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# Intermolecular Hydroalkoxylation of Terminal Alkynes Catalyzed by a Dipyrrinato Rhodium(I) Complex with Unusual Selectivity

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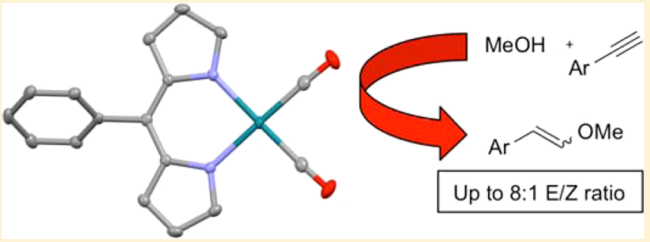
Supporting Information

**ABSTRACT:** An operationally simple and atom-economical method for the *E*-selective preparation of enol ethers is described. A novel dicarbonyl(5-phenyldipyrrinato)rhodium complex, **2**, was prepared in four synthetic steps, characterized by X-ray crystallography and NMR spectroscopy, and then investigated as a catalyst for the intermolecular hydroalkoxylation of terminal alkynes. Solvent and substrate studies were used to gain insight into the mechanism of the reaction. Cyclic voltammetry was also used to investigate the electronic properties of **2**. The rhodium(I)-catalyzed intermolecular alkyne hydroalkoxylation reaction reported here mediates excellent substrate transformation with a high degree of *E*/*Z* selectivity which is opposite to that reported previously using alternative catalysts.



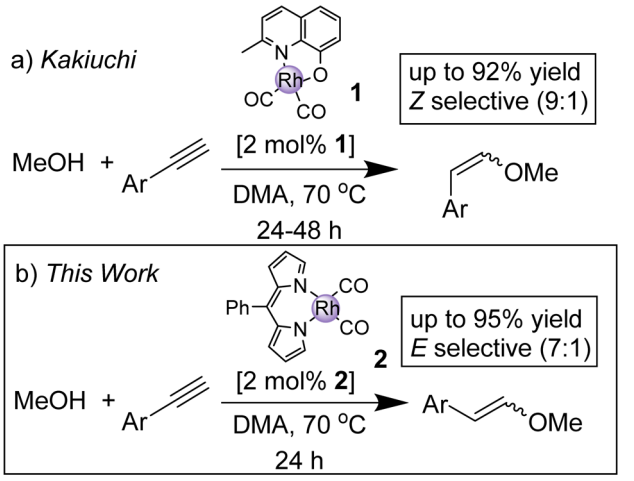

## INTRODUCTION

The development of atom-economical methods for the intermolecular hydroalkoxylation of alkynes is important, because the reactive enol ethers formed are versatile building blocks in organic synthesis.[1] Enol ethers can be hydrolyzed to yield aldehydes and ketones,[2] employed as substrates for cross-coupling[3] and ring-closing metathesis[4] reactions. Enol ethers can also be utilized as building blocks in cycloaddition transformations[5] and have consequently proved to be useful intermediates in the programmed synthesis of bioactive molecules[6] with medicinal applications.[7]

The potential utility of transition-metal-catalyzed addition of oxygen nucleophiles to triple bonds has driven the growth of interest in the intermolecular hydroalkoxylation of alkynes, and this area has been comprehensively reviewed.[8] There are two mechanisms that are broadly accepted for this reaction: coordination of the transition metal to the triple bond, enabling nucleophilic attack by the oxygen, or the formation of a vinylidene intermediate. The latter is more commonly observed for terminal alkynes, as the mechanism is thought to involve a $\beta$-hydride elimination step following deprotonation of the terminal alkyne. Irrespective of the mechanism, controlling the regioselectivity of the products formed following intermolecular hydroalkoxylation has persisted as a major challenge, and general and reliable methods are still sought after. In 2011, Kakiuchi and co-workers made significant progress toward controlling the regioselectivity of the reaction by demonstrating that the intermolecular hydroalkoxylation reaction could be catalyzed under mild conditions using an 8-quinolinolato rhodium complex (**1**) (Scheme 1a) to selectively form (*Z*)-enol ethers with no observable quantity of the undesired Markovnikov product formed.[9]

While the application of dipyrrin-based molecules for the assembly of fluorescent dyes[10] is well established, the use of bidentate dipyrrinato (dpm) ligands as scaffolds for promoting

**Scheme 1. Hydroalkoxylation of Terminal Alkynes: (a) *Z* Selective, Kakiuchi; (b) *E* Selective, This Work**

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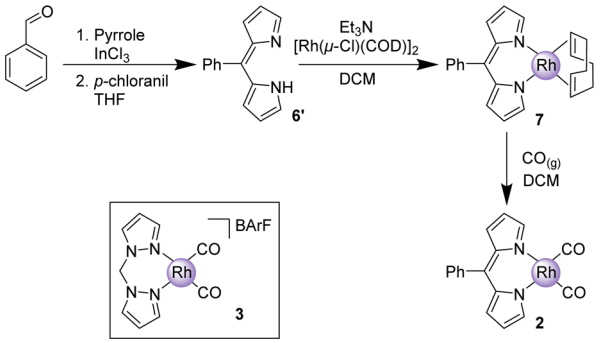
transition-metal-mediated catalysis have not been as extensively investigated. The Betley research group have made several significant advances in the area of C−H bond activation using iron and cobalt dpm complexes as catalysts.[11,12] Several other groups have utilized the dpm motif within larger polydentate ligand architectures, forming complexes with Ge and Ti for polymerizing $CO_2$ and epoxides.[13] Considering the utility of complexes of first-row transition metals with dipyrrinato ligands for catalysis, there are remarkably few examples of rhodium dpm complexes that have been used for catalysis. The catalytic properties of rhodium dipyrrinato complexes have barely been investigated, with only one example in the literature using Rh(III) for catalyzing the transfer hydrogenation of terephthalaldehyde[14] and no examples of catalysis using Rh(I).

We became interested in investigating Rh(I) dpm complexes as catalysts due to their structural similarity as well as a relative electronic difference in comparison to our previously reported positively charged bis(pyrazol-1-yl)methane (bpm) Rh(I) and Ir(I) complexes, which have proven to be effective catalysts for hydroelementation reactions.[15] We were also interested in the potential of the planar geometry of Rh(I) dpm complexes in forming the basis of efficient hybrid catalyst materials[16] or effective new bimetallic catalysts,[15e] since previous examples containing the bpm ligand motif can adopt various, easily interconvertible conformations that prevent the determination of a well-defined intermetallic distance.[17] Here we report dicarbonyl(5-phenyldipyrrinato)rhodium ([$Rh(CO)_2$dpm], **2**) as a catalyst for the intermolecular hydroalkoxylation of alkynes (Figure 1b) and show that this complex can promote the synthesis of enol ethers with stereoselectivity opposite to that observed in Kakiuchi's study.

## RESULTS AND DISCUSSION

The complex [$Rh(CO)_2$dpm] (**2**) was readily prepared in four synthetic steps with an overall yield of 15% (Scheme 2).[18]

**Scheme 2. Synthesis of [$Rh(CO)_2$dpm] (2) and Structure of the Closely Related Analogue [$Rh(CO)_2$bpm][BArF] (3)**




Benzaldehyde was condensed with excess pyrrole in the presence of an $InCl_3$ Lewis acid catalyst, followed by oxidation of the newly formed 5-phenyldipyrromethane using *p*-chloranil to furnish **6′** in 31% yield over the two steps. **6′** was deprotonated at the N position of the pyrrole ring with triethylamine in the presence of $[Rh(\mu\text{-Cl})(COD)]_2$ following a method similar to that reported by Yadav.[18b] The intermediate complex [Rh(COD)dpm] (**7**) formed was purified by column chromatography and then treated with CO gas to give **2** as a dark orange solid in 51% yield over two steps.

Single crystals of **2** suitable for X-ray analysis were grown by slow cooling of a hot, saturated solution of the complex in toluene (Figure 1). The X-ray crystal structure confirms the anticipated square-planar geometry of the primary coordination sphere of **2** (Figure 1). The conformation of the flat rhodacycle in complex **2** is in contrast to the distorted-boat conformation adopted by the rhodacycle of complex **3** (Scheme 2).[15a] Complex **2** has a mirror plane through the atoms C9a−C5a−Rh1. The Rh−N1a/N1a$^i$ bond lengths of 2.065 Å in complex **2** are shorter than the Rh−N bond lengths in the analogous complex **3** due to the anionic charge of the dpm ligand. The Rh−C1/C1$^i$ bond lengths of 1.855 Å in complex **2** are also slightly shorter than the analogous bonds in complex **3**. The N1a−Rh1−N1a$^i$ bond angle of 87° implies only a slight distortion from the ideal angle of 90°. Additionally, the six-membered metallacycle of complex **2** is close to being planar, with the largest torsion angle within the metallacycle which consists of the atoms C5a−C4a−N1a−Rh1 being 3.04°.

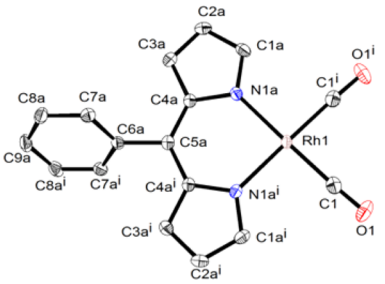



**Figure 1.** Molecular structure of complex **2**. Hydrogen atoms have been omitted for clarity. Ellipsoids are at the 50% probability level. Selected bond lengths (Å) and angles (deg): Rh−C1$^i$ 1.855, Rh−C1 1.855, Rh−N1a$^i$ 2.065, Rh−N1a 2.065; C1$^i$−Rh1−C1 86.69, C1−Rh1−N1a$^i$ 92.38, N1a$^i$−Rh1−N1a 88.58, N1a−Rh1−C1$^i$ 92.38.

The electron structure of the primary coordination sphere of complex **2** is likely to closely match that of the 8-quinolinolato rhodium complex **1**, and so we reasoned that the dipyrrinato Rh(I) complex **2** would have potential as a hydroalkoxylation catalyst. A test run of the **2**-catalyzed hydroalkoxylation reaction was carried out using phenylacetylene (**4a**) and methanol as substrates. Pleasingly, phenylacetylene (**4a**) was cleanly converted to (2-methoxyvinyl)benzene (**5a**) when stirred in methanol/*N*,*N*-dimethylacetamide (DMA) at 70 °C for 24 h in the presence 2 mol% of **2**, as determined by $^1$H NMR spectroscopy (Table 1, entry 1). The reaction showed no Markovnikov addition product, and the *E*:*Z* product ratio was 6:1. Interestingly, the product selectivity was opposite to that reported by Kakiuchi.[9] Reducing the catalyst loading to 1 mol % did not affect substrate conversion and actually moderately improved the selectivity of the reaction to a 7:1 ratio of *E*:*Z* isomers (Table 1 entry 2). After purification, the isolated yield of combined *E*:*Z* products was 95%.

To verify the effect of oxygen and water, which can lead to deactivation/decomposition of organometallic catalysts or compete with substrates to occupy binding sites, the catalyzed hydroalkoxylation reaction was repeated in the presence of $O_2$ (Table 1, entry 3) or water (Table 1, entry 4), respectively. The intermolecular hydroalkoxylation reaction under investigation was shown to be sensitive to oxygen (Table 1, entry 3) with a reduction in conversion to 50% observed when the reaction was undertaken in the presence of oxygen, accompanied by a slight increase in selectivity for the *E* product (8:1). The reaction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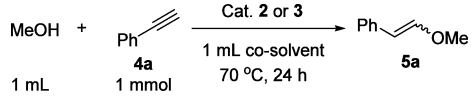
*Organometallics* XXXX, XXX, XXX−XXX

**Table 1. Hydroalkoxylation of Phenylacetylene under Various Reaction Conditions**




| Entry | Cosolvent | Catalyst | Catalyst loading (mol %) | Conversion of **4a** (%)[a] | *E*:*Z* ratio of **5a** |
|---|---|---|---|---|---|
| 1 | DMA | **2** | 2 | >98 | 6:1 |
| 2 | DMA | **2** | 1 | >98 | 7:1 |
| 3[b] | DMA/$O_2$ | **2** | 1 | 50 | 8:1 |
| 4[c] | DMA/$H_2O$ | **2** | 1 | 57 | 2:1 |
| 5 | DMA | **3** | 1 | N/A[d] | N/A |
| 6 | DMF | **2** | 1 | >98 | 5:1 |
| 7 | DMSO | **2** | 1 | >98 | 5.4:1 |
| 8 | THF | **2** | 1 | 43 | N/A |
| 9 | MeCN | **2** | 1 | 33 | N/A |
| 10 | Acetone | **2** | 1 | 24 | N/A |
| 11 | - | **2** | 1 | 34 | N/A |

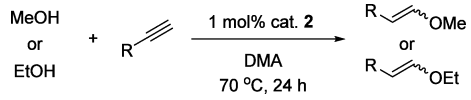
[a]Determined by $^1$H NMR spectroscopy. Conversion was determined by comparing the ratio of the alkyne proton resonance (ca. 3 ppm) and product alkene resonance (5−7 ppm) using $^1$H NMR spectroscopy. [b]Solvents were aerated prior to reaction. [c]Solvents were wetted with 10 drops of water. [d]Unidentifiable decomposition products observed.

resulted in 57% conversion in the presence of water with significantly lower product selectivity and a trace amount of aldehyde (Table 1, entry 4). Interestingly, the closely related bis(pyrazol-1-yl)methane complex **3** is a poor catalyst for this reaction, resulting only in substrate decomposition to unidentifiable products under reaction conditions similar to those used here for **2** (Table 1, entry 5).

The effect of the cosolvent on the product formation was further investigated following these initial studies (Table 1). The previously observed excellent substrate conversion was retained in both DMF and DMSO (Table 1, entries 6 and 7), but the selectivity of the reaction was less pronounced. Moving to less polar cosolvents such as EtOAc, THF, and acetone resulted in poor conversions, and using these cosolvents several uncharacterized byproducts were formed during the reaction (Table 1, entries 8−10). Surprisingly, the reaction proceeds very poorly in neat MeOH, suggesting that the cosolvent plays an important role in the reaction (Table 1, entry 11).

With an effective protocol for the selective synthesis of (*E*)-(2-methoxyvinyl)benzene in hand, we commenced an investigation into substrate scope using readily available substrates (Table 2). Substituting the methanol with ethanol did not affect the conversion, but product formation was significantly less selective, dropping to a 3:1 *E*:*Z* ratio (Table 2, entry 2). Introducing an electron-donating or -withdrawing group in the para position of the aryl acetylene under investigation had no effect on the efficacy of the reaction (Table 2, entries 3−5). However, when both ortho and para positions were occupied by methyl groups (Table 2, entry 6), the substrate conversion decreased significantly, most likely due to steric hindrance. The hydroalkoxylation of an alkyne substrate with no aryl substituents, 1-octyne, with methanol resulted in poor conversion (14%, Table 2, entry 7), with predominant formation of the *E* isomer. Replacing the saturated alkyl substituents with a cyclic alkene led to high levels of conversion to **5h**. Interestingly, substituting the phenyl ring with pyridine

**Table 2. Hydroalkoxylation of Selected Alkyne Substrates**




| Entry | Substrate | Product | Conv.[a] | *E*/*Z* ratio[b] |
|---|---|---|---|---|
| 1 | **4a** | **5a** | >98% (95%) | 7:1 |
| 2 | **4a** | **5b** | >98% (75%) | 3:1 |
| 3 | **4c** | **5c** | >98% (90%) | 4:1 |
| 4 | **4d** | **5d** | >98% (84%) | 5:1 |
| 5 | **4e** | **5e** | >98% (75%) | 6:1 |
| 6 | **4f** | **5f** | 72% (50%) | 3:1 |
| 7 | **4g** | **5g** | 14% | *E*-isomer only |
| 8 | **4h** | **5h** | >98% (85%) | *E*-isomer only |
| 9 | **4i** | **5i** | 28% | 1:3 |
| 10 | **4j** | **5j** | 0% | N/A |
| 11 | **4k** | **5k** | 0% | N/A |

[a]Isolated yield *in* parentheses. [b]*E*:*Z* ratio determined by $^1$H NMR spectroscopy.

(Table 2, entry 9) subdues the reaction efficiency with inversed product selectivity in comparison to entries 1−6. Using internal aromatic and alkyl alkynes (Table 2, entries 11 and 12) did not yield any hydroalkoxylation products.

The observation that complex **2** only promotes the transformation of terminal alkynes suggests that complex **2**



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*Organometallics* XXXX, XXX, XXX−XXX

may also form a vinylidene complex as a reaction intermediate on reaction with the terminal alkynes, as proposed by Kakiuchi et al.[9] and supported by the computer simulation by Wang et al.[19] Formation of such a complex involves migration of the terminal proton via a 1,2-$\beta$-hydride transfer before attack by the alcohol.

The mechanism of the *inter*molecular hydroalkoxylation of terminal acetylenes using **2** would appear to be very different from the mechanism of intramolecular hydroalkoxylation of alkynes using the bpm-based complex **3** that we have intensively investigated in our laboratory.[20] In the case of the latter, we have clearly shown using low-temperature NMR spectroscopy that *intra*molecular dihydroalkoxylation is readily promoted and the reaction proceeds via $\pi$ coordination of the alkyne substrate to the metal center followed by the sequential addition of two hydroxyl groups.[15a] We have not unambiguously determined the mechanism of the anti-Markovnikov addition of methanol to terminal acetylenes using complex **2**. However, it is likely that product formation is directed via a vinylidene rhodium intermediate[8c] that precludes Markovnikov addition as well as the reaction of internal alkynes that do not have the requisite terminal alkynyl proton. The origin of the observed *E* selectivity is the subject of current investigation in our laboratory.

To gain further insight into the reaction mechanism, the electrochemical properties of complex **2** and the structurally similar complex **3** were investigated using cyclic voltammetry (CV, Figure 2) under inert conditions. Measurements were

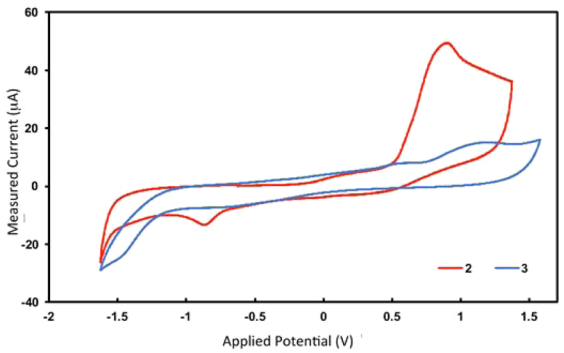


**Figure 2.** Cyclic voltammograms of complex **2** (red) and complex **3** (blue), both 1 mM in 0.1 M $[Bu_4N][PF_6]/CH_2Cl_2$ supporting electrolyte at 100 mV/s.

initiated at 0 V at a scan rate of +100 mV/s. Electrode potentials reported herein are referenced to the ferrocene/ferrocenium couple, and the voltammograms are plotted without correction.

The cyclic voltammogram of complex **2** (Figure 2, red) indicates an irreversible anodic peak at +0.96 V. A small reduction peak was observed at −0.88 V. On comparison with the cyclic voltammograms of other planar Rh(I) complexes containing anionic ligands and CO coligands,[21] the anodic peak at +0.96 V was assigned to be the Rh(I)/Rh(III) oxidation process, whereas the reduction peak at −0.88 V corresponds to the reduction of a Rh(III) species. The different intensities in the anodic and cathodic peaks in the cyclic voltammogram of complex **2** suggested that the oxidized Rh(III) species may have been decomposing or diffusing into the bulk solution.[21] In addition, a small shoulder at 1.14 V grew after multiple scans (see the Supporting Information), indicating the formation of a second oxidized species. In contrast, complex **3** (Figure 2, blue) showed an irreversible anodic peak at +1.14 V and no observable reduction peak or multiple oxidized products. The current intensity of this peak is substantially lower than the anodic peaks of complex **2**, despite both Rh(I) complexes being examined by CV at 1 mM concentration. The reduced current intensity of **3** may be due to the bulkiness of the $BArF^-$ counterion reducing the diffusion coefficient or possible partial ion pairing in $CH_2Cl_2$.[22]

From the voltammograms, complex **2** was shown to oxidize at a potential less positive than that of complex **3** by 180 mV. Should the *inter*molecular hydroalkoxylation reaction proceed via the vinylidene formation mechanism, complex **2** could lead to an intermediate more stable than that formed on using complex **3**, whereas the *intra*molecular catalyzed reactions may proceed via a different mechanism involving a Rh(I) ion (such as $\pi$ coordination to the triple bond). The second oxidized species observed in the voltammogram of complex **2** may also in fact be the active species during catalysis.

## CONCLUSIONS

In summary, we have determined that the dipyrrinato rhodium(I) complex **2** is an effective catalyst for the intermolecular hydroalkoxylation of terminal alkynes. In this case it is likely that the reaction occurs via a vinylidene intermediate, as internal alkynes were shown to be unreactive with methanol under the reaction conditions investigated. The intermolecular hydroalkoxylation reaction catalyzed by complex **2** was shown to be robust and selective for a range of substrates, with good to excellent yields and preferential formation of the *E* product in most cases. Cyclic voltammetry reveals that the potential at which the Rh(I) metal center of complex **2** is oxidized is 180 mV lower than the bis-pyrazole Rh(I) complex **3**, suggesting that a more readily accessible Rh(III) center may play an important role in the hydroalkoxylation reaction. However, we cannot rule out the possibility that a second more active species may be formed during the reaction, which may go some way in explaining the sensitivity of the reaction to the cosolvent. Overall, the surprising catalytic activity promoted by a Rh(I) complex containing the well-known dipyrrinato ligand suggests that interesting catalyst scaffolds could be assembled using this readily accessed planar moiety.

## EXPERIMENTAL SECTION

**General Procedures.** All manipulations of metal complexes and air-sensitive reagents were carried out using standard Schlenk techniques; catalysis experiments were carried out using a Radleys Discovery Technologies GreenHouse Parallel Synthesizer and standard Schlenk techniques under an $N_2$(g) atmosphere. Unless otherwise stated, chemicals were purchased from Alfa Aesar Inc. or Aldrich Chemical Co. Inc. and used as received. Rhodium(III) chloride hydrate was purchased from Precious Metals Online P/L and used without further purification. Pyrrole was distilled before use. $[Rh(\mu\text{-}Cl)(COD)]_2$,[23] 5-phenyldipyrromethane (**6**),[18a] and 5-phenyldipyrrin (**6′**)[24] were synthesized according to reported procedures. Solvents for catalysis were deoxygenated with $N_2$.

For the purposes of air-sensitive manipulations and preparation of metal complexes, solvents were dispensed from a PuraSolv solvent purification system and stored under a nitrogen or argon atmosphere in glass ampules fitted with J. Young Teflon valves. Nitrogen gas for Schlenk line operation came from in-house liquid nitrogen boil-off. Bulk compressed gases of nitrogen (>99.5%) and carbon monoxide (>99.5%) were obtained from Air Liquide.

**X-ray Crystallography.** Suitable single crystals of **2** selected under the polarizing microscope (Leica M165Z) were picked up on a


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*Organometallics* XXXX, XXX, XXX−XXX

MicroMount (MiTeGen, USA) consisting of a thin polymer tip with a wicking aperture. The X-ray diffraction measurements were carried out on a Bruker Kappa-II CCD diffractometer at 150 K by using graphite-monochromated Mo K$\alpha$ radiation ($\lambda$ = 0.710723 Å). The single crystal, mounted on the goniometer using cryo loops for intensity measurements, was coated with paraffin oil and then quickly transferred to the cold stream using an Oxford Cryo stream attachment. Symmetry-related absorption corrections using the program SADABS[25] were applied, and the data were corrected for Lorentz and polarization effects using Bruker APEX2 software.[26] All structures were solved by direct methods, and full-matrix least-squares refinements were carried out using SHELXL.[27] The non-hydrogen atoms were refined anistropically. Key crystallographic data and refinement details are given in Table S1. in the Supporting Information.

**Synthesis of the Intermediate Complex [Rh(COD)dpm] (7).** $Et_3N$ (0.96 mL, 6.89 mmol) was added to a solution of **6′** in DCM/MeOH (194 mg, 0.88 mmol; 30 mL of DCM and 20 mL of MeOH) followed by $[Rh(\mu\text{-Cl})(COD)]_2$ (216 mg, 0.88 mmol). The resultant dark red solution was stirred for 1 h at room temperature. The solvent was evaporated under reduced pressure. The residue was redissolved in DCM and then passed through an alumina column (neutral or basic; eluent hexane/DCM 2/1 v/v). The clear red fractions were combined, and the solvent was evaporated to yield **7** as a dark red solid (274 mg, 0.636 mmol, 72%). $^1$H NMR (300.2 MHz, $CD_2Cl_2$): $\delta$ 1.88−2.16 (m, 4H, COD $-CH_2-$), 2.38−66 (m, 4H, COD $-CH_2-$), 4.50−60 (m, 4H, COD $=CH-$), 6.27 (dd, $^3J_{H-H}$ = 4.3 Hz, $^3J_{H-H}$ = 1.6 Hz, 2H, Py*H*), 6.35 (dd, $^3J_{H-H}$ = 4.3 Hz, $^4J_{H-H}$ = 1.2 Hz, 2H, Py*H*), 7.10 (m, 2H, Py*H*), 7.28−53 (m, 5H, Ar*H*). The complex was used for the carbonylation step without full characterization.

**Synthesis of the Complex [Rh(CO)$_2$dpm] (2).** **7** (250 mg, 0.57 mmol) was dissolved in a minimum amount of DCM and degassed with three freeze−pump−thaw cycles. The dark red solution was stirred under a CO(g) atmosphere for 2 h. The mixture produced a dark brown precipitate in a yellow solution. The precipitate was filtered, washed with pentane (3 × 20 mL), and dried in vacuo to yield **2** as a dark orange solid (156 mg, 0.414 mmol, 72%). $^1$H NMR (300.2 MHz, $CD_2Cl_2$): $\delta$ 6.43 (dd, $^3J_{H-H}$ = 4.4 Hz, $^3J_{H-H}$ = 1.6 Hz, 2H, Py*H*4), 6.55 (dd, $^3J_{H-H}$ = 4.3 Hz, $^4J_{H-H}$ = 1.1 Hz, 2H, Py*H*3), 7.28−59 (m, 5H, Ar*H*), 7.78 (m, 2H, Py*H*5). $^{13}$C NMR (75 MHz, $CD_2Cl_2$): $\delta$ 118.67 (PyC3), 127.67 (*m*-ArC), 129.08 (*p*-ArC), 130.79 (*o*-ArC), 132.44 (PyC4), 136.78 (PyC2), 138.15 (*i*-ArC), 155.30 (PyC5), 155.33 (methine *C*), 186.75 (CO). Anal. Found: C, 54.02; H, 2.96; N, 7.38. Calcd for $C_{17}H_{11}N_2O_2Rh$: C, 53.99; H, 2.93; N, 7.41.

**General Procedure for Catalyzed Hydroalkoxylation.** Substrate and cosolvent screenings were carried out in a Radleys Discovery Technologies Parallel Synthesizer. Alcohol (0.5 mL), cosolvent (0.5 mL), alkyne (0.455 mmol), and catalyst (1.9 mg, 5.0 $\mu$mol, 1.1 mol %) were charged into test tubes with a magnetic stirrer bar and placed in the Synthesizer. The reaction chamber was carefully evacuated and refilled with nitrogen gas over five cycles and then heated to 70 °C with stirring for 24 h. When they were cooled to room temperature, the reaction mixtures were diluted to 1.5 mL with $Et_2O$ and washed with LiCl solution (0.1 M, 2 × 2 mL). The organic phase was dried with saturated brine solution (3 mL) and $Na_2SO_4$, and the solvent was removed in vacuo. Products were analyzed using $^1$H NMR spectroscopy.

Scaled-up reactions were carried out in Schlenk flasks under a $N_2$(g) atmosphere. Reagents were charged into Schlenk flasks, stoppered, and heated with stirring at 70 °C for 24 h. When the mixtures were cooled, crude products were diluted with $Et_2O$ (20 mL) and washed with LiCl solution (0.1 M, 2 × 30 mL). The organic phase was dried with saturated brine solution (30 mL) and $Na_2SO_4$, filtered, and then concentrated in vacuo. Crude products were purified on silica gel column pretreated with $Et_3N$.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.5b00561.

Additional experimental details, $^1$H NMR spectra, and crystallographic data (PDF)

X-ray crystal structure information for **2** (CIF)

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### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS


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