# Synthesis and Catalytic Properties of Two Trinuclear Complexes of Rhodium and Iridium with the N-Heterocyclic Tris-carbene Ligand TIMEN$^{iPr}$

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Two trinuclear complexes of rhodium and iridium have been obtained by reaction of the tris-N-heterocyclic carbene ligand TIMEN$^{iPr}$ and $[(COD)MCl]_2$ or $[(COD)_2M](BF_4)$ (M = Rh and Ir). The new complexes have been fully characterized by means of NMR spectroscopy and single-crystal X-ray diffraction studies. The trinuclear rhodium complex shows efficient activity in cyclization of acetylenic carboxylic acids, ranking among the highest known for this type of reaction.

## Introduction

Since the preparation of the first catalysts based on N-heterocyclic carbene (NHC) ligands by Herrmann and co-workers,[1] many researchers have focused their efforts on the design of novel NHC ligands and complexes with diverse topologies that can compete with or show superior catalytic activity over their phosphine analogues.[2] While complexes of monodentate NHCs exhibit high catalytic activity in a wide variety of reactions,[3,4] certain chelating NHCs yield catalysts with considerably improved air and thermal stability.[5,6] Well-known examples include bidentate, Pincer-type, and polydentate carbene ligands with tripodal geometry.[5,7−13] Among the first complexes employing bis-NHC ligands were the palladium complexes $[py(NHC)_2Pd(Br)](Br)$ and $[CH_2(NHC)_2Pd(I)_2]$, which were mainly used for C−C bond formation catalysis,[3,14] followed by a series of Rh,[15−19] Ir,[19−21] Ru,[22,23] Co,[12] and other complexes[24] for a variety of applications in catalysis and small molecule activation.

We recently reported the synthesis of a variety of tripodal N-heterocyclic carbene ligands and their coordination to a series of main group (Tl),[9] group 11 (Cu, Ag, Au),[10,11] and late second- and third-row transition metal ions (Rh[8] and Ir[25]). The preparation of the

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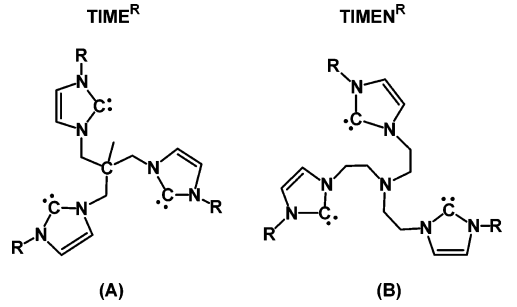
**Scheme 1**



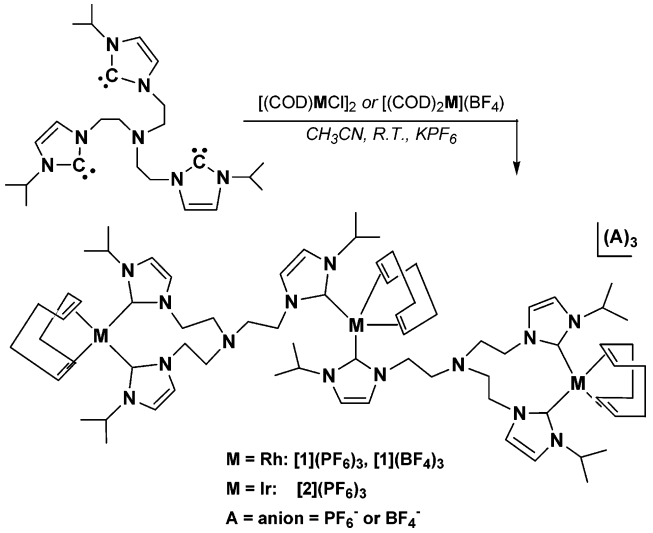

precursor [1,1,1-tris(3-alkylimidazolium-2-yl)methyl]-ethane trichloride, $[H_3TIME^R]Cl_3$, provided access to a new family of C-anchored tris-carbene ligands, [1,1,1-tris(3-alkylimidazol-2-ylidene)methyl]ethane ($TIME^R$ with R = Me, *t*-Bu; Scheme 1A), which coordinates to metal ions to form bi- and trimetallic complexes.[11−13] Despite the structural flexibility of this ligand, mononuclear complexes, in which the ligand binds to the metal ion in a tripodal fashion, remained elusive. In contrast, employing the N-anchored analogues tris[2-(3-alkylmethylimidazol-2-ylidene)ethyl]-amine, $TIMEN^R$ (R = alkyl, aryl; Scheme 1B), afforded the first tripodal carbene complexes of Co,[12] Ni,[13] and Cu.[11] Our studies revealed a remarkable flexibility of the tripodal ligand system TIMEN, stabilizing trigonal planar (tris-carbene coordination), distorted trigonal pyramidal (with or without coordination of the anchoring nitrogen donor), tetrahedral, and octahedral coordination polyhedra. In an extension of this work, we here present the isopropyl-derivatized ligand, [$TIMEN^{iPr}$], and report on its coordination to Rh and Ir. The synthesis, characterization, and catalytic activity of these novel complexes with respect to cyclization of acetylenic carboxylic acids are described. X-ray diffraction studies on single crystals of the Rh and Ir complexes revealed trinuclear molecular structures in the solid state.

## Results and Discussion

The tris-carbene ligand tris[2-(3-isopropylimidazol-2-ylidene)ethyl]amine ($TIMEN^{iPr}$) was prepared by deprotonation of the corresponding imidazolium salt with potassium *tert*-butoxide in THF following the previously described methods.[12,13] Addition of the metal starting materials $[(COD)MCl]_2$ or $[(COD)_2M](BF_4)$ (M = Rh and Ir) to a solution of $TIMEN^{iPr}$ in acetonitrile afforded formation of the complexes $[(TIMEN^{iPr})_2M_3(COD)_3](A)_3$ (A = $PF_6^-$ or $BF_4^-$, Scheme 2). The complexes were purified by column chromatography and isolated as crystalline solids in moderate yield (40−50%).

The $^1H$ and $^{13}C$ NMR spectra of $[(TIMEN^{iPr})_2Rh_3(COD)_3](A)_3$ ([**1**]$(PF_6)_3$ and [**1**]$(BF_4)_3$) and $[(TIMEN^{iPr})_2Ir_3(COD)_3](PF_6)_3$ ([**2**]$(PF_6)_3$) are consistent with a low symmetry of the complex cations in solution. The aliphatic region of both $^1H$ NMR (300 MHz) spectra shows an unresolved set of signals between 1 and 5.5 ppm, which is likely an overlay of the signals from the three diastereotopic couples of the $CH_2$ bridging groups, the 1,5-cyclooctadiene ligands, and the isopropyl N-wingtips of the NHC ligand. Five additional singlets arise from the set of imidazol-2-ylidene rings: four signals with unity intensity were assigned to the azole

**Scheme 2**




rings at the terminal metal centers, and one more signal with twice the intensity was assigned to the set of accidentally degenerate hydrogens of the central bis-carbene moiety. The metalation of the ligand is confirmed by the $^{13}C$ NMR spectra in DMSO-$d_6$. Compound [**1**]$(PF_6)_3$ shows three doublets at $\delta$ 177.8, 177.7, and 177.2 ($^1J_{Rh-C}$ = 53 Hz) due to the three different types of metalated C atoms, thus suggesting that an idealized $C_2$ symmetry is present in the complex. Solutions of [**2**]-$(PF_6)_3$ in DMSO-$d_6$ show five signals between 174.9 and 172.1 ppm, suggesting an asymmetric structure in which two (out of six) carbene resonances show accidental degeneracy.

The molecular structures of [**1**]$(PF_6)_3$ and [**2**]$(PF_6)_3$ were confirmed by means of single-crystal X-ray crystallography. Figure 1 shows the molecular diagram of trication $[\mathbf{1}]^{3+}$ in crystals of [**1**]$(PF_6)_3 \cdot 2CH_3CN \cdot Et_2O$ (iridium complex [**2**]$(PF_6)_3$ shows a similar molecular structure in crystals of [**2**]$(PF_6)_3 \cdot 4CH_2Cl_2$, see ESI). The molecular structure confirms the trinuclear nature of [**1**]$(PF_6)_3$ in the solid state. Two $TIMEN^{iPr}$ ligands exhibit coordination to three different Rh(I) atoms. The three Rh atoms exhibit a pseudo-square-planar coordination. Two of the three arms of the carbene ligands are chelating to one Rh atom; the third branch, together with that of a second ligand, are bound to a central metal, resulting in a cis-conformation of the tris-carbene ligand. The nitrogen anchor remains uncoordinated. The Rh−C distances (2.029−2.073 Å) are similar to those of other reported Rh complexes.[15,17−19] The ligand bite angles of 93.65° and 93.81° to the Rh(I) ions are larger than those reported for other bis-carbene Rh complexes.[26] This is likely due to steric requirements resulting from the formation of the 10-membered rings upon coordination of the tris-carbene ligand to the Rh ions. The heterocyclic imidazole-2-ylidene rings are nearly perpendicular to the square planar Rh coordination plane, with angles ranging from 80.0° to 83.5°.

The iridium complex [**2**]$(PF_6)_3$ shows a molecular structure very similar to that shown for [**1**]$(PF_6)_3$ in the solid state. The Ir−C distances (2.052−2.065 Å) range among other reported Ir complexes.[25] As shown for [**1**]-

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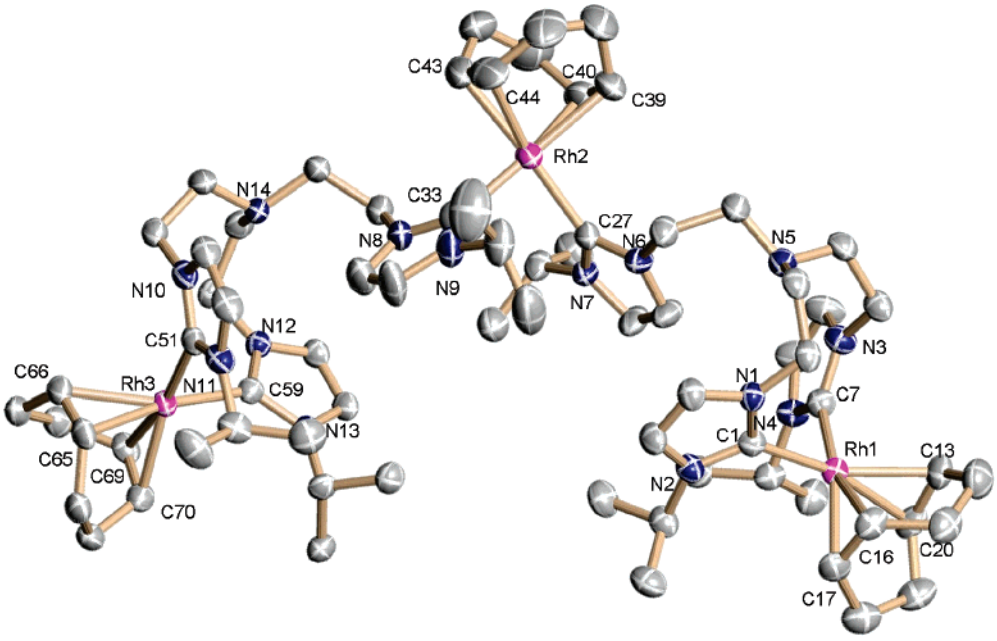
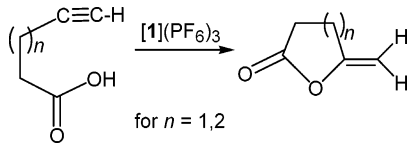



**Figure 1.** X-ray molecular structure of trication $[\mathbf{1}]^{3+}$ in crystals of $[\mathbf{1}](PF_6)_3 \cdot 2CH_3CN \cdot Et_2O$ (hydrogen atoms, anions, and cocrystallized solvent molecules have been omitted for clarity).

**Scheme 3**




$(PF_6)_3$, the ligand bite angles (95.0° and 95.3°) are larger than those found for other Ir related complexes[25] due to the reasons described above.

The catalytic properties of $[\mathbf{1}](PF_6)_3$ and $[\mathbf{2}](PF_6)_3$ were tested for reactions such as hydrosilylation and hydrothiolation of alkynes and cyclization of acetylenic carboxylic acids. On the basis of the molecular structure of the complexes, we expected their activity to be low in all catalytic reactions requiring an oxidative addition in the catalytic cycle.[18,25,26] We have recently studied the oxidation potential of a series of Rh(I) complexes with different chelating bis-carbene ligands, and we concluded that the angle between the azole ring planes and the coordination plane of the complex determines whether oxidation is possible.[26] The planes of the imidazole-2-ylidene rings of $[\mathbf{1}](PF_6)_3$ and $[\mathbf{2}](PF_6)_3$ are essentially perpendicular to the square plane of the complex and are thereby sterically hindering the formation of pseudo-octahedral M(III) complexes. Accordingly, our compounds were inactive with respect to catalyzing hydrosilylation and hydrothiolation of alkynes. Interestingly, the Rh compound $[\mathbf{1}](PF_6)_3$ showed good activity toward the catalytic cyclization of acetylenic carboxylic acids (Scheme 3).

The catalytic formation of five- and six-membered ring systems containing oxygen is an important application in homogeneous catalysis given their essential relevance to the pharmaceutical industry. Several cationic Rh(I) complexes reportedly have shown good catalytic activity in this reaction.[27,28]

**Table 1. Selected Bond Lengths and Angles in $[\mathbf{1}](PF_6)_3$ and $[\mathbf{2}](PF_6)_3$**

| | $[\mathbf{1}](PF_6)_3$ (M = Rh) | $[\mathbf{2}](PF_6)_3$ (M = Ir) |
|---|---|---|
| | Bond Lengths (Å) | |
| M(1)−C(1) | 2.062(3) | 2.052(6) |
| M(1)−C(7) | 2.063(3) | 2.058(6) |
| M(2)−C(27) | 2.058(3) | 2.054(6) |
| M(2)−C(33) | 2.029(4) | 2.047(6) |
| M(3)−C(51) | 2.056(3) | 2.065(5) |
| M(3)−C(59) | 2.073(3) | 2.044(6) |
| | Angles (deg) | |
| C(1)−M(1)−C(7) | 93.65(12) | 95.3(2) |
| C(27)−M(2)−C(33) | 89.91(14) | 91.4(2) |
| C(51)−M(3)−C(59) | 93.81(11) | 95.0(2) |

**Table 2. Cyclization of 4-Pentynoic Acid and 5-Hexynoic Acid Using $[\mathbf{1}](PF_6)_3$ as Catalyst[a]**

| entry | substrate | temp (°C) | catalyst (%) | time (h) | yield (%) | TON |
|---|---|---|---|---|---|---|
| 1 | 4-pentynoic acid | 50 | 0.50 | 16 | >99 | 200 |
| 2 | | 50 | 0.05 | 48 | 94 | 1880 |
| 3 | | 50 | 5.00 | 4 | >99 | 20 |
| 4[b] | | 50 | 0.50 | 72 | 40 | 80 |
| 5 | | 25 | 5.00 | 72 | 95 | 19 |
| 6 | | 80 | 0.50 | 2 | 97 | 19 |
| 7 | 5-hexynoic acid | 50 | 0.50 | 12 days | 26 | 52 |
| 8 | | 50 | 5.00 | 5 days | 90 | 18 |

[a] Conditions: in an NMR tube, 0.5 mmol of substrate, 0.75 mL of acetonitrile-$d_3$ as solvent. [b] Reactions performed with acetone-$d_6$ as solvent.

The reactions were performed at different temperatures in an NMR tube containing 0.75 mL of acetonitrile-$d_3$, with catalyst loadings ranging from 0.05 to 5 mol %. From the data shown in Table 2, we can conclude that the cyclization of 4-pentynoic acid is much more favorable than the cyclization of 5-hexynoic acid, as seen in other previously reported work.[27,28] For the reactions performed at 50 °C, our catalyst showed comparable

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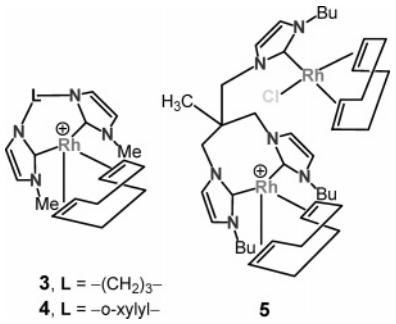
**Scheme 4**




activity to complexes reported previously, although it also showed good activity at room temperature with catalyst loadings of 5 mol % (entry 5), thus displaying higher activity than previously reported Rh(I) catalysts.[27,28] Catalyst loadings of 0.05 mol % also showed an efficient catalytic activity, with nearly complete cyclization of 4-pentynoic acid in 48 h (entry 2), resulting in the highest TON (1880) obtained for this reaction so far. When the reaction was performed at 80 °C with a catalyst loading of 0.5 mol %, the reaction achieved completion in only 2 h (entry 6). The catalytic activity is solvent dependent, as evident by the lower activity observed when the reaction was performed in acetone-$d_6$ (entry 4).

To compare the catalytic activity of [**1**]$(PF_6)_3$ to related NHC−Rh(I) complexes, we studied the cyclization of acetylenic carboxylic acids using mono- and dinuclear complexes **3**−**5** (Scheme 4) previously prepared in our group. For this reaction, however, complexes **3**−**5** showed no catalytic activity. Steric hindrance in close proximity to the metal center may cause this lack of catalytic activity. The long propyl and *o*-xylyl linker in monometallic bis(carbene) complexes **3** and **4**, which imposes severe orientation restrictions on the imidazole planes, likely renders these compounds inert toward oxidative addition reactions, a critical step in the cyclization reaction.[26] The tridentate $TIME^{Me}$ ligand of dinuclear complex **5** is coordinated to two Rh ions in bidentate chelating and monodentate bridging fashion.[25] On the basis of the observations for complexes **3** and **4**, we also expected lack of catalytic activity for the very similar bis(carbene) Rh(I) fragment in **5** (same linker length). Instead, we anticipated catalytic activity to be centered at the monocarbene Rh fragment. However, solutions of dinuclear **5** showed no catalytic activity. From these results we cannot unambiguously conclude which is the reactive entity in complex [**1**]$(PF_6)_3$. However, we propose that the catalytic activity of [**1**]$(PF_6)_3$ is centered at the least hindered central bis(carbene) Rh fragment.

## Conclusions

We synthesized new Rh and Ir complexes of the tris-carbene $TIMEN^{iPr}$ ligand system. The molecular structures of the complexes $[(TIMEN^{iPr})_2M_3(COD)_3](PF_6)_3$ revealed coordination of two carbene ligands, which are simultaneously chelating and bridging three metal centers via their carbenoid carbon atoms. The catalytic activity of the complexes was tested in a series of reactions and revealed efficient activity in cyclization of acetylenic carboxylic acids. The conditions for cyclization were optimized, and the observed catalytic activity of the reported Rh complexes ranks among the highest known for this type of reaction.

## Experimental Section

**General Procedures.** Manipulation of air-sensitive compounds was performed under a controlled dry nitrogen atmosphere using standard Schlenk-line techniques and inert-gas gloveboxes (MBraun Labmaster by M. Braun, Inc.). Solvents were purified using a two-column solid-state purification system (Glasscontour System, Joerg Meyer, Irvine, CA), transferred to the glovebox without exposure to air, and stored over molecular sieves and/or sodium metal. NMR solvents were obtained from Cambridge Isotope Laboratories, degassed, and stored over activated molecular sieves prior to use. Metal precursor $[(COD)_2Rh](BF_4)$ was prepared according to literature procedures.[29] All NMR spectra were recorded at room temperature (20 °C) in $CDCl_3$, acetonitrile-$d_3$, DMSO-$d_6$, and acetone-$d_6$ solutions on Varian spectrometers operating at 400/300 MHz ($^1$H NMR) and 100 MHz ($^{13}$C NMR). Elemental analyses were obtained in a EA 1108 CHNS-O Carlo Erba analyzer. High-resolution mass spectral data were obtained on a Thermo Finnigan MAT900XP spectrometer (UCSD Mass Spec Facility). 3-Nitrobenzyl alcohol was used as the matrix, and polypropylene glycol was used as the internal reference.

**1-Isopropylimidazole, $Im^{iPr}$.** A flask cooled to 0−5 °C was charged with formaldehyde (37 wt %, 94.2 g, 1.16 mol), isopropylamine (99.37 mL, 1.16 mol), ammonium carbonate (55.73 g, 0.58 mol), glyoxal (168.4 g, 1.16 mol), and 700 mL of $CH_3OH$. The mixture was left to stir at room temperature overnight. After evaporating the volatiles, the crude brown material was purified by vacuum distillation to yield a yellow liquid (60.64 g; yield 47.5%).

$^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 7.40 (s, 1H), 6.92 (s, 1H), 6.84 (s, 1H), 4.20 (q, 1H), 1.36 (s, 3H), 1.34 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta$ 135.02, 128.88, 116.55, 49.10, 23.85.

**[$H_3TIMEN^{iPr}$] $(PF_6)_3$.** A 50 mL flask equipped with a reflux condenser was charged with tris(2-chloroethyl)amine (12.82 g, 62.7 mmol) and 1-isopropylimidazole (20.69 g, 188 mmol). The mixture was heated to 150 °C for 3 days during which a brown solid formed. The solid was dissolved in methanol and filtered. The resulting brown solution was evaporated to dryness to yield the crude product, $[H_3TIMEN^{iPr}]Cl_3$. The hygroscopic hydrochloride salt was dissolved in methanol and converted to stable $[H_3TIMEN^{iPr}](PF_6)_3$ by adding a solution of $NaPF_6$ (31.58 g, 188 mmol) in methanol. The white hexafluorophosphate salt precipitated immediately, was collected by filtration, and washed with small portions of cold methanol. The solid was then dissolved in acetone and filtered. Solvent was removed from the filtrate, and the resulting solid was dried under vacuum (37.88 g; yield 70%). $^1$H NMR (300 MHz, DMSO-$d_6$): $\delta$ 9.11 (s, 3H), 7.88 (s, 3H), 7.63 (s, 3H), 4.63 (q, $^3J_{H-H}$ = 6.60 Hz, 3H), 4.17 (t, $^3J_{H-H}$ = 6.00 Hz, 6H), 2.99 (t, $^3J_{H-H}$ = 5.7 Hz, 6H), 1.49 (s, 9H), 1.47 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-$d_6$): $\delta$ 135.40, 123.30, 121.02, 53.11, 52.74, 46.80, 23.13. HR-MS (FAB): 718.2773 (M − $PF_6$); calcd 718.2780.

**[$(TIMEN^{iPr})_2Rh_3(COD)_3$]$(PF_6)_3$, [1]$(PF_6)_3$.** A solution of $[(COD)RhCl]_2$ (300 mg, 0.61 mmol) in acetonitrile was added dropwise to a solution of $TIMEN^{iPr}$ in acetonitrile (345 mg, 0.81 mmol). The reaction mixture was stirred for 1 h, and the volume was reduced under vacuum. After reducing the volume, ether was added and a yellow solid formed immediately. The yellow solid was collected by filtration and washed with ether. The resulting solid was purified by column chromatography. Elution with acetone and $KPF_6$ allowed the separation of a

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yellow band containing [**1**]$(PF_6)_3$. The product was recrystallized from $CH_3CN$/ether (400 mg; yield 52%). $^1H$ NMR (300 MHz, acetonitrile-$d_3$, aliphatic region omitted for clarity): $\delta$ 7.27, 7.13, 7.09, 6.45, 5.83 (imidazole-*H*). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-$d_6$): $\delta$ 178.81 (d, 2C, $^1J_{C-Rh}$ = 53.1 Hz, C-Rh), 178.74 (d, 2C, $^1J_{C-Rh}$ = 53.0 Hz, C-Rh), 177.20 (d, 2C, $^1J_{C-Rh}$ = 53.8 Hz, C-Rh), 122.34 (2C, C-imidazole), 121.23 (C-imidazole), 119.69 (C-imidazole), 119.45 (C-imidazole), 117.54 (C-imidazole), 88.63 (set of signals assigned to COD), 59.95 (set of signals assigned to COD), 52.77, 52.23, 51.96 (set of signals assigned to N*C*$H_2$*C*$H_2$-imid), 49.87 (*C*H$(CH_3)_2$), 34.65 (*C*H$(CH_3)_2$), 31.05, 30.76 (COD), 27.77 (*C*H$(CH_3)_2$), 25.27 (COD), 24.54 (2C,$CH_3$), 23.54(2C,$CH_3$), 23.25 (2C,$CH_3$). Anal. Calcd for $C_{72}H_{114}F_{18}N_{14}P_3Rh_3$ (1919.38): C, 45.05; H, 5.99; N, 10.22. Found: C, 45.11; H, 6.04; N, 10.15. FAB MS *m/z* (fragment): 1773.9 $[M - PF_6]^+$.

**[(TIMEN$^{iPr}$)$_2$Rh$_3$(COD)$_3$](BF$_4$)$_3$,** [**1**](**BF$_4$**)$_3$**.** A solution of $[(COD)_2Rh](BF_4)$ (200 mg, 0.49 mmol) in acetonitrile was added dropwise to a solution of TIMEN$^{iPr}$ in acetonitrile (140 mg, 0.33 mmol). The reaction mixture was stirred for 1 h, and the volume was reduced under vacuum. After reducing the volume, ether was added and a yellow solid appeared immediately. The yellow solid was collected by filtration and washed with ether. The resulting solid was purified by column chromatography. Elution with $CH_2Cl_2$/acetone allowed the separation of a yellow band containing [**1**]$(BF_4)_3$. The product was recrystallized with $CH_2Cl_2$/ether (100 mg; yield 35%). $^1H$ NMR (300 MHz, acetonitrile-$d_3$; aliphatic region omitted for clarity): $\delta$ 7.30, 7.15, 7.10, 6.46, 5.83 (imidazole-*H*). Anal. Calcd for $C_{72}H_{114}F_{12}N_{14}B_3Rh_3$ (1744.90): C, 49.56; H, 6.59; N, 11.24. Found: C, 49.61; H, 6.50; N, 11.20.

**[(TIMEN$^{iPr}$)$_2$Ir$_3$(COD)$_3$](PF$_6$)$_3$,** [**2**](**PF$_6$**)$_3$**.** A solution of $[(COD)IrCl]_2$ (300 mg, 0.45 mmol) in acetonitrile was added dropwise to a solution of TIMEN$^{iPr}$ (253 mg, 0.59 mmol) in acetonitrile. The reaction mixture was stirred for 1 h, and the volume was reduced under vacuum. After reducing the volume, ether was added and an orange solid appeared immediately. The orange solid was collected by filtration and washed with ether. The resulting solid was purified by column chromatography. Elution with acetone and $KPF_6$ allowed the separation of an orange band containing [**2**]$(PF_6)_3$. The product is recrystallized from $CH_2Cl_2$/ether (250 mg; yield 38%). $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ 8.57, 7.45, 7.38, 7.17, 7.09 (imidazole-*H*). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-$d_6$): $\delta$ 174.92 (2C, C-Ir), 174.79 (C-Ir), 174.73 (C-Ir), 173.50 (C-Ir), 172.09 (C-Ir), 135.30 (C-imidazole), 129.48 (2C, C-imidazole), 128.88 (2C, C-imidazole), 125.90 (C-imidazole), 122.26 (2C, C-imidazole), 122.04 (C-imidazole), 120.85 (C-imidazole), 119.24 (2C, C-imidazole), 76.35, 76.15 (COD), 59.01, 58.16 (COD), 53.07, 52.65, 52.24 (set of signals assigned to N*C*$H_2$*C*$H_2$-imid), 47.86 (*C*H$(CH_3)_2$), 31.42 (COD), 25.40 (2C, $CH_3$), 24.76 (2C, $CH_3$), 24.38 (*C*H$(CH_3)_2$), 23.32 (*C*H$(CH_3)_2$, 23.06 (2C, $CH_3$). Anal. Calcd for $C_{72}H_{114}F_{18}N_{14}P_3Ir_3$ (2187.31): C, 39.54; H, 5.25; N, 8.97. Found: C, 39.66; H, 5.09; N, 9.08. FAB MS *m/z* (fragment): 2041.5 $[M - PF_6]^+$.

**Cyclization of Acetylenic Carboxylic Acids.** A typical procedure was performed as follows. In a 5 mm NMR tube, 0.5 mmol of substrate (4-pentynoic acid or 5-hexynoic acid) and [**1**]$(PF_6)_3$ (0.05, 0.5, or 5%) were dissolved in 0.75 mL of deuterated solvent (acetonitrile-$d_3$ or acetone-$d_6$). The mixture was heated at different temperatures (25, 50, and 80 °C) by immersion in an oil bath. The progress of the reaction was monitored by $^1H$ NMR, according to the data of the products obtained from the literature.[27]

**X-ray Diffraction Studies.** Single-crystals suitable for X-ray diffraction were grown from slow diffusion of ether in a saturated solution of [**1**]$(PF_6)_3$ in acetonitrile and slow evaporation of a saturated solution of [**2**]$(PF_6)_3$ in $CH_2Cl_2$. Crystals of [**1**]$(PF_6)_3$ and [**2**]$(PF_6)_3$ were mounted on a glass fiber in a random orientation.

Diffraction intensity data for [**1**]$(PF_6)_3$·$Et_2O$·$2CH_3CN$ (**1**) and [**2**]$(PF_6)_3$·$4CH_2Cl_2$ (**2**) were collected with a Bruker Smart Apex CCD diffractometer at 100(2) K. The structures were solved using the direct methods, completed by subsequent difference Fourier syntheses, and refined by full matrix least-squares procedures on $F^2$. SADABS [Sheldrick, G. M. *SADABS* (2.01), Bruker/Siemens Area Detector Absorption Correction Program, Bruker AXS: Madison, WI, 1998] absorption corrections were applied ($T_{min}/T_{max}$= 0.87 (**1**) and 0.79 (**2**)). The asymmetric unit of **1** contains one molecule of diethyl ether and two molecules of acetonitrile. These molecules are highly disordered and were treated by the SQUEEZE program [Van der Sluis, P.; Spek, A. L. *Acta Crystallogr.*, *Sect. A* **1990**, *A46*, 194−201]. Corrections of the X-ray data by SQUEEZE gave 152 electrons/cell; the required value is 128 electrons/cell. All nonhydrogen atoms were refined with anisotropic displacement coefficients. The hydrogen atoms were treated as idealized contributions and refined in a rigid group model.

**Crystallographic Details for [(TIMEN$^{iPr}$)$_2$Rh$_3$(COD)$_3$](PF$_6$)$_3$·Et$_2$O·2CH$_3$CN,** [**1**](**PF$_6$**)$_3$·**Et$_2$O·2CH$_3$CN:** $C_{80}H_{130}F_{18}N_{16}OP_3Rh_3$, $M_w$ = 2075.64, yellow crystal, triclinic, space group $P\bar{1}$, $a$ = 14.7154(12) Å, $b$ = 17.0629(14) Å, $c$ = 20.5292(17) Å, $\alpha$ = 68.6210(10)°, $\beta$ = 81.0570(10)°, $\gamma$ = 76.3760(10)°, $V$ = 4651.1(7) Å$^3$, $D_c$ = 1.482 g cm$^{-3}$, $\mu$ = 0.665 mm$^{-1}$, $Z$ = 2, Mo K$\alpha$ radiation ($\lambda$ = 0.71073), 39 382 reflections collected, 20 156 unique ($R_{int}$ = 0.0227). GOF = 1.038. Final $R$ indices [$I > 2\sigma(I)$], R1 = 0.0449, wR2 = 0.1240.

**Crystallographic Details for [(TIMEN$^{iPr}$)$_2$Ir$_3$(COD)$_3$](PF$_6$)$_3$·4CH$_2$Cl$_2$,** [**1**](**PF$_6$**)$_3$·**4CH$_2$Cl$_2$:** $C_{76}H_{122}Cl_8F_{18}N_{14}P_3Ir_3$, $M_w$ = 2526.99, orange crystal, triclinic, space group $P\bar{1}$, $a$ = 14.7904(14) Å, $b$ = 17.4200(16) Å, $c$ = 20.3569(19) Å, $\alpha$ = 67.6560(10)°, $\beta$ = 81.5490(10)°, $\gamma$ = 78.1680(10)°, $V$ = 4734.2(8) Å$^3$, $D_c$ = 1.773 g cm$^{-3}$, $\mu$ = 4.567 mm$^{-1}$, $Z$ = 2, Mo K$\alpha$ radiation ($\lambda$ = 0.71073), 40 318 reflections collected, 20 521 unique ($R_{int}$ = 0.0278). GOF = 1.040. Final $R$ indices [$I > 2\sigma(I)$], R1 = 0.0418, wR2 = 0.1079.

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**Supporting Information Available:** Crystallographic details, complete listing of structural parameters (CIF), and ORTEP diagram of [**2**]$^{3+}$. This material is available free of charge via the Internet at http//pubs.acs.org

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