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Rapid Access to Derivatized, Dimeric, Ring-Substituted Dichloro(cyclopentadienyl)rhodium(III) and Iridium(III) Complexes

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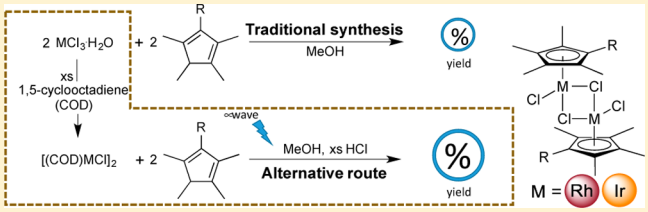
Supporting Information

ABSTRACT: The present work describes the design and synthesis of a series of rhodium and iridium dimers $[(\eta^5\text{-ring})MCl]_2(\mu^2\text{-Cl})_2$ (where $(\eta^5\text{-ring})MCl = (\eta^5\text{-Me}_4C_5R)Rh(III)Cl$ or $(\eta^5\text{-Me}_4C_5R)Ir(III)Cl$) using a new and efficient 1 h procedure. Rhodium and iridium dimeric complexes were synthesized via a microwave reaction. The modified HMe_4C_5R (R = isopropyl, *n*-butyl, isobutyl, *sec*-butyl, *n*-pentyl, *n*-hexyl, *n*-heptyl, *n*-octyl, phenyl, benzyl, phenethyl, cyclohexyl, and cyclopentyl) type ligands were synthesized by reaction of 2,3,4,5-tetramethylcyclopent-2-en-1-one with the respective Grignard reagent (RMgX), followed by elimination of water under acidic conditions to produce the tetramethyl(alkyl or aryl)cyclopentadienes in moderate to excellent yields (40−98%). Reaction of the HMe_4C_5R ligands with $[M(COD)](\mu^2\text{-Cl})_2$ (M = Rh, Ir; COD = 1,5-cyclooctadiene) gave the dimeric complexes $[(\eta^5\text{-Me}_4C_5R)MCl]_2(\mu^2\text{-Cl})_2$ in yields ranging from 47% to 96%. The derivatized dimers were tested for antimicrobial activity, showing activity against *Mycobacterium smegmatis* and improved activity with derivatized R groups against *Staphylococcus aureus* and MRSA 43300. The characterization of these complexes was completed by NMR spectroscopy, single-crystal X-ray diffraction, high-resolution mass spectrometry, and elemental analysis.



INTRODUCTION

The importance of cyclopentadienyl ligands to the development of organometallic chemistry cannot be overstated.[1−7] Metal complex chemistry of cyclopentadienyl systems was further elaborated with the use of pentamethylcyclopentadienyl ligands that blocked unwanted reactions of the metal center with cyclopentadiene C−H bonds.[8−10] Our group has focused on the synthesis of $\eta^5\text{-Me}_4C_5R$-type complexes of rhodium and iridium with an eye toward developing both catalytic and biological chemistry of these metals.[11−13] Rhodium and iridium dimers of the type $[(\eta^5\text{-Me}_5C_5)MCl]_2(\mu^2\text{-Cl})_2$ (M = Rh, Ir) are employed in various catalytic systems[14−27] and are useful synthetic precursors in half-sandwich chemistry.[28]

Rhodium and iridium dimers have many uses in catalytic applications, as do the subsequent half-sandwich complexes synthesized from their respective dimers.[11,29−31] The literature features an abundance of half-sandwich (piano-stool) complexes with various chelating agents including acacs,[32] amino alcohols,[30,33,34] amino acids,[12] ethylenediamines,[13] C,N chelating ligands,[35] hydroxyquinolines,[36,37] and bipyridyls.[38] The facile synthesis of these compounds allows half-sandwich complexes to be easily tailored for catalytic or biological applications. Recently, $\eta^4\text{-Me}_5C_5H$ complexes have been shown to be effective catalysts for H_2 evolution and an essential intermediate in the catalytic reduction of NAD.[39,40] This development opens the door for modified complexes, as they can help influence H migration onto the η^5-ring via select R groups that can direct that migration. Various substituents on substituted cyclopentadienes may facilitate and/or direct substrates into best alignment with the metal center. As a result, this may lead to unique complexes with catalytic properties yet to be explored. In addition to catalysis, chain length of $\eta^5\text{-Me}_4C_5R$ rhodium and iridium dimeric complexes has been shown to affect biological activity.[12,41,42] Therefore, expanding the library of varying chain lengths is of particular interest. However, syntheses of most derivatized $\eta^5\text{-Me}_4C_5R$ rhodium and iridium dimeric complexes proceed with low yields.[11,38,43−45] As a result, we have investigated a more efficient procedure than the conventional method, which aims to exploit the benefits of a microwave reactor.

Microwave reactors have been shown to expedite the synthesis of organic and organometallic reactions, providing an alternative to time-consuming conventional techniques.[46−50] Traditionally, the synthesis of rhodium and iridium dimers requires alcoholic solvents, and these solvents are excellent hydrogen-bonding solvents for microwave irradiation. In addition, the increased temperature and pressure provided by a closed system used in the microwave reactors are advantageous synthetic conditions that are absent in benchtop reflux.

Modified $\eta^5\text{-Me}_4C_5R$ rhodium and iridium dimers have been explored, but not to the depth that would be required to understand how "R" affects sandwich and half-sandwich compound chemistry. Moreover, most of the dimers previously reported were synthesized in low yield. The work reported herein describes the successful use of a microwave reactor to

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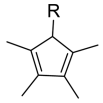
synthesize iridium and rhodium dimeric cyclopentadienyl complexes with yields ranging from 47% to 96%. This alternate approach was developed based on modifications to previously reported methodology in order to provide an efficient and cost-effective pathway to further rhodium and iridium dimers. This article describes the highly efficient, microwave reactor assisted synthesis of a series of η^5-ring (η^5-Me_4C_5R) complexes in only 1 h.

RESULTS AND DISCUSSION

General Comments and Naming Scheme. The numbering scheme used throughout this paper to discuss the various ligands and corresponding complexes may be found in Chart 1.

Chart 1. List of Various HMe_4C_5R Dienes Synthesized



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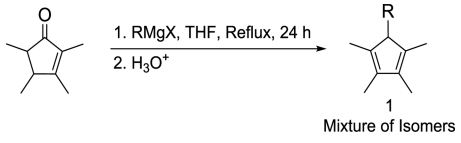
1a = R = CH_2CH_3 1b = R = $(CH_2)_2CH_3$
1c = R = $CH(CH_3)_2$ 1d = R = $(CH_2)_3CH_3$
1e = R = $CH_2CH(CH_3)_2$ 1f = R = $CH(CH_3)(CH_2CH_3)$
1g = R = $(CH_2)_4CH_3$ 1h = R = $(CH_2)_5CH_3$
1i = R = $(CH_2)_6CH_3$ 1j = R = $(CH_2)_7CH_3$
1k = R = Ph 1l = R = CH_2Ph
1m = R = $(CH_2)_2Ph$ 1n = R = Cyh
1o = R = Cyp

Cyclopentadienyl Ligand Synthesis. One approach to synthesizing HMe_4C_5R dienes is via lithiation of 2-bromo-2-butene followed by reaction with the appropriate ester or lactone.[10,51] This synthesis requires multiple steps and is an unfavorable method for producing a series of HMe_4C_5R ligands. Therefore, we decided a more rational approach to synthesizing a series of HMe_4C_5R ligands is via Grignard reactions with 2,3,4,5-tetramethylcyclopent-2-enone. While this has been used previously to make pentamethylcyclopentadiene[52] and a few other unsymmetrically substituted pentaalkylcyclopentadienyl compounds,[53,54] we extend this method to utilize a wide variety of Grignard reagents that are commercially available to develop an extensive library of unsymmetrical Cp*-type ligands and Rh and Ir dimers as precursors to half-sandwich compounds.

The modified HMe_4C_5R variants were synthesized via reaction of 1.25 molar equiv of a Grignard reagent and 2,3,4,5-tetramethylcyclopent-2-enone in anhydrous THF. The resulting reaction produced an alcohol intermediate; subsequently, elimination of water under acidic conditions gave the corresponding diene (Scheme 1).

Purification of the final HMe_4C_5R dienes was carried out via column chromatography on silica gel using hexanes as the eluent. The solvent was removed under reduced pressure to obtain the ligand as a yellow oil. The ^{1}H NMR spectra of the

Scheme 1. General Scheme for the Modifications of HMe_4C_5R Dienes



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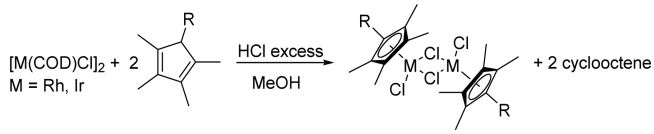
Mixture of Isomers

HMe_4C_5R ligands are quite complex since the reaction does not form a single isomer. Multiple double-bond positions around the asymmetrically substituted ring are produced including having a double bond exo to the ring (Figures S1–S6). Fortunately, all isomers can react under the synthesis conditions to form the desired cyclopentadienyl metal complexes.

Microwave Synthesis vs Conventional Synthesis. Rhodium(III) and iridium(III) dimers $[(\eta^5\text{-}Me_4C_5R)MCl]_2(\mu^2\text{-}Cl)_2$ (M = Rh, Ir) are conventionally obtained from refluxing $MCl_3{\cdot}xH_2O$ and pentamethylcyclopentadiene in aqueous alcohol for 36–48 h.[55] In addition to long reaction times, conventional syntheses of $[(\eta^5\text{-}Me_4C_5R)MCl]_2(\mu^2\text{-}Cl)_2$ (M = Rh, Ir) pentasubstituted cyclopentadiene derivatives yield less than 50% in some cases.[11,38,43−45] An alternative to the conventional synthesis of $[(\eta^5\text{-}Me_4C_5R)MCl]_2(\mu^2\text{-}Cl)_2$ involves oxidation of the rhodium(I) and iridium(I) cyclooctadiene, COD, dimers with concentrated HCl.[56] As COD is displaced with stronger coordinating ligands, dimeric cyclooctadiene compounds are excellent precursors to cyclopentadienyl dimers that are more challenging to synthesize. Therefore, the synthesis of modified pentasubstituted cyclopentadienyl iridium and rhodium dimeric species was carried out using an adaptation of a previously reported literature procedure (Scheme 2) in combination with a microwave reactor.[56]

Scheme 2. General Scheme for the Synthesis of $[(\eta^5\text{-}Me_4C_5R)MCl]_2(\mu^2\text{-}Cl)_2$ from $[M(COD)]_2(\mu^2\text{-}Cl)_2$ (M = Rh, Ir)



The reaction of $[M(COD)]_2(\mu^2\text{-}Cl)_2$ with 3.5–5 equiv of the HMe_4C_5R in the presence of HCl led to formation of the corresponding $[(\eta^5\text{-}Me_4C_5R)MCl]_2(\mu^2\text{-}Cl)_2$. For rhodium, the yellow suspension of $[Rh(COD)]_2(\mu^2\text{-}Cl)_2$ and diene was microwaved for 1 h to yield a red precipitate or a red solution. Similarly, for iridium, the orange suspension formed an orange precipitate or an orange solution after being microwaved for 1 h. In both syntheses, the solvent was removed under reduced pressure and the crude product was recrystallized from dichloromethane (DCM) and hexanes to yield the desired product as a red powder (Rh) or an orange powder (Ir). Upon removal of the sample from the microwave, we noticed a small amount of byproduct, which was decanted from the methanolic solution of the dimer prior to the workup. Further investigation of this byproduct led us to identify excess diene, as expected, as well as cyclooctene by NMR spectroscopy (Figure S67). This finding contrasts that of an earlier publication suggesting cyclooctane is the fate of the reduced diene.[56]

The iridium dimers were obtained in yields ranging from 47% to 96% (Table 1), whereas the rhodium dimers were obtained in yields ranging from 50% to 89% (Table 2). A few reactions of rhodium complexes did not go to completion, giving instead a mixture of desired product and starting material. This phenomenon was not observed for reactions of iridium complexes, which suggests that $[Rh(COD)]_2(\mu^2\text{-}Cl)_2$ does not oxidize as readily as $[Ir(COD)]_2(\mu^2\text{-}Cl)_2$. This leads us to the conclusion that the rate of oxidation of [Rh-

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Table 1. Comparison of Iridium Dimers Synthesized Conventionally and with a Microwave Reactor

iridium dimer	conventional yield[a]	microwave yield[b,c]	overall yield[e]
2a	45%, (16%)[44]	50%	46%
2b	17%	61%	57%
2c	56%	70%	64%
2d	20%	55%	51%
2e	NR[d]	76%	70%
2f	NR[d]	96%	88%
2g	16%	86%	79%
2h	9%	57%	52%
2i	4%	47%	43%
2j	(58%)[61]	83%	77%
2k	(39%)[62]	69%	64%
2l	42%	87%	80%
2m	23%	84%	78%
2n	49%	48%	45%
2o	NR[d]	60%	55%

[a]The reaction was carried out using $IrCl_3 \cdot xH_2O$ and the corresponding ligand refluxed in MeOH for 48 h under N_2. [b]The reaction was carried out in a microwave pressure tube for 1 h. [c]Isolated yield. [d]No reaction. [e]Based on a 92% yield for $[Ir(COD)]_2(\mu^2\text{-}Cl)_2$. [f]Yields in parentheses are reported literature values.

Table 2. Comparison of Various Rhodium Dimers Synthesized Conventionally and with a Microwave Reactor

rhodium dimer	conventional yield[a]	microwave yield[b,c]	overall yield[e]
3a	(95%)[44]	79%	74%
3b	47%	80%	75%
3c	(72%),[63] (77%)[64]	50%	47%
3d	3%	63%	59%
3e		89%	83%
3f		54%[d]	51%
3g		77%	72%
3h		73%	68%
3i		52%	49%
3j		52%	49%
3k	(71%),[65] (78%)[60]	75%	70%
3l	35%	89%	83%
3m	66%, (45%)[45]	77%	72%
3n		64%[d]	60%
3o		54%[d]	51%

[a]The reaction was carried out using $RhCl_3 \cdot xH_2O$ and the corresponding ligand refluxed in MeOH for 48 h under N_2. [b]The reaction was carried out in a microwave pressure tube for 1 h. [c]Isolated yield. [d]Reacted yield. [e]Based on a 94% yield for $[Rh(COD)]_2(\mu^2\text{-}Cl)_2$. [f]Yields in parentheses are reported literature values.

$(COD)]_2(\mu^2\text{-}Cl)_2$ is slower than the rate of complex formation. The yields reported are for the conditions listed in the Experimental Section. In general, reaction performed on larger scales led to higher yields.

Microwave-facilitated reaction of modified dienes with $[M(COD)]_2(\mu^2\text{-}Cl)_2$ showed a significantly improved yield for most complexes in comparison to that obtained by conventional heating methods. The ^1H NMR pattern of the Me_4C_5R complexes is very straightforward since there is no longer an isomer issue. Modified dimers exhibit two singlets from the chemically nonequivalent methyl groups of the η^5-Me_4C_5R ring upon introduction of the R group, dissimilar to the typical $[(\eta^5\text{-}Me_5C_5)MCl]_2(\mu^2\text{-}Cl)_2$, which exhibits a singlet for all methyl groups. In the case of *sec*-butyl, more peaks are seen due to the presence of a chiral center on the ligand. All complexes synthesized exhibited a typical piano-stool arrangement with chloro bridges between the metal centers and a terminal chloride bound to the metal, similarly to other reported iridium and rhodium dimers.[11,38,44,57−60]

The conventional syntheses for rhodium dimers with long chains and saturated rings yielded numerous undesired and unidentifiable side products. Consequently, these reactions gave low yields, as the product could not be isolated from impurities, despite great efforts. As a result, only rhodium dimers with short chains or conjugated rings were successfully synthesized and purified via the conventional method. Modified cyclopentadienyl dimers synthesized via the alternative route between $[Rh(COD)]_2(\mu^2\text{-}Cl)_2$ and the appropriate HMe_4C_5R proceeded without any complications or difficulties in purifying the final product. The difficulties encountered when following the conventional synthesis emphasize not only the importance of the alternative method in synthesizing difficult dimers but also the efficiency and cost effectiveness of this synthetic pathway.

Characterization. The $[(\eta^5\text{-ring})MCl]_2(\mu^2\text{-}Cl)_2$ complexes described in this paper have been structurally characterized using high-resolution mass spectrometry (HRMS), ^1H NMR, ^{13}C NMR, X-ray diffraction (XRD), and elemental analysis. A notable trend was observed with the methylene adjacent to the η^5-ring among Me_4C_5R chains ranging from *n*-propyl to *n*-octyl. The ^1H NMR spectrum of each methylene did not show a well-resolved triplet as expected, which implies slightly hindered rotation of the alkyl chain. A variable-temperature NMR study was conducted to investigate this hypothesis using complex **2b** on a 500 MHz NMR (Figure S68). At 70 °C (a), there was little difference between the spectrum at room temperature (b). When the temperature was lowered to −10 °C (c), the methylene began to resolve into a more triplet-like shape than observed at higher temperatures. This result corroborates our hypothesis that the methylene adjacent to the η^5-ring of longer chain complexes experiences hindered rotation.

Molecular Structures. The crystal structures of complexes **2a**, **2d**, **2e**, **2f**, **2g**, **2m**, **2o**, **3a**, **3b**, **3d**, **3e**, **3g**, **3h**, **3l**, **3m**, **3n**, and **3o** were determined by single-crystal X-ray diffraction. X-ray crystallographic data are listed in the Supporting Information (Tables S1−S4), and the cif files for all structures are also available. The $[(\eta^5\text{-ring})MCl]_2(\mu^2\text{-}Cl)_2$ complexes exhibit a pseudotetrahedral, piano-stool geometry around the metal center with the η^5-ring occupying the "seat" position and three chloride ligands (two bridging and one terminal) making up the "legs" of the stool. Examination of the various metal complexes reveals little to no difference between the M−C(centroid), M−Cl, and M−Cl(bridging) bond distances. Greater variability is observed with bond angles for both iridium and rhodium complexes. Rhodium complexes had larger X_1−M−X_2, X_1−M−Cl, and X_2−M−Cl bond angles, whereas iridium complexes had a larger M−Cl−M bond angle.

A thermal ellipsoid plot of **3m**, the [bis(phenethylcyclopentadienyl)dirhodium tetrachloride) compound, is provided in Figure 1 as an exemplar. For **3m**, the asymmetric unit is half of the dinuclear complex with the full complex generated by the inversion operation. In Figure 1, the generated atoms are labeled with (i) to show they are produced by the inversion operation. Thermal ellipsoid plots and full listings of angles and bonds for 18 structures can be found in the Supporting Information. In addition, cif files are provided in the Supporting Information.

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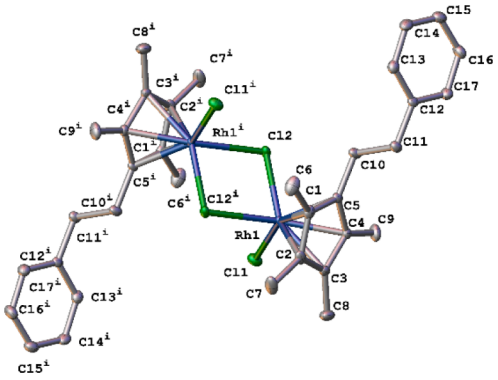

Figure 1. Thermal ellipsoid plot of the phenethylcylopentadienyl rhodium dimer, **3m**. Ellipsoids are shown at 50% probability.

It is worth noting that complexes **3a**, **3h**, and **3n** exhibited disorder within their respective structures, and those disorders were easily handled with two-site models. While most compounds crystallized without lattice solvent, complexes **3b**, **2g**, **3g**, and **3n** had solvent present within the crystal lattice. Complex **3b** crystallizes both without solvent and as a structure with dichloromethane in the lattice. Comparison of the two shows the structures have varied chain behavior, with the propyl chain projecting out from the ring in the case of the dichloromethane solvate, while the solventless structure finds those chains folding back over the Cp ring (Figures S71 and S72). In addition, the structure with dichloromethane exhibited a shorter Rh−Rh distance between metal centers (Table S3). There are short C−H−Cl interactions between the H on dichloromethane and Cl on Rh as well that could account for the differing bond distances.

At this time, this is the first complete study of modified η^5-ring dimers with group 9 metals. Each of these modified complexes showed that rhodium and iridium behave similarly in the solid state. These results suggest that various substituents on the η^5-ring do not show a significant change in structure.

Antimicrobial Results. We, and others, have been exploring the biological activity of rhodium and iridium sandwich compounds. The bulk of work examining the activity of metal complexes for medicinal purposes has been directed toward anticancer activity.[35,41,62,66] We, on the other hand, have become more interested in the activity against resistant bacterial strains such as tuberculosis and MRSA.[12,13] While our previous work was with piano-stool complexes of amino acids and ethylenediamines, we find that the dimers reported here also show high antimicrobial activity. The complexes reported herein were tested against various strains of microbes, showing that long chains impart improved activity against *S. aureus*, *E. coli*, *M. smegmatis*, and MRSA (Tables 3 and 4). Rhodium appears to have greater antimicrobial activity than its iridium counterpart. Complexes **2i** and **3i** exhibited improved activity across all microbes, with the exception of *M. smegmatis*. These results of improved potency with increasing chain length are consistent with similar findings by Lucas et al.[41] for anticancer activity. An in-depth structure−activity relationship study is under way with $[(\eta^5\text{-ring})MCl]_2(\mu^2\text{-Cl})_2$ complexes as well as their corresponding half-sandwich compounds with a variety of ligands. Overall, as we found for amino acid complexes, the dimers are most effective against mycobacteria.[12,13] Further work on additional mycobacteria including tuberculosis is planned.

Table 3. Antimicrobial Activity of Derivatized Iridium Complexes

	MIC[a] (μM)			
bacteria line	IrCp*[b]	**2g**	**2i**	**2o**
S. aureus	600 ± 0	90 ± 40	44 ± 19	184 ± 80
E. coli	630 ± 0	550 ± 0	173 ± 75	550 ± 0
M. smegmatis	10 ± 0	18 ± 0	17 ± 0	18 ± 0
MRSA 43300	630 ± 0	70 ± 0	44 ± 19	180 ± 80

[a]Minimal inhibitory concentration. [b]$[(Cp^*)IrCl]_2(\mu^2\text{-Cl})_2$. All results are the averages of triplicates and are expressed as means ± standard deviation.

Table 4. Antimicrobial Activity of Derivatized Rhodium Complexes

	MIC[a] (μM)			
bacteria line	RhCp*[b]	**3g**	**3i**	**3o**
S. aureus	400 ± 0	228 ± 100	133 ± 0	340 ± 0
E. coli	400 ± 0	680 ± 0	320 ± 0	688 ± 0
M. smegmatis	4 ± 0	5 ± 1.6	4.2 ± 1.5	6 ± 0
MRSA 43300	400 ± 0	143 ± 48	107 ± 45	344 ± 0

[a]Minimal inhibitory concentration. [b]$[(Cp^*)RhCl]_2(\mu^2\text{-Cl})_2$. All results are the averages of triplicates and are expressed as means ± standard deviation.

CONCLUSIONS

An extensive library of iridium and rhodium dimeric complexes of the form $[(\eta^5\text{-ring})MCl]_2(\mu^2\text{-Cl})_2$ was synthesized and characterized. The use of a microwave reactor reduced the conventional reaction time of 48 h to 1 h.

Until now, nine of the modified dimers have been described using the conventional method. In this paper, we report comparable, if not improved, yields via a microwave route. The other 21 modified dimers reported here allow for a complete comparison of the substituent effect on modified cyclopentadienes with various R groups between iridium and rhodium.

In summary, this work has shown that modular design is greatly facilitated by the use of a microwave reactor. This new route lessens the number and amounts of reagents used, involves less chromatography, and reduces the amount of rhodium and iridium metal lost during reactions. The range of new substituted Cp^{*R} dimers allows for examining the potential structure/activity relationships not only in the biological arena but in the catalytic arena as well.[43,64] Rhodium and iridium derivatized dimeric species are being explored further in catalysis, with preliminary results showing both iridium and rhodium dimers catalyze diols into their corresponding lactones without a need for additional ligand substitution.[34] More details on the effect of substitution of the Cp ring will be forthcoming.

EXPERIMENTAL SECTION

All materials for synthesis, purification, and characterization were used as received unless otherwise stated. Snap ring tops and 10 mL pressure tubes were purchased from CEM Corporation. $RhCl_3 \cdot xH_2O$ and $IrCl_3 \cdot xH_2O$ were purchased from Pressure Chemical (Pittsburgh, PA, USA). Heptylmagnesium chloride and 2,3,4,5-tetramethylcyclopent-2-en-1-one were purchased from Alfa Aesar (Ward Hill, MA, USA). Reagent-grade solvents, ethyl-tetramethylcyclopentadiene (**1a**), tetramethyl(*n*-propyl)cyclopentadiene (**1b**), benzylmagnesium chloride, cyclohexylmagnesium chloride, cyclopentylmagnesium bromide, phenylmagnesium bromide, phenethylmagnesium chloride, isopropylmagnesium

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bromide, butylmagnesium chloride, isobutylmagnesium chloride, *sec*-butylmagnesium chloride, pentylmagnesium bromide, hexylmagnesium bromide, and octylmagnesium bromide were purchased from Sigma-Aldrich (St. Louis, MO, USA). Deuterated solvents for NMR spectroscopy were obtained from Cambridge Isotope Laboratories. Elemental analyses were performed by Atlantic Microlabs (Norcross, GA, USA). ^{1}H NMR and ^{13}C NMR spectra were collected on a Varian MR-400 NMR spectrometer. ^{13}C NMR spectra were correspondingly recorded at 101 MHz. HRMS were collected on an Agilent 6220 Accurate Mass TOF LC-MS.

Synthesis of HMe_4C_5R Dienes. Unless otherwise stated, all reactions were conducted under a N_2 atmosphere.

General Procedure of HMe_4C_5R Dienes. A solution of the respective Grignard reagent (18.1 mmol) in THF was added to a stirred solution of 2,3,4,5-tetramethyl-2-cyclopentenone (2.00 g, 15.2 mmol) in anhydrous THF (20 mL). The mixture was refluxed for 24 h, then cooled to 0 °C and quenched with HCl. This solution was warmed to room temperature and agitated for 2 h. The mixture was diluted with diethyl ether (30 mL) and washed with water (3 × 30 mL), and the organic layer was dried over $MgSO_4$. The products were concentrated under reduced pressure and purified by column chromatography (silica gel, hexanes) to afford the product and isomers as a yellow oil. The ^{1}H NMR spectra of the dienes are complex due to the signal overlap of the isomers. Both ^{1}H and ^{13}C NMR spectra of dienes **1i**, **1m**, and **1n** are reproduced in the Supporting Information (Figures S1−S6) to illustrate that complexity. We relied on HRMS and success in further reactions as proof of synthesis. Dienes **1c**−**1h** and **1j**−**1o** have previously been reported.[11,38,67−73]

*Synthesis of 5-isopropyl-2,3,4,5-tetramethylcyclopenta-1,3-diene (**1c**).* Yield: 1.04 g (44%).

*Synthesis of 5-butyl-1,2,3,4-tetramethylcyclopenta-1,3-diene (**1d**).* Yield: 2.53 g (98%).

*Synthesis of 5-isobutyl-1,2,3,4-tetramethylcyclopenta-1,3-diene (**1e**).* Yield: 2.49 g (96%). HRMS/APCI+ (*m*/*z*): calcd for $C_{13}H_{23}$ 179.1800; found 179.1798.

*Synthesis of 5-(sec-butyl)-1,2,3,4-tetramethylcyclopenta-1,3-diene (**1f**).* Yield: 1.02 g (40%). HRMS/APCI+ (*m*/*z*): calcd for $C_{13}H_{23}$ 179.1800; found 179.1794.

*Synthesis of 1,2,3,4-tetramethyl-5-pentylcyclopenta-1,3-diene (**1g**).* Yield: 1.76 g (63%). HRMS/ESI+ (*m*/*z*): calcd for $C_{14}H_{23}$ 191.1800; found 191.1792.

*Synthesis of 5-hexyl-1,2,3,4-tetramethylcyclopenta-1,3-diene (**1h**).* Yield: 0.651 g (52%).

*Synthesis of 5-heptyl-1,2,3,4-tetramethylcyclopenta-1,3-diene (**1i**).* Yield: 2.53 g (79%). HRMS/APCI+ (*m*/*z*): calcd for $C_{16}H_{29}$ 221.2269; found 221.2264.

*Synthesis of 1,2,3,4-tetramethyl-5-octylcyclopenta-1,3-diene (**1j**).* Yield: 2.61g (77%).

*Synthesis of (2,3,4,5-tetramethylcyclopenta-2,4-dien-1-yl)-benzene (**1k**).* Yield: 2.78 g (97%).

*Synthesis of ((2,3,4,5-tetramethylcyclopenta-2,4-dien-1-yl)-methyl)benzene (**1l**).* Yield: 2.58 g (84%).

*Synthesis of (2-(2,3,4,5-tetramethylcyclopenta-2,4-dien-1-yl)-ethyl)benzene (**1m**).* Yield: 2.51 g (77%). HRMS/APCI+ (*m*/*z*): calcd for $C_{17}H_{23}$ 227.1800; found 227.1799.

*Synthesis of (2,3,4,5-tetramethylcyclopenta-2,4-dien-1-yl)-cyclohexane (**1n**).* Yield: 2.18 g (74%).

*Synthesis of 2,3,4,5-tetramethyl[1,1′-bi(cyclopentane)]-2,4-diene (**1o**).* Yield: 1.57 g (57%). HRMS/APCI+ (*m*/*z*): calcd for $C_{14}H_{21}$ 191.1800; found 191.1794.

General Procedure for Synthesis of $[(\eta^5\text{-}Me_4C_5R)IrCl]_2(\mu^2\text{-}Cl)_2$. A microwave pressure tube was fitted with the appropriate amounts of the respective $[Ir(COD)]_2(\mu^2\text{-}Cl)_2$, HMe_4C_5R, in 4 mL of methanol with 0.5 mL of concentrated HCl. The reaction mixture was heated to 115 °C at 50 W and 150 psi and held for 1 h, yielding an orange solution. The solvent was evaporated under reduced pressure, and the resulting powder recrystallized from DCM and cold hexanes, collected via filtration, and washed with cold hexanes. Complexes **2a**, **2b**, **2c**, **2k**, **2l**, **2m**, and **2n** have previously been reported and were identified via spectral comparison.[11,38,44,74,75]

*Synthesis of $[Cp^{*ethyl}IrCl]_2(\mu^2\text{-}Cl)_2$ (**2a**).* Following the general procedure, $[Ir(COD)]_2(\mu^2\text{-}Cl)_2$ (0.100 g, 0.149 mmol), **1a** (0.045 g, 0.298 mmol), and 0.5 mL of HCl were reacted in methanol (4 mL) to give **2a** (0.061 g, 50% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.16−2.10 (q, 4H, $^2J_{HH}$ = 7.7 Hz, 2 CH_2), 1.58 (s, 12H, 4 $CpCH_3$), 1.56 (s, 12H, 4 $CpCH_3$), 1.07−1.03 (t, 6H, $^2J_{HH}$ = 7.7 Hz, 2 CH_3). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 89.06 (*Cp*C), 86.49 (*Cp*C), 86.18 (*Cp*C), 17.56 (CH_2), 11.63 (CH_3), 9.30 ($CpCH_3$), 9.13 ($CpCH_3$). Anal. Calcd for $C_{22}H_{34}Cl_4Ir_2$: C, 32.04; H, 4.16. Found: C, 31.88; H, 3.96.

*Synthesis of $[Cp^{*n\text{-}propyl}IrCl]_2(\mu^2\text{-}Cl)_2$ (**2b**).* Following the general procedure, $[Ir(COD)]_2(\mu^2\text{-}Cl)_2$ (0.100 g, 0.149 mmol), **1b** (0.0851 g, 0.521 mmol), and 0.5 mL of HCl were reacted in methanol (4 mL) to give **2b** (0.078 g, 61% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.13−2.09 (m, 4H, 2 $CH_2CH_2CH_3$), 1.59 (s, 12H, 4 $CpCH_3$), 1.57 (s, 12H, 4 $CpCH_3$), 1.49−1.40 (m, 4H, 2 $CH_2CH_2CH_3$), 0.94−0.90 (app t, 6H, 2 CH_3). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 87.96 (*Cp*C), 86.52 (*Cp*C), 86.52 (*Cp*C), 26.16 ($CH_2CH_2CH_3$), 21.00 ($CH_2CH_2CH_3$), 14.36 (CH_3), 9.55 ($CpCH_3$), 9.47 ($CpCH_3$). HRMS/ESI+ (*m*/*z*): $C_{24}H_{38}[^{193}Ir]_2Cl_3$ 817.1298; found 817.1331.

*Synthesis of $[Cp^{*isopropyl}IrCl]_2(\mu^2\text{-}Cl)_2$ (**2c**).* Following the general procedure, $[Ir(COD)]_2(\mu^2\text{-}Cl)_2$ (0.100 g, 0.149 mmol), **1c** (0.0851 g, 0.521 mmol), and 0.5 mL of HCl were reacted in methanol (4 mL) to give **2c** (0.089 g, 70% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.54−2.43 (m, 2H, 2 *CH*), 1.68 (s, 12H, 4 $CpCH_3$), 1.60 (s, 12H, 4 $CpCH_3$), 1.29−1.27 (d, 12H, $^2J_{HH}$ = 7.1 Hz, 4 CH_3). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 90.38 (*Cp*C), 86.47 (*Cp*C), 86.21 (*Cp*C), 25.39 ($CH(CH_3)_2$), 20.78 ($CH(CH_3)_2$), 10.40 ($CpCH_3$), 9.68 $CpCH_3$). HRMS/ESI+ (*m*/*z*): $C_{24}H_{38}[^{193}Ir]_2Cl_3$ 817.1298; found 817.1326. Anal. Calcd for $C_{24}H_{38}Cl_4Ir_2$: C, 33.80; H, 4.49. Found: C, 34.01; H, 4.48.

*Synthesis of $[Cp^{*n\text{-}butyl}IrCl]_2(\mu^2\text{-}Cl)_2$ (**2d**).* Following the general procedure, $[Ir(COD)]_2(\mu^2\text{-}Cl)_2$ (0.300 g, 0.447 mmol), **1d** (0.159 g, 0.893 mmol), and 0.5 mL of HCl were reacted in methanol (4 mL) to give **2d** (0.109 g, 55% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.15−2.11 (m, 4H, 2 $CH_2(CH_2)_2CH_3$), 1.60 (s, 12H, 4 $CpCH_3$), 1.58 (s, 12H, 4 $CpCH_3$), 1.41−1.28 (m, 8H, 2 $CH_2(CH_2)_2CH_3$), 0.91−0.88 (app t, 6H, 2 CH_3). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 88.26 (*Cp*C), 86.57 (*Cp*C), 86.55 (*Cp*C), 29.97 ($CH_2CH_2CH_2CH_3$), 24.05 ($CH_2CH_2CH_2CH_3$), 23.00 ($CH_2CH_2CH_2CH_3$), 14.04 (CH_3), 9.55 ($CpCH_3$), 9.51 ($CpCH_3$). HRMS/ESI+ (*m*/*z*): $C_{26}H_{42}[^{193}Ir]_2Cl_3$ 845.1611; found 845.1617. Anal. Calcd for $C_{26}H_{42}Cl_4Ir_2$: C, 35.45; H, 4.81. Found: C, 35.61; H, 4.80.

*Synthesis of $[Cp^{*isobutyl}IrCl]_2(\mu^2\text{-}Cl)_2$ (**2e**).* Following the general procedure, $[Ir(COD)]_2(\mu^2\text{-}Cl)_2$ (0.200 g, 0.298 mmol), **1e** (0.186 g, 1.04 mmol), and 0.5 mL of HCl were reacted in methanol (4 mL) to give **2e** (0.199 g, 76% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.06−2.04 (d, 4H, $^2J_{HH}$ = 7.5 Hz, 2 CH_2), 1.77−1.66 (m, 2H, 2 *CH*), 1.61 (s, 12H, 4 $CpCH_3$), 1.60 (s, 12H, 4 $CpCH_3$), 0.90−0.89 (d, 12H, $^2J_{HH}$ = 6.7 Hz, 4 CH_3). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 87.48 (*Cp*C), 87.00 (*Cp*C), 86.59 (*Cp*C), 33.13 ($CH_2CH(CH_3)_2$), 27.91 ($CH_2CH(CH_3)_2$), 22.83 ($CH_2CH(CH_3)_2$), 10.08 ($CpCH_3$), 9.55 ($CpCH_3$). HRMS/ESI+ (*m*/*z*): $C_{26}H_{42}[^{193}Ir]_2Cl_3$ 845.1611, found 845.1602. Anal. Calcd for $C_{26}H_{42}Cl_4Ir_2$: C, 35.45; H, 4.81. Found: C, 35.66; H, 4.70.

*Synthesis of $[Cp^{*sec\text{-}butyl}IrCl]_2(\mu^2\text{-}Cl)_2$ (**2f**).* Following the general procedure, $[Ir(COD)]_2(\mu^2\text{-}Cl)_2$ (0.500 g, 0.744 mmol), **1f** (0.465 g, 2.61 mmol), and 0.5 mL of HCl were reacted in methanol (4 mL) to give **2f** (0.6276 g, 96% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.23−2.18 (m, 2H, *CH*), 1.68 (s, 6H, 2 $CpCH_3$), 1.66−1.67 (m, 2H, *CHH*), 1.66 (s, 6H, 2 $CpCH_3$), 1.62 (s, 6H, 2 $CpCH_3$), 1.58 (s, 6H, 2 $CpCH_3$), 1.53−1.43 (m, 2H, *CHH*), 1.33−1.31 (d, 6H, $^2J_{HH}$ = 7.2 Hz, CH_3CH), 0.90−0.86 (t, 6H, $^2J_{HH}$ = 7.4 Hz, CH_2CH_3). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 91.03 (*Cp*C), 90.44 (*Cp*C), 87.08 (*Cp*C), 86.29 (*Cp*C), 85.01 (*Cp*C), 32.04 (*CH*), 27.71 (CH_2), 18.47 (CH_3CH), 12.84 (CH_3CH_2), 10.77 ($CpCH_3$), 10.40 ($CpCH_3$), 9.82 ($CpCH_3$), 9.61 ($CpCH_3$). HRMS/ESI+ (*m*/*z*): $C_{26}H_{42}[^{193}Ir]_2Cl_3$ 845.1611; found 845.1695. Anal. Calcd for $C_{26}H_{42}Cl_4Ir_2$: C, 35.45; H, 4.81. Found: C, 35.19; H, 4.71.

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Synthesis of [Cp$^{n\text{-pentyl}}$IrCl]$_2$(μ^2-Cl)$_2$ (**2g**).* Following the general procedure, [Ir(COD)]$_2$(μ^2-Cl)$_2$ (0.100 g, 0.149 mmol), **1g** (0.100 g, 0.521 mmol), and 0.5 mL of HCl were reacted in methanol (4 mL) to give **2g** (0.116 g, 86% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.14−2.11 (m, 4H, 2 CH_2(CH$_2$)$_3$CH$_3$), 1.61 (s, 12H, 4 CpCH_3), 1.59 (s, 12H, 4 CpCH_3), 1.43−1.34 (m, 4H, 2 CH$_2$CH_2(CH_2)$_2$CH$_3$), 1.34−1.24 (m, 8H, 2 CH$_2$CH$_2$(CH_2)$_2$CH$_3$), 0.88−0.85 (app t, 6H, 2 CH_3). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 88.23 (CpC), 86.49 (CpC), 86.46 (CpC), 31.90 (CH$_2$), 27.43 (CH$_2$), 24.16 (CH$_2$), 22.48 (CH$_2$), 13.95 (CH$_3$), 9.51 (CpCH$_3$), 9.48 (CpCH$_3$). HRMS/ESI+ (m/z): $C_{28}H_{46}[^{193}Ir]_2Cl_3$ 873.1924; found 873.1965. Anal. Calcd for $C_{28}H_{46}Cl_4Ir_2$: C, 37.00; H, 5.10. Found: C, 37.60; H, 5.08.

Synthesis of [Cp$^{n\text{-hexyl}}$IrCl]$_2$(μ^2-Cl)$_2$ (**2h**).* Following the general procedure, [Ir(COD)]$_2$(μ^2-Cl)$_2$ (0.300 g, 0.447 mmol), **1h** (0.230 g, 1.12 mmol), and 0.5 mL of HCl were reacted in methanol (4 mL) to give **2h** (1.56 g, 52% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.14−2.10 (m, 4H, 2 CH_2(CH$_2$)$_4$CH$_3$), 1.61 (s, 12H, 4 CpCH_3), 1.59 (s, 12H, 4 CpCH_3), 1.42−1.23 (m, 16H, 2 CH$_2$(CH_2)$_4$CH$_3$), 0.88−0.84 (app t, 6H, 2 CH_3). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 88.34 (CpC), 86.60 (CpC), 86.56 (CpC), 31.65 (CH$_2$), 29.53 (CH$_2$), 27.76 (CH$_2$), 24.26 (CH$_2$), 22.62 (CH$_2$), 14.16 (CH$_3$), 9.54 (CpCH$_3$), 9.51 (CpCH$_3$). HRMS/ESI+ (m/z): $C_{30}H_{50}[^{193}Ir]_2Cl_3$ 901.2237; found 901.2145. Anal. Calcd for $C_{30}H_{50}Cl_4Ir_2$: C, 38.46; H, 5.38. Found: C, 38.46; H, 5.38.

Synthesis of [Cp$^{n\text{-heptyl}}$IrCl]$_2$(μ^2-Cl)$_2$ (**2i**).* Following the general procedure, [Ir(COD)]$_2$(μ^2-Cl)$_2$ (0.250 g, 0.372 mmol), **1i** (0.287 g, 1.30 mmol), and 0.5 mL of HCl were reacted in methanol (4 mL) to give **2i** (0.168, 47% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.14−2.10 (m, 4H, 2 CH_2(CH$_2$)$_5$CH$_3$), 1.60 (s, 12H, 4 CpCH_3), 1.59 (s, 12H, 4 CpCH_3), 1.41−1.34 (m, 4H, 2 CH$_2$CH_2(CH$_2$)$_4$CH$_3$), 1.31−1.21 (m, 16H, CH$_2$CH$_2$(CH_2)$_4$CH$_3$), 0.88−0.84 (app t, 6H, 2 CH_3). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 88.32 (CpC), 86.59 (CpC), 86.53 (CpC), 31.82 (CH$_2$), 29.84 (CH$_2$), 29.18 (CH$_2$), 27.81 (CH$_2$), 24.27 (CH$_2$), 22.75 (CH$_2$), 14.23 (CH$_3$), 9.57 (CpCH$_3$), 9.52 (CpCH$_3$). HRMS/ESI+ (m/z): $C_{32}H_{54}[^{193}Ir]_2Cl_3$ 929.2550; found 929.2531. Anal. Calcd for $C_{32}H_{54}Cl_4Ir_2$: C, 39.83; H, 5.64. Found: C, 39.89; H, 5.60.

Synthesis of [Cp$^{n\text{-octyl}}$IrCl]$_2$(μ^2-Cl)$_2$ (**2j**).* Following the general procedure, [Ir(COD)]$_2$(μ^2-Cl)$_2$ (0.200 g, 0.298 mmol), **1j** (0.349 g, 1.49 mmol), and 0.5 mL of HCl were reacted in methanol (4 mL) to give **2j** (0.246 g, 83% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.14−2.10 (app t, 4H, 2 CH_2(CH$_2$)$_6$CH$_3$), 1.61 (s, 12H, 4 CpCH_3), 1.59 (s, 12H, 4 CpCH_3), 1.44−1.34 (m, 4H, 2 CH$_2$CH_2(CH$_2$)$_5$CH$_3$), 1.33−1.19 (m, 20H, 2 CH$_2$CH$_2$(CH_2)$_5$CH$_3$), 0.88−0.85 (app t, 6H, 2 CH_3). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 88.33 (CpC), 86.60 (CpC), 86.54 (CpC), 31.95 (CH$_2$), 29.88 (CH$_2$), 29.47 (CH$_2$), 29.27 (CH$_2$), 27.81 (CH$_2$), 24.28 (CH$_2$), 22.78 (CH$_2$), 14.23 (CH$_3$), 9.58 (CpCH$_3$), 9.54 (CpCH$_3$). HRMS/ESI+ (m/z): $C_{34}H_{58}[^{193}Ir]_2Cl_3$ 957.2863; found 957.2828. Anal. Calcd for $C_{34}H_{58}Cl_4Ir_2$: C, 41.12; H, 5.89. Found: C, 41.28; H, 5.74.

Synthesis of [Cp^{phenyl}IrCl]$_2$(μ^2-Cl)$_2$ (**2k**).* Following the general procedure, [Ir(COD)]$_2$(μ^2-Cl)$_2$ (0.250 g, 0.372 mmol), **1k** (0.295 g, 1.49 mmol), and 0.5 mL of HCl were reacted in methanol (4 mL) to give **2k** (0.237 g, 69% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58−7.55 (m, 4H, ArH), 7.37−7.34 (m, 6H, ArH), 1.72 (s, 12H, 4 CpCH_3), 1.63 (s, 12H, 4 CpCH_3). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 130.34 (ArC), 129.94 (ArC), 128.79 (ArC), 128.58 (ArC), 93.64 (CpC), 85.61 (CpC), 82.10 (CpC), 10.50 (CpCH$_3$), 9.77 (CpCH$_3$). HRMS/ESI+ (m/z): calcd for $C_{30}H_{34}[^{193}Ir]_2Cl_3$ 885.0985; found 885.1018. Anal. Calcd for $C_{30}H_{34}Ir_2Cl_4$: C, 39.13; H, 3.72. Found: C, 38.89; H, 3.51.

Synthesis of [Cp^{benzyl}IrCl]$_2$(μ^2-Cl)$_2$ (**2l**).* Following the general procedure, [Ir(COD)]$_2$(μ^2-Cl)$_2$ (0.100 g, 0.149 mmol), **1l** (0.111 g, 0.521 mmol), and 0.5 mL of HCl were reacted in methanol (4 mL) to give **2l** (0.123 g, 87% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30−7.27 (m, 2H, ArH), 7.26−7.25 (m, 2H, ArH), 7.23−7.18 (m, 2H, ArH), 7.11−7.09 (m, 4H, ArH), 3.57 (s, 4H, 2 CH_2), 1.65 (s, 12H, 4 CpCH_3), 1.63 (s, 12H, 4 CpCH_3). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 136.97 (ArC), 128.88 (ArC), 128.38 (ArC), 126.90 (ArC), 87.68 (CpC), 86.90 (CpC), 85.93 (CpC), 30.58 (CH$_2$), 9.97 (CpCH$_3$), 9.53 (CpCH$_3$). HRMS/ESI+ (m/z): calcd for $C_{32}H_{38}[^{193}Ir]_2Cl_3$ 913.1298; found 913.1347. Anal. Calcd for $C_{32}H_{38}Ir_2Cl_4$: C, 40.51; H, 4.04. Found: C, 40.40; H, 3.98.

Synthesis of [Cp^{phenethyl}IrCl]$_2$(μ^2-Cl)$_2$ (**2m**).* Following the general procedure, [Ir(COD)]$_2$(μ^2-Cl)$_2$ (0.200 g, 0.298 mmol), **1m** (0.336 g, 1.49 mmol), and 0.5 mL of HCl were reacted in methanol (4 mL) to give **2m** (0.245 g, 84% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25−7.16 (m, 6H, ArH), 7.04−7.02 (m, 4H, ArH), 2.77−2.73 (t, 4H, $^2J_{HH}$ = 7.3 Hz, 2 PhCH$_2$CH$_2$), 2.48−2.45 (t, 4H, $^2J_{HH}$ = 7.3 Hz, 2 PhCH$_2$CH$_2$), 1.55 (s, 12H, 4 CpCH_3), 1.36 (s, 12H, 4 CpCH_3). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 140.14 (ArC), 128.64 (ArC), 128.46 (ArC), 126.35 (ArC), 87.22 (CpC), 86.30 (CpC), 86.29 (CpC), 33.60 (PhCH$_2$CH$_2$), 26.60 (PhCH$_2$CH$_2$), 9.27 (CpCH$_3$), 9.09 (CpCH$_3$). HRMS/ESI+ (m/z): calcd for $C_{34}H_{42}[^{193}Ir]_2Cl_3$ 941.1611; found 941.1616. Anal. Calcd for $C_{34}H_{42}Ir_2Cl_4$: C, 41.80; H, 4.33. Found: C, 41.92; H, 4.22.

Synthesis of [Cp^{cyclohexyl}IrCl]$_2$(μ^2-Cl)$_2$ (**2n**).* Following the general procedure, [Ir(COD)]$_2$(μ^2-Cl)$_2$ (0.200 g, 0.298 mmol), **1n** (0.152 g, 0.744 mmol), and 0.5 mL of HCl were reacted in methanol (4 mL) to give **2n** (0.079 g, 48% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.08−2.01 (m, 2H, 2 CH), 1.93−1.89 (m, 4H, 2 CH$_2$), 1.78−1.74 (m, 4H, 2 CH$_2$), 1.67 (s, 12H, 4 CpCH_3), 1.59 (s, 12H, 4 CpCH_3), 1.43−1.22 (m, 10H, CH$_2$), 1.18−1.09 (m, 2H, CH$_2$). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 90.77 (CpC), 85.99 (CpC), 84.81 (CpC), 35.75 (CH), 30.88 (CH$_2$), 27.10 (CH$_2$), 26.20 (CH$_2$), 10.70 (CpCH$_3$), 9.74 (CpCH$_3$). HRMS/ESI+ (m/z): calcd for $C_{30}H_{46}[^{193}Ir]_2Cl_3$ 897.1924; found 897.1946. Anal. Calcd for $C_{30}H_{46}Ir_2Cl_4$: C, 38.62; H, 4.97. Found: C, 38.77; H, 4.92.

Synthesis of [Cp^{cyclopentyl}IrCl]$_2$(μ^2-Cl)$_2$ (**2o**).* Following the general procedure, [Ir(COD)]$_2$(μ^2-Cl)$_2$ (0.250 g, 0.372 mmol), **1o** (0.248 g, 1.30 mmol), and 0.5 mL of HCl were reacted in methanol (4 mL) to give **2o** (0.213 g, 59% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.63−2.54 (m, 2H, 2 CH), 2.09−2.02 (m, 4H, 2 CH$_2$), 1.74−1.71 (m, 2H, CH$_2$), 1. 68 (s, 12H, 4 CpCH_3), 1.67−1.60 (m, 10H, CH$_2$), 1.59 (s, 12H, 4 CpCH_3). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 89.60 (CpC), 86.07 (CpC), 85.92 (CpC), 36.05 (CH), 31.34 (CH$_2$), 26.67 (CH$_2$), 10.46 (CpCH$_3$), 9.72 (CpCH$_3$). HRMS/ESI+ (m/z): calcd for $C_{28}H_{42}[^{193}Ir]_2Cl_3$ 869.1611; found 869.1567.

General Procetdure for Synthesis of [(η^5-Me$_4$C$_5$R)RhCl]$_2$(μ^2-Cl)$_2$. A microwave pressure tube was fitted with the appropriate amounts of the respective [Rh(COD)]$_2$(μ^2-Cl)$_2$, HMe$_4$C$_5$R, in 4 mL of methanol with 0.5 mL of concentrated HCl. The reaction mixture was heated to 115 °C at 50 W and 150 psi and held for 1 h, yielding a red solution. The solvent was evaporated under reduced pressure, and the resulting powder recrystallized from DCM and cold hexanes, collected via filtration, and washed with cold hexanes. Complexes **3a**, **3c**, **3k**, **3m**, and **3n** have previously been reported and were identified by HRMS as well as by comparison of NMR spectra with those reported in the literature.[43−45,63,65]

Synthesis of [Cp^{ethyl}RhCl]$_2$(μ^2-Cl)$_2$ (**3a**).* Following the general procedure, [Rh(COD)]$_2$(μ^2-Cl)$_2$ (0.250 g, 0.507 mmol), **1a** (0.244 g, 1.62 mmol), and 0.5 mL of HCl were reacted in methanol (4 mL) to give **3a** (0.259 g, 79% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.27−2.23 (q, 4H, $^2J_{HH}$ = 7.7 Hz, 2 CH$_2$), 1.61 (s, 12H, 4 CpCH_3), 1.60 (s, 12H, 4 CpCH_3), 1.01−0.97 (t, 6H, $^2J_{HH}$ = 7.7 Hz, 2 CH$_3$). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 97.41−97.31 (d, J_{CRh} = 9.3 Hz, CpC), 94.76−94.66 (d, J_{CRh} = 9.2 Hz, CpC), 94.00−93.91 (d, J_{CRh} = 9.1 Hz, CpC), 17.61 (CH$_2$), 11.55 (CH$_3$), 9.51 (CpCH$_3$), 9.30 (CpCH$_3$). HRMS/ESI+ (m/z): calcd for $C_{22}H_{34}Cl_3Rh_2$ 608.9836; found 608.9761.

Synthesis of [Cp$^{n\text{-propyl}}$RhCl]$_2$(μ^2-Cl)$_2$ (**3b**).* Following the general procedure, [Rh(COD)]$_2$(μ^2-Cl)$_2$ (0.150 g, 0.304 mmol), **1b** (0.200 g, 1.22 mmol), and 0.5 mL of HCl were reacted in methanol (4 mL) to give **3b** (0.164 g, 80% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.27−2.23 (m, 4H, 2 CH$_2$CH$_2$CH$_3$), 1.64 (s, 12H, 4 CpCH_3), 1.62 (s, 12H, 4 CpCH_3), 1.45−1.36 (m, 4H, 2 CH$_2$CH$_2$CH$_3$), 0.94−0.91 (app t, 6H, 2 CH$_3$). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 96.19−96.10 (d, J_{CRh} = 9.4 Hz, CpC), 94.73−94.64 (d, J_{CRh} = 9.2 Hz, CpC), 94.36−94.27 (d, J_{CRh} = 9.3 Hz, CpC), 26.06 (CH$_2$CH$_2$CH$_3$), 20.91 (CH$_2$CH$_2$CH$_3$), 14.33 (CH$_3$), 9.61 (CpCH$_3$), 9.55 (CpCH$_3$). HRMS/ESI+ (m/z):

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calcd for $C_{24}H_{38}Cl_3Rh_2$ 637.0149; found 637.0173. Anal. Calcd for $C_{24}H_{38}Cl_4Rh_2$: C, 42.76; H, 5.68. Found: C, 42.47; H, 5.68.

Synthesis of [Cp^{isopropyl}RhCl]$_2$(μ^2-Cl)$_2$ (**3c**).* Following the general procedure, [Rh(COD)]$_2$(μ^2-Cl)$_2$ (0.100 g, 0.203 mmol), **1c** (0.112 g, 0.710 mmol), and 0.5 mL of HCl were reacted in methanol (4 mL) to give **3c** (0.067 g, 50% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.66−2.55 (m, 2H, 2 C*H*), 1.72 (s, 12H, 4 CpCH_3), 1.60 (s, 12H, 4 CpCH_3), 1.31−1.29 (d, 12H, $^2J_{HH}$ = 7.1 Hz, 4 CH_3). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 97.71−97.62 (d, J_{CRh} = 9.1 Hz, Cp*C*), 95.44−95.34 (d, J_{CRh} = 10.0 Hz, Cp*C*), 94.22−94.13 (d, J_{CRh} = 9.2 Hz, Cp*C*), 25.09 (CH(CH$_3$)$_2$), 20.79 (CH(*C*H$_3$)$_2$), 10.51 (Cp*C*H$_3$), 9.62 (Cp*C*H$_3$). HRMS/ESI+ (*m*/*z*): calcd for $C_{24}H_{38}Cl_3Rh_2$ 637.0149; found 637.014.

Synthesis of [Cp$^{n\text{-}butyl}$RhCl]$_2$(μ^2-Cl)$_2$ (**3d**).* Following the general procedure, [Rh(COD)]$_2$(μ^2-Cl)$_2$ (0.200 g, 0.406 mmol), **1d** (0.289 g, 1.62 mmol), and 0.5 mL of concentrated HCl were reacted in methanol (4 mL) to give **3d** (0.180 g, 63%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.27−2.24 (m, 4H, 2 CH_2(CH$_2$)$_2$CH$_3$), 1.63 (s, 12H, 4 CpCH_3), 1.61 (s, 12H, 4 CpCH_3), 1.38−1.27 (m, 8H, 2 CH$_2$(CH_2)$_2$CH$_3$), 0.90−0.87 (app t, 6H, 2 CH_3). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 96.33−96.24 (d, J_{CRh} = 9.6 Hz, Cp*C*), 94.64−94.55 (d, J_{CRh} = 9.2 Hz, Cp*C*), 94.26−94.17 (d, J_{CRh} = 9.2 Hz, Cp*C*), 29.76, 23.85, 22.90, 13.96 (*C*H$_3$), 9.54 (Cp*C*H$_3$), 9.54 (Cp*C*H$_3$). HRMS/ESI+ (*m*/*z*): calcd for $C_{26}H_{42}Cl_3Rh_2$ 665.0462; found 665.0447. Anal. Calcd for $C_{26}H_{42}Cl_4Rh_2$, C, 44.47; H, 6.03. Found: C, 44.55; H, 5.96.

Synthesis of [Cp^{isobutyl}RhCl]$_2$(μ^2-Cl)$_2$ (**3e**).* Following the general procedure, [Rh(COD)]$_2$(μ^2-Cl)$_2$ (0.200 g, 0.406 mmol), **1e** (0.362 g, 2.03 mmol), and 0.5 mL of HCl were reacted in methanol (4 mL) to give **3e** (0.252 g, 89% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.19−2.17 (d, 4H, $^2J_{HH}$ = 7.5 Hz, 2 CH_2), 1.73−1.64 (m, 2H, 2 C*H*), 1.63 (s, 12H, 4 CpCH_3), 1.62 (s, 12H, 4 CpCH_3), 0.88−0.87 (d, 12H, $^2J_{HH}$ = 6.7 Hz, 4 CH_3). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 95.58−95.49 (d, J_{CRh} = 9.4 Hz, Cp*C*), 94.74−94.66 (d, J_{CRh} = 9.2 Hz, Cp*C*), 94.70−94.61 (d, J_{CRh} = 9.2 Hz, Cp*C*), 32.93 (*C*H$_2$CH(CH$_3$)$_2$), 27.98 (CH$_2$CH(CH$_3$)$_2$), 23.84 (CH$_2$CH(*C*H$_3$)$_2$), 10.09 (Cp*C*H$_3$), 9.58 (Cp*C*H$_3$). HRMS/ESI+ (*m*/*z*): $C_{26}H_{42}Cl_3Rh_2$ 665.0462; found 665.0459. Anal. Calcd for $C_{26}H_{42}Cl_4Rh_2$: C, 44.47; H, 6.03. Found: C, 44.18; H, 5.96.

Synthesis of [Cp$^{sec\text{-}butyl}$RhCl]$_2$(μ^2-Cl)$_2$ (**3f**).* Following the general procedure, [Rh(COD)]$_2$(μ^2-Cl)$_2$, **1f** (0.289 g, 1.62 mmol), and 0.5 mL of HCl were reacted in methanol (4 mL). Upon cooling, an orange-yellow powder (0.123 g) formed in a red solution. The powder was isolated and the red solution evaporated under reduced pressure. The resulting red powder was recrystallized from DCM and cold hexanes and collected by filtration. The red powder was washed with cold hexanes to give **3f** in a reacted yield of 0.0589 g (54%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.37−2.28 (m, 2H, 2 C*H*), 1.72 (s, 6H, 2 CpCH_3), 1.69 (s, 6H, 2 CpCH_3), 1.67−1.64 (m, 2H, CH*H*), 1.61 (s, 6H, 2 CpCH_3), 1.60 (s, 6H, 2 CpCH_3), 1.51−1.42 (m, 2H, C*H*H), 1.39−1.37 (d, 6H, $^2J_{HH}$ = 7.1 Hz, CH_3CH), 0.90−0.86 (t, 6H, $^2J_{HH}$ = 7.4 Hz, CH$_2$CH_3). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 98.37−98.29 (d, J_{CRh} = 8.8 Hz, Cp*C*), 97.61−97.53 (d, J_{CRh} = 8.9 Hz, Cp*C*), 95.35−95.25 (d, J_{CRh} = 10.1 Hz, Cp*C*), 95.29−95.20 (d, J_{CRh} = 9.0 Hz, Cp*C*), 92.83−92.73 (d, J_{CRh} = 9.4 Hz, Cp*C*), 31.65 (CH), 27.79 (CH$_2$), 18.41 (CH$_3$CH), 12.65 (CH$_3$CH$_2$), 10.89 (Cp*C*H$_3$), 10.45 (Cp*C*H$_3$), 9.83 (Cp*C*H$_3$), 9.44 (Cp*C*H$_3$). HRMS/ESI+ (*m*/*z*): $C_{26}H_{42}Cl_3Rh_2$ 665.0462; found 665.0472.

Synthesis of [Cp$^{n\text{-}pentyl}$RhCl]$_2$(μ^2-Cl)$_2$ (**3g**).* Following the general procedure, [Rh(COD)]$_2$(μ^2-Cl)$_2$ (0.200 g, 0.406 mmol), **1g** (0.312 g, 1.62 mmol), and 0.5 mL of HCl were reacted in methanol (4 mL) to give **3g** (0.227 g, 77%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.27−2.23 (m, 4H, 2 CH_2(CH$_2$)$_3$CH$_3$), 1.63 (s, 12H, 4 CpCH_3), 1.62 (s, 12H, 4 CpCH_3), 1.38−1.24 (m, 12H, CH$_2$(CH_2)$_3$CH$_3$), 0.87−0.84 (app t, 6H, 2 CH_3). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 96.44−96.34 (d, J_{CRh} = 9.3 Hz, Cp*C*), 94.69−94.60 (d, J_{CRh} = 9.1 Hz, Cp*C*), 94.29−94.19 (d, J_{CRh} = 9.2 Hz, Cp*C*), 31.88 (CH$_2$), 27.33 (CH$_2$), 24.10 (CH$_2$), 22.50 (CH$_2$), 13.96 (CH$_3$), 9.58 (Cp*C*H$_3$), 9.56 (Cp*C*H$_3$). HRMS/ESI+ (*m*/*z*): calcd for $C_{28}H_{46}Cl_3Rh_2$ 693.0775; found 693.0788. Anal. Calcd for $C_{28}H_{46}Cl_4Rh_2$: C, 46.05; H, 6.35. Found: C, 45.77; H, 6.16.

Synthesis of [Cp$^{n\text{-}hexyl}$RhCl]$_2$(μ^2-Cl)$_2$ (**3h**).* Following the general procedure, [Rh(COD)]$_2$(μ^2-Cl)$_2$ (0.200 g, 0.304 mmol), **1h** (0.344 g, 1.62 mmol), and 0.5 mL of HCl were reacted in methanol (4 mL) to give **3h** (0.224 g, 73% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.26−2.23 (m, 4H, 2 CH_2(CH$_2$)$_4$CH$_3$), 1.63 (s, 12H, 4 CpCH_3), 1.61 (s, 12H, 4 CpCH_3), 1.37−1.24 (m, 16H, 2 CH$_2$(CH_2)$_4$CH$_3$), 0.87−0.84 (app t, 6H, 2 CH_3). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 96.41−96.31 (d, J_{CRh} = 9.4 Hz, Cp*C*), 94.68−94.59 (d, J_{CRh} = 9.1 Hz, Cp*C*), 94.26−94.17 (d, J_{CRh} = 9.3 Hz, Cp*C*), 31.61 (CH$_2$), 29.46 (CH$_2$), 27.62 (CH$_2$), 24.14 (CH$_2$), 22.58 (CH$_2$), 14.13 (CH$_3$), 9.57 (Cp*C*H$_3$), 9.55 (Cp*C*H$_3$). HRMS/ESI+ (*m*/*z*): calcd for $C_{30}H_{50}Cl_3Rh_2$ 721.1088; found 721.1106.

Synthesis of [Cp$^{n\text{-}heptyl}$RhCl]$_2$(μ^2-Cl)$_2$ (**3i**).* Following the general procedure, [Rh(COD)]$_2$(μ^2-Cl)$_2$ (0.150 g, 0.304 mmol), **1i** (0.344 g, 1.62 mmol), and 0.5 mL of HCl were reacted in methanol (4 mL) to give **3i** (0.125g, 52% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.26−2.22 (m, 4H, 2 CH_2(CH$_2$)$_5$CH$_3$), 1.63 (s, 12H, 4 CpCH_3), 1.61 (s, 12H, 4 CpCH_3), 1.33−1.22 (m, 20H, CH$_2$(CH_2)$_5$CH$_3$), 0.87−0.83 (app t, 6H, 2 CH_3). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 96.41−96.32 (d, J_{CRh} = 9.5 Hz, Cp*C*), 94.69−94.60 (d, J_{CRh} = 9.2 Hz, Cp*C*), 94.26−94.17 (d, J_{CRh} = 9.2 Hz, Cp*C*), 31.77 (CH$_2$), 29.76 (CH$_2$), 29.13 (CH$_2$), 27.66 (CH$_2$), 24.13 (CH$_2$), 22.17 (CH$_2$), 14.20 (CH$_3$), 9.57 (Cp*C*H$_3$), 9.55 (Cp*C*H$_3$). HRMS/ESI+ (*m*/*z*): calcd for $C_{32}H_{54}Cl_3Rh_2$ 749.1401; found 749.1413. Anal. Calcd for $C_{32}H_{54}Cl_4Rh_2$: C, 48.88; H, 6.92. Found: C, 49.11; H, 6.87.

Synthesis of [Cp$^{n\text{-}octyl}$RhCl]$_2$(μ^2-Cl)$_2$ (**3j**).* Following the general procedure, [Rh(COD)]$_2$(μ^2-Cl)$_2$ (0.200 g, 0.304 mmol), **1j** (0.344 g, 1.62 mmol), and 0.5 mL of HCl were reacted in methanol (4 mL) to give **3j** (0.173 g, 52% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.26−2.22 (app t, 4H, 2 CH_2(CH$_2$)$_6$CH$_3$), 1.63 (s, 12H, 4 CpCH_3), 1.61 (s, 12H, 4 CpCH_3), 1.29−1.23 (m, 24H, CH$_2$(CH_2)$_6$CH$_3$), 0.87−0.84 (app t, 6H, 2 CH_3). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 96.41−96.32 (d, J_{CRh} = 9.5 Hz), 94.69−94.60 (d, J_{CRh} = 9.2 Hz, Cp*C*), 94.26−94.17 (d, J_{CRh} = 9.2 Hz, Cp*C*), 32.23 (CH$_2$), 30.12 (CH$_2$), 29.74 (CH$_2$), 29.53 (CH$_2$), 27.98 (CH$_2$), 24.46 (CH$_2$), 23.07 (CH$_2$), 14.53 (CH$_3$), 9.89 (Cp*C*H$_3$), 9.87 (Cp*C*H$_3$). HRMS/ESI+ (*m*/*z*): calcd for $C_{34}H_{58}Cl_3Rh_2$ 777.1717; found 777.1701. Anal. Calcd for $C_{34}H_{58}Cl_4Rh_2$: C, 50.14; H, 7.18. Found: C, 50.43; H, 7.09.

Synthesis of [Cp^{phenyl}RhCl]$_2$(μ^2-Cl)$_2$ (**3k**).* Following the general procedure, [Rh(COD)]$_2$(μ^2-Cl)$_2$ (0.200 g, 0.406 mmol), **1k** (0.322 g, 1.62 mmol), and 0.5 mL of HCl were reacted in methanol (4 mL) to give **3k** (0.225 g, 75%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66−7.64 (m, 4H, Ar*H*), 7.39−7.36 (m, 6H, Ar*H*), 1.71 (s, 12H, 4 CpCH_3), 1.68 (s, 12H, 4 CpCH_3). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 130.36 (Ar*C*), 129.02 (Ar*C*), 128.74 (Ar*C*), 128.41 (Ar*C*), 100.47−100.39 (d, J_{CRh} = 8.6 Hz, Cp*C*), 93.67−93.58 (d, J_{CRh} = 9.0 Hz, Cp*C*), 90.70−90.60 (d, J_{CRh} = 10.2 Hz, Cp*C*), 10.75 (Cp*C*H$_3$), 9.75 (Cp*C*H$_3$). HRMS/ESI+ (*m*/*z*): calcd for $C_{30}H_{34}Cl_3Rh_2$ 704.9836; found 704.9854.

Synthesis of [Cp^{benzyl}RhCl]$_2$(μ^2-Cl)$_2$ (**3l**).* Following the general procedure, [Rh(COD)]$_2$(μ^2-Cl)$_2$ (0.200 g, 0.406 mmol), **1l** (0.344 g, 1.62 mmol), and 0.5 mL of HCl were reacted in methanol (4 mL) to give **3l** (0.276 g, 89% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28−7.25 (m, 2H, Ar*H*), 7.24−7.18 (m, 4H, Ar*H*), 7.08−7.06 (m, 4H, Ar*H*), 3.71 (s, 4H, 2 CH_2), 1.67 (s, 12H, 4 CpCH_3), 1.65 (s, 12H, 4 CpCH_3). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 136.17 (Ar*C*), 128.81 (Ar*C*), 128.26 (Ar*C*), 126.86 (Ar*C*), 95.09−95.00 (d, J_{CRh} = 9.1 Hz, Cp*C*), 94.94−94.85 (d, J_{CRh} = 9.0 Hz, Cp*C*), 93.98−93.88 (d, J_{CRh} = 9.5 Hz, Cp*C*), 30.14 (CH$_2$), 9.87 (Cp*C*H$_3$), 9.44 (Cp*C*H$_3$). HRMS/ESI+ (*m*/*z*): calcd for $C_{32}H_{38}Cl_3Rh_2$ 733.0149; found 733.0158. Anal. Calcd for $C_{32}H_{38}Cl_4Rh_2$: C, 49.90; H, 4.97. Found: C, 50.49; H, 5.19.

Synthesis of [Cp^{phenethyl}RhCl]$_2$(μ^2-Cl)$_2$ (**3m**).* Following the general procedure, [Rh(COD)]$_2$(μ^2-Cl)$_2$ (0.150 g, 0.304 mmol), **1m** (0.274 g, 1.22 mmol), and 0.5 mL of HCl were reacted in methanol (4 mL) to give **3m** (0.186 g, 77% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23−7.14 (m, 6H, Ar*H*), 6.99−6.97 (m, 4H, Ar*H*), 2.72−2.69 (t, 4 H, $^2J_{HH}$ = 7.3 Hz, 2 PhCH_2CH$_2$), 2.61−2.57 (t, 4 H, $^2J_{HH}$ = 7.3 Hz, 2 PhCH$_2$CH_2), 1.57 (s, 12H, 4 CpCH_3), 1.36 (s, 12H, 4 CpCH_3).

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$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ 139.75 (ArC), 128.60 (ArC), 128.50 (ArC), 126.47 (ArC), 94.82–94.73 (d, J_{CRh} = 9.1 Hz, CpC), 94.61–94.52 (d, J_{CRh} = 9.5 Hz, CpC), 94.44–94.35 (d, J_{CRh} = 9.2 Hz, CpC), 33.37 ($PhCH_2CH_2$), 26.45 ($PhCH_2CH_2$), 9.32 ($CpCH_3$), 9.12 ($CpCH_3$). HRMS/ESI+ (m/z): calcd for $C_{34}H_{38}Cl_3Rh_2$ 761.0462; found 761.0466. Anal. Calcd for $C_{34}H_{42}Cl_4Rh_2$: C, 51.15; H, 5.30. Found: C, 50.89; H, 5.18.

Synthesis of $[Cp^{*cyclohexyl}RhCl]_2(\mu^2\text{-}Cl)_2$ ***(3n)***. Following the general procedure, $[Rh(COD)]_2(\mu^2\text{-}Cl)_2$ (0.200 g, 0.406 mmol), **1n** (0.332 g, 1.62 mmol), and 0.5 mL of HCl were reacted in methanol (4 mL). Upon cooling, an orange-yellow powder (0.091 g) formed in a red solution. The powder was isolated and the red solution evaporated under reduced pressure. The resulting red powder was recrystallized from DCM and cold hexanes and collected by filtration. The red powder was washed with cold hexanes to give **3n** in a reacted yield of 0.106 g (64%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.20–2.12 (m, 2H, 2 CH), 2.01–1.98 (m, 4H, 2 CH_2), 1.79–1.75 (m, 4H, 2 CH_2), 1.71 (s, 12H, 4 $CpCH_3$), 1.59 (s, 12H, 4 $CpCH_3$), 1.44–1.25 (m, 10H, CH_2), 1.19–1.08 (m, 2H, CH_2). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ 97.95–97.86 (d, J_{CRh} = 8.9 Hz, CpC), 94.08–93.99 (d, J_{CRh} = 9.1 Hz, CpC), 93.83–93.74 (d, J_{CRh} = 9.1 Hz, CpC), 35.39 (CH), 30.76 (CH_2), 26.83 (CH_2), 26.12 (CH_2), 10.78 ($CpCH_3$), 9.66 ($CpCH_3$). HRMS/ESI+ (m/z): calcd for $C_{30}H_{46}Cl_3Rh_2$ 717.0775; found 717.0782. Anal. Calcd for $C_{30}H_{46}Cl_4Rh_2$: C, 47.77; H, 6.15. Found: C, 47.27; H, 5.88.

Synthesis of $[Cp^{*cyclopentyl}RhCl]_2(\mu^2\text{-}Cl)_2$ ***(3o)***. Following the general procedure, $[Rh(COD)]_2(\mu^2\text{-}Cl)_2$ (0.150 g, 0.304 mmol), **1o** (0.232 g, 1.22 mmol), and 0.5 mL of HCl were reacted in methanol (4 mL). Upon cooling, an orange-yellow powder (0.031 g) formed in a red solution. The powder was isolated and the red solution evaporated under reduced pressure. The resulting red powder was recrystallized from DCM and cold hexanes and collected by filtration. The red powder was washed with cold hexanes to give **3o** in a reacted yield of 0.095 g (54%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.71–2.62 (m, 2H, 2 CH), 2.13–2.06 (m, 4H, 2 CH_2), 1. 72 (s, 12H, 4 $CpCH_3$), 1.69–1.62 (m, 12H, CH_2), 1.60 (s, 12H, 4 $CpCH_3$). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ 97.15–97.05 (d, J_{CRh} = 9. 0 Hz, CpC), 94.56–94.47 (d, J_{CRh} = 9.0 Hz, CpC), 93.97–93.88 (d, J_{CRh} = 9.3 Hz, CpC), 35.63 (CH), 31.60 (CH_2), 26.69 (CH_2), 10.56 ($CpCH_3$), 9.63 ($CpCH_3$). HRMS/ESI+ (m/z): calcd for $C_{28}H_{42}Cl_3Rh_2$ 689.0462; found 689.0503.

Biological Testing. MICs were measured by broth microdilution of fresh overnight cultures according to the Clinical and Laboratory Standards Institute (CCLI) guidelines with cation-adjusted Mueller–Hinton broth and an inoculum of 105 CFU mL^{-1}.[76] Stocks of the compounds were dissolved in Mueller–Hinton broth. The MIC (μg mL^{-1}) was defined as the lowest concentration of compound completely inhibiting the appearance of turbidity by eye and confirmed by absorbance 540 nm. The MBC (μg mL^{-1}) was defined as the lowest concentration of compound reducing the colony count by 99.9% of the colony count in the initial, compound-free, inoculated well after 24 h of incubation. All results represent the average of three independent measurements. Both MIC and MBC experiments were also performed using brain heart infusion broth, resulting in similar data for both MIC and MBC. For Tables 3 and 4, the units of μg mL^{-1} were converted to μM.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.6b00580.

An appendix that contains ^{1}H and ^{13}C NMR spectra for all compounds listed in this paper as well as crystallographic tables and thermal ellipsoid plots of all compounds characterized by single-crystal X-ray diffraction (PDF)

File containing all of the information including structure factors for all compounds characterized by XRD (CIF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Cuenca, T.; Royo, P. *Coord. Chem. Rev.* **1999**, *193–195*, 447–498.
(2) Thornberry, M. P.; Slebodnick, C.; Deck, P. A.; Fronczek, F. R. *Organometallics* **2001**, *20* (5), 920–926.
(3) Thornberry, M. P.; Slebodnick, C.; Deck, P. A.; Fronczek, F. R. *Organometallics* **2000**, *19* (25), 5352–5369.
(4) Deck, P. a.; Jackson, W. F.; Fronczek, F. R. *Organometallics* **1996**, *15* (25), 5287–5291.
(5) Wilkinson, G. *J. Organomet. Chem.* **1975**, *100* (1), 273–278.
(6) Werner, H. *Angew. Chem., Int. Ed.* **2012**, *51* (25), 6052–6058.
(7) Slocum, D. W.; Ernst, C. R. Electronic Effects in Metallocenes and Certain Related Systems. In *Advances in Organometallic Chemistry*; Wiley, 1972; Vol. *10*, pp 79–11410.1016/S0065-3055(08)60338-X.
(8) Wolczanski, P. T.; Bercaw, J. E. *Organometallics* **1982**, *1* (6), 793–799.
(9) Brintzinger, H.; Bercaw, J. E. *J. Am. Chem. Soc.* **1971**, *93* (8), 2045–2046.
(10) Threlkel, R. S.; Bercaw, J. E. *J. Organomet. Chem.* **1977**, *136* (1), 1–5.
(11) Morris, D. M.; McGeagh, M.; De Peña, D.; Merola, J. S. *Polyhedron* **2014**, *84* (0), 120–135.
(12) Karpin, G. W.; Merola, J. S.; Falkinham, J. O. *Antimicrob. Agents Chemother.* **2013**, *57* (7), 3434–3436.
(13) Karpin, G. W.; Morris, D. M.; Ngo, M. T.; Merola, J. S.; Falkinham, J. O., III. *MedChemComm* **2015**, *6* (8), 1471–1478.
(14) Chen, S.; Lu, G.; Cai, C. *RSC Adv.* **2015**, *5* (17), 13208–13211.
(15) Gunay, A.; Mantell, M. A.; Field, K. D.; Wu, W.; Chin, M.; Emmert, M. H. *Catal. Sci. Technol.* **2015**, *5* (2), 1198–1205.
(16) Xia, Y.; Liu, Z.; Feng, S.; Zhang, Y.; Wang, J. *J. Org. Chem.* **2015**, *80* (1), 223.
(17) Kim, K.; Hong, S. H. *J. Org. Chem.* **2015**, *80* (8), 4152–4156.
(18) Matsu-Ura, T.; Sakaguchi, S.; Obora, Y.; Ishii, Y. *J. Org. Chem.* **2006**, *71* (21), 8306–8308.
(19) Fujita, K.; Takahashi, Y.; Owaki, M.; Yamamoto, K.; Yamaguchi, R. *Org. Lett.* **2004**, *6* (16), 2785–2788.
(20) Fujita, K.; Furukawa, S.; Yamaguchi, R. *J. Organomet. Chem.* **2002**, *649* (2), 289–292.
(21) Fujita, K.; Li, Z.; Ozeki, N.; Yamaguchi, R. *Tetrahedron Lett.* **2003**, *44* (13), 2687–2690.
(22) Kawahara, R.; Fujita, K.; Yamaguchi, R. *Adv. Synth. Catal.* **2011**, *353* (7), 1161–1168.
(23) Saidi, O.; Bamford, M. J.; Blacker, A. J.; Lynch, J.; Marsden, S. P.; Plucinski, P.; Watson, R. J.; Williams, J. M. J. *Tetrahedron Lett.* **2010**, *51* (44), 5804–5806.
(24) Kumaran, E.; Leong, W. K. *Organometallics* **2015**, *34* (9), 1779–1782.
(25) Iuchi, Y.; Obora, Y.; Ishii, Y. *J. Am. Chem. Soc.* **2010**, *132* (8), 2536–2537.

DOI: 10.1021/acs.organomet.6b00580
Organometallics XXXX, XXX, XXX–XXX

(26) Izumi, A.; Obora, Y.; Sakaguchi, S.; Ishii, Y. *Tetrahedron Lett.* **2006**, *47* (52), 9199−9201.
(27) Koda, K.; Matsu-ura, T.; Obora, Y.; Ishii, Y. *Chem. Lett.* **2009**, *38* (8), 838−839.
(28) Liu, J.; Wu, X.; Iggo, J. A.; Xiao, J. *Coord. Chem. Rev.* **2008**, *252* (5−7), 782−809.
(29) Suzuki, T.; Matsuo, T.; Watanabe, K.; Katoh, T. *Synlett* **2005**, 1453−1455.
(30) Suzuki, T.; Ghozati, K.; Katoh, T.; Sasai, H. *Org. Lett.* **2009**, *11* (19), 4286−4288.
(31) Suzuki, T.; Morita, K.; Tsuchida, M.; Hiroi, K. *J. Org. Chem.* **2003**, *68* (4), 1601−1602.
(32) Collins, J. E.; Castellani, M. P.; Rheingold, A. L.; Miller, E. J.; Geiger, W. E.; Rieger, A. L.; Rieger, P. H. *Organometallics* **1995**, *14* (3), 1232−1238.
(33) Suzuki, T.; Yamada, T.; Watanabe, K.; Katoh, T. *Bioorg. Med. Chem. Lett.* **2005**, *15* (10), 2583−2585.
(34) Suzuki, T.; Morita, K.; Tsuchida, M.; Hiroi, K. *Org. Lett.* **2002**, *4* (14), 2361−2363.
(35) Millett, A. J.; Habtemariam, A.; Romero-Canelón, I.; Clarkson, G. J.; Sadler, P. J. *Organometallics* **2015**, *34* (11), 2683−2694.
(36) Śliwińska, U.; Pruchnik, F. P.; Ułaszewski, S.; Latocha, M.; Nawrocka-Musiał, D. *Polyhedron* **2010**, *29* (6), 1653−1659.
(37) Thai, T.-T.; Therrien, B.; Süss-Fink, G. *Inorg. Chem. Commun.* **2009**, *12* (8), 806−807.
(38) Liu, Z.; Habtemariam, A.; Pizarro, A. M.; Fletcher, S. A.; Kisova, A.; Vrana, O.; Salassa, L.; Bruijnincx, P. C.; Clarkson, G. J.; Brabec, V.; et al. *J. Med. Chem.* **2011**, *54* (8), 3011−3026.
(39) Quintana, L. M. A.; Johnson, S. I.; Corona, S. L.; Villatoro, W.; Goddard, W. A.; Takase, M. K.; VanderVelde, D. G.; Winkler, J. R.; Gray, H. B.; Blakemore, J. D. *Proc. Natl. Acad. Sci. U. S. A.* **2016**, *113* (23), 6409−6414.
(40) Pitman, C. L.; Finster, O. N. L.; Miller, A. J. M. *Chem. Commun.* **2016**, *52* (58), 9105−9108.
(41) Lucas, S. J.; Lord, R. M.; Basri, A. M.; Allison, S. J.; Phillips, R. M.; Blacker, A. J.; McGowan, P. C. *Dalt. Trans* **2016**, *45* (16), 6812−6815.
(42) Karpin, G. W.; Morris, D. M.; Ngo, M. T.; Merola, J. S.; Falkinham, J. O. *MedChemComm* **2014**, *6*, 1471.
(43) Piou, T.; Rovis, T. *Nature* **2015**, *527* (V), 1−5.
(44) Dooley, T.; Fairhurst, G.; Chalk, C. D.; Tabatabaian, K.; White, C. *Transition Met. Chem.* **1978**, *3* (1), 299−302.
(45) Gusev, O. V.; Sergeev, S.; Saez, I. M.; Maitlis, P. M. *Organometallics* **1994**, *13* (5), 2059−2065.
(46) Baghurst, D. R.; Michael, D.; Mingos, P.; Watson, M. J. *J. Organomet. Chem.* **1989**, *368* (3), C43−C45.
(47) Baghurst, D. R.; Cooper, S. R.; Greene, D. L.; Mingos, D. M. P.; Reynolds, S. M. *Polyhedron* **1990**, *9* (6), 893−895.
(48) Strauss, C.; Trainor, R. *Aust. J. Chem.* **1995**, *48* (June), 1665−1692.
(49) Larhed, M.; Hallberg, A. *Drug Discovery Today* **2001**, *6* (8), 406−416.
(50) Gedye, R.; Smith, F.; Westaway, K.; Ali, H.; Baldisera, L.; Laberge, L.; Rousell, J. *Tetrahedron Lett.* **1986**, *27* (3), 279−282.
(51) Blacker, J.; Treacher, K.; Screen, T. *Unsaturated carbocyclic compounds linked to solid supports as ligands for transition metal-catalyzed hydrogenation and metathesis reactions.* PCT Int. Appl. WO2009093059A2, 2009.
(52) Fendrick, C. M.; Schertz, L. D.; Mintz, E. A.; Marks, T. J.; Bitterwolf, T. E.; Horine, P. A.; Hubler, T. L.; Sheldon, J. A.; Belin, D. D. Large-Scale Synthesis of 1,2,3,4,5-Penta-Methylcyclopentadiene. In *Inorganic Syntheses*; John Wiley & Sons, Inc., 1992; pp 193−198.
(53) Evans, W. J.; Forrestal, K. J.; Ziller, J. W. *Polyhedron* **1998**, *17* (23−24), 4015−4021.
(54) Liu, Z.; Habtemariam, A.; Pizarro, A. M.; Fletcher, S. A.; Kisova, A.; Vrana, O.; Salassa, L.; Bruijnincx, P. C. A.; Clarkson, G. J.; Brabec, V.; et al. *J. Med. Chem.* **2011**, *54* (8), 3011−3026.
(55) White, C.; Yates, A.; Maitlis, P. M. *Inorg. Synth.* **1992**, *29*, 228.
(56) El Amouri, H.; Gruselle, M.; Jaouén, G. *Synth. React. Inorg. Met.-Org. Chem.* **1994**, *24* (3), 395−400.
(57) Abramov, P. A.; Sokolov, M. N.; Virovets, A. V.; Fedin, V. P. *J. Struct. Chem.* **2009**, *50* (1), 162−165.
(58) Churchill, M. R.; Julis, S. A. *Inorg. Chem.* **1977**, *16* (6), 1488−1494.
(59) Churchill, M. R.; Julis, S. A.; Rotella, F. J. *Inorg. Chem.* **1977**, *16* (5), 1137−1141.
(60) Miyano, Y.; Nakai, H.; Hayashi, Y.; Isobe, K. *J. Organomet. Chem.* **2007**, *692* (1−3), 122−128.
(61) Morris, D. M. Design and Modification of Half-Sandwich Ir(III), Rh(III), and Ru(II) Amino Acid Complexes for Application in Asymmetric Transfer Hydrogenation Reactions; Thesis, Virginia Tech, 2015.
(62) Liu, Z.; Habtemariam, A.; Pizarro, A. M.; Clarkson, G. J.; Sadler, P. J. *Organometallics* **2011**, *30* (17), 4702−4710.
(63) Jardim, G. A. M.; da Silva Júnior, E. N.; Bower, J. F. *Chem. Sci.* **2016**, *7* (6), 3780−3784.
(64) Piou, T.; Rovis, T. *J. Am. Chem. Soc.* **2014**, *136* (32), 11292−11295.
(65) Cadenbach, T.; Gemel, C.; Schmid, R.; Fischer, R. A. *J. Am. Chem. Soc.* **2005**, *127* (48), 17068−17078.
(66) Guo, Z.; Sadler, P. J. *Angew. Chem., Int. Ed.* **1999**, *38* (11), 1512−1531.
(67) Suzuki, Y.; Yasumoto, T.; Mashima, K.; Okuda, J. *J. Am. Chem. Soc.* **2006**, *128* (39), 13017−13025.
(68) Seidel, R. W.; Ganesamoorthy, C.; Loerke, S.; Winter, M. V.; Gemel, C.; Fischer, R. A. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **2013**, *69* (6), 573−576.
(69) Uemura, M.; Fujita, M. Transition metal compound, polymerization-initiator system comprising the same, and process for producing polymer. JP2007217290 (A), 2007.
(70) Ngubane, S.; Hakansson, M.; Jagner, S.; Moss, J. R.; Sivaramakrishna, A. *J. Organomet. Chem.* **2008**, *693* (2), 343−348.
(71) Flores, J. C.; Wood, J. S.; Chien, J. C. W.; Rausch, M. D. *Organometallics* **1996**, *15* (23), 4944−4950.
(72) McArdle, P.; Ryder, A. G.; Cunningham, D. *Organometallics* **1997**, *16* (12), 2638−2645.
(73) Ma, Z.; Wang, N.; Guo, K.; Zheng, X.; Lin, J. *Inorg. Chim. Acta* **2013**, *399*, 126−130.
(74) Merola, J. S.; Morris, D.; De Weerd, N. *Acta Crystallogr., Sect. E: Struct. Rep. Online* **2013**, *69*, m176.
(75) Miguel-Garcia, J. A.; Adams, H.; Beiley, N. A.; Maitlis, P. M. *J. Organomet. Chem.* **1991**, *413* (1−3), 427−444.
(76) Maisuria, B. B.; Actis, M. L.; Hardrict, S. N.; Falkinham, J. O.; Cole, M. F.; Cihlar, R. L.; Peters, S. M.; MacRi, R. V.; Sugandhi, E. W.; Williams, A. a.; et al. *Bioorg. Med. Chem.* **2011**, *19* (9), 2918−2926.

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Organometallics XXXX, XXX, XXX−XXX