPh$_4$]. 2,2-(Bis(*N*-methylimidazol-2-yl))propane (40 mg, 0.2 mmol) in methanol (3 mL) was added to a solution of $[Rh(CO)_2Cl]_2$ (36 mg, 93 μmol) in methanol (5 mL) at room temperature. The mixture was stirred for 1 h before adding excess sodium tetraphenylborate (30 mg) in methanol (3 mL). The precipitate that formed immediately was isolated by filtration and washed with methanol, affording 2,2-(bis(*N*-methylimidazol-2-yl)propane)dicarbonylrhodium(I) tetraphenylborate as a silver-black solid (82 mg, 61%), mp 172−176 °C (dec). Anal. Found: C, 65.0; H, 5.4; N, 8.3. $C_{37}H_{36}BN_4O_2Rh$ requires: C, 65.1; H, 5.3; N, 8.2. ^{1}H NMR (400 MHz, acetone-d_6): δ 7.34 (m, 8H, *o-H*), 7.31 (d, 2H, $^3J_{H4-H5}$ = 1.6 Hz, *H4*), 7.19 (d, 2H, *H5*), 6.91 (m, 8H, *m-H*), 6.77 (m, 4H, *p-H*), 4.07 (s, 6H, N−CH_3), 2.44 (s, 6H, C-(CH_3)$_2$) ppm. ^{13}C{^{1}H} NMR (100 MHz, acetone-d_6): δ 186.0 (d, $^1J_{Rh-CO}$ = 68.2 Hz, Rh-*C*O), 165.6−164.6 (m, B-*C*), 151.2 (*C2*), 137.4 (*o-C*), 130.5 (*C4*), 126.8 (*C5*), 126.4 (*m-C*), 122.6 (*p-C*), 43.7 (*C*-(CH_3)$_2$), 39.4 (N-*C*H_3), 32.3 (C-(CH_3)$_2$) ppm. ν (KBr): 2089 (Rh−CO), 2027 (Rh−CO) cm^{-1}. MS *m/z*: (ES^+) 363 (100%, $[Rh(bip)(CO)_2]^+$). *m/z* (%): 434 (M^+, 77), 406 (47), 378 (100), 349 (11), 276 (29), 149 (31). ν (KBr): 2054 (Rh−CO), 1993 (Rh−CO) cm^{-1}.

(e) Synthesis of [Ir(bik)(CO)$_2$][BPh$_4$]. Solutions of bis(*N*-methylimidazol-2-yl)ketone (60 mg, 0.32 mmol) in methanol (3 mL) and sodium tetraphenylborate (120 mg, 0.35 mmol) in methanol (3 mL) were added to a solution of $[Ir(COD)Cl]_2$ (90 mg, 0.13 mmol) in methanol (10 mL) and hexane (3 mL) at room temperature. A dark red precipitate formed immediately. The mixture was stirred for 1 h, degassed, and placed under an atmosphere of carbon monoxide gas. The red solid became yellow within 5 min. The mixture was left to stir at room temperature for 24 h. The yellow solid was isolated by filtration and washed with hexane and methanol, affording (bis(*N*-methylimidazol-2-yl)ketone)dicarbonyliridium(I) tetraphenylborate (143 mg, 73%), mp 160 °C (darkens), 201−202 °C (dec), which was used without further purification. ^{1}H NMR (tetrahydrofuran-d_8, 290 K): δ 7.52 (s, 2H, *H4*), 7.29 (m, 8H, *o-H*), 7.24 (s, 2H, *H5*), 6.82 (m, 8H, *m-H*), 6.67 (m, 4H, *p-H*), 3.79 (s, 6H, N-CH_3) ppm. ^{13}C{^{1}H} NMR (tetrahydrofuran-d_8): δ 172.3 (Ir-*C*O), 166.3 (*C*=O), 165.8−164.3 (m, B-*C*), 139.4 (*C2*), 137.1 (*o-C*), 135.0 (*C4*), 131.5 (*C5*), 125.8 (*m-C*), 122.0 (*p-C*), 39.0 (N-*C*H_3) ppm. ν (KBr): 2082 (Rh−CO), 2015 (Rh−CO) cm^{-1}. MS *m/z*: (ES^+) 439 (100%, $[Ir(bik)(CO)_2]^+$).

(f) Synthesis of [Ir(bbnzim)(CO)$_2$][BPh$_4$]. Bis(*N*-methylbenzimidazol-2-yl)methane (45 mg, 0.16 mmol) in methanol (5 mL) was added to a solution of $[Ir(COD)Cl]_2$ (50 mg, 75 μmol) in methanol (10 mL) and hexane (3 mL) at room temperature. The mixture was stirred for 30 min before adding a solution of sodium tetraphenylborate (70 mg, 0.2 mmol) in methanol (5 mL). A bright yellow precipitate formed. The mixture was degassed and placed under an atmosphere of carbon monoxide gas and stirred for 2 days. The yellow solid was isolated by filtration and washed with hexane and methanol to give (bis(*N*-methylbenzimidazol-2-yl)methane)-dicarbonyliridium(I) tetraphenylborate (109 mg, 86%), mp 194−196 °C (dec), which was used without further purification. Anal. Found: C, 61.1; H, 4.4; N, 6.8. $C_{43}H_{36}BIrN_4O_2$ requires: C, 61.2; H, 4.3; N, 6.6. ^{1}H NMR (400 MHz, acetone-d_6): δ 8.05−8.02 (m, 2H, *H5* or *H4*), 7.85−7.83 (m, 2H, *H7*), 7.63−7.60 (m, 4H, *H6* and *H5* or *H4*), 7.34 (m, 8H, *o-H*), 6.89 (m, 8H, *m-H*), 6.73 (m, 4H, *p-H*), 5.05 (s, 2H, CH_2), 4.18 (s, 6H, N−CH_3) ppm. ^{13}C{^{1}H} NMR (100 MHz, acetone-d_6): δ 173.3 (s, Ir-*C*O), 166.0−164.1 (m, B-*C*), 150.9 (*C2*), 140.7 (*C8* or *C9*), 136.8 (*o-C*), 135.3 (*C8* or *C9*), 126.6 and 126.1 (*C4* or *C5* and *C6*), 126.0 (*m-C*), 122.2 (*p-C*), 117.9 (*C4* or *C5*), 113.1 (*C7*), 32.1 (N-*C*H_3), 25.8 (*C*H_2) ppm. ν (KBr): 2074 (Ir−CO), 2005 (Ir−CO) cm^{-1}. MS *m/z*: (ES^+) 525 (100%, $[Ir(bbnzim)(CO)_2]^+$).

General Procedures for Catalytic Reactions. Rhodium(I)- and iridium(I)-catalyzed reactions were performed on a small scale under nitrogen, in NMR tubes fitted with a concentric Teflon valve. The substrate was typically added to the catalyst dissolved in deuterated solvent, in a NMR tube at room temperature. The catalytic reactions were performed at elevated temperature by heating in an oil bath at the desired temperature or heating within the NMR spectrometer, in the case of time course experiments. The temperature within the magnet was calibrated using ethylene glycol.[39] Products were confirmed by comparison with spectral NMR data from the literature and by comparison with authentic samples.

The conversion of starting material to product was determined by integration of the product resonances relative to the substrate resonances in the ^{1}H NMR spectrum. 100% conversion was taken to be the time where no remaining substrate peaks were evident. The turnover rate (N_t h^{-1}) was calculated as the number of moles of product/mol of catalyst/hour and was usually calculated at the point of 50% conversion of substrate to product.

Cyclization of 4-Pentyn-1-amine (8a) to 2-Methyl-1-pyrroline (11). The rhodium(I)- and iridium(I)-catalyzed cyclization of 4-pentyn-1-amine (**8a**) led to 2-methyl-1-pyrroline (**11**) as the single product. A typical reaction was performed as follows:

4-Pentyn-1-amine (**8a**) (56 mg, 0.67 mmol) was added to [Rh(bim)(CO)$_2$][BPh$_4$] (**1a**) (6 mg, 9.2 μmol) in tetrahydrofuran-d_8 (0.5 mL) in a NMR tube under an atmosphere of nitrogen. The mixture was heated at 60 °C, and ^{1}H spectra were recorded at regular intervals. The product, 2-methyl-1-pyrroline (**11**), was formed quantitatively from starting material after 14 h. Assignment of the product was based on comparison of the ^{1}H and ^{13}C NMR spectra of **11** with the ^{1}H and ^{13}C NMR spectra of an authentic sample of 2-methyl-1-pyrroline. ^{1}H NMR (tetrahydrofuran-d_8): δ 3.67 (m, 2H, CH_2C=N), 2.39 (t, 2H, $^3J_{CH2-CH2}$ = 7.9 Hz, CH_2N), 1.91 (s, 3H, CH_3), 1.78 (m, 2H, CH_2) ppm. ^{13}C{^{1}H} NMR (tetrahydrofuran-d_8): δ 173.6 (*C*=N), 61.6 (*C*H_2N), 39.0 (*C*H_2C=N), 23.7 (*C*H_2CH_2N), 19.3 (*C*H_3) ppm.

Cyclization of 3-Butyn-1-amine (7a) to 1-Pyrroline (12). The catalyzed cyclization of 3-butyn-1-amine (**7a**) was attempted using complexes **1a**, **2a**, and **2b** in tetrahydrofuran-d_8 at 60 °C and at reflux. No new products were found in reactions with complexes

(39) Amman, C.; Meier, P.; Merbach, A. E. *J. Magn. Reson.* **1982**, *46*, 319−321.

2a and **2b**. Catalysis with complex **1a** resulted in the formation of 1-pyrroline (**12**). Assignment of the product was based on comparison of the ^{1}H NMR spectra with literature data.[40]

3-Butyn-1-amine (**7a**) (20 mg, 0.29 mmol) was added to [Rh(bim)(CO)$_2$][BPh$_4$] (**1a**) (3 mg, 4.6 μmol) in tetrahydrofuran-d_8 (0.5 mL) in a NMR tube under an atmosphere of nitrogen. The mixture was heated at reflux in an oil bath for 24 h. 1-Pyrroline (**12**) was formed in 20% conversion from starting material. ^{1}H NMR (tetrahydrofuran-d_8): δ 7.44 (s, 1H, CH), 3.73 (m, 2H, CH_2C═N), 2.44 (t, 2H, $^3J_{H5-H4}$ = 8.0 Hz, CH_2N), 1.73 (m, 2H, CH_2) ppm. ^{13}C{^{1}H} NMR (tetrahydrofuran-d_8): δ 165.7 (*C*═N), 62.0 (*C*H$_2$N), 37.2 (*C*H$_2$C═N), 21.4 (*C*H$_2$) ppm.

Cyclization of 3-Pentyn-1-amine (7b) to 2-Methyl-1-pyrroline (11). The cyclization of 3-pentyn-1-amine (**7b**) to 2-methyl-1-pyrroline (**11**) was catalyzed by complexes **1a**, **1b**, **2a**, and **2b** in tetrahydrofuran-d_8 at 60 °C. Assignment of the product was based on comparison of the ^{1}H and ^{13}C NMR spectra of **11** with the ^{1}H and ^{13}C NMR spectra of an authentic sample of 2-methyl-1-pyrroline. A typical reaction was performed as follows:

3-Pentyn-1-amine (**7b**) (34 mg, 0.41 mmol) was added to [Rh(bim)(CO)$_2$][BPh$_4$] (**1a**) (4 mg, 6.1 μmol) in tetrahydrofuran-d_8 (0.5 mL) in a NMR tube under an atmosphere of nitrogen. The mixture was heated at 60 °C in the spectrometer magnet, and ^{1}H spectra were recorded every 10 min using an automated time course program. 2-Methyl-1-pyrroline (**11**) was formed with 63% conversion from starting material after 12 h.

Cyclization of 4-Hexyn-1-amine (8b) in Tetrahydrofuran-d_8 at 60 °C. The cyclization of 4-hexyn-1-amine (**8b**) in tetrahydrofuran-d_8 at 60 °C was catalyzed by complexes **1a**, **1b**, **2a**, and **2b**. A typical reaction was performed as follows:

4-Hexyn-1-amine (**8b**) (20 mg, 0.2 mmol) was added to [Rh(bim)(CO)$_2$][BPh$_4$] (**1a**) (2 mg, 3 μmol) in tetrahydrofuran-d_8 (0.5 mL) in a NMR tube. The mixture was heated at 60 °C in the NMR spectrometer magnet, and ^{1}H spectra were recorded every 10 min using an automated time course program. The major product, 2-ethyl-1-pyrroline (**13**), was formed with 68% conversion from starting material after 16 h. The minor product 2-methyl-3,4,5,6-tetrahydropyridine (**14**) was formed in 7% conversion. Complete conversion was achieved within 48 h. Assignment of the products was based on comparison of the ^{1}H and ^{13}C NMR spectra of the product with literature spectral data.

2-Ethyl-1-pyrroline (13).[18] ^{1}H NMR (tetrahydrofuran-d_8): δ 3.68 (m, 2H, CH_2C═N), 2.39 (t, 2H, $^3J_{H5-H4}$ = 8.1 Hz, CH_2N), 2.26 (q, 2H, $^3J_{CH2-CH3}$ = 7.5 Hz, CH_2CH$_3$), 1.78 (m, 2H, CH_2), 1.09 (t, 3H, CH_3) ppm. ^{13}C{^{1}H} NMR (tetrahydrofuran-d_8): δ 177.4 (*C*═N), 61.5 (*C*H$_2$N), 37.4 (*C*H$_2$C═N), 27.2 (*C*H$_2$CH$_2$N), 23.4 (*C*H$_2$CH$_3$), 10.9 (*C*H$_3$) ppm.

2-Methyl-3,4,5,6-tetrahydropyridine (14).[31] ^{1}H NMR (tetrahydrofuran-d_8): δ 3.42 (m, 2H, CH_2C═N), 2.05 (t, 2H, $^3J_{H6-H5}$ = 6.4 Hz, CH_2N), 2.05 (s, 3H, CH_3), 1.56 (m, 2H, CH_2), 1.46 (m, 2H, CH_2) ppm. ^{13}C{^{1}H} NMR (tetrahydrofuran-d_8): δ 166.1 (*C*═N), 49.8 (*C*H$_2$N), 30.5 (*C*H$_2$C═N), 27.4 (*C*H$_3$), 22.8 (*C*H$_2$), 20.7 (*C*H$_2$) ppm.

Cyclization of 4-Hexyn-1-amine (8b) in Tetrahydrofuran-d_8 at Reflux. The cyclization of 4-hexyn-1-amine (**8b**) in tetrahydrofuran-d_8 at reflux was catalyzed by complexes **1a**, **1b**, **2a**, and **2b**. A typical reaction was performed as follows:

4-Hexyn-1-amine (**8b**) (45 mg, 0.47 mmol) was added to [Rh(bim)(CO)$_2$][BPh$_4$] (**1a**) (5 mg, 7.6 μmol) in tetrahydrofuran-d_8 (0.5 mL) in a NMR tube. The mixture was heated at reflux in an oil bath, and ^{1}H spectra were recorded at regular intervals. 2-Ethyl-1-pyrroline (**13**) was formed in 85% conversion from starting material after 6.5 h. The minor product 2-methyl-3,4,5,6-tetrahydropyridine (**14**) was formed in 9% conversion.

(40) Cantrell, G. K.; Geib, S. J.; Meyer, T. Y. *Organometallics* **2000**, *19*, 3562−3568.

Cyclization of 5-Hexyn-1-amine (9) to 2-Methyl-3,4,5,6-tetrahydropyridine (14). The cyclization of 5-hexyn-1-amine (**9**) to 2-methyl-3,4,5,6-tetrahydropyridine (**14**) was catalyzed by complexes **1a**, **1b**, **2a**, and **2b** in tetrahydrofuran-d_8 at reflux. Assignment of the product was based on comparison of the ^{1}H and ^{13}C NMR spectra with literature data.[31] A typical reaction was performed as follows:

5-Hexyn-1-amine (**9**) (44 mg, 0.45 mmol) was added to [Ir(bim)(CO)$_2$][BPh$_4$] (**1b**) (5 mg, 6.7 μmol) in tetrahydrofuran-d_8 (0.5 mL) in a NMR tube under an atmosphere of nitrogen. The mixture was heated at reflux in an oil bath, and ^{1}H spectra were recorded at regular intervals. 2-Methyl-3,4,5,6-tetrahydropyridine (**14**) was formed in 95% conversion from starting material after 24 h.

Attempted Cyclization of 6-Heptyn-1-amine (10). The catalyzed cyclization of 6-heptyn-1-amine (**10**) was attempted with complexes **1a**, **1b**, **2a**, and **2b**. No new cyclized products were detected. A typical reaction was performed as follows:

6-Heptyn-1-amine (**10**) (40 mg, 0.36 mmol) was added to [Rh(bim)(CO)$_2$][BPh$_4$] (**1a**) (5.5 mg, 8.4 μmol) in tetrahydrofuran-d_8 (0.5 mL) in a NMR tube under an atmosphere of nitrogen. The mixture was heated at 60 °C in the spectrometer magnet, and ^{1}H spectra were recorded every 10 min using an automated time course program. The ^{1}H NMR spectrum showed no evidence of the desired cyclic product after 16 h. The tube was placed in an oil bath at reflux for 48 h, after which time no new products had formed.

Cyclization of 4-Phenyl-3-butyn-1-amine (7c) to 2-Phenyl-1-pyrroline (16). The cyclization of 4-phenyl-3-butyn-1-amine (**7c**) in tetrahydrofuran-d_8 at 60 °C was catalyzed by the complexes **1a**, **1b**, **2a**, and **2b**. A typical reaction was performed as follows:

[Rh(bpm)(CO)$_2$][BPh$_4$] (**2a**) (5.0 mg, 8.0 μmol) was weighed into an NMR tube and dissolved in freshly distilled, dry, and degassed tetrahydrofuran-d_8 (0.6 mL). 4-Phenyl-3-butyn-1-amine (**7c**) (63 mg, 0.43 mmol) was injected directly into the NMR tube. The reaction was monitored by ^{1}H NMR while being heated at 60 °C. 2-Phenyl-1-pyrroline (**16**) was formed in quantitative conversion from the starting material after 2.5 h. The product was identified by comparison of the ^{1}H and ^{13}C NMR data with literature data.[25]

^{1}H NMR (300 MHz, tetrahydrofuran-d_8): δ 7.85 (m, 2H, Ar*H*), 7.33 (m, 3H, Ar*H*) 3.95 (tt, 2H, $^3J_{H5-H4}$ = 7.2 Hz, $^4J_{H5-H3}$ = 1.9 Hz, *H5*), 2.86 (tt, 2H, $^3J_{H3-H4}$ = 7.9 Hz, $^4J_{H3-H5}$ = 1.9 Hz, *H3*), 1.93 (p, 2H, $^3J_{H4-H5}$ = 7.2 Hz, $^3J_{H4-H3}$ = 7.9 Hz, *H4*) ppm. ^{13}C NMR (75 MHz, tetrahydrofuran-d_8): δ 172.3 (*C*═N), 135.9 (Ar*C*), 130.4 (Ar*C*H), 128.7 (Ar*C*H), 128.2 (Ar*C*H), 62.1 (*C5*), 35.0 (*C3*), 23.3 (*C4*) ppm.

Cyclization of 5-Phenyl-4-pentyn-1-amine (8c) to 2-Benzyl-1-pyrroline (17). The cyclization of 5-phenyl-4-pentyn-1-amine (**8c**) in dioxane-d_8 at 95 °C was catalyzed by the complexes **1a**, **1b**, **2a**, and **2b**. A typical reaction was performed as follows:

[Rh(bim)(CO)$_2$][BPh$_4$] (**1a**) (6.0 mg, 9.2 μmol) was weighed into an NMR tube and suspended in dioxane-d_8 (0.6 mL). 5-Phenyl-4-pentyn-1-amine (**8c**) (31 mg, 1.9 mmol) was injected directly into the NMR tube. The mixture was heated at 95 °C, and ^{1}H NMR spectra were recorded at regular intervals. 2-Benzyl-1-pyrroline (**17**) was formed with 96% conversion from starting material after 2.3 h. The product was identified by comparison of the ^{1}H and ^{13}C NMR data with literature data.[18]

^{1}H NMR (300 MHz, dioxane-d_8): δ 7.27−7.15 (m, 5H, Ar*H*), 3.73 (tt, 2H, $^3J_{H5-H4}$ = 7.2 Hz, $^4J_{H5-H3}$ = 1.7 Hz, *H5*), 3.61 (s, 2H, CH_2Ph), 2.32 (t, 2H, $^3J_{H3-H4}$ = 7.9 Hz, $^4J_{H3-H5}$ = 1.7 Hz, *H3*), 1.74 (p, $^3J_{H4-H5}$ = 7.2 Hz, $^3J_{H4-H3}$ = 7.9 Hz, 2H, *H4*) ppm. ^{13}C NMR (75 MHz, dioxane-d_8): δ 175.4 (*C*═N), 138.3 (Ar*C*), 129.5 (Ar*C*H), 128.9 (Ar*C*H), 126.8 (Ar*C*H), 61.2 (*C5*), 40.6 (*C*H$_2$Ph), 36.6 (*C3*) 23.0 (*C4*) ppm.

Acknowledgment. We gratefully acknowledge the Australian Government for Australian Postgraduate Scholarships (S.B. and S.L.R.) and the Australian Research Council for funding. We would also like to thank Ms. Jackie Morgan for her invaluable assistance with compound preparation. We would like to thank Prof. Todd Marder and Dr. Michael Whittlesey for helpful discussions.

OM700428Q