ORGANOMETALLICS

Article

Cite This: *Organometallics* XXXX, XXX, XXX–XXX

pubs.acs.org/Organometallics

Pyrene-Connected Tetraimidazolylidene Complexes of Iridium and Rhodium. Structural Features and Catalytic Applications

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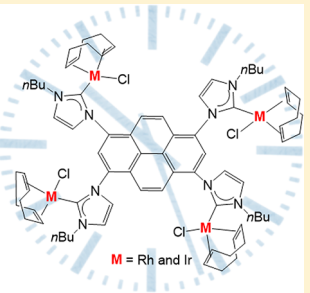
Supporting Information

ABSTRACT: A pyrene-connected tetra-imidazolium salt has been prepared starting from commercially available 1,3,6,8-tetrabromopyrene, and used as tetra-NHC precursor in the preparation of tetranuclear Rh(I) and Ir(I) complexes. The tetra-NHC ligand displays axial chirality upon coordination to the MCl(cod) (M = Rh and Ir) fragments, giving rise to right- and left-handed helix conformations. The catalytic activity of the resulting complexes was studied in two relevant reactions that lead to the formation of five- and six-membered oxygen-containing heterocycles, namely, the cyclization of acetylenic carboxylic acid and the coupling of diphenylcyclopropenone with substituted phenylacetylenes.



INTRODUCTION

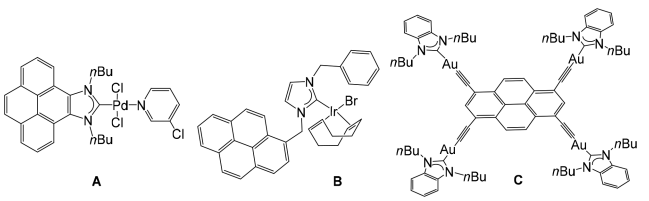
The widespread use of N-heterocyclic carbene (NHC) ligands arises from their extraordinary stereoelectronic versatility and their capability to incorporate a wide variety of additional functional groups.[1] The presence of these additional functions makes the resulting complexes good candidates for undergoing supramolecular interactions since they may establish reversible noncovalent interactions with the other reaction partners (substrate, additive, and counterion). The introduction of these interactions by design is an important tool for modifying the properties of a metal-based catalyst, and constitutes the basis of supramolecular catalysis.[2] In addition, over the past years, discrete supramolecular complexes held together by M–C_{NHC} bonds have become of interest, and this required the preparation of poly-NHC ligands with suitable topologies that offer the possibility of forming self-assembled structures.[3]

Our group has been particularly interested in studying the catalytic behavior of NHC-based complexes bearing extended polyaromatic systems as additional functions. We demonstrated that, due to the ability of polyaromatic groups to afford π-stacking noncovalent interactions, their catalytic properties clearly differ from those shown by analogues lacking these polyaromatic systems.[4] In line with this, a series of NHC-based complexes containing pyrene in their structure were prepared. Employing pyrene-containing palladium[5] (**A**, Chart 1), nickel,[5] rhodium,[6] iridium,[7] and gold[8] complexes, we further explored the importance of π-stacking interactions in homogeneously catalyzed reactions. The inherent capability of pyrene to afford π-stacking interactions with graphitic surfaces also allowed to support pyrene-tagged complexes,[6,7,9] such as complex **B** in Chart 1,[7] onto reduced graphene oxide and to study the activity and recyclability properties of the resulting heterogenized catalysts. Additionally, and taking advantage of the fluorescent properties of pyrene, we prepared NHC-based complexes with interesting photophysical properties.[10]

More recently, we prepared a tetra-Au(I) complex connected by 1,3,6,8-tetraethynylpyrene, which turned out to be one of the most efficient Au-based fluorescence emitters in solution reported to date (**C**, Chart 1).[11]

All of these findings illustrate how pyrene-adorned NHC-metal complexes constitute an interesting family of materials with unusual photophysical and catalytic properties. In this new work, we report the preparation of a pyrene-connected tetra-imidazolium salt and its use as tetra-NHC precursor in the preparation of rhodium and iridium complexes. The catalytic properties of the rhodium and iridium complexes were studied in the cyclization of acetylenic carboxylic acids and in the cycloaddition of diphenylcyclopropenone and alkynes.

Chart 1



RESULTS AND DISCUSSION

The pyrene-tetra-imidazolium salt **2** was prepared by a three-step procedure starting from commercially available 1,3,6,8-tetrabromopyrene, as displayed in Scheme 1. Treatment of 1,3,6,8-tetrabromopyrene with 4 equiv of imidazole in the presence of CuI and K_2CO_3 in refluxing DMF resulted in the formation of neutral tetraimidazolyl-pyrene compound **1**.

Received: August 30, 2018

DOI: 10.1021/acs.organomet.8b00633
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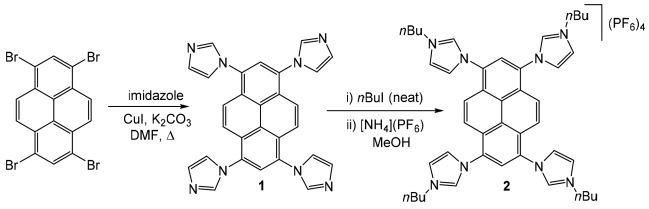
Scheme 1. Synthesis of Tetra-imidazolium Salt 2



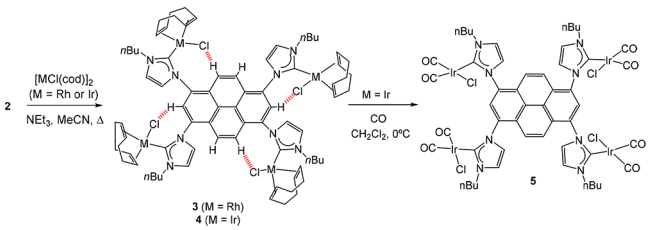
Compound **1** was isolated as a highly insoluble dark green solid, in almost quantitative yield.

The N-quaternization of the four imidazole rings of compound **1** with *n*-BuI and subsequent anion metathesis using $[NH_4](PF_6)$ in methanol afforded the hexafluorophosphate tetra-imidazolium salt **2**. Compound **2** was isolated as a dark brown solid, in a 65% overall yield.

The ^{1}H NMR spectrum in acetone-d_6 of the pyrene-containing tetra-imidazolium salt **2** shows the resonance due to the four equivalent acidic protons of the NCHN groups at 9.7 ppm. The ^{13}C NMR spectrum shows the resonance due to the carbon atoms of the NCHN groups at 139.1 ppm. The ESI-MS spectrum (positive ions) of **2** exhibits an intense peak at *m*/*z* 279.9, which was assigned to $[M - 3(PF_6)]^{3+}$.

We initially considered that compound **2** could be used as the precursor of a bis-$C_{NHC}CC_{NHC}$-*pincer* ligand, in which the two potential *pincer* arms are linearly opposed and connected by an aromatic skeleton. However, all our attempts to achieve this coordination mode to Rh(III) and Ir(III) by the metalation/transmetalation strategy using $Zr(NMe_2)_4$[12] were unsuccessful. Instead, the reaction of **2** with $[MCl(cod)]_2$ (M = Rh or Ir) afforded the tetrametallic complexes **3** and **4** (Scheme 2). Complexes **3** and **4** were characterized by NMR

Scheme 2. Synthesis of Tetrametallic Complexes 3−5

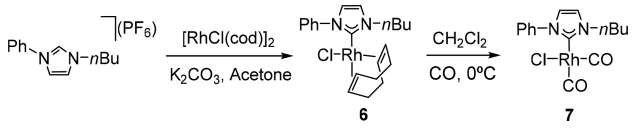


spectroscopy, electrospray mass spectrometry, and elemental analysis. Both the ^{1}H and ^{13}C NMR spectra are in agreement with the two-fold symmetry of the complexes, and with the presence of only one of the possible rotational isomers. The observed tetra-NHC ligand/cod ratio obtained from ^{1}H NMR integration along with the positive ion ESI-MS signals at 802.9 and 981.7 *m*/*z*, assigned to $[M - 2Cl]^{2+}$, confirmed the formation of the tetranuclear complexes **3** and **4**, respectively.

Whereas the presence of a singlet at 8.49 ppm indicates the equivalency of four of the protons of the pyrene core of the tetra-imidazolium salt **2**, these protons are no longer equivalent in complexes **3** and **4**, due to the restricted rotation about the $C_{pyr}-N_{imid}$ and the $M-C_{carbene}$ bonds, upon coordination of the MCl(cod) fragment. These resonances appear as two doublets at 9.85 and 8.11 ppm (complex **3**) and at 9.35 and 7.97 ppm (complex **4**). One of the two doublets is downfield shifted, thus strongly suggesting the presence of weak hydrogen-bonding interactions with the chloride ligands, as illustrates the drawing of **3** and **4** in Scheme 2. This situation indicates that the symmetry of the complex in solution is C_2, rather than that expected for a 1,3,6,8-(symmetrically)-tetrasubstituted pyrene (C_{2v}). As a result of this loss of symmetry, complexes **3** and **4** feature two different sets of metalated carbon atoms, thus showing two carbene carbon resonances in their ^{13}C NMR spectra [185.5 and 183.6 ppm ($^1J_{Rh-C}$ = 51 Hz) for **3**, and 182.4 and 181.2 ppm for **4**]. We did not observe changes in the ^{1}H NMR spectra of complexes **3** and **4** upon performing VT-NMR experiments in $CDCl_3$.

In order to estimate the electron-donating character of the tetra-NHC ligand, we transformed tetra-iridium complex **4** into its carbonyl derivative **5** (Scheme 2) by bubbling carbon monoxide through a solution of the complex in dichloromethane at 0 °C. Complex **5** displays only one carbene-carbon resonance at 180.7 ppm in the ^{13}C NMR spectrum, indicating that the rotation about the $Ir-C_{carbene}$ bond is no longer restricted, and thus suggesting a pseudo-C_{2v} symmetry for the complex in solution. Complex **5** displays two strong CO stretching bands at 1977 and 2064 cm^{-1}, which allowed us to calculate the Tolman Electronic Parameter (TEP) as 2047 cm^{-1}, by using well-known correlations.[13] For comparative purposes, we prepared the complex [1-*n*-butyl-3-phenyl-imidazol-2-ylidene]dicarbonylchlororhodium (**7**, Scheme 3),

Scheme 3. Synthesis of Monometallic Complexes 6 and 7



which can be regarded as the mono-rhodium counterpart of **5**. For this complex, we found a TEP value of 2045 cm^{-1}, thus indicating that the electron-donating strength of the tetra-NHC ligand in **5** is similar to that shown by 1-*n*-butyl-3-phenylimidazol-2-ylidene (in **7**).

The X-ray diffraction studies confirmed the molecular structure of complex **4** and revealed the presence of two independent molecules in the asymmetric unit. Each molecule consists of four *n*-butyl-imidazolylidene-Rh(I)Cl(cod) units connected by the pyrene core. The two molecules are enantiomers as, upon coordination, the tetra-NHC ligand displays axial chirality. The top view of one of the enantiomers is given in Figure 1 (top), and shows a helical (or screw-shaped) geometry, giving rise to a left-handed helix conformation.

As can be observed from the side view of the molecular structure of **4** (Figure 1, bottom), the two metal units at the pyrene 1- and 6-positions are above the plane formed by the pyrene central unit, placing the chloride ligands in close proximity to the protons at the 2- and 7-positions, at an average distance of 2.84 Å. In a similar manner, the two metal units at the pyrene 3- and 8-positions are below the pyrene plane, placing the chloride atoms in close proximity to the protons at the 4- and 9-positions, at an average distance of 2.90 Å. This is in agreement with our observations in the ^{1}H NMR of complexes **3** and **4**, and indicate the presence of weak hydrogen-bonding interactions, which are also evident in the solid state. The imidazolylidene rings deviate from the plane of the pyrene core by an average angle of 64°. The Supporting Information includes different perspective views of the other enantiomer of **4**.

DOI: 10.1021/acs.organomet.8b00633
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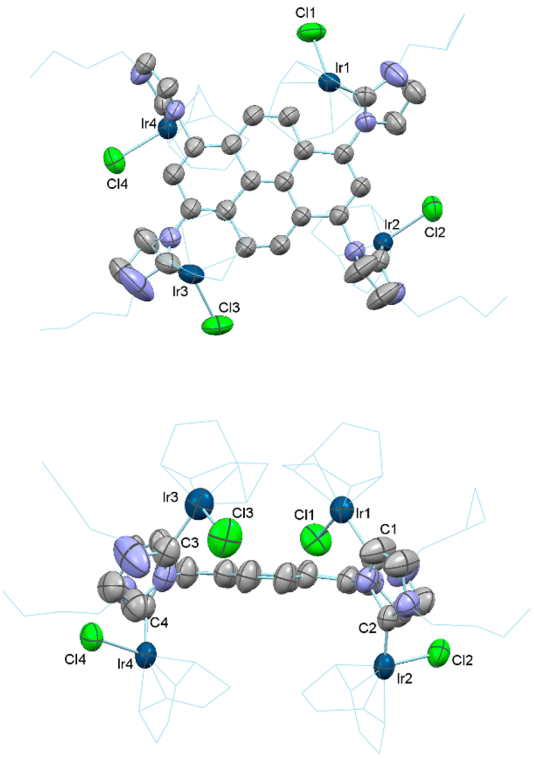


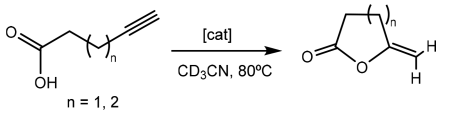
Figure 1. Top and side views of one of the enantiomers of **4**. Solvent ($CHCl_3$ and CH_2Cl_2) and hydrogen atoms have been removed for clarity. *n*-Butyl substituents and 1,5-cylooctadiene ligands are shown in the wireframe form. Selected distances (Å): Ir1−C1 2.07(4), Ir2−C2 1.84(4), Ir3−C3 2.07(5), Ir4−C4 1.88(4).

In order to evaluate the catalytic activity of the isolated complexes, we selected organic transformations typically catalyzed by Rh(I), namely, the cyclization of acetylenic carboxylic acids[14] and the synthesis of cyclopentadienones.[15] These two reactions are of practical relevance to the pharmaceutical industry because they allow the formation of five- and six-membered oxygen-containing heterocycles. We believe that these two reactions constitute two excellent models for the comparison of the activity of our new complexes with the related mononuclear ones, in order to evaluate if the presence of the four metal units in the catalyst, or the presence of the pyrene core, have any relevant role in the activity of our systems.

Complexes **3** and **4** were first tested in the intramolecular cyclization of 4-pentynoic and 5-hexynoic acid, which leads to the formation of five- and six-membered rings, respectively. The reactions were performed in an NMR tube containing 0.75 mL of CD_3CN with different catalyst loadings (10^{-3}−1 mol %), at 80 °C.

The results shown in Table 1, indicate that the iridium complex outperforms the rhodium one, both in the cyclization of 4-pentynoic and 5-hexynoic acids. Complexes **3** and **4** achieved full conversion to γ-methylene-γ-butyrolactone after 2.5 h, using a catalyst loading of 1 mol %. With a catalyst loading of 0.1 mol % (0.4 mol % based on the concentration of metal), full conversion was achieved by complex **4** in 4 h, whereas a longer reaction time (21 h) was required for complex **3** (compare entries 2 and 6). At a catalyst loading of 0.01 mol % (0.04 mol % based on metal), the iridium complex achieved full conversion after 21 h (entry 7). In agreement with previous reports,[14c,d,16] the cyclization of 5-hexynoic acid

Table 1. Catalytic Cyclization of Acetylenic Carboxylic Acids[a]



entry	substrate	cat.	cat. loading (mol %)	time (h)	conversion (%)[b]
1	4-pentynoic acid	**3**	1	2.5	>99
2	4-pentynoic acid	**3**	0.1	21	>99
3	4-pentynoic acid	**3**	0.01	21	35
4	4-pentynoic acid	**3**	0.001	21	16
5	4-pentynoic acid	**4**	1	2.5	>99
6	4-pentynoic acid	**4**	0.1	4	>99
7	4-pentynoic acid	**4**	0.01	21	>99
8	4-pentynoic acid	**4**	0.001	21	9
10	4-pentynoic acid	**6**	0.4	21	>99
11	4-pentynoic acid	**6**	0.04	21	>99
12	4-pentynoic acid	**6**	0.004	21	12
13	5-hexynoic acid	**3**	0.1	192	83
14	5-hexynoic acid	**3**	0.01	216	0
15	5-hexynoic acid	**4**	0.1	192	79
16	5-hexynoic acid	**4**	0.01	192	21
17	5-hexynoic acid	**6**	0.4	192	31
18	5-hexynoic acid	**6**	0.04	216	0

[a]Reaction conditions: in an NMR tube, 0.5 mmol acetylenic acid, catalyst **3**, **4**, or **6**, CD_3CN (0.75 mL), 80 °C. [b]Conversions were determined by ^1H NMR spectroscopy using 1,3,5-trimethoxybenzene as internal standard.

resulted much less efficient; complexes **3** and **4** required 8 days of reaction to afford 80% conversion (entries 13 and 15).

In order to study if the use of tetrametallic complexes produced an improvement in the catalytic efficiencies compared to those provided by their monometallic analogues, we prepared the mono-rhodium complex [1-*n*-butyl-3-phenyl-imidazol-2-ylidene](1,5-cyclooctadiene)chlororhodium, **6** (Scheme 3). Unfortunately, our attempts to isolate a pure sample of the mono-iridium complex were unsuccessful.

In the cyclization of 4-pentynoic acid, the mono-rhodium complex **6** performed better than its tetrametallic counterpart (complex **3**) when using catalyst loadings of 0.4 and 0.04 mol % based on the concentration of the metal. Nevertheless, using a catalyst loading of 0.004 mol %, the two catalysts led to similar outcomes (compare entries 4 and 12). In order to explain this behavior, we studied the time-dependent reaction profiles of the cyclization of 4-pentynoic acid using different concentrations of **3**, and we determined the reaction order with respect to the catalyst, by plotting the concentration of the product against a normalized time scale $t[\mathrm{cat}]^n$ (being *n* the order of the catalyst).[17] The power value gives the right reaction order with respect to the catalyst when the corrected conversion curves overlay. Four catalyst loadings of 1, 0.1, 0.01, and 0.001 mol % were employed to determine the reaction order in catalyst.

Visual analysis of the reaction profiles depicted in Figure 2 indicates that the order in catalyst is 1 (Figure 2b), although the curve for the higher concentration (1 mol %) is clearly out of the fit. This result is explained as a consequence of the low solubility of catalyst **3** in acetonitrile (the same applies to the iridium catalyst **4**; see the Supporting Information for details), and therefore, once the saturation concentration has been

DOI: 10.1021/acs.organomet.8b00633
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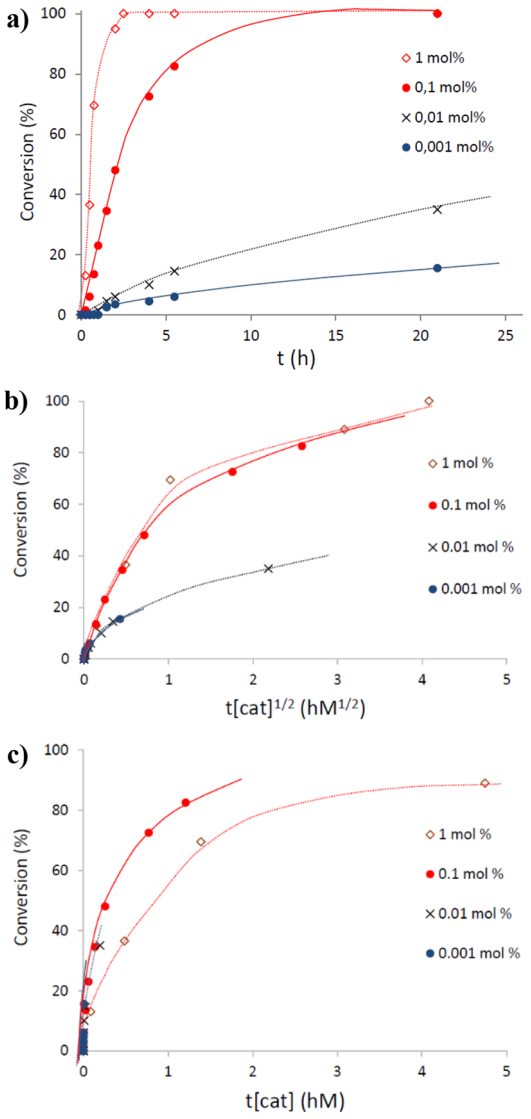
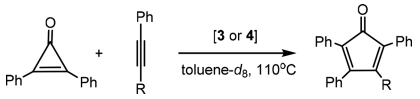


Figure 2. (a) Time-dependent reaction profile of the cyclization reaction of 4-pentynoic acid using catalyst **3**. (b) Reaction profile with normalized time scale assuming a catalyst order of 1/2. (c) Reaction profile with normalized time scale assuming a catalyst order of 1. Reaction conditions are the same as those shown in Table 1. In all three graphics, the evolution is shown as consumption of 4-pentynoic acid. Lines are only to guide the eye.

reached, increasing the amount of catalyst added to the reaction media does not produce any improvement in the reaction rate. This result clearly contrasts with our previous findings using other pyrene-containing ligands, for which fractional reaction orders were observed, as a consequence of the formation of nonactive dimers by π-stacking self-association of the catalyst.[7,8] The different solubility of **3** and **6** explains why, at higher concentrations, the monometallic complex outperforms the tetrametallic one, while, at lower concentrations, both catalysts display similar activity, as expected for two complexes with quasi-identical stereo-electronic properties. Furthermore, the first-order reaction found with respect to the concentration of **3** (and **4**) suggests that the cooperativity between the metal units in both tetrametallic catalysts is negligible.

In order to widen the study on the catalytic activities of complexes **3** and **4**, we decided to test them in the [3 + 2] cycloaddition reaction of cyclopropenones and alkynes (Table 2). This reaction, first reported by Wenders and co-workers,

Table 2. [3 + 2] Cycloaddition Reactions of Diphenylcyclopropenone with Substituted Phenylacetylenes[a]



entry	R	cat.	cat. loading (mol %)	time (h)	conversion (%)[b]
1	CO_2Et	**3**	1	24	72
2	CO_2Et	**3**	0.5	24	60
3	CO_2Et	**3**	0.1	48	71
4	CH_3	**3**	0.1	48	64
5	H	**3**	0.1	48	30
6	CO_2Et	**4**	1	24	95
7	CO_2Et	**4**	0.5	24	75
8	CO_2Et	**4**	0.1	24	92
9	CH_3	**4**	0.1	24	44
10	H	**4**	0.1	24	30

[a]Reaction conditions: 0.225 mmol of diphenylcyclopropenone, 0.15 mmol of alkyne, catalyst **3** or **4**, toluene-d_8 (0.3 M), 110 °C. [b]Conversions were determined by ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene as internal standard.

constitutes a selective and high-yielding route to valuable cyclopentadienones (CPDs).[15a] Using 1 mol % of Rh(I) complex **3**, the [3 + 2] cycloaddition of diphenylcyclopropenone and ethylpropionate gave the corresponding CPD in 72% after 24 h at 110 °C (entry 1). The catalytic activity of **3** compares well with those given by other Rh(I) complexes described in the literature, bearing NHC[15b] and cyclic(amino)(aryl)carbene ligands.[15c]

In all cases, the tetra-iridium complex **4** showed higher catalytic activity than **3** in the reaction of diphenylcyclopropenone with ethylphenylpropiolate (compare entries 1−3 and 6−8), and constitutes one of the best catalysts described to date for this type of transformation. As well as **3**, **4** showed moderate catalytic activity in the reactions using 1-phenyl-1-propyne and phenylacetylene.

CONCLUSIONS

In summary, we described a new pyrene-tetra-imidazolium salt that we used for the preparation of a series of Rh(I) and Ir(I) pyrene-tetra-NHC complexes. The coordination of MCl(cod) units results in the formation of helix-type structures dominated by the restricted rotation about the $C_{pyr}-N_{imid}$ and $M-C_{NHC}$ bonds, which yield hydrogen-bonding interactions between the chloride ligands and the protons of the pyrene connector. The two complexes were tested in the cyclization of acetylenic carboxylic acids, and in the reaction of diphenylcyclopropenone with substituted phenylacetylenes to form cyclopentadienones. In the first of these two reactions, the activity of the tetrametallic catalysts is similar to the activity shown by a monometallic analogue, only at low concentrations. At higher concentrations, the monometallic complex outperforms the tetrametallic one. This behavior is explained as a consequence of the low solubility of the tetrametallic catalyst, which leads to a maximum concentration of the catalyst when the saturation of the solution has been reached. In the coupling of diphenylcyclopropenone with substituted phenylacetylenes,

DOI: 10.1021/acs.organomet.8b00633
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the tetra-iridium complex (**4**) shows higher activity than the tetra-rhodium one (**3**). Although there is clearly room for improvement, to the best of our knowledge, complex **4** is the first iridium complex tested in this reaction.

EXPERIMENTAL SECTION

General Considerations. Anhydrous solvents were dried using a solvent purification system (SPS M BRAUN) or purchased and degassed prior to use by purging them with dry nitrogen. All the reagents and solvents were used as received from commercial suppliers. Column chromatography was performed on silica gel Merck 60, 62−200 mm unless otherwise stated, using mixtures of solvents. NMR spectra were recorded on a Varian Innova 500 MHz or on a Bruker 400/300 MHz, using DMSO-d_6, acetone-d_6, or $CDCl_3$ as solvent. Elemental analyses were carried out on a TruSpec Micro Series. Infrared spectra (FT-IR) were performed on a Bruker EQUINOX 55 spectrometer with a spectral window of 4000−600 cm^{-1}. Electrospray Mass Spectra (ESI-MS) were recorded on a Micromass Quatro LC instrument. MeOH, CH_3CN, or CH_2Cl_2 was used as mobile phase, and nitrogen was employed as the drying and nebulizing gas.

Synthesis of the Rh(I) and Ir(I) Complexes. *Synthesis of 1-n-Butyl-3-phenylimidazolium Hexafluorophosphate.* Imidazole (1.3 g, 19.6 mmol, 4 equiv), $CuSO_4$ (196 mg, 1.23 mmol, 0.25 equiv), and K_2CO_3 (2 g, 14.7 mmol, 3 equiv) were placed together in a high pressure Schlenk tube fitted with a Teflon cap. The tube was evacuated and filled with nitrogen three times. Iodobenzene (0.56 mL, 4.9 mmol, 1 equiv) was added, and the resulting suspension was heated at 150 °C for 24 h. After this time, the resulting solid was washed with water (3 × 40 mL) and filtrated using a Büchner. The solid was extracted with MeOH (3 × 20 mL). 1-Phenylimidazole, which was isolated as an oil after removal of the volatiles, was employed in the next step without further purification. Yield: 400 mg (57%). A mixture of 1-phenylimidazole (400 mg, 2.8 mmol, 1 equiv) and *n*-BuI (0.3 mL, 2.8 mL, 1 equiv) in dry THF (20 mL) was heated at 110 °C in a high pressure Schlenk tube fitted with a Teflon cap, during 12 h. After removal of the volatiles, 1-*n*-butyl-3-phenylimidazolium iodide was isolated as a brown oil. A mixture of 1-*n*-butyl-3-phenylimidazolium iodide (885 mg, 2.7 mmol, 1 equiv) and $[NH_4](PF_6)$ (550 mg, 3.4 mmol, 1.25 equiv) in MeOH (15 mL) was heated at 40 °C overnight. After removal of the volatiles, the crude was washed with dichloromethane and the insoluble salts were separated by filtration. The desired product was isolated as an off-white solid after precipitation in a mixture dichloromethane/diethyl ether. Yield: 900 mg (93%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.08 (s, 1H, NC*H*N), 7.61−7.48 (m, 7H; 5H, CH_{phenyl} and 2H, CH_{imid}), 4.36 (t, $^3J_{H\text{-}H}$ = 8 Hz, 2H, NCH_2CH$_2$CH$_2$CH$_3$), 1.98−1.91 (m, 2H, NCH$_2$CH_2CH$_2$CH$_3$), 1.46−1.40 (m, 2H, NCH$_2$CH$_2$CH_2CH$_3$), 0.98 (t, $^3J_{H\text{-}H}$ = 8 Hz, 3H, NCH$_2$CH$_2$CH$_2$CH_3). ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$): δ −72.3 (d). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ −144.32 (m). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 134.4 (NCHN), 134.3 (C$_{q\ phenyl}$), 130.7 (CH$_{phenyl}$), 127.8 (CH$_{phenyl}$), 123.1 (CH$_{imid}$), 122.3 (CH$_{phenyl}$), 121.5 (CH$_{imid}$), 50.6 (NCH$_2$CH$_2$CH$_2$CH$_3$), 31.9 (NCH$_2$-CH$_2$CH$_2$CH$_3$), 19.5 (NCH$_2$CH$_2$CH$_2$CH$_3$), 13.4 (NCH$_2$CH$_2$CH$_2$-CH$_3$). Electrospray MS (cone 20 V) (*m*/*z*, fragment): 201.2 [M − PF$_6$]$^+$ (calcd. for [M − PF$_6$]$^+$: 201.3). Anal. Calcd for $C_{13}H_{17}N_2PF_6$·CH_2Cl_2 (431.18): C, 39.00; H, 4.44; N, 6.50. Found: C, 39.42; H, 4.18; N, 6.99.

Synthesis of the Neutral Precursor ***1***. A mixture of 1,3,6,8-tetrabromopyrene (500 mg, 0.97 mmol, 1 equiv), imidazole (265.6 mg, 3.86 mmol, 4 equiv), K_2CO_3 (1079 mg, 7.73 mmol, 8 equiv), and CuI (73.6 mg, 0.39 mmol, 0.4 equiv) were placed together in a high pressure Schlenk tube fitted with a Teflon cap. The tube was evacuated and filled with nitrogen three times. The solids were suspended in anhydrous DMF (12 mL), and the resulting solution was heated at 160 °C for 72 h. Then, the reaction mixture was allowed to reach room temperature. Distilled water (75 mL) was added, and the suspension was stirred for 2 h. The resulting solid was collected by filtration using a Büchner and washed with water. Compound **1** was isolated as a highly insoluble dark green solid. Yield: 452.0 mg (>99%). ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.43 (br s, 2H, CH_{pyrene}), 8.27 (br s, 4H, NC*H*N), 8.08 (br s, 4H, CH_{pyrene}), 7.85 (br s, 2H, CH_{imid}), 7.36 (br s, 2H, CH_{imid}). Electrospray MS (cone 20 V) (*m*/*z*, fragment): 467.2 [M + H]$^+$ (calc. for [M + H]$^+$: 467.2).

Synthesis of the Tetra-imidazolium Salt ***2***. Under aerobic conditions, a mixture of compound **1** (517 mg, 1.11 mmol, 1 equiv) and *n*-BuI (16 mL, 89 mmol, 80 equiv) was heated in a thick-walled Schlenk tube fitted with a Teflon cap at 100 °C for 72 h. After cooling at room temperature, the excess of *n*-BuI was distilled under vacuum. The resulting black solid residue was washed several times with diethyl ether and ethyl acetate, and collected by filtration. The iodide salt (500 mg, 0.42 mmol, 1 equiv) was dissolved in MeOH (15 mL) and treated with $[NH_4](PF_6)$ (342.3 mg, 2.10 mmol, 5 equiv). The suspension was heated at 40 °C overnight. Compound **2** was collected by filtration as a brown solid. Yield: 885 mg (71%). ^{1}H NMR (400 MHz, acetone-d_6): δ 9.72 (s, 4H, NC*H*N), 9.06 (s, 2H, CH_{pyr}), 8.49 (s, 4H, CH_{pyr}), 8.31 (s, 4H, CH_{imid}), 8.26 (s, 4H, CH_{imid}), 4.62 (t, $^3J_{H\text{-}H}$ = 8 Hz, 8H, NCH_2CH$_2$CH$_2$CH$_3$), 2.18−2.10 (m, 8H, NCH$_2$CH_2CH$_2$CH$_3$), 1.58−1.49 (m, 8H, NCH$_2$CH$_2$CH_2-CH$_3$), 1.02 (t, $^3J_{H\text{-}H}$ = 8 Hz, 12H, NCH$_2$CH$_2$CH$_2$CH_3). ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$): δ −72.3 (d). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ −144.4 (m). ^{13}C{^{1}H} NMR (100 MHz, acetone-d_6): δ 139.1 (NCHN), 131.2 (C$_{q\ pyr}$), 128.8 (C$_{q\ pyr}$), 126.9 (CH$_{pyr}$), 126.4 (CH$_{pyr}$), 125.9 (CH$_{imid}$), 125.2 (C$_{q\ pyr}$), 124.8 (CH$_{imid}$), 51.3 (NCH$_2$CH$_2$CH$_2$CH$_3$), 32.5 (NCH$_2$CH$_2$CH$_2$CH$_3$), 20.2 (NCH$_2$-CH$_2$CH$_2$CH$_3$), 13.7 (NCH$_2$CH$_2$CH$_2$CH$_3$). Electrospray MS (cone 20 V) (*m*/*z*, fragment): 173.7 [M − 4(PF$_6$)]$^{4+}$, 279.9 [M − 3(PF$_6$)]$^{3+}$, 492.3 [M − 2(PF$_6$))]$^{2+}$ (calcd. for [M − 4(PF$_6$)]$^{4+}$: 173.6, [M − 3(PF$_6$)]$^{3+}$: 279.8, [M − 2(PF$_6$))]$^{2+}$: 492.2). Anal. Calcd for $C_{44}H_{54}N_8P_4F_{24}$·$2CH_2Cl_2$ (1444.68): C, 38.24; H, 4.05; N, 7.76. Found: C, 38.43; H, 3.92; N, 7.82.

Synthesis of the Tetrametallic Complexes ***3−5***. *General Procedure for Complexes* ***3*** *and* ***4***. Compound **2** (1 equiv) was placed in a Schlenk tube. The tube was evacuated and filled with nitrogen three times. The solid was suspended in dry CH_3CN and NEt_3 (50 equiv) was added to the suspension. The resulting solution was heated at 40 °C for 45 min. The corresponding metal precursor (2.2 equiv of [RhCl(cod)]$_2$ or [IrCl(cod)]$_2$) was placed in a second Schlenk tube. The tube was evacuated and filled with nitrogen three times. The solid was then suspended in dry CH_3CN and subsequently cannulated over the first Schlenk. The resulting mixture was heated under reflux overnight. Once at room temperature, the resulting yellow precipitate was collected by filtration. The crude product was purified by column chromatography. Elution with a 9:1 CH_2Cl_2/acetone mixture afforded a bright red band that contained the desired complex.

Synthesis of ***3***. A mixture of [RhCl(cod)]$_2$ (127.8 mg, 0.260 mmol) in dry CH_3CN (10 mL) was cannulated to a suspension of **2** (150 mg, 0.118 mmol) and NEt_3 (0.82 mL, 5.9 mmol) in dry CH_3CN (30 mL). After the general workup, complex **3** was isolated as a bright yellow solid. Yield: 107.1 mg (54%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.86 (d, $^3J_{H\text{-}H}$ = 7 Hz, 2H, CH_{pyr}), 8.98 (s, 2H, CH_{pyr}), 8.15 (d, $^3J_{H\text{-}H}$ = 1.5 Hz, 2H, CH_{imid}), 8.11 (d, $^3J_{H\text{-}H}$ = 7 Hz, 2H, CH_{pyr}), 7.40 (d, $^3J_{H\text{-}H}$ = 1.5 Hz, 2H, CH_{imid}), 7.21 (d, $^3J_{H\text{-}H}$ = 1.5 Hz, 2H, CH_{imid}), 7.20 (d, $^3J_{H\text{-}H}$ = 1.5 Hz, d, 2H, CH_{imid}), 5.27−5.21 (m, 4H, NCH_2-CH$_2$CH$_2$CH$_3$), 4.88−4.78 (m, 8H, CH_{cod}), 4.71−4.61 (m, 8H, CH_{cod}), 4.50−4.43 (m, 4H, NCH_2CH$_2$CH$_2$CH$_3$), 3.35 (q, 3H, C$H_{2\ cod}$), 3.29 (q, 3H, C$H_{2\ cod}$). The rest of the signals corresponding to the *n*-butyl and cod ligands are displayed in the region between 2.50 and 0.30 ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 185.5 (d, Rh-C$_{carbene}$, $^1J_{Rh\text{-}C}$ = 51 Hz), 183.6 (d, Rh-C$_{carbene}$, $^1J_{Rh\text{-}C}$ = 51 Hz), 134.4 (C$_{q\ pyr}$), 134.4 (C$_{q\ pyr}$), 128.1 (CH$_{imid}$), 127.6 (CH$_{imid}$), 127.3 (C$_{q\ pyr}$), 127.0 (C$_{q\ pyr}$), 125.5 (CH$_{imid}$), 125.1 (C$_{q\ pyr}$), 123.9 (CH$_{imid}$), 122.1 (CH$_{pyr}$), 121.8 (CH$_{pyr}$), 121.7 (CH$_{pyr}$), 98.3 (d, Rh-CH$_{cod}$, $^1J_{Rh\text{-}C}$ = 6.75 Hz), 98.1 (d, Rh-CH$_{cod}$, $^1J_{Rh\text{-}C}$ = 6.75 Hz), 97.5 (d, Rh-CH$_{cod}$, $^1J_{Rh\text{-}C}$ = 7.5 Hz), 96.9 (d, Rh-CH$_{cod}$, $^1J_{Rh\text{-}C}$ = 7.5 Hz), 69.7 (d, Rh-CH$_{cod}$, $^1J_{Rh\text{-}C}$ = 14.25 Hz), 69.4 (d, Rh-CH$_{cod}$, $^1J_{Rh\text{-}C}$ = 14.25 Hz), 68.7 (d, Rh-CH$_{cod}$, $^1J_{Rh\text{-}C}$ = 13.5 Hz), 66.6 (d, Rh-CH$_{cod}$, $^1J_{Rh\text{-}C}$ = 13.5 Hz), 52.0 (NCH$_2$CH$_2$CH$_2$CH$_3$), 51.1 (NCH$_2$CH$_2$CH$_2$CH$_3$), 35.06

DOI: 10.1021/acs.organomet.8b00633
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(CH_2 cod), 33.1 ($NCH_2CH_2CH_2CH_3$), 33.1 ($NCH_2CH_2CH_2CH_3$), 31.5 (CH_2 cod), 31.0 (CH_2 cod), 30.5 (CH_2 cod), 29.7 (CH_2 cod), 28.6 (CH_2 cod), 28.4 (CH_2 cod), 27.1 (CH_2 cod), 20.3 ($NCH_2CH_2CH_2CH_3$), 20.3 ($NCH_2CH_2CH_2CH_3$), 14.1 ($NCH_2CH_2CH_2CH_3$), 14.0 ($NCH_2CH_2CH_2CH_3$). Electrospray MS (cone 20 V) (*m*/*z*, fragment): 802.9 $[M - 2Cl]^{2+}$ (calcd. for $[M - 2Cl]^{2+}$: 802.2). Anal. Calcd for $C_{76}H_{98}N_8Rh_4Cl_4 \cdot CH_2Cl_2$ (1762.03): C, 52.49; H, 5.72; N, 6.36. Found: C, 51.95; H, 5.86; N, 6.97.

Synthesis of ***4****.* A mixture of $[IrCl(cod)]_2$ (137.6 mg, 0.173 mmol) in dry CH_3CN (8 mL) was cannulated to a suspension of **2** (100 mg, 0.079 mmol) and NEt_3 (0.55 mL, 3.925 mmol) in dry CH_3CN (20 mL). After the general workup, complex **4** was isolated as a bright orange solid. Yield: 87.7 mg (54%). ^1H NMR (300 MHz, $CDCl_3$): δ 9.36 (d, $^3J_{H-H}$ = 9.5 Hz, 2H, CH_{pyr}), 8.82 (s, 2H, CH_{pyr}), 7.98 (d, $^3J_{H-H}$ = 9.5 Hz, 2H, CH_{pyr}), 7.92 (d, $^3J_{H-H}$ = 1.5 Hz, 2H, CH_{imid}), 7.41 (d, $^3J_{H-H}$ = 1.5 Hz, 2H, CH_{imid}), 7.23 (d, $^3J_{H-H}$ = 1.5 Hz, 2H, CH_{imid}), 7.20 (d, $^3J_{H-H}$ = 1.5 Hz, 2H, CH_{imid}), 5.01−4.94 (m, 4H, $NCH_2CH_2CH_2CH_3$), 4.55−4.44 (m, 8H, CH_{cod} and 4H, $NCH_2CH_2CH_2CH_3$), 4.32−4.27 (m, 8H, CH_{cod}), 3.03−3.00 (m, 3H, CH_2 cod), 2.92−2.88 (m, 3H, CH_2 cod). The rest of the signals corresponding to the *n*-butyl and cod ligands are displayed in the region between 2.15 and 0.10 ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 182.4 (Ir-$C_{carbene}$), 181.2 (Ir-$C_{carbene}$), 133.7 (C_q pyr), 133.5 (C_q pyr), 128.4 (CH_{imid}), 127.7 (CH_{imid}), 127.4 (C_q pyr), 126.8 (C_q pyr), 124.8 (CH_{imid}), 124.7 (C_q pyr), 123.4 (CH_{imid}), 121.4 (CH_{pyr}), 121.4 (CH_{pyr}), 121.1 (CH_{pyr}), 84.3 (CH_{cod}), 84.2 (CH_{cod}), 84.0 (CH_{cod}), 82.5 (CH_{cod}), 53.4 (CH_{cod}), 53.1 (CH_{cod}), 52.6 (CH_{cod}), 51.7 ($NCH_2CH_2CH_2CH_3$), 50.8 ($NCH_2CH_2CH_2CH_3$), 50.4 (CH_{cod}), 35.8 (CH_2 cod), 33.6 (CH_2 cod), 33.1 ($NCH_2CH_2CH_2CH_3$), 32.9 ($NCH_2CH_2CH_2CH_3$), 32.3 (CH_2 cod), 31.2 (CH_2 cod), 30.5 (CH_2 cod), 29.4 (CH_2 cod), 29.0 (CH_2 cod), 27.6 (CH_2 cod), 20.2 ($NCH_2CH_2CH_2CH_3$), 20.2 ($NCH_2CH_2CH_2CH_3$), 14.0 ($NCH_2CH_2CH_2CH_3$), 14.0 ($NCH_2CH_2CH_2CH_3$). Electrospray MS (cone 20 V) (*m*/*z*, fragment): 981.7 $[M - 2Cl]^{2+}$ (calcd. for $[M - 2Cl]^{2+}$: 981.3). Anal. Calcd for $C_{76}H_{98}N_8Ir_4Cl_4$ (2034.34): C, 44.87; H, 4.86; N, 5.51. Found: C, 45.16; H, 5.62; N, 5.13.

Synthesis of ***5****.* CO gas was passed through a solution of complex **4** (30 mg, 0.015 mmol) in CH_2Cl_2 (10 mL) at 0 °C, for 30 min. After this time, the solution was concentrated under reduced pressure and precipitated with hexane. The corresponding carbonyl derivative precipitated as a pale yellow solid in quantitative yield. ^1H NMR (400 MHz, $CDCl_3$): δ 8.36 (br, 2H, CH_{pyr}), 8.03 (br, 4H, CH_{pyr}), 7.49 (s, 4H, CH_{imid}), 7.33 (s, 4H, CH_{imid}), 4.57 (br, 4H, $NCH_2CH_2CH_2CH_3$), 4.46 (br, 4H, $NCH_2CH_2CH_2CH_3$), 2.07−2.02 (m, 8H, $NCH_2CH_2CH_2CH_3$), 1.54−1.51 (m, 8H, $NCH_2CH_2CH_2CH_3$), 1.06 (t, $^3J_{H-H}$ = 9.5 Hz, 12H, $NCH_2CH_2CH_2CH_3$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 180.7 (Ir-$C_{carbene}$), 175.6 (Ir-CO), 168.1 (Ir-CO), 133.3 (C_q pyr), 129.0 (C_q pyr), 125.4 (CH_{pyr}), 125.0 (CH_{pyr}), 125.0 (CH_{imid}), 124.8 (C_q pyr), 122.0 (CH_{imid}), 51.6 ($NCH_2CH_2CH_2CH_3$), 32.9 ($NCH_2CH_2CH_2CH_3$), 20.0 ($NCH_2CH_2CH_2CH_3$), 13.9 ($NCH_2CH_2CH_2CH_3$). IR (KBr): 2064 ($\nu_{C\equiv O}$), 1977 ($\nu_{C\equiv O}$) cm^{-1}. Electrospray MS (cone 20 V) (*m*/*z*, fragment): 1791.3 $[M - Cl]^+$ (calcd. for $[M - Cl]^+$: 1789.1). Anal. Calcd for $C_{52}H_{50}N_8O_8Ir_4Cl_4 \cdot CH_2Cl_2$ (1910.62): C, 33.32; H, 2.74; N, 5.86. Found: C, 33.25; H, 2.96; N, 6.21.

Synthesis of the Monometallic Complexes ***6*** *and* ***7****. Synthesis of* ***6****.* 1-*n*-Butyl-3-phenylimidazolium hexafluorophosphate (50 mg, 0.144 mmol, 1 equiv), $[RhCl(cod)]_2$ (35.5 mg, 0.072 mmol, 0.5 equiv), and K_2CO_3 (60 mg, 0.432 mmol, 3 equiv) were placed together in a high pressure Schlenk. The resulting mixture was dissolved in acetone (3 mL) and stirred for 20 h at 60 °C. After this time, the mixture was cooled to room temperature. The solution was then filtered and the volatiles were removed under vacuum. The resulting solid was dissolved in CH_2Cl_2, filtered through a pad of Celite, and the solvent was removed under vacuum. The crude solid was purified by column chromatography. Elution with CH_2Cl_2 afforded a bright orange band that contained the desired complex. Yield: 53.5 mg (83.5%). ^1H NMR (400 MHz, $CDCl_3$): δ 8.22−8.20 (m, 2H, CH_{Ph}), 7.55−7.50 (m, 2H, CH_{Ph}), 7.45−7.40 (m, 1H, CH_{Ph}), 7.17 (d, $^3J_{H-H}$ = 2 Hz, 1H, CH_{imid}), 7.02 (d, $^3J_{H-H}$ = 2 Hz, 1H, CH_{imid}), 5.26−5.22 (m, 1H, CH_{cod}), 5.18−5.11 (m, 1H, CH_{cod}), 4.87−4.77 (m, 1H, $NCH_2CH_2CH_2CH_3$), 4.44−4.34 (m, 1H, $NCH_2CH_2CH_2CH_3$), 3.42−3.37 (m, 1H, CH_{cod}), 2.78−2.73 (m, 1H, CH_{cod}), 2.32−2.22 (m, 2H, CH_2 cod), 2.11−1.99 (m, 2H, CH_2 cod), 1.96−1.71 (m, 4H, CH_2 cod and 2H, $NCH_2CH_2CH_2CH_3$), 1.57−1.46 (m, 2H, $NCH_2CH_2CH_2CH_3$), 1.06 (t, $^3J_{H-H}$ = 12 Hz, 3H, $NCH_2CH_2CH_2CH_3$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 182.2 (d, Rh-$C_{carbene}$, $^1J_{Rh-C}$ = 49 Hz), 140.5 (C_q Ph), 128.8 (CH_{Ph}), 127.9 (CH_{Ph}), 124.7 (CH_{Ph}), 121.9 (CH_{imid}), 120.9 (CH_{imid}), 95.7 (d, Rh-CH_{cod}, $^1J_{Rh-C}$ = 7 Hz), 72.1 (d, Rh-CH_{cod}, $^1J_{Rh-C}$ = 14 Hz), 71.3 (d, Rh-CH_{cod}, $^1J_{Rh-C}$ = 14 Hz), 52.0 ($NCH_2CH_2CH_2CH_3$), 33.0 (CH_2 cod), 32.4 ($NCH_2CH_2CH_2CH_3$), 31.2 (CH_2 cod), 29.8 (CH_2 cod), 29.2 (CH_2 cod), 20.3 ($NCH_2CH_2CH_2CH_3$), 14.1 ($NCH_2CH_2CH_2CH_3$). Electrospray MS (cone 20 V) (*m*/*z*, fragment): 411.3 $[M - Cl]^+$ (calcd. for $[M - Cl]^+$: 411.1). Anal. Calcd for $C_{21}H_{28}N_2RhCl \cdot 2CH_2Cl_2$ (616.68): C, 44.80; H, 5.23; N, 4.54. Found: C, 44.67; H, 5.39; N, 4.83.

Synthesis of ***7****.* CO gas was passed through a solution of complex **6** (33 mg, 0.074 mmol) in CH_2Cl_2 (10 mL) at 0 °C, for 30 min. After this time, the solvent was removed under vacuum. The corresponding carbonyl derivative was obtained as a yellow solid in quantitative yield. Complex **7** was found unstable in solution as well as in the solid state, which prevented a correct elemental analysis. ^1H NMR (300 MHz, $CDCl_3$): δ 7.73−7.71 (m, 2H, CH_{Ph}), 7.51−7.44 (m, 3H, CH_{Ph}), 7.28−7.27 (d, $^3J_{H-H}$ = 2 Hz, 1H, CH_{imid}), 7.17−7.16 (d, $^3J_{H-H}$ = 2 Hz, 1H, CH_{imid}), 4.61−4.52 (m, 1H, $NCH_2CH_2CH_2CH_3$), 4.19−4.10 (m, 1H, $NCH_2CH_2CH_2CH_3$), 1.98−1.88 (m, 2H, $NCH_2CH_2CH_2CH_3$), 1.46−1.39 (m, 2H, $NCH_2CH_2CH_2CH_3$), 1.00 (t, $^3J_{H-H}$ = 7.3 Hz, 3H, $NCH_2CH_2CH_2CH_3$). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 187.2 (d, Rh-$C_{carbene}$, $^1J_{Rh-C}$ = 53.25 Hz), 181.2 (d, Rh-CO, $^1J_{Rh-C}$ = 77.25 Hz), 172.66 (d, Rh-CO, $^1J_{Rh-C}$ = 41.25 Hz), 139.8 (C_q Ph), 129.3 (CH_{Ph}), 128.9 (CH_{Ph}), 125.5 (CH_{Ph}), 122.9 (CH_{imid}), 122.3 (CH_{imid}), 52.1 ($NCH_2CH_2CH_2CH_3$), 32.3 ($NCH_2CH_2CH_2CH_3$), 19.9 ($NCH_2CH_2CH_2CH_3$), 13.9 ($NCH_2CH_2CH_2CH_3$). IR (KBr): 2067 ($\nu_{C\equiv O}$), 1997 ($\nu_{C\equiv O}$) cm^{-1}.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.8b00633.

NMR spectra of 1-*n*-butyl-3-phenylimidazolium hexafluorophosphate, compounds **1** and **2**, and complexes **3**−**7**, X-ray crystallographic data of complex **4**, and the time-dependent reaction profile of the cyclization reaction of 4-pentynoic acid using catalyst **4** (PDF)

Accession Codes

CCDC 1864607 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

DOI: 10.1021/acs.organomet.8b00633
Organometallics XXXX, XXX, XXX−XXX

■ ACKNOWLEDGMENTS

We gratefully acknowledge financial support from the Universitat Jaume I (UJI-B2017-07 and P11B2015-24). We are grateful to the Serveis Centrals d'Instrumentació Científica (SCIC-UJI) for providing spectroscopic facilities. We also thank Dr. Louise N. Dawe (Wilfrid Laurier University) for her valuable advice on the refinement of the structure of complex **4**.

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DOI: 10.1021/acs.organomet.8b00633
Organometallics XXXX, XXX, XXX−XXX