Reactive Indolyl Complexes of Group 9 Metals

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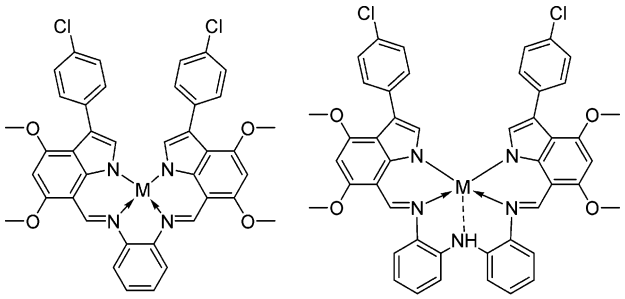
A series of novel indolyl−imine ligand precursors have been synthesized. In particular, bidentate, tridentate, and potentially tetradentate ligands were prepared, each containing both indolyl sp^2-N and imine sp^2-N donors. A series of neutral rhodium(I) and iridium(I) complexes of these ligands were synthesized, including monometallic and bimetallic complexes. The X-ray structures of three of the monometallic complexes with bidentate indolyl−imine ligands were determined. In each complex, the metal center was in a square planar conformation, as expected for Rh(I) and Ir(I) complexes. The five- and six-membered metallocycles formed on complexation of the metal with the ligands were all planar, and the aromaticity of the ligands was maintained. The Rh(I) complex with the tridentate indolyl ligand (L) reacted at room temperature with CH_2Cl_2 to form the Rh(III) chloromethyl complex [Rh(L)(CO)-(CH_2Cl)(Cl)] via oxidative addition of the C−Cl bond of CH_2Cl_2. The Rh/Ir(I) indolyl−imine complexes are efficient catalysts for the intramolecular cyclization of 4-pentynoic acid to form γ-methylene-γ-butyrolactone. A dinuclear Rh(I) complex was the most active catalyst, demonstrating a significant degree of bimetallic cooperativity.

Introduction

Heterocyclic donors, in particular N-heterocyclic carbenes (NHCs), have attracted significant attention as ligands in homogeneous catalysis over the past decade. Metal complexes with N-heterocyclic carbene ligands[1] are, in many cases, more robust than analogous complexes containing phosphine or nitrogen donor ligands, because of their ability to form strong σ-donor bonds. Other heterocyclic ligands containing nitrogen donors such as pyrrole, carbazole, and indole rings display strong σ-donor properties similar to those of carbenes. In particular, indolyl ligands generate a very powerful anionic sp^2-N σ-donor group upon deprotonation and can bind strongly to positively charged metal ions. Indolyl-based ligand systems have been designed to include more labile donors such as imines as well as take advantage of the strongly binding N-donor of the indolyl system, and have been complexed with first-row transition metals Co, Ni, Cu, Zn, and Mn (**1**−**3**).[2] The complexes with Mn (**1**) are active as catalysts for the epoxidation of alkenes.[3] To date, mixed indolyl−imine complexes with group 9 metals such Rh and Ir have not been studied.

In the search for active catalysts, metal complexes containing N-donor ligands as well as phosphine and N-heterocyclic carbene donors have been investigated. Metal complexes with phosphine ligands as well as metal complexes containing the strongly binding NHC ligands are active catalysts for a large number of organic transformations. Incorporating both the stability of complexes with strongly bound ligands and the reactivity of complexes with labile ligands, there are many examples of metal complexes with mixed polydentate donor ligands, in particular complexes with NHC-imine,[4] NHC-hydroxy/alkoxy/phenoxy,[5] NHC-amine/amido,[6] NHC-sulfide,[7] NHC-phosphine,[7,8] and NHC-pyrazolyl ligands.[9] Mixed phosphine−N-donor ligands include ligands containing phosphine and sp^3 amino donors, and sp^2 pyrazolyl[10] or imidazolyl[11] donors. Applications of these metal complexes with mixed donors in catalysis have, however, been limited. Among the P−N donor ligands, the phosphine−pyrazolyl and phosphine−imidazolyl ligands have been used for the preparation of late transition metal (Rh and Ir) complexes and act as efficient C−X



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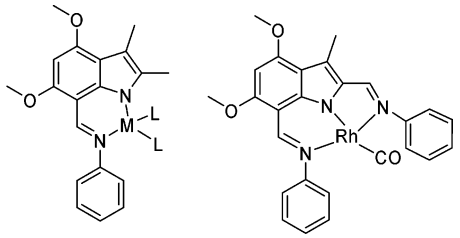
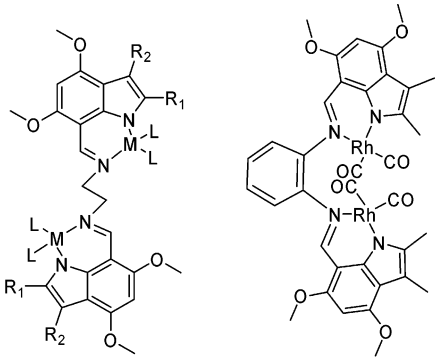
bond formation catalysts for allylic substitution,[12] hydrogenation,[12] hydrothiolation,[13] and asymmetric hydrogenation of alkenes[14] and imines.[15] Metal complexes containing two or more metal centers with multidentate ligands are also known to be active catalysts for a variety of transformations, in particular hydroformylation catalyzed by Rh_2[16] and Ru_2[17] complexes; alkene[18] and alkyne[19] hydrogenation catalyzed by Ir_2 complexes; and nitrile hydration catalyzed by Ni_2[20] and Pd_2[21,22] species. Of particular interest are bimetallic complexes that display cooperative effects between the metals, enhancing the rate of catalysis.[22]

We report here the synthesis and structural characterization of a new series of the novel bi-, tri-, and tetradentate indolyl−imine ligand precursors as well as their Rh(I) and Ir(I) complexes (**4**−**14**) and the solid-state structures of **4**, **6**, **7**, and **16**. The catalytic activity of the monometallic and bimetallic Rh/Ir(I) complexes for the intramolecular hydroalkoxylation of pentynoic acid is also investigated. The effect of the presence of two metals in a single catalyst on catalytic efficiency is described using bimetallic complex **14**.



M=Rh **4** L=CO, **5** L,L=COD
M=Ir **6** L,L=COD **7** L=CO

8



M=Ir, L,L=COD **9** R_1 = H, R_2 = Me; **10** R_1 = Me, R_2 = Me
M=Rh, L=CO **11** R_1 = H, R_2 = Me; **12** R_1 = Me, R_2 = Me; **13** R_1 = H, R_2 = ^{t}Bu

14

Results and Discussion

Synthesis and Characterization of Mixed Indolyl−Imine Ligands. The synthesis of the indolyl−imine ligand precursors (**15**−**20**) involves a three-step preparation following a modified method of Black et al.[2c,23,24] The first step is to obtain the activated 4,6-dimethoxyindole, which involves the direct cyclization of an arylaminoketone with lithium bromide under neutral conditions in a one-pot process.[23] Subsequently, the formylindoles were synthesized via the Vilsmeier reaction at the 2- and/or 7-positions.[24] The targeted ligand precursors (**15**−**20**) were then obtained following Schiff base condensation of the formylindoles with a series of alkyl and aryl amines.[2c]

The monoanionic bidentate (**15**) and tridentate indolyl−imine (**16**) ligand precursors were synthesized by refluxing the appropriate formylindole with an excess amount of aniline in toluene under nitrogen and in the presence of a catalytic amount

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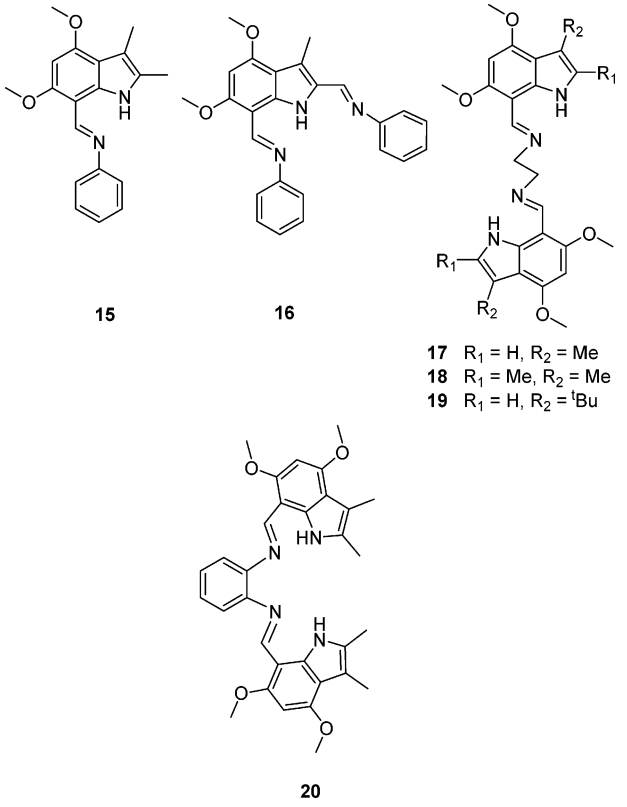

of glacial acetic acid and 4 Å molecular sieves.[25] The dianionic tetradentate bis(indolyl−imine) ligand precursors **17**−**20** were also prepared via condensation of 7-formylindole with the corresponding alkyl and aryl diamine. In contrast to the bidentate (**15**) and tridentate (**16**) indolyl−imine ligand precursors, the tetradentate (**17**−**20**) ligand precursors have the flexibility to support the formation of bimetallic complexes.

A broad resonance between 10.58 and 11.46 ppm due to the indole N−H proton was observed in the ^{1}H NMR spectra of the indolyl−imine precursors **15**−**20** at ambient temperature, and the downfield shift of this resonance is indicative of hydrogen bonding to the imino nitrogens. This suggests that only the *E*-configuration of the imino C═N double bond is present in solution,[25] which was confirmed by the solid-state structure of the tridentate indolyl−imine precursor **16** as determined by X-ray diffraction (Figure 1).

Crystals of **16** suitable for X-ray analysis were obtained by slow evaporation of a saturated solution of CH_2Cl_2/toluene. The molecular structure of this tridentate ligand precursor reveals a planar geometry. The two imino C═N linkages [C(9)−N(2) 1.2851(18) Å and C(19)−N(3) 1.2836(18) Å] are similar to those reported in the literature for similar tridentate imino ligands.[25]

Synthesis and Characterization of Rh and Ir(I) Complexes Containing Indolyl−Imine Ligands. Synthesis of Dicarbonyl and 1,5-Cyclooctadiene Rh(I) Complexes with Bidentate Indolyl−Imine Ligands (4, 5). The monoanionic bidentate indolyl−imine ligand **15′** was generated and used in situ by reacting the precursor ligand **15** with excess sodium acetate in CH_2Cl_2 solution. Reaction of equimolar quantities of [Rh(μ-Cl)(CO)$_2$]$_2$ and the deprotonated **15′** in CH_2Cl_2 at ambient temperature gave the neutral dicarbonyl indolyl−imine Rh(I) complex [Rh(15′)(CO)$_2$] (**4**) in excellent yield (98%) (Scheme 1). The bright orange complex **4** was isolated as an air- and water-stable solid. By reacting the dimeric [Rh(COD)OEt]$_2$ with 2 equiv of bidentate indolyl−imine ligand **15** in a CH_2Cl_2 solution, complex [Rh(15′)(COD)] (**5**) was obtained as an orange solid in moderate yield (68%) (Scheme 1).

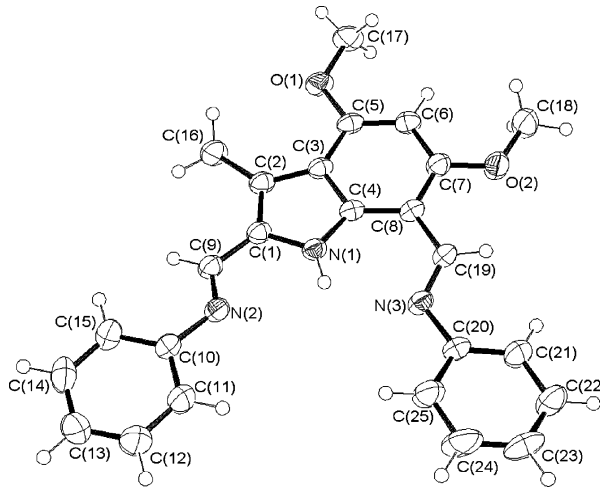

Figure 1. ORTEP representation of tridentate ligand precursor **16** shown with 50% probability ellipsoids.

The solid-state IR spectrum of **4** showed three intense peaks including a broad shoulder at 2052 cm^{-1} and a symmetrical doublet at 1997 and 1985 cm^{-1}, which were attributed to the carbonyl stretching frequencies. However, the liquid-state IR (in CD_2Cl_2) showed only two bands at 2066 and 1998 cm^{-1}, as is commonly observed for Rh(I) dicarbonyl complexes.[26] The solid-state spectrum showed more absorption bands in this region possibly due to the presence of two chemically different molecules in the solid state (vide infra). The ^{13}C{^{1}H} NMR spectrum of **4** displayed two doublet resonances at 187.93 and 187.01 ppm ($^1J_{Rh-C}$ = 69 and 63 Hz) characteristic of two Rh-bound carbonyl ligands.[26,27] In the ^{1}H NMR (CD_2Cl_2) spectrum of **4** and **5**, the indolyl NH resonance at 10.58 ppm disappeared upon complexation with the metal precursors, confirming the binding of the anionic ligand to the rhodium center. Additionally, the high-field shift of the imine proton to 8.74 and 8.24 ppm, in **4** and **5**, respectively, and the doublet resonance observed with coupling to ^{103}Rh ($^3J_{Rh-H}$ = 2.3 Hz) confirmed the imine coordination to the Rh center.

Synthesis of 1,5-Cyclooctadiene and Dicarbonyl Ir(I) Complexes with Bidentate Indolyl−Imine Ligands (6, 7). Complex [Ir(15′)(COD)] (**6**) was synthesized using the same method as was employed for the synthesis of complex **4** (Scheme 1). Deprotonation of the bidentate indolyl−imine ligand precursor **15** with sodium acetate in dichloromethane before addition to a solution of [Ir(μ-Cl)(COD)]$_2$ in dichloromethane led to the formation of **6** in good yield (94%). The dicarbonyl indolyl−imine Ir(I) (**7**) complex was synthesized by displacement of COD from **6** in either a suspension of a methanol/hexane mixture or a dichloromethane solution under an atmosphere of carbon monoxide (Scheme 1). The isolated orange precipitate **7** was recrystallized from dichloromethane as red crystals in moderately high yield (79%). The Ir analogues **6** and **7** show very similar IR and ^{1}H NMR spectroscopic data to those of **4** and **5**.

Synthesis of a Carbonyl Rh(I) Complex with the Tridentate Indolyl−Imine Ligand (8). The deprotonated monoanionic

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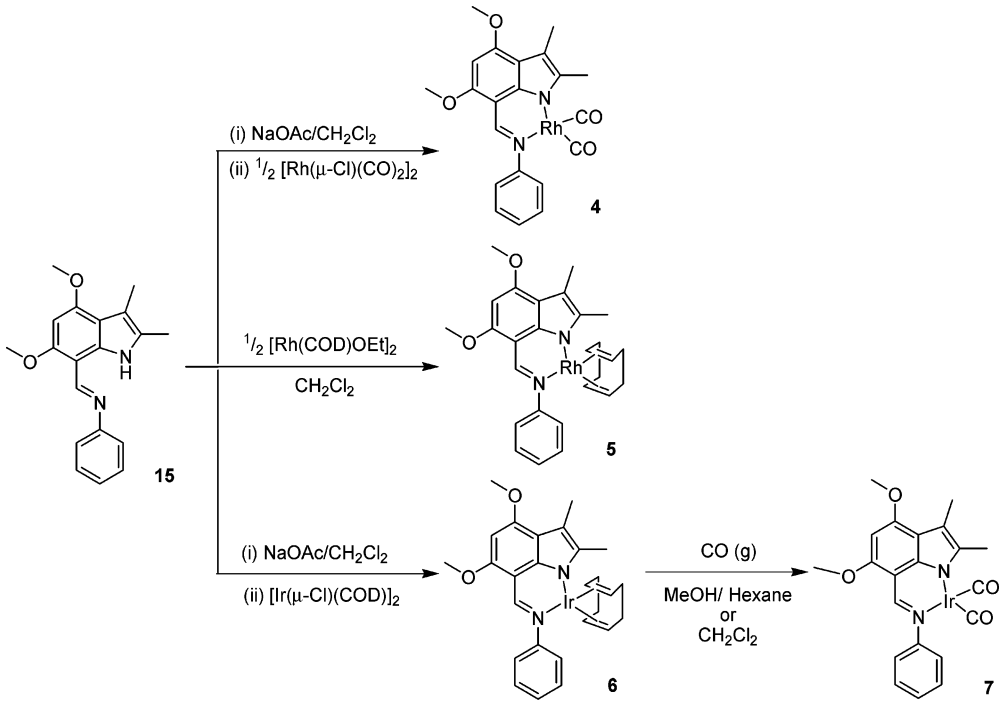
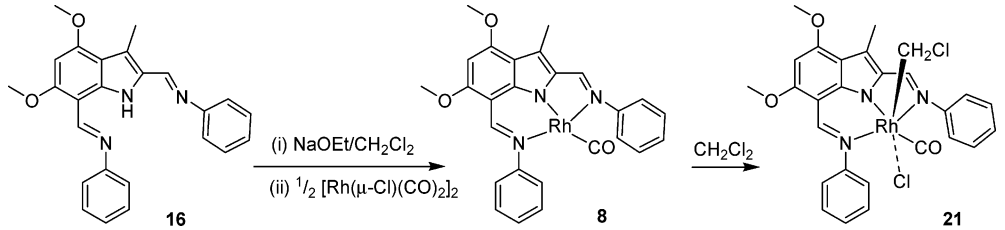
Scheme 1



Scheme 2



tridentate ligand **16′** was prepared in situ by mixing the corresponding tridentate ligand precursor **16** with a base in dichloromethane. This mixture was added dropwise to a dichloromethane solution of the dimeric $[Rh(\mu\text{-}Cl)(CO)_2]_2$ (Scheme 2). The reaction proceeded cleanly to yield complex **8** as a dark maroon solid (71%) when sodium ethoxide was used as the base. In contrast, using sodium acetate as the base led to a mixture of products.

For **8**, one carbonyl stretching band was observed in each of the solid- and liquid-state IR spectra at 1952 and 1962 cm^{-1}, respectively, characteristic of Rh(I) carbonyl complexes with monoanionic tridentate ligands.[28,29]

The ^1H NMR ($(CD_3)_2CO$) spectrum of **8** showed two doublet resonances due to coupling between the imine CH protons and ^{103}Rh ($^3J_{Rh-H}$ = 3.8 Hz). This coupling constant is within the range typically observed (3.5−3.9 Hz) for similar square planar Rh(I) complexes, confirming that both imino "arms" are bound to the Rh center in **8**.[28,30]

Oxidative Addition of CH_2Cl_2 to the Carbonyl Rh(I) Complex with a Tridentate Indolyl−Imine Ligand (8). The relatively low ν(CO) frequency 1952 cm^{-1} observed for **8** indicates there is a high electron density at the Rh center, making it a good candidate for oxidative addition reactions.[31] The square planar Rh(I) complex **8** in CD_2Cl_2, in an NMR tube sealed with a concentric Teflon Young's tap under an inert atmosphere, underwent oxidative addition of CD_2Cl_2 to form the octahedral Rh(III) derivative **21-*d*$_2$** (Scheme 2). The transformation to **21-*d*$_2$** took 2 days for complete conversion. The IR spectrum of **21-*d*$_2$** showed a carbonyl stretching frequency of complex **21** at 2085 cm^{-1}, which is significantly shifted to higher wavenumber compared to that observed for complex **8**, as expected on oxidative addition of an alkyl halide to a square planar Rh(I) carbonyl complex. Similar oxidative addition reactions have been reported for MeI addition to bis(imino)carbazolide,[28] α-diimine,[32] and pyridylbis(carbene)[31] Rh(I) carbonyl complexes.

On reaction of **8** with protio-dichloromethane to form **21**, ^1H NMR resonances due to the activated chloromethyl moiety were observed as two sets of doublets of doublets at 4.02 and 3.77 ppm, with a $^2J_{Rh-H}$ coupling constant of 3.0 Hz.[30,33] Resonances due to the Rh-bound carbonyl ligand at 184.54 ppm ($^1J_{Rh-C}$ = 58 Hz) in the $^{13}C\{^1H\}$ NMR spectrum and the chloromethyl carbon atom at 37.84 ppm with a $^1J_{Rh-C}$ coupling constant of 27 Hz were observed at similar chemical shifts to equivalent nuclei in similar Rh(III) complexes.[33,34]

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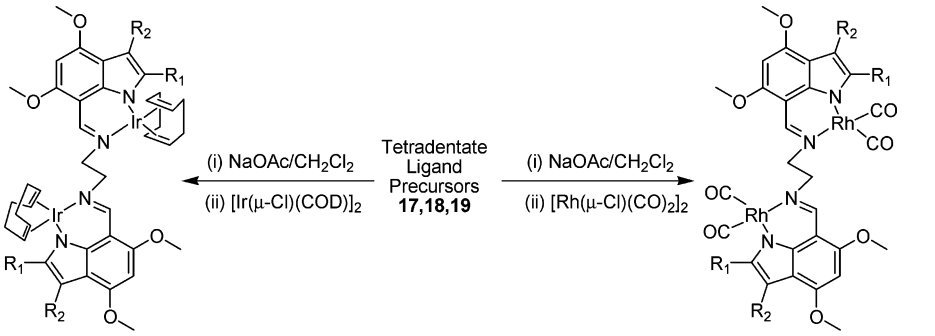
Scheme 3



9 R_1 = H, R_2 = Me
10 R_1 = Me, R_2 = Me

11 R_1 = H, R_2 = Me
12 R_1 = Me, R_2 = Me
13 R_1 = H, R_2 = ^{t}Bu

Synthesis of Ir/Rh(I) Complexes with Tetradentate Ligands (9−14). The dianionic tetradentate bis(indolyl−imine) ligand **17′** was prepared by reaction of the tetradentate ligand precursor **17** with excess sodium acetate in dichloromethane solution.[2c] The Ir/Rh(I) complexes **9** and **11** were synthesized by the reaction of an equimolar amount of the deprotonated tetradentate bis(indolyl−imine) ligand **17′** generated in situ with a dichloromethane solution of the respective metal precursors, [Ir(*μ*-Cl)(COD)]$_2$ or [Rh(*μ*-Cl)(CO)$_2$]$_2$ (Scheme 3). An immediate precipitation of the metal complex was observed in each case. The complexes were isolated after washing with hexane and methanol. The poor solubility of these complexes in common organic solvents made complete characterization difficult.

Complexes **10** and **12**, with methyl groups substituted at the C2- and C3-positions of the indolyl donor, and complex **13** with a bulky *tert*-butyl group at the C3-position of the indole ring were prepared in an attempt to improve the solubility of the metal complexes. Unfortunately, all of the isolated tetradentate bis(indolyl−imine) Ir/Rh(I) complexes with an ethylene-bridged backbone were insoluble in common organic solvents, which precluded complete characterization. The IR spectra of these complexes are discussed below.

The ligand precursor **20** contains a phenyl bridge between the two bidentate indolyl−imine ligands in place of the ethylene backbone of ligand precursors **17**−**19**. The neutral tetracarbonyl dirhodium(I) complex **14** was synthesized in excellent yield (95%) using ligand precursor **20** and following the same synthetic approach to that used for the synthesis of **11**−**13** (Scheme 3). This phenyl-bridged tetradentate bis(indolyl−imine) Rh(I) complex (**14**) was soluble in chloroform and THF and was fully characterized. A variable-temperature ^{1}H NMR experiment of **14** in $CDCl_3$ showed that the unresolved broad resonances observed at ambient temperature decoalesced at a lower temperature (213 K), confirming the presence of two indolyl−imine ligand units that are nonidentical at low temperature and highly fluxional (with magnetically equivalent protons) at room temperature (Figure 2).

IR Spectra of Bimetallic Complexes 11−14. The IR spectra of the bimetallic tetradentate carbonyl complexes **11**−**14** each contained two carbonyl stretching frequencies between 2058 and 1976 cm^{-1}, indicating the presence of two different metal-bound terminal CO groups. The *ν*(CO) stretching frequencies were very similar for all four complexes. The presence of two *ν*(CO) stretching frequencies in each case suggested these were all symmetrical, bimetallic systems.

Molecular Structures of Metal Complexes. Metal Complexes with Bidentate Ligands 4, 6, and 7. Crystals of **4** and **6** suitable for X-ray analysis were obtained by slow diffusion of pentane and hexane into concentrated CH_2Cl_2 solutions of **4** and **6**, respectively. A crystal of **7** suitable for X-ray analysis was obtained by slow evaporation of a saturated CH_2Cl_2 solution of **7**. The molecular structures of **4**, **6**, and **7** show that each complex has a square planar geometry about the metal center comprising one bidentate indolyl−imine ligand (**15′**), which provides two nitrogen donor atoms, and either two carbonyl donors (**4**, **7**) or a 1,5-cyclooctadiene unit (**6**) as the co-ligands.

The X-ray data for **4** are presented in Table 1, and selected bond lengths and angles in Table 2. For **4**, the bidentate anionic indolyl−imine ligand (**15′**) is essentially planar within the six-membered metallocycle (Figure 3), with the exception of the phenyl subsitituent on the imine-N. The bite angle N(1)−Rh-(1)−N(2) of 89.07(7)° is close to the ideal 90° required for square planar complexes. Complex **4** has a Rh(1)−N(1) (indolyl) bond length of 2.0662(17) Å and a Rh(1)−N(2) (imino) bond length of 2.0807(18) Å, which are comparable to the Rh−N imino bond lengths in previously reported complexes with mixed imino−phosphine[32] and imino−pyridyl[35] ligands. To date, there have been no other reports of indolyl−imine Rh complex structures.

The ORTEP illustration of the molecular structure of neutral complex **6** is presented in Figure 4, crystal data and structure refinement data are tabulated in Table 1, and selected bond lengths and angles are given in Table 2. The bond lengths of complex **6** for the Ir(1)−N(1) (indolyl) and Ir(1)−N(2) (imino) bonds were 2.0905(19) and 2.110(2) Å, respectively. The Ir atom is centered in an essentially square planar arrangement consisting of two N atoms of the bidentate indolyl−imine ligand (**15′**) and the centers of the C═C bonds of the COD ligand. The planar six-membered metallocycle results in a N(1)−Ir(1)−N(2) bond angle of 87.53(7)°, implying only a slight distortion from the ideal 90° value. This indicates a very low level of ring strain due to the binding of the indolyl−imine ligand.

The ORTEP representation of the neutral complex **7** is presented in Figure 5. Relevant molecular parameters are listed in Table 2, while all other crystallographic data are presented in Table 1. A geometry was displayed by complex **7** similar to those of **4** and **6**, with a four-coordinate square planar geometry about the Ir center and the monoanionic bidentate indolyl−imine ligand essentially planar within the six-membered iridacycle. In comparison with complex **6**, the substitution of the sterically

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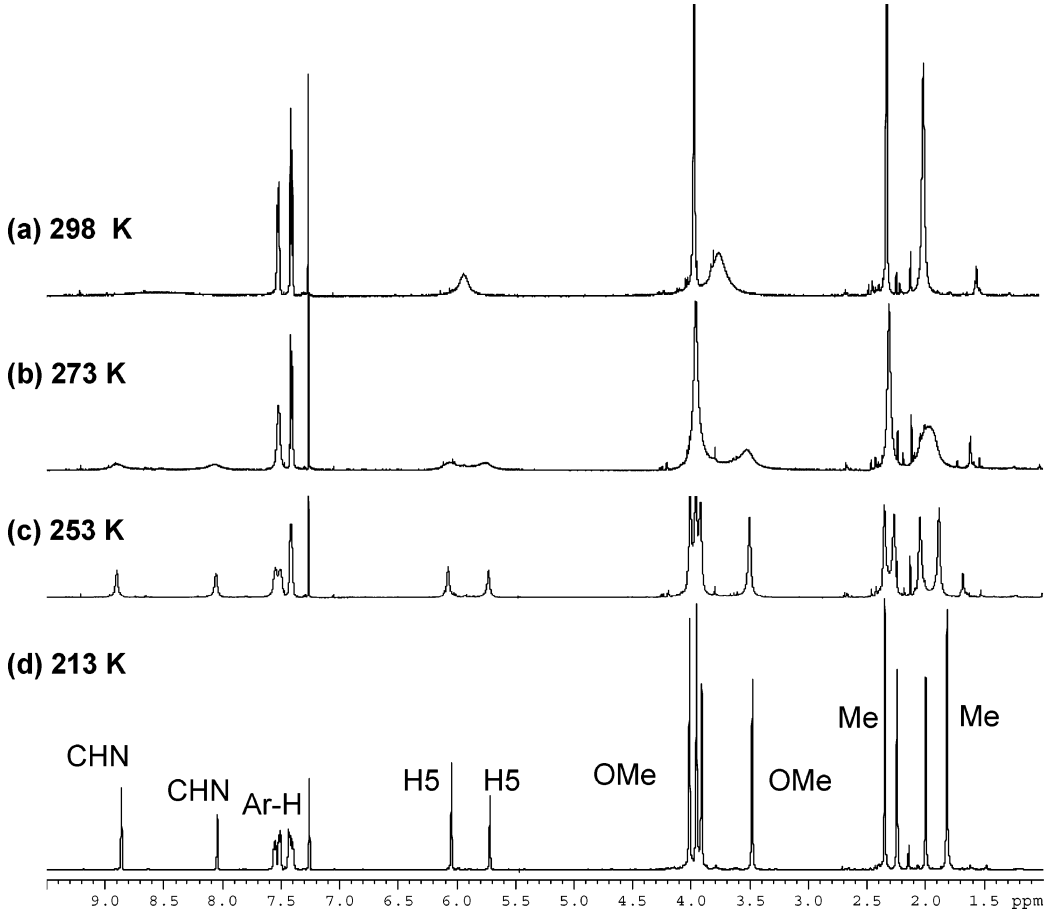

Figure 2. Variable-temperature ^{1}H NMR (500 MHz, $CDCl_3$) spectra of complex **14**: (a) 298 K, (b) 273 K, (c) 253 K, and (d) 213 K.

Table 1. Crystallographic Data for [Rh(15′)(CO)$_2$] (4), [Ir(15′)(COD)] (6), [Ir(15′)(CO)$_2$] (7), and Tridentate Ligand Precursor (16)

	[Rh(15′)(CO)$_2$] (**4**)	[Ir(15′)(COD)] (**6**)	[Ir(15′)(CO)$_2$] (**7**)	**16**
formula of refinement model	$C_{21}H_{19}N_2O_4Rh$	$C_{27}H_{34}IrN_2O_{3.50}$	$C_{21}H_{19}Ir_1N_2O_4$	$C_{25}H_{23}N_3O_2$
MW	466.29	634.76	555.58	397.46
cryst syst	monoclinic	triclinic	monoclinic	monoclinic
space group	$P2_1/n$ (#14)	$P\bar{1}$ (#2)	$P2_1/n$ (#14)	$P2_1/c$ (#14)
a/Å	11.1206(4)	7.7020(14)	11.099(2)	12.8861(14)
b/Å	27.5135(10)	12.171(2)	27.469(6)	8.4980(9)
c/Å	13.4874(5)	14.506(3)	13.464(3)	19.738(2)
α/deg		103.233(3)		
β/deg	111.600(2)	101.973(3)	111.39(3)	107.691(2)
γ/deg		104.272(3)		
V/Å^3	3836.9(2)	1231.6(4)	3822.4(13)	2059.2(4)
D_c/g cm^{-3}	1.614	1.712	1.931	1.282
Z	8	2	8	4
cryst size/mm	0.253 × 0.065 × 0.030	0.35 × 0.30 × 0.20	0.31 × 0.038 × 0.018	0.49 × 0.39 × 0.30
cryst color	red	red	red	red
cryst habit	needle	prism	needle	prism
temp/K	150(2)	150(2)	150(2)	150(2)
λ(Mo Kα)/Å	0.71073	0.71073	0.71073	0.71073
μ(Mo Kα)/mm^{-1}	0.920	5.454	7.016	0.083
T(empirical)$_{min,max}$	0.890, 1.00	0.228, 0.336	0.626, 0.881	0.856, 1.00
$2\theta_{max}$/deg	56.58	56.70	56.66	56.64
hkl range	−14 14, −36 36, −17 17	−10 10, −16 16, −18 18	−14 14, −36 36, −17 17	−16 16, −11 11, −25 26
N	92484	12277	72145	20134
N_{ind}(R_{merge})	9530(0.0341)	5759(0.0174)	9516(0.0423)	5003(0.0279)
N_{obs} − ($I > 2\sigma(I)$)	8062	5560	7682	3754
N_{var}	513	309	513	277
R1[a] ($I > 2\sigma$(I)), wR2[a] (all)	0.0276, 0.0627	0.0173, 0.0459	0.0263, 0.0936	0.0480, 0.1376
GoF	1.175	1.047	0.971	1.047
residual extrema/e$^-$ Å^{-3}	−0.456, 0.430	−0.724, 1.309	−0.585, 0.875	−0.195, 0.373

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$ for $F_o > 2\sigma(F_o)$ and $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_c^2)^2]\}^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + (AP)^2 + BP]$, $P = (F_o^2 + 2F_c^2)/3$, and A and B are listed in the crystal data information supplied.

demanding COD ligand with the smaller CO ligands in complex **7** results in a slightly larger bite angle of 88.57(13)° for the N(1)−Ir−N(2) angle in the bidentate indolyl−imine ligand iridacycle. The Ir(1)−N(1) (indolyl-N) bond length of 2.071-

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg)[a] for the Inner Coordination Spheres of [Rh(15′)(CO)$_2$] (4), [Ir(15′)(COD)] (6), and [Ir(15′)(CO)$_2$] (7)

[Rh(15′)(CO)$_2$] (**4**)		[Ir(15′)(COD)] (**6**)		[Ir(15′)(CO)$_2$](**7**)	
Rh(1)−C(20)	1.858(2)	Ir(1)−C(20)	2.119(2)	Ir(1)−C(20)	1.855(5)
Rh(1)−C(21)	1.865(3)	Ir(1)−C(23)	2.125(2)	Ir(1)−C(21)	1.854(5)
Rh(1)−N(1)	2.0662(17)	Ir(1)−C(24)	2.139(2)	Ir(1)−N(1)	2.071(3)
Rh(1)−N(2)	2.0807(18)	Ir(1)−C(27)	2.154(2)	Ir(1)−N(2)	2.075(3)
		Ir(1)−N(1)	2.0905(19)		
C(20)−Rh(1)−C(21)	82.32(10)	Ir(1)−N(2)	2.110(2)	C(21)−Ir(1)−C(20)	82.8(2)
C(20)−Rh(1)−N(1)	98.20(9)			C(21)−Ir(1)−N(1)	177.90(18)
C(21)−Rh(1)−N(1)	177.96(10)	N(1)−Ir(1)−N(2)	87.53(7)	C(20)−Ir(1)−N(1)	98.55(18)
C(20)−Rh(1)−N(2)	172.63(9)	N(1)−Ir(1)−C(20)	90.12(8)	C(21)−Ir(1)−N(2)	90.13(17)
C(21)−Rh(1)−N(2)	90.46(9)	N(2)−Ir(1)−C(20)	152.31(9)	C(20)−Ir(1)−N(2)	172.65(18)
N(1)−Rh(1)−N(2)	89.07(7)	N(1)−Ir(1)−C(23)	156.12(9)	N(1)−Ir(1)−N(2)	88.57(13)
		N(2)−Ir(1)−C(23)	90.02(8)		
Rh(2)−C(41)	1.860(2)	C(20)−Ir(1)−C(23)	81.14(9)	Ir(2)−C(41)	1.849(5)
Rh(2)−C(42)	1.868(2)	N(1)−Ir(1)−C(24)	164.91(9)	Ir(2)−C(42)	1.858(5)
Rh(2)−N(1)	2.0662(17)	N(2)−Ir(1)−C(24)	92.46(8)	Ir(2)−N(3)	2.066(3)
Rh(2)−N(2)	2.0816(18)	C(20)−Ir(1)−C(24)	96.74(9)	Ir(2)−N(4)	2.077(3)
		C(23)−Ir(1)−C(24)	38.92(9)		
C(41)−Rh(2)−C(42)	82.51(10)	N(1)−Ir(1)−C(27)	98.45(8)	C(41)−Ir(2)−C(42)	83.08(19)
C(41)−Rh(2)−N(3)	98.54(8)	N(2)−Ir(1)−C(27)	168.10(8)	C(41)−Ir(2)−N(3)	98.69(17)
C(42)−Rh(2)−N(3)	178.10(9)	C(20)−Ir(1)−C(27)	38.71(9)	C(42)−Ir(2)−N(3)	177.54(17)
C(41)−Rh(2)−N(4)	172.21(8)	C(23)−Ir(1)−C(27)	88.58(9)	C(41)−Ir(2)−N(4)	172.82(17)
C(42)−Rh(2)−N(4)	89.75(8)	C(24)−Ir(1)−C(27)	79.09(9)	C(42)−Ir(2)−N(4)	89.75(17)
N(3)−Rh(2)−N(4)	89.23(7)			N(3)−Ir(2)−N(4)	88.47(13)

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

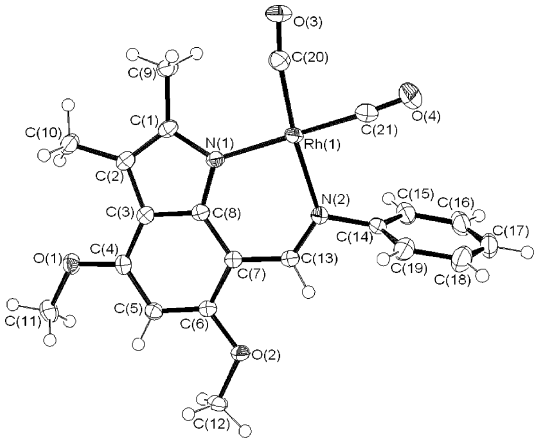

Figure 3. ORTEP representation of [Rh(15′)(CO)$_2$] (**4**) shown with 50% probability ellipsoids. Only one of the two independent molecules in the asymmetric unit is shown.

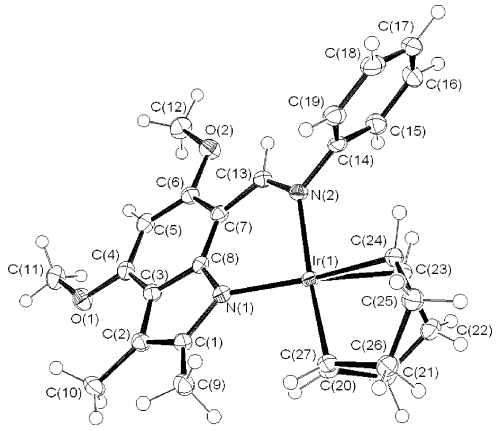

Figure 4. ORTEP representation of [Ir(15′)(COD)] (**6**) shown with 50% probability ellipsoids. Disordered solvent molecules have been omitted for clarity.

(3) Å and the Ir(1)−N(2) (imino) bond length of 2.075(3) Å of **7** are each slightly longer than those of the Ir dicarbonyl analogue, **6**, possibly because the carbonyl ligands make the Ir center more electron deficient through π-back-bonding, causing the indolyl−imine ligand to bind more strongly.

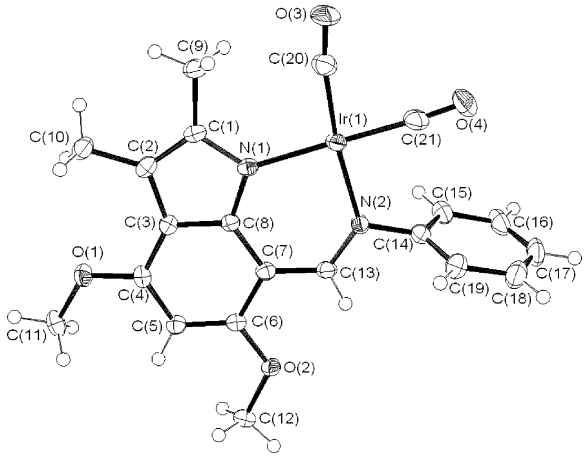

Figure 5. ORTEP representation of [Ir(15′)(CO)$_2$] (**7**) shown with 50% probability ellipsoids. Only one of the two independent molecules in the asymmetric unit is shown.

Catalyzed Intramolecular Hydroalkoxylation. Transition metal catalyzed reactions such as the intramolecular cyclization of acetylenic carboxylic acids offer a potentially efficient approach to the synthesis of five- and six-membered ring systems containing oxygen.[36] Industrially, this catalytic process is particularly useful for the preparation of pharmaceuticals, flavors, and fragrances.[36b] The metal-catalyzed intramolecular cyclization of 4-alkynyl carboxylic acids to form the five-membered exocyclic enol lactones (**22**, Scheme 4) has been performed previously using Rh,[36a,37] Pd,[36a] and Hg[36a,b] complexes. Rh(I) complexes with sp^2-N donor ligands[36b] and cationic

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(37) (a) Marder, T. B.; Chan, D. M. T.; Fultz, W. C.; Milstein, D. *J. Chem. Soc., Chem. Commun.* **1988**, 996−998. (b) Marder, T. B.; Chan, D. M. T.; Fultz, W. C.; Calabrese, J. C.; Milstein, D. *J. Chem. Soc., Chem. Commun.* **1987**, 1885−1887.

Scheme 4

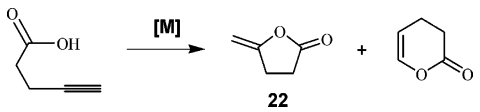

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Table 3. Efficiency of Catalyzed Intramolecular Cyclization of 4-Pentynoic Acid to Exocyclic γ-Methylene-γ-butyrolactone (22) Using Rh(I) and Ir(I) Complexes with Indoyl Ligands (65 °C, 2 mol % catalyst, N_2 atmosphere, NMR scale)

catalyst	deuterated solvents	4-pentynoic acid amount (mg)	reaction time (h)	% conversion	N_t[c] (h^{-1})
4[a,b]	$CDCl_3$	26.9	3.4	>98	31
4[a,b]	$(CD_3)_2CO$	26.9	3.0	>95	35
4[a,b]	CD_3CN	26.9	4.6	>96	5
4[a,b]	CD_3OD	26.9	3.9	40	
5	$(CD_3)_2CO$	17.3	2.8	7	
5	CD_3OD	17.3	2.8	53	17
6	$(CD_3)_2CO$	26.9	6.2	94	26
6	CD_3OD	26.9	2.5	>98	52
7	$CDCl_3$	26.4	9.9	73	5
7	$(CD_3)_2CO$	26.4	90	60	<5
8	$(CD_3)_2CO$	27.9	20	61	<5
14	$CDCl_3$	17.2	3.5	>98	142

[a] 2.3mol % catalyst. [b] 60 °C. [c] N_t (h^{-1}) is the amount of product/mole of catalyst/hour at the point of 50% conversion of substrate to product.

Rh/Ir(I) complexes of the tris-carbene (TIMEN) tris[2-(3-isopropylimidazol-2-ylidenne)ethyl]amine ligand system[38] are efficient catalysts for the intramolecular cyclization of acetylenic carboxylic acids.

Preliminary studies of the efficiency of the neutral Rh/Ir(I) complexes with a bidentate indolyl−imine ligand system, [Rh(15′)$(CO)_2$] (**4**), [Rh(15′)(COD)] (**5**), [Ir(15′)(COD)] (**6**), and [Ir(15′)$(CO)_2$] (**7**), the Rh(I) tridentate indolyl−imine complex [Rh(16′)(CO)] (**8**), and the Rh(I) tetradentate bis(indolyl−imine) complex [Rh_2(20′)$(CO)_4$] (**14**) as catalysts for the cyclization of 4-pentynoic acid were carried out. The catalyzed reactions of 4-pentynoic acid were performed on an NMR scale with 2 mol % catalyst loading at elevated temperature (~60 °C), in a variety of deuterated solvents. The reaction progress was monitored at regular intervals using ^{1}H NMR spectroscopy. Percentage conversion was determined by integration of the product resonances relative to the substrate resonances in the ^{1}H NMR spectrum. The turnover rate (N_t) was calculated as the amount of product/mole of catalyst/hour at the point of 50% conversion of substrate to product, unless otherwise stated. The results are presented in Table 3.

[Ir(15′)(COD)] (**6**) was the most efficient catalyst of the monometallic complexes, with quantitative conversion to products in under 2.5 h and an efficiency of 52 h^{-1} turnovers at 50% conversion. The monometallic Rh(I) dicarbonyl system [Rh(15′)$(CO)_2$] (**4**) achieved quantitative conversion in 3 h, with an efficiency of 35 h^{-1} turnovers. [Rh(15′)(COD)] (**5**) gave an efficiency of 17 h^{-1}, while [Ir(15′)$(CO)_2$] (**7**) gave a low N_t of 5 h^{-1}. The efficiency of the catalysts investigated was strongly dependent on the solvent used (Table 3). Previous reports of Rh-, Pd-, and Hg-based catalysts[36a,37] with primarily phosphine ligands achieved less than quantitative conversion in over 16 h. The most efficient catalyst reported to date by Mas-Marzá et al, a cationic Rh(I) complex of a tris-carbene ligand, achieves quantitative conversion of the pentynoic acid substrate in under 3 h, which is comparable to the efficiency of the Rh/Ir(I) indolyl complexes reported here.[39]

The most efficient catalyst was the Rh(I) bimetallic complex **14**, which promoted the quantitative conversion of starting material after 3.5 h with a turnover number of 142 h^{-1} in $CDCl_3$. Comparing this with the equivalent Rh(I) monometallic species (**4**) (which had a turnover number of 35 h^{-1} for the corresponding transformation), a significant degree of cooperation between the two metal centers of the bimetallic complex **14** during the catalyzed reaction was indicated. Jones and James[22] have proposed an index of cooperativity to provide a numerical estimate of the catalytic activity the complex appears to possess beyond the expected value. The value of this index for complex **14** under investigation here, based on the turnover frequency at 50% conversion, is 2.1, indicating that the reactivity of the metal complex is enhanced by a cooperative mechanism whereby the second metal center enhances the efficiency of the first. In comparison, the cooperativity indices for the bimetallic Rh(I) catalysts for hydroformylation reported previously[22] are as high as 422 or 34, suggesting a significantly greater degree of cooperativity than observed here.

Conclusions

A series of novel indolyl−imine ligands with a variety of binding modes have been synthesized. In particular, bidentate and tridentate ligands were prepared and additionally a ligand that can act as either a tetradentate ligand or a bis-bidentate ligand. A series of neutral rhodium(I) and iridium(I) complexes of these indolyl ligand derivatives have also been synthesized. In each complex, the metal center was in a square planar conformation, as expected for Rh(I) and Ir(I) complexes. The five- and six-membered metallocycles formed on complexation of the metal with the ligands were all planar, and the aromaticity of the ligands was maintained. The Rh(I) complex with the tridentate indolyl ligand (**8**) reacted at room temperature with CH_2Cl_2 to form the Rh(III) chloromethyl complex [Rh(16′)(CO)(CH_2Cl)(Cl)] (**21**) via oxidative addition of the C−Cl bond of CH_2Cl_2.

The Rh/Ir(I) indolyl−imine complexes (**4**−**6** and **14**) are efficient catalysts for the intramolecular cyclization of 4-pentynoic acid to form γ-methylene-γ-butyrolactone (**22**). In this work, the dinuclear complex [Rh_2(20′)$(CO)_4$] (**14**) was the most active catalyst and produced exclusively the five-membered exocyclic lactone γ-methylene-γ-butyrolactone (**22**), with a turnover rate of 142 h^{-1} and quantitative conversion in 3.5 h. The equivalent monometallic complex **4** gave a much lower turnover rate of 35 h^{-1}. Calculation of the cooperativity index for **14** suggests that the catalyzed reaction follows a mechanism that involves intramolecular intermetallic cooperativity. The next most efficient catalyst was the monometallic [Ir(15′)(COD)] (**6**), with a faster quantitative conversion time of 2.5 h and a slower initial turnover rate of 52 h^{-1}. These reaction rates are among the best reported for the catalyzed hydroalkoxylation of 4-pentynoic acid to **22**.

Experimental Section

General Procedures. All manipulations of metal complexes and air-sensitive reagents were carried out using standard Schlenk techniques or in a nitrogen-filled glovebox. Tetrahydrofuran, hexane, toluene, and pentane were dried by distillation under argon from benzophenone and sodium shavings. Methanol was predried over activated 4 Å molecular sieves and distilled from magnesium turnings. Dichloromethane was dried over and distilled from calcium

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(39) Mas-Marza, E.; Sanau, M.; Peris, E. *Inorg. Chem.* **2005**, *44*, 9961−9967.

hydride. The indolyl derivatives, the metal precursors $[Rh(\mu\text{-}Cl)(CO)_2]_2$,[40a] $[Rh(\mu\text{-}Cl)(COD)]_2$,[40b] $[Rh(\mu\text{-}OEt)(COD)]_2$,[40c] and $[Ir(\mu\text{-}Cl)(COD)]_2$,[40d] and 4-pentynoic acid[40e] were prepared according to published procedures. All other reagents were purchased from Aldrich or Ajax Finechem and used as supplied. Nuclear magnetic resonance spectra were recorded at ambient temperature unless otherwise stated. Elemental analyses (C, H, N) were carried out at the Campbell Microanalytical Laboratory, University of Otago, New Zealand. Electrospray mass spectra were carried out at the Biological Mass Spectrometry Facility, University of NSW. Single-crystal X-ray structure analyses were obtained at the Crystal Structure Analysis Facility, School of Chemistry, University of Sydney.

Synthesis of 7-(4,6-Dimethoxy-2,3-dimethylindol-2-yl)iminobenzene (15). A mixture of 4,6-dimethoxy-2,3-dimethylindole-7-carbaldehyde (1.00 g, 4.29 mmol), aniline (0.40 mL, 8.58 mmol), and 4 Å molecular sieves (4.0 g) in toluene (150 mL) with glacial acetic acid (5 drops) was refluxed for 1 day under a nitrogen atmosphere. The solution was cooled to rt, the molecular sieves were filtered off, and the solvent was evaporated under reduced pressure to yield a pale yellow solid. The crude product (0.80 g, 2.61 mmol, 65%) was purified by washing from hot acetonitrile. Mp: 168−170 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.58 (bs, 1H, N*H*), 9.02 (s, 1H, C*H*N), 7.41−7.37 (m, 2H, Ar-*H*), 7.27−7.16 (m, 3H, Ar-*H*), 6.17 (s, 1H, *H5*), 3.97, 3.94 (2s, 6H, OCH_3) 2.36, 2.33 (2s, 6H, CH_3). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 156.82 (*C*HN), 158.73, 158.42, 135.83, 128.92, 113.66, 106.90, 102.29 (*Ar*), 153.57, 129.22, 125.00, 121.37 (*Ar′*), 86.98 (*C5*), 57.04, 55.48 (O*C*H$_3$), 11.46, 10.67 (*C*H$_3$). IR (KBr): ν_{NH} 3390 (m), $\nu_{CH=N}$ 1623 (s) cm^{-1}. ES-MS *m*/*z* (%): 309 ([LH]$^+$, 100). Anal. Calcd for ($C_{19}H_{20}N_2O$ + 0.6H_2O): C, 71.09; H, 6.72; N, 8.73. Found: C, 71.17; H, 6.65; N, 8.58.

Synthesis of 4,6-Dimethoxy-3-methylindol-2,7-diylidenaminobenzene (16). A mixture of 4,6-dimethoxy-3-methylindole-2,7-dicarbaldehyde (1.50 g, 6.06 mmol), aniline (2.20 mL, 24.2 mmol), and 4 Å molecular sieves (4.0 g) in toluene (100 mL) with 5 drops of glacial acetic acid was heated under reflux for 2 days under a nitrogen atmosphere. The solution was cooled to rt, the molecular sieves were filtered off, and the solvent was evaporated under reduced pressure. The crude product was purified by washing from hot acetonitrile to yield a brick red solid (1.87 g, 77%). Red single crystals of **16** were obtained by slow evaporation of a saturated solution of CH_2Cl_2/toluene. Mp: 190−192 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 11.46 (bs, 1H, N*H*), 9.05 (s, 1H, C*H′*N), 8.52 (s, 1H, C*H*N), 7.42−7.17 (m, 10H, Ar-*H*), 6.16 (s, 1H, *H5*), 4.00, 3.97 (2s, 6H, OCH_3), 2.64 (s, 3H, CH_3). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 161.07 (*C*H′N), 129.90 (*C*HN), 155.42, 152.84, 152.40, 147.74, 137.80, 130.91, 128.97, 128.93, 125.25, 124.98, 121.28, 121.00, 119.61, 113.92, 102.07 (*Ar*), 86.78 (*C5*), 56.42, 55.29 (−O*C*H$_3$), 10.50 (*C*H$_3$). IR (KBr) ν_{NH} 3380 (m), $\nu_{CH=N}$ 1610 (br, m) cm^{-1}. ES-MS *m*/*z* (%): 399 ([LH]$^+$, 100). Anal. Calcd for ($C_{25}H_{23}N_3O_2$ + 0.5H_2O): C, 73.87; H, 5.95; N, 10.34. Found: C, 73.57; H, 5.89; N, 10.40.

Synthesis of 1,2-Di(4,6-dimethoxy-2,3-dimethylindol-7-ylidenamino)ethane (18). A mixture of 4,6-dimethoxy-2,3-dimethylindole-7-carbaldehyde (1.00 g, 4.29 mmol), 1,2-diaminoethane (0.4 mL, 4.39 mmol), and 4 Å molecular sieves (2.0 g) in toluene (100 mL) was heated under reflux for a day under nitrogen. The solution was allowed to cool, the molecular sieves were removed by filtration, and the solvent of the filtrate was evaporated under reduced pressure. The crude product was washed with hexane, diethyl ether, and ethyl acetate and the solvent evaporated in vacuo to yield the compound as a pale yellow solid (0.65 g, 2.11 mmol, 55%). Mp: 260−262 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.49 (bs, 1H, N*H*), 8.85 (s, 1H, C*H*N), 6.12 (s, 1H, *H5*), 3.95 (s, 2H, CH_2), 3.92, 3.84 (2s, 6H, OCH_3) 2.30, 2.11 (2s, 6H, CH_3). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 158.62 (*C*HN), 157.39 (*Ar*), 136.18, 129.14, 113.90, 106.60, 101.99 (*Ar*), 87.34 (*C5*), 63.43 (*C*H$_2$), 57.40, 55.65 (−O*C*H$_3$), 11.29, 10.86 (*C*H$_3$). IR (KBr): ν_{NH} 3343 (m), $\upsilon_{CH=N}$ 1625 (s) cm^{-1}. ES-MS *m*/*z* (%): 491 ([LH]$^+$, 100). Anal. Calcd for ($C_{28}H_{34}N_4O_4$ + 0.4H_2O): C, 67.56; H, 7.05; N, 11.25. Found: C, 67.84; H, 6.83; N, 11.22.

Synthesis of 1,2-Di(4,6-dimethoxy-3-tertbutylindol-7-ylidenamino)ethane (19). A mixture of 4,6-dimethoxy-3-tertbutylindole-7-carbaldehyde (0.75 g, 2.87 mmol), 1,2-diaminoethane (0.38 mL, 5.75 mmol), and 4 Å molecular sieves (2.0 g) in toluene (100 mL) was heated under reflux for 18 h under nitrogen. The solution was allowed to cool, the molecular sieves were removed by filtration, and the solvent of the filtrate was evaporated under reduced pressure. The crude product was recrystallized from CH_2Cl_2/hexane to yield the compound as a pale green solid (0.55 g, 1.01 mmol, 70%). Mp: 196−198 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 11.04 (bs, 1H, N*H*), 8.84 (s, 1H, C*H*N), 6.71 (s, 1H, *H2*), 6.19 (s, 1H, *H5*), 3.92 (s, 2H, CH_2), 3.99, 3.86 (2s, 6H, OCH_3), 1.40 (d, 9H, C(CH_3)$_3$). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 158.23 (*C*HN), 157.71, 156.54, 138.70, 127.25, 118.48, 111.23, 101.59 (*Ar*), 87.12 (*C5*), 62.93 (*C*H$_2$), 56.97, 55.00 (−O*C*H$_3$), 31.46 (*C*(CH$_3$)$_3$), 31.32 (C(*C*H$_3$)$_3$). ES-MS *m*/*z* (%): 547 ([LH]$^+$, 100).

Synthesis of 1,2-Di(4,6-dimethoxy-2,3-dimethylindol-7-ylidenamino)benzene (20). A mixture of 4,6-dimethoxy-2,3-dimethylindole-7-carbaldehyde (1.00 g, 4.29 mmol), 1,2-diaminobenzene (0.23 g, 2.10 mmol), and 4 Å molecular sieves (2.0 g) in toluene (80 mL) was heated under reflux for 18 h. The solution was cooled, the molecular sieves were removed by filtration, and the solvent was evaporated under reduced pressure. The product was recrystallized from $CHCl_3$/hexane to yield a yellow microcrystalline solid (0.46 g, 0.855 mmol, 41%). Mp: 274−278 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.73 (bs, 1H, N*H*), 9.10 (s, 1H, C*H*N), 7.24 (m, 2H, Ar-*H*), 6.14 (s, 1H, *H5*), 3.95, 3.87 (2s, 6H, OCH_3) 2.27, 1.64 (2s, 6H, CH_3). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 156.08(*C*HN), 158.08, 157.85, 135.53, 129.12, 113.31, 106.08, 102.43 (*Ar*), 146.25, 119.14, 113.31 (*Ar′*), 86.49 (*C5*), 56.66, 55.17 (O*C*H$_3$), 10.33, 9.96 (*C*H$_3$). IR (KBr): ν_{NH} 3299 (w); $\nu_{CH=N}$ 1621 (m) cm^{-1}. ES-MS *m*/*z* (%): 539 ([LH]$^+$, 100). Anal. Calcd for $C_{32}H_{34}N_4O_4$: C, 71.35; H, 6.36; N, 10.40. Found: C, 71.10; H, 6.40; N, 10.40.

Synthesis of 4,6-Dimethoxy-2,3-dimethylindol-7-ylidenaminobenzyl Rhodium(I) Dicarbonyl, [Rh(15′)(CO)$_2$] (4). A mixture of imine **15** (0.11 g, 0.358 mmol) with NaOAc (0.08 g, 0.974 mmol) in CH_2Cl_2 (10 mL) was stirred for 0.5 h under an inert atmosphere. This mixture was added to a solution of $[Rh(\mu\text{-}Cl)(CO)_2]_2$ (0.0695 g, 0.179 mmol) in CH_2Cl_2 (5 mL) and stirred for another 2 h before the solvent was evaporated in vacuo and washed with diethyl ether and methanol, yielding complex **4** as an orange solid (0.165 g, 0.35 mmol, 98%). Single crystals suitable for X-ray analysis were obtained by slow diffusion of pentane into a concentrated CH_2Cl_2 solution of complex **5**. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 8.74 (d, $^3J_{Rh-H}$ = 2.3 Hz, 1H, C*H*N), 7.47−7.39 (m, 4H, Ar-*H*), 7.33−7.27 (m, 1H, Ar-*H*), 6.15 (s, 1H, *H5*), 4.00, 3.92 (2s, 6H, OCH_3) 2.56, 2.42 (2s, 6H, CH_3). ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2): δ 187.47 (d, $^1J_{Rh-C}$ = 69 Hz, *C*O), 185.53 (d, $^1J_{Rh-C}$ = 63 Hz, *C*O), 160.53 (*C*HN), 162.02, 161.69, 114.27, 110.62, 102.93 (*Ar*), 156.49, 129.36, 126.84, 124.70 (*Ar′*), 86.13 (*C5*), 56.99, 56.01 (O*C*H$_3$), 17.54 (*C2*), 12.10 (*C3*). IR (KBr): ν_{CO} 2052 (br), 1997, 1985 (s); $\nu_{CH=N}$ 1610 (s) cm^{-1}. IR (thin film): ν_{CO} 2066 (m), 1998 (m); $\nu_{CH=N}$ 1610 (s) cm^{-1}. ESMS *m*/*z* (%): 467 ([MH$^+$], 100). Anal. Calcd for $C_{21}H_{21}N_2O_4Rh$: C, 53.86; H, 4.52; N, 5.98. Found: C, 53.96; H, 4.11; N, 5.79.

Synthesis of 4,6-Dimethoxy-2,3-dimethylindol-7-ylidenaminobenzyl Rhodium(I) Cyclooctadiene, [Rh(15′)(COD)] (5). Method 1. Complex **4** (0.1 g, 0.214 mmol) was heated under reflux with

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excess 1,5-cyclooctadiene in methanol, under nitrogen for 1 day. The brown precipitate obtained was filtered and washed with hexane to yield the product as an orange solid (0.030 g, 0.058 mmol, 27%).

Synthesis of 4,6-Dimethoxy-2,3-dimethylindol-7-ylidenaminobenzyl Rhodium(I) Cyclooctadiene, [Rh(15′)(COD)] (5). Method 2. A mixture of imine **15** (0.10 g, 0.324 mmol) with [Rh(μ-OEt)(COD)]$_2$ (0.0831 g, 0.162 mmol) was stirred in CH_2Cl_2 (10 mL) for 2 h before the solvent was evaporated in vacuo and washed with pentane and methanol, yielding complex **5** as an orange solid (0.114 g, 0.22 mmol, 68%). Mp: 126−131 °C. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 8.25 (d, $^3J_{Rh-H}$ = 2.3 Hz, 1H, C*H*N), 7.40−7.20 (m, 5H, Ar-*H*), 6.04 (s, 1H, *H5*), 4.60, 3.35, 2.24, 1.73−1.69, 1.63−1.53 (*COD*), 3.98, 3.90 (2s, 6H, OCH_3), 2.34, 2.22 (2s, 6H, CH_3). ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2): δ 156.98 (*C*HN), 159.87, 159.76, 142.69, 139.43, 1214.21, 110.17, 104.60 (*Ar*), 156.98, 128.33, 125.37, 124.09 (*Ar*), 84.25 (*C5*), 78.50 (d, $^1J_{Rh-C}$ = 13 Hz, *COD*), 76.69 (d, $^1J_{Rh-C}$ = 12 Hz, *COD*), 30.45, 29.72 (*COD*), 56.35, 55.06 (OCH_3), 14.68, 11.15 (CH_3). IR (KBr): ν_{NH} 3408 (br), $\upsilon_{CH=N}$ 1608 (s) cm^{-1}. ESMS *m*/*z* (%): 519 ([MH$^+$], 49). Anal. Calcd for ($C_{27}H_{31}RhN_2O_2$ + 0.5CH_2Cl_2): C, 58.88; H, 5.75; N, 4.99. Found: C, 58.58; H, 5.89; N, 4.94.

Synthesis of 4,6-Dimethoxy-2,3-dimethylindol-7-ylidenaminobenzyl Iridium(I) Cyclooctadiene, [Ir(15′)(COD)] (6). A mixture of imine **15** (0.15 g, 0.487 mmol) with NaOAc (0.11 g, 1.34 mmol) in CH_2Cl_2 (10 mL) was stirred for 0.5 h under an inert atmosphere. This mixture was added to a solution of [Ir(μ-Cl)(COD)]$_2$ (0.180 g, 0.268 mmol) in CH_2Cl_2 (5 mL). The reacting mixture was stirred for another 2 h before the solvent was concentrated to dryness and washed with diethyl ether and methanol, yielding complex **6** as a yellowish-brown solid (0.277 g, 0.455 mmol, 94%). Red single crystals suitable for X-ray analysis were obtained by slow diffusion of pentane into a concentrated CH_2Cl_2 solution of complex **6**. Mp < 100 °C (dec). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 8.36 (s, 1H, C*H*N), 7.40−7.35 (m, 2H, Ar-*H*), 7.27−7.21 (m, 3H, Ar-*H*), 6.05 (s, 1H, *H5*), 4.57, 3.07, 2.04, 1.50, 1.37 (*COD*), 3.97, 3.89 (2s, 6H, OCH_3) 2.37, 2.27 (2s, 6H, CH_3). ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2): δ 156.03 (*C*HN), 161.10, 161.02, 154.40, 144.12, 139.29, 128.85, 126.57, 125.43, 113.85, 112.50, 104.56 (*Ar*), 85.69 (*C5*), 63.03, 59.27, 31.96, 30.78 (*COD*), 56.98, 55.90 (OCH_3), 15.42, 11.85 (CH_3). IR (KBr): ν_{NH} 3427 (br), $\nu_{CH=N}$ 1608 (s) cm^{-1}. ESMS *m*/*z* (%): 609 ([MH$^+$], 100). Anal. Calcd for $C_{27}H_{31}IrN_2O_2$: C, 53.36; H, 5.14; N, 4.61. Found: C, 53.8; H, 5.15; N, 4.52.

Synthesis of 4,6-Dimethoxy-2,3-dimethylindol-7-ylidenaminobenzyl Ir(I) Dicarbonyl, [Ir(15′)(CO)$_2$] (7). A brown solution of complex **6** (0.100 g, 0.164 mmol) in CH_2Cl_2 (10 mL) was exposed to 1 atm of CO at rt for 3 h. The solvent was removed in vacuo and the crude product washed with hexane. The orange product was isolated by column chromatography on silica (CH_2Cl_2 eluent) as an air-stable red crystalline solid (0.0723 g, 0.130 mmol, 79%). Mp: 228−230 °C. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 8.85 (s, 1H, C*H*N), 7.50−7.30 (m, 5H, Ar-*H*), 6.21 (s, 1H, *H5*), 4.04 3.95(2s, 6H, OCH_3) 2.60 2.46(2s, 6H, CH_3). ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2): δ 175.09, 174.55 (*C*O), 161.69 (*C*HN), 161.45, 159.35, 154.29, 143.65, 136.86, 128.48, 126.70, 124.60, 112.89, 111.23, 102.66 (Ar-*C*), 86.05 (*C5*), 56.25, 55.44 (OCH_3), 16.70 (*C2*), 11.40 (*C3*). IR (KBr): ν_{CO} 2041 (br), 1982, 1968 (s), $\nu_{CH=N}$ 1607 (s) cm^{-1}. IR (thin film): ν_{CO} 2053 (m), 1979 (m), $\nu_{CH=N}$ 1607 (s) cm^{-1}. ESMS *m*/*z* (%): 557 ([M],75). Anal. Calcd for $C_{21}H_{21}IrN_2O_4$; C, 45.23; H, 3.80; N, 5.02. Found: C, 45.45; H, 3.71; N, 4.87.

Synthesis of Rh(I) Tridentate Indolyl−imine Carbonyl, [Rh(16′)(CO)] (8). A mixture of **16** (0.10 g, 0.252 mmol) with NaOEt (0.35 g, 1.22 mmol) in CH_2Cl_2 (10 mL) was stirred for 0.5 h under an inert atmosphere. This mixture was added to a solution of [Rh(μ-Cl)(CO)$_2$]$_2$ (0.052 g, 0.13 mmol) in CH_2Cl_2 (5 mL). This mixture was stirred for another 4 h before the solvent was concentrated to 3 mL and the product precipitated by the addition of hexane. The solid was isolated by filtration, washed with methanol and water, and dried in vacuo, yielding complex **8** as a reddish-brown solid (0.095 g, 0.180 mmol, 71%). ^{1}H NMR (300 MHz, $(CD_3)_2CO$): δ 8.34 (d, $^3J_{Rh-H}$ = 3.8 Hz, 1H, C*H*N), 8.11 (d, $^3J_{Rh-}$H = 3.8 Hz, 1H, C*H*N), 7.36−7.25 (m, 6H, Ar-*H*), 7.23−7.13 (m, 4H, Ar-*H*), 6.14 (s, 1H, *H5*), 4.07, 3.99 (2s, 6H, OCH_3), 2.65 (s, 3H, CH_3). ^{13}C{^{1}H} NMR (75 MHz, $(CD_3)_2CO$): δ 193.60 (d, $^1J_{Rh-C}$ = 72 Hz, *C*O), (*C*HN), 166.43, 165.19, 161.95, 157.92, 154.34, 144.92, 138.53, 128.52, 128.13, 126.27, 125.26, 124.17, 122.99, 122.24, 113.12, 102.68 (*Ar*), 86.87 (*C5*), 55.93, 55.45 (OCH_3), 11.25 (*C3*). IR (KBr): ν_{CO} 1952 (s) cm^{-1}. Anal. Calcd for ($C_{26}H_{23}N_3O_3Rh$ + 1.5H_2O): C, 56.23; H, 4.72; N, 7.57. Found: C, 56.57; H, 4.26; N, 7.46.

General Procedure for the Synthesis of 1,2-Di(4,6-dimethoxy-2,3-dimethylindol-7-ylidenamino)ethane Diiridium/Dirhodium-(I) Tetracarbonyl/Dicyclooctadiene, [Ir$_2$(17′-19′)(COD)$_2$]/[Rh$_2$-(17′-19′)(CO)$_4$] (9−13). A mixture of 1 equiv of the tetradentate ligand precursors (**17**−**19**) and 3 equiv of NaOAc in CH_2Cl_2 (10 mL) was stirred for 0.5 h under an inert atmosphere. This mixture was added to a solution of 1.2 equiv of [Ir(μ-Cl)(COD)]$_2$/[Rh(μ-Cl)(CO)$_2$]$_2$ in CH_2Cl_2 (5 mL) and stirred for a further 2 h before the solvent was evaporated in vacuo. The residue was washed with diethyl ether and methanol and dried under vacuum.

1,2-Di(4,6-dimethoxy-3-methylindol-7-ylidenamino)ethane Diiridium(I) Biscycloctadiene, [Ir$_2$(17′)(COD)$_2$] (9). Yield: 88%. Mp < 287−290 °C (dec). ES-MS *m*/*z* (%): 1061([M]$^+$, 30), 952 ([M − COD]$^+$, 25).

1,2-Di(4,6-dimethoxy-2,3-dimethylindol-7-ylidenamino)-ethane Diiridium(I) Biscycloctadiene, [Ir$_2$(17′)(COD)$_2$] (10). Yield: 91%. Anal. Calcd for $C_{44}H_{56}Ir_2N_4O_4$ + 1.5CH_2Cl_2 + H_2O: C, 44.26; H, 4.98; N, 4.54. Found: C, 44.32; H, 4.74; N, 4.89.

1,2-Di(4,6-dimethoxy-2,3-dimethylindol-7-ylidenamino)-ethane Dirhodium(I) Tetracarbonyl, [Rh$_2$(17′)(CO)$_4$] (11). Yield: 92%. Mp < 245−250 °C (dec). IR (KBr): ν_{CO} 2055, 1976 (s) cm^{-1}. Anal. Calcd for $C_{30}H_{28}N_4O_8Rh_2$ + 0.7CH_2Cl_2: C, 44.01; H, 3.54; N, 6.69. Found: C, 43.92; H, 3.53; N, 6.67.

1,2-Di(4,6-dimethoxy-2,3-dimethylindol-7-ylidenamino)-ethane Dirhodium(I) Tetracarbonyl, [Rh$_2$(17′)(CO)$_4$] (12). Yield: 90%. IR (KBr): ν_{CO} 2049, 1976 (s) cm^{-1}. Anal. Calcd for $C_{32}H_{32}N_4O_8Rh_2$ + 0.6CH_2Cl_2: C, 45.67; H, 3.90; N, 6.53. Found: C, 45.83; H, 3.94; N, 6.52.

1,2-Di(3-*tert*-butyl-4,6-dimethoxyindol-7-ylidenamino)-ethane Dirhodium(I) Tetracarbonyl, [Rh$_2$(19′)(CO)$_4$] (13). Yield: 86%. IR (KBr): ν_{CO} 2058, 1984 (s); $\nu_{CH=N}$ 1592 (s) cm^{-1}. ES-MS *m*/*z* (%): 806 ([M − 2CO]$^+$, 80).

Synthesis of 1,2-(4,6-Dimethoxy-2,3-dimethylindol-7-ylidenamino)benzene Rhodium(I) Dicarbonyl, [Rh$_2$(20′)(CO)$_4$] (14). A mixture of the ligand precursor **20** (0.10 g, 0.186 mmol) and NaOAc (0.10 g, 1.22 mmol) in CH_2Cl_2 (10 mL) was stirred for 0.5 h under an inert atmosphere. This mixture was added to a solution of [Rh(μ-Cl)(CO)$_2$]$_2$ (0.0722 g, 0.186 mmol) in CH_2Cl_2 (5 mL). This mixture was stirred for another 2 h before the solvent was reduced to ∼3 mL and hexane added to precipitate the product. The solid was washed with water and the solvent evaporated in vacuo, yielding complex **14** as an orange solid (0.152 g, 0.177 mmol, 95%). Mp < 195−200 °C (dec). ^{1}H NMR (500 MHz, $CDCl_3$, 213 K): δ 8.86, 8.04 (2s, 2H, C*H*N), 7.56−7.51 (m, 2H, Ar-*H*), 7.44−7.26 (m, 2H, Ar-*H*), 6.05, 5.72 (2s, 2H, *H5*), 4.02, 3.95, 3.91, 3.48 (4s, 12H, OCH_3), 2.35, 2.24, 2.00, 1.82 (4s, 12H, CH_3). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 298 K): δ 187.02, 186.10 (*C*O), 160.96, 161.12, 157.34, 152.72, 142.82, 137.91, 126.90, 123.57, 113.93, 109.36, 103.17 (Ar-*C*), 84.98 (*C5*), 56.20, 55.36 (OCH_3), 16.22, 11.66 (CH_3). IR (KBr) ν_{CO} 2049, 1989 (s) cm^{-1}. ES-MS *m*/*z* (%): 798 ([M − 2(CO)], 100). Anal. Calcd for $C_{36}H_{36}N_4O_8Rh_2$ + 2CH_2Cl_2 + H_2O: C, 43.79; H, 3.67; N, 5.38. Found: C, 43.9; H, 3.53; N, 5.42.

Synthesis of Rh(III) (Chloromethyl) Carbonyl Chloride, [Rh(16′)(CO)(CH_2Cl)(Cl)] (21). On a NMR scale, complex **8** was dissolved in CH_2Cl_2 and left to stand for 2 days. Pentane (2 equiv) was added to precipitate the product as a brown solid. The solvent was removed in vacuo to yield complex **21**. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 8.13 (d, $^3J_{Rh-H}$ = 3.0 Hz, 1H, *H8*), 7.84 (d, $^3J_{Rh-H}$ = 3.0 Hz, 1H, *H9*), 7.64−7.61 (m, 3H, Ar-*H*), 7.45−7.30 (m, 7H, Ar-*H*), 5.99 (s, 1H, *H5*), 4.07 (s, 3H, *H11*), 3.97 (s, 3H, *H12*), 4.02, 4.00 (dd, $^2J_{Rh-H}$ = 3.0 Hz, 1H, *H13*), 3.78, 3.76 (dd, $^2J_{Rh-H}$ = 3.0 Hz, 1H, *H14*), 2.76 (s, 3H, *H10*). ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2): δ 184.54 (d, $^1J_{Rh-C}$ = 58 Hz, *C*O), 158.77 (*C9*), 156.83 (*C8*), 167.05, 166.96, 156.83, 152.38, 141.84, 137.09, 129.40, 129.12, 127.88, 127.40, 126.39, 123.4, 113.32, 101.20, 101.17 (*Ar*), 87.10 (*C5*), 56.81 (*C12*), 56.35 (*C11*), 37.84 (d, $^1J_{Rh-C}$ = 27 Hz, 1H, *C*H_2Cl), 12.5 (*C10*). IR (KBr): ν_{CO} 2085 (s) cm^{-1}. IR (thin film): ν_{CO} = 2091 (s) cm^{-1}. ES-MS *m*/*z* (%): 576 ([(M − Cl), 52], 548 ([(M − Cl − CO), 100].

X-ray Structure Determination of Compounds 4, 6, 7, and 16. A single crystal of **16** was grown by slow evaporation of a saturated solution of CH_2Cl_2/toluene, single crystals of **4** and **6** were grown by slow diffusion of pentane into a concentrated solution of CH_2Cl_2, and single crystals of **7** were grown by evaporation of a saturated solution of CH_2Cl_2. Crystal data collection parameters are summarized in Table 2. Data for complex **6** and ligand precursor **16** were collected with ω scans to approximately 56° 2θ using a Bruker SMART 1000. For complex **4** and complex **7**, data were collected with φ and ω scans to approximately 56° 2θ using a Bruker-Nonius APEX2-X8-FR591. Both diffractometers employed graphite-monochromated Mo Kα radiation generated from a sealed tube in the former and a rotating anode in the latter (0.71073 Å). Data integration and reduction were undertaken with SAINT and XPREP,[41a,b] and subsequent computations were carried out using the WinGX-32 graphical user interface.[41c] Multiscan empirical absorption corrections were applied to the data using the program SADABS.[41d] The structures were solved by direct methods using SIR97,[41e] then refined and extended with SHELXL-97.[41f] Ordered non-hydrogen atoms with occupancies greater than or equal to 0.5 were refined anisotropically. Carbon-bound hydrogen atoms were included in idealized positions and refined using a riding model. Nitrogen-bound hydrogen atoms were first located in the Fourier difference map before refining with bond length restraints fixed at 0.88(2) Å.

Specific Details for 6. There is a region of disordered electron density within this structure, which lies very close to and across a crystallographic inversion site. Attempts were made to model this electron density as disordered thf and cyclohexane molecules with rigid body restraints; however, these attempts were unsuccessful. This electron density was subsequently modeled as isotropic water molecules, with a total occupancy of three water molecules per unit cell. The oxygen-bound hydrogen atoms were not structurally evident in the difference Fourier map and were not included in the model.

General Method for the Catalytic Cyclization of 4-Pentynoic Acid. In a NMR tube, 4-pentynoic acid (0.275 mol) and a catalytic amount of the catalyst (2 mol %) were dissolved in deuterated solvents (0.75 mL) under an atmosphere of argon. The mixture was heated at 60 or 65 °C, and the reaction progress was monitored by ^{1}H NMR spectroscopy at regular intervals. The product spectra were consistent with the data reported in the literature.

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Supporting Information Available: Crystallographic data for **4**, **6**, **7**, and **16** is available as CIF files free of charge via the Internet at http://pubs.acs.org.

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(41) (a) *SMART*, *SAINT*, and *XPREP*; Bruker Analytical X-ray Instruments Inc.: Madison, WI, 1995. (b) *APEX*, *SAINT*, and *XPREP*, Area detector control and data integration and reduction software; Bruker-Nonius Analytical X-ray Instruments Inc.: Madison, WI, 2003. (c) *WinGX-32*, System of programs for solving, refining and analysing single-crystal X-ray diffraction data for small molecules. Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837. (d) Sheldrick, G. M. *SADABS: Empirical Absorption and Correction Software*; University of Göttingen, Institüt für Anorganische Chemie der Universität: Tammanstrasse 4, D-3400 Göttingen, Germany, 1999−2003. (e) Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giocavazzo, C.; Guagliardi, A.; Moliterni, A. G. C.; Polidori, G.; Spagna, S. *J. Appl. Crystallogr.* **1999**, *32*, 115. (f) Sheldrick, G. M. *SHELX-97, Programs for Crystal Structure Analysis*; University of Göttingen, Institüt für Anorganische Chemie der Universität: Tammanstrasse 4, D-3400 Göttingen, Germany, 1997.