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Notes

Facile, Near-Quantitative, Aqueous Routes to Nearly Any [Cp*Ru(η^6-arene)]Cl Compound

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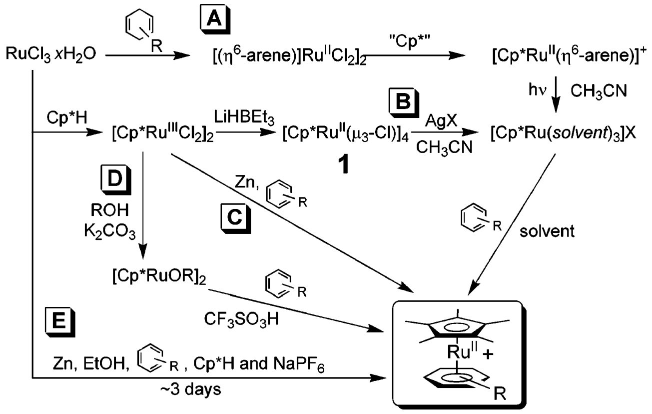
*Summary: Facile syntheses of water-soluble [Cp*Ru(arene)]Cl compounds exploiting the extraordinary properties of [Cp*Ru(μ_3-Cl)]$_4$ in aqueous media are described. These methods produce no byproducts, involve little to no workup, and are applicable to almost any simple arene.*

Introduction

[Cp^{R}M(η^6-arene)]$^{n+}$ (M = Fe^{II}, Ru^{II}, Ir^{III}, Rh^{III}) compounds are generally air-, water-, and heat-stable organometallic sandwich compounds that have been extensively studied by chemists of all disciplines.[1−3] The positive charge and electron-withdrawing nature of the [Cp^{R}M]$^{n+}$ moieties enhances the electrophilicity of arenes and activates them toward a variety of synthetically useful organic transformations, most notably nucleophilic additions and substitutions, benzylic deprotonation, and Pd-catalyzed cross-coupling reactions.[2−4] Recently, much attention has focused on [CpRu^{II}(arene)]$^+$ and [Cp*Ru^{II}(arene)]$^+$ compounds due to their (i) broad accessibility relative to their Fe analogues, (ii) low cost relative to their Ir^{III}/Rh^{III} analogues, and (iii) ease of arene recovery (typically via UV irradiation).[5] Indeed, [Cp^{R}Ru(arene)]$^+$ compounds have shown promise in natural product synthesis,[6] in radioisotopic labeling of biomolecules,[7] in crystal engineering,[8] as charge-transfer materials,[9] and as supramolecular anion receptors.[10]Moreover, [Cp^{R}Ru(arene)]$^+$ compounds can serve as precursors to [Cp^{R}Ru]$^+$ species that are known to catalyze a variety of organic transformations, many of which are C−C bond forming reactions.[11] It is therefore important to optimize protocols for the synthesis of [Cp^{R}Ru(arenes)]$^+$.[12]

Scheme 1. Reaction Routes to [Cp*Ru(η^6-arenes)]X



The arenophilic nature of the [Cp*Ru]$^+$ fragment is well documented, and thus several procedures exist for the synthesis of simple [Cp*Ru(arene)]$^+$ compounds. The most popular procedures (Scheme 1) employ putative or well-defined [Cp*Ru(solvent)$_3$]$^+$ species, available via UV irradiation of [Cp*Ru(benzene)]$^+$ (route **A**),[5,13] halide abstraction from [Cp*Ru^{II}(μ_3-Cl)]$_4$ (**1**) (route **B**),[8] or zinc reduction of [Cp*Ru^{III}Cl$_2$]$_2$ (route **C**)[14,15] in the appropriate solvents. An alternative route involves the two-step synthesis of the alkoxy-coordinated [Cp*Ru(OR)]$_2$ (route **D**),[16,17] which, in the presence of a proton donor, metalates arenes. Also reported is a one-pot synthesis of [Cp*Ru(arene)]$^+$ compounds via direct reaction of RuCl$_3$ with Cp*H and Zn in ethanol (Scheme 1, route **E**).[18,19] Though these methods are generally quite useful, each has its relative shortcomings and there remains room for improvement. Some of these shortcomings include the use of toxic or expensive Sn or Ag reagents (routes **A** and **B**, respectively), subquantitative (routes **A**−**D**)

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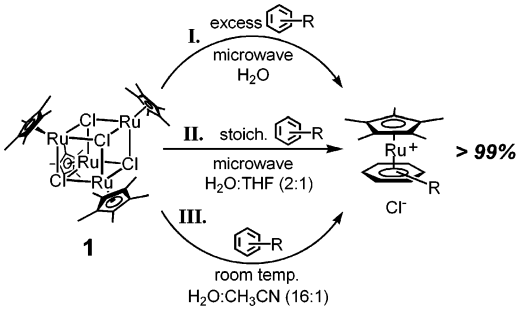
Scheme 2. Three Methods to [Cp*Ru(η^6-arenes)]Cl

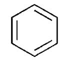
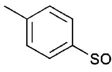
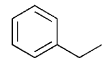
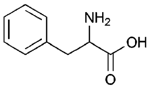
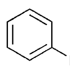
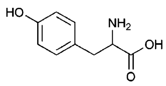
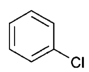
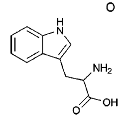
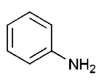
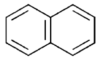
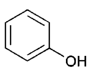
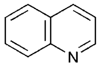
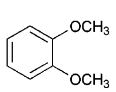
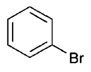
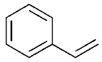
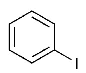
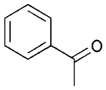
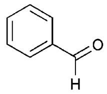
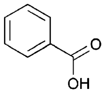
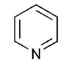
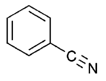
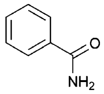


or even low (route **E**) yields, and the need for organic solvents (routes **A**−**D**), revealing an incompatibility with many biomolecules (e.g., proteins). As with any reaction, the ideal protocol would employ simple or mild reaction conditions, proceed in aqueous solution, give quantitative yields, produce no byproducts, involve little to no workup, and be widely applicable. We report herein three general methods for $[Cp^*Ru(arene)]^+$ synthesis that embody, as much as possible, the aforementioned principles (Scheme 2). These methods are not grossly different from the approaches described above (routes **B**−**D**) but, rather, exploit the extraordinary properties of **1**, or the *chloride* salt of $[Cp^*Ru(solvent)_3]^+$, in aqueous (or mostly aqueous) media, affording water-soluble [Cp*Ru(η^6-arene)]Cl compounds in near-quantitative yields. To our knowledge, the only other report of aqueous $[Cp^RRu(arene)]^+$ synthesis exploits a water solubilizing, amino-derivatized Cp ligand that necessitates an extensive synthesis.[20]

Results and Discussion

Method I. With the goal of optimizing protocols for the synthesis of $[Cp^*Ru(arenes)]^+$, we discovered that the readily available[21] **1** reacts directly with arenes in pure, anaerobic water at elevated temperatures, without the need for chloride abstraction. The procedure is fast, extremely convenient, and essentially quantitative, giving water-soluble [Cp*Ru(η^6-arene)]Cl compounds—even for arenes that are insoluble in water. The typical reaction (method I) involves combination of **1** and the chosen arene (8:1 arene−Ru) in degassed H_2O, followed by microwave irradiation in a sealed vessel (0−50 W to maintain ca. 130 °C) for ca. 10 min. The dark, brick red color of **1** serves as a convenient indicator of reaction progress, affording near-colorless solutions by completion. For most arenes, **1** reacts cleanly and completely, resulting in solutions that contain only the desired product, excess unreacted arene, and water. Typically, the excess arene can be removed under reduced pressure or by trituration of the crude salt in organic solvent, yielding pure product in near-quantitative yields. It is important to point out that this protocol is an aqueous relative of the method used by Chaudret and co-workers (route **C**),[14,15] wherein “Zn-reduced solutions” of $[Cp^*Ru^{III}Cl_2]_2$ in ethanol, acetone, THF, or toluene—which are, in effect, solutions of residual $ZnCl_2$ and **1** (or [Cp*Ru(solvent)$_3$]Cl)—were used to metalate arenes, with the resulting $[Cp^*Ru(arenes)]^+$ compounds typically being isolated as their $[PF_6]^-$ salts. Notably, these researchers have expressed concern about the scalability of their reaction due to “deposition of the ruthenium complex on zinc”[22] and have abandoned the procedure for the synthesis of some $[Cp^*Ru(arenes)]^+$. Additionally, direct reaction of **1** with neat arene solvents (e.g., toluene[15] and hexamethylbenzene[23]) has also been reported previously, but the reaction rates are known to be extremely slow, give low yields, and are not amenable to a wide variety of arenes.

Table 1. Microwave-Assisted Metalation of Arenes with 1 in H_2O[a]

arene	Cp*Ru-(η^6-arene)Cl	Yield (%)	Arene	Cp*Ru-(η^6-arene)Cl	Yield (%)
	**2**	95[b]		**13**	94[e,f]
	**3**	>99		(±)-**14**	93[f]
	**4**	>99		(±)-**15**	94[f]
	**5**	>99		(±)-**16a** (±)-**16b**	88[f]
	**6**	>99		**17**	87[h]
	**7**	>99		(±)-**18**	78[f,i]
	**8**	>99		**19**	64[c]
	**9**	97		**20**	86[d]
	**10**	>99		**21**	52[g]
	**11**	>99		**22**	0
	**12a**	33 + 66[j]	, **12b**		

[a] Reaction mixtures were heated at 130 °C (0−50 W) for 10−30 min with 8:1 arene−Ru in degassed H_2O. [b] The product also contained 5% [Cp^{*OH}Ru(benzene)]Cl. [c] The product also contained 19% [Cp^{*OH}Ru(bromobenzene)]Cl and 17% **2**. [d] The product also contained 14% [Cp^{*OH}Ru(iodobenzene)]Cl. [e] Isolated as a zwitterion. [f] Reactions resulted in >99% spectroscopic yield, remaining product lost in workup. [g] The product also contained 40% [Cp*Ru(phenylmethanediol)]Cl and 8% [Cp*Ru((4-(hydroxymethyl)phenyl)methanol)]Cl. [h] The product also contained 4% [Cp^{*OH}Ru(naphthalene)]Cl. [i] Coordination occurs at the carbocyclic ring. [j] The product also contained 66% **12b**.

To explore the breadth of method I, a variety of arenes were subjected to this protocol and the outcomes are highlighted in Table 1. All compounds in this paper were isolated as their chloride salts, with the exception of the zwitterionic **13**, and were characterized by ^1H and ^{13}C NMR, IR, ESI-MS, and, for

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[20] Grotjahn, D. B.; Joubran, C.; Combs, D.; Brune, D. C. *J. Am. Chem. Soc.* **1998**, *120*, 11814−11815.

[21] The synthesis of **1** is straightforward and high yielding (ca. 80% overall from $RuCl_3 \cdot xH_2O$, Scheme 1). Moreover, unlike its precursor, $[Cp^*Ru^{III}Cl_2]_2$, **1** can be made in bulk and stored under nitrogen for prolonged periods of time.[8]

[22] Chaudret, B.; He, X. D.; Huang, Y. S. *J. Chem. Soc., Chem. Commun.* **1989**, 1844−1846.

[23] Koelle, U.; Kossakowski, J. *J. Chem. Soc., Chem. Commun.* **1988**, 549−551.

8 and **12b**, single-crystal X-ray diffraction[24] (see the Supporting Information). The cations of **8**, **12b**, **20**, and (±)-**24** have not been previously reported.

Generally, method I tolerates most functional groups, including alkyl, fluoro, chloro, hydroxyl, amino, methoxy, vinyl, acetyl, carboxyl, and sulfonate. The three aryl amino acids (±)-phenylalanine, (±)-tyrosine, and (±)-tryptophan reacted quantitatively according to ^{1}H NMR spectroscopy, though removal of the excess unreacted arenes required a Sephadex column and lowered the isolated yields slightly. Notably, reaction with (±)-tryptophan gave a roughly equal mixture of the possible diastereomeric products, (±)-**16a** and (±)-**16b**. Products **2**−**16,** **19**, and **20** are air, water, and heat stable, though **12a** hydrolyzes to **12b** at elevated temperatures in water. Unsurprisingly,[25] the [Cp*Ru(arene)]$^+$ compounds of the fused aromatics **17** and (±)-**18** decompose slowly in warm solutions exposed to air, the former being qualitatively more stable. Indeed, even as a solid, (±)-**18** decomposes slowly in air, marked by a gradual darkening of the material. As expected, quinoline is metalated exclusively at the carbocylic ring, and we were unable to synthesize [Cp*Ru(η^6-pyridine)]Cl (**22**) by method I (an alternative methodology proved successful; *vide infra*). The more sensitive bromo- and iodo-substituted arenes gave moderate yields of **19** (64%) and **20** (86%) along with significant amounts of their respective Cp*^{OH}-substituted impurity.[26] Reaction with bromobenzene additionally resulted in **2** (17%), an apparent product of disproportionation. Reaction with benzonitrile gave primarily the hydrolysis product **12b** (66%) and only 33% of **12a**. Metalation of benzaldehyde gave **21** (52%) along with two additional complexes that we tentatively assign as [Cp*Ru(phenylmethanediol)]Cl (40%) and [Cp*Ru((4-(hydroxymethyl)phenyl)methanol)]Cl (8%) by ESI-MS and ^{1}H NMR (see the Supporting Information).

We note that method I can also be performed thermally, without the need for microwave irradiation. Indeed, similar results were obtained when identical reactions were carried out in a sealed flask that was heated in an oil bath at 115 °C. Reactions times, however, ranged from 1 to 3 days and the yields tended to be slightly lower due to slow degradation of **1** under these conditions (see the Supporting Information).

Method II. Although method I is efficient at high arene:Ru ratios, 1:1 stoichiometric reactions proceed very slowly or do not proceed at all. The reaction of **1** with (±)-phenylalanine at a 1:1 ratio of arene to Ru went to less than 20% completion after microwave irradiation at 130 °C for 1 h. To facilitate reactions at stoichiometric arene to Ru ratios, method II employs 2:1 water−THF as the reaction solvent, thus increasing the solubility of both **1** and the arenes in the reaction solvent. The ability to conduct stoichiometric metalations is advantageous for arenes that (i) are valuable (e.g., the products of multistep syntheses), (ii) are to be multiply metalated (e.g., polyaromatic hydrocarbons), or (iii) are difficult to separate from their resulting [Cp*Ru(arene)]Cl products (e.g., amino acids).

Table 2. Microwave-Assisted Metalation of Arenes by 1 at 1:1 Arene−Ru Ratios[a]

arene	Cp*Ru(arene)Cl	yield (%)
benzene	**2**	>95[b]
ethylbenzene	**3**	>99
chlorobenzene	**5**	>99
phenol	**7**	>99
benzoic acid	**11**	>99
(±)-tryptophan	(±)-**16a**,**b**	>99
(±)-cryptophane-E[c]	[(±)-**23**⊂THF]Cl$_6$	97

[a] Reaction mixtures were heated at 130 °C (0−50 W) for 15 min with 28 μmol **of 1** and 0.11 mmol of arene (1:1 arene−Ru) in 3 mL of H_2O and 1.5 mL of THF. [b] With an additional 5% [Cp*^{OH}Ru(benzene)]Cl impurity. [c] Heated at 135 °C (0−100 W) for 30 min with 10.7 μmol of (±)-cryptophane E and 18.7 μmol of **1** (6:7 arene−Ru) in 2 mL of H_2O and 1 mL of THF, giving exclusively hexametalated [(Cp*Ru)$_6$((±)-cryptophane-E)⊂THF]Cl$_6$.

Table 3. Room-Temperature Metalation of Arenes[a]

arene	Cp*Ru(arene)Cl	yield (%)
phenol	**7**	>99
toluenesulfonic acid	**13**[b]	>99
(±)-tryptophan	(±)-**16a**,**b**	98
(±)-quinoline	(±)-**18**	>99
benzonitrile	**12a**	>99
pyridine	**22**	97
(1*R*,2*S*)-(−)-*N*-methylephedrine	(±)-**24**	>99

[a] Reactions were performed by dissolving 28 μmol of **1** in 500 μL of CH_3CN (heated and then cooled to ca. 25 °C), followed by the addition of a solution of 0.11 mmol of arene in 8 mL of H_2O (ca. 25 °C); this mixture was sealed under nitrogen and reacted overnight. [b] Isolated as a zwitterion.

Method II reactions—identical to method I, but employing 1:1 ratios of arene to Ru and 2:1 H_2O−THF as the solvent—generally proceed quantitatively in 15−30 min (Table 2). Workup involves merely the removal of the solvent. Thus, the diastereomeric mixture (±)-**16a**,**b** is isolated in quantitative yield, without the need to remove excess nonmetalated (±)-tryptophan. To assess the utility of method II for metalating polyaromatics, the supramolecular host (±)-cryptophane-E was subjected to a similar protocol with only a slight excess (6:7 arene−Ru) of **1**. (±)-Cryptophane-E is a molecular "container" with six alkoxy-substituted aryl moieties per molecule, and its hexametalation has previously been reported by us via route **B** (78% yield).[10] Under conditions of method II, (±)-cryptophane-E is hexametalated cleanly, giving [(Cp*Ru)$_6$((±)-cryptophane-E⊂THF)]Cl$_6$ ([(±)-**23**⊂THF]Cl$_6$) in 97% yield. Conveniently, excess unreacted/decomposed **1** precipitates from the solution after exposure to air and is easily removed by filtration.

Method III. Though microwave reactions provide a convenient method to rapidly metalate most simple arenes, the metalation of water-soluble, heat-sensitive arenes (biomolecules etc.) necessitates stoichiometric reaction at or near room temperature. This can be achieved by first dissolving **1** in minimal amounts of CH_3CN, presumably forming the water-soluble [Cp*Ru(CH_3CN)$_3$]Cl, followed by addition of an aqueous solution of the arene such that the ratio of H_2O to CH_3CN is roughly 16:1 (method III). As with methods I and II, the formation of [Cp*Ru(η^6-arene)]Cl products is near-quantitative, though reaction times are considerably longer (ca. 8−20 h) under stoichiometric conditions (Table 3). Again, reaction progress can be conveniently followed by a gradual change of the solution color from yellow to near-colorless. Again also, the workup involves only the removal of solvent. Notably, under the mild conditions of method III, reaction with benzonitrile affords pure **12a** with no trace of hydrolysis product **12b** (appears in 66% yield by method I). This result clearly demonstrates the effectiveness of this procedure for the mild, near-quantitative [Cp*Ru]$^+$ functionalization of water-soluble arenes of questionable thermal stability. Remarkably, method III also proved highly useful for the η^6 metalation of heterocyclics such as quinoline and pyridine,

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(24) CCDC 634128 and 634129 contain supplementary crystallographic data for **8** and **12b**. These data can be obtained online free of charge (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K., fax (+44) 1223-336-033, or deposit@ccdc.cam.ac.uk).

(25) McNair, A. M.; Mann, K. R. *Inorg. Chem.* **1986**, *25*, 2519−2527.

(26) The impurities, [Cp*^{OH}Ru(η^6-arene)]Cl (Cp*^{OH} = η^5-1-(hydroxymethyl)-2,3,4,5-tetramethylcyclopentadienyl anion), found in the synthesis of **2**, **17**, **19**, and **20** are analogous to the "Cp*^{OMe}" impurity described by Lindel and coworkers[7] in their one-step methanolic synthesis of [Cp*Ru(arene)]$^+$ compounds (Scheme 1, route **D**). Lindel's proposed explanation for the occurrence of "Cp*^{OMe}" can similarly explain the observation of Cp*^{OH} species here.

giving both (±)-**18** and **22** in near-quantitative yield. The improvement afforded by this protocol in the synthesis of **22** is a striking example of the power of this aqueous methodology that merits additional comment. Chaudret *et al*. have previously synthesized **22** by route **C**, but it was impure and was obtained in only ~46% yield.[15] The metalation of pyridine is dependent on the interconversion between η^1 and η^6 coordination to the $[Cp^*Ru]^+$ moiety. Notably, ^1H NMR of the aqueous reaction mixture (16:1 H_2O-CH_3CN, method III) of $[Cp^*Ru(CH_3CN)_3]Cl$ and a stoichiometric amount of pyridine after *ca.* 8 h revealed no trace of **22** but significant formation of the η^1 complex, presumably $[Cp^*Ru(\eta^1\text{-pyridine})(CH_3CN)_2]Cl$. Interestingly, the formation of **22** requires removal of CH_3CN from the reaction mixture, resulting in quantitative formation in the complete absence of CH_3CN. The failure of method I (8:1 arene−Ru) to produce **22** is likely due to the excess of pyridine, which presumably drives the equilibrium exclusively to the η^1-coordinated species.

Finally, it should be noted that a logical extension of the methods presented herein requires a protocol for the mild, stoichiometric metalation of water-insoluble arenes (e.g., bromobenzene, which was not quantitatively metalated by method I). It seems clear that direct reaction of **1** with arenes in weakly coordinating organic solvents (e.g., THF) would work well for the mild preparation of many such [Cp*Ru(arene)]Cl compounds. Indeed, Chaudret and co-workers have successfully employed their “Zn-reduced solutions” for the high-yield synthesis of [Cp*Ru(benzene)]Cl and $[Cp^*Ru(benzene)][PF_6]$. Direct reaction of arenes with **1**, however, should greatly facilitate workup by providing clean solutions with no possibility for Zn^{II}-containing byproducts.

Conclusion

In conclusion, we have described three facile, near-quantitative, aqueous (or near-aqueous) routes to nearly any [Cp*Ru(arene)]Cl. Though several reasonable methods are currently available for the synthesis of $[Cp^*Ru(arene)]^+$ compounds, the clear facility, universality, and near-quantitative nature of the aqueous methods reported here significantly expands the scope of $[Cp^*Ru(arene)]^+$ chemistry. In particular, this chemistry opens the door to aqueous applications of the water-soluble chloride salts, compounds which have not been widely available previously.

Experimental Section

General Procedures. THF and CH_3CN were obtained from Fisher (Pittsburgh, PA), degassed with nitrogen, and used without further purification. All arenes were obtained from Acros (Pittsburgh, PA) or Aldrich (Milwaukee, WI) and were used without further purification. H_2O was deionized, distilled, and degassed in house. **1**[8] and cryptophane-E[27] were prepared according to previously reported literature procedures. All reactions were carried out under a nitrogen atmosphere using standard Schlenk and/or glovebox techniques. All microwave reactions were performed in a CEM Discover microwave reactor using a 10 mL sealed glass microwave reaction vessel fitted with a stir bar.

Instrumentation. ^1H (300.1 MHz) and ^{13}C (75.5 MHz) NMR were carried out on a Varian Unity Inova spectrometer. All NMR spectra were collected at 25 °C unless otherwise noted and were indirectly referenced using residual solvent signals as internal standards (references: ^1H NMR, D_2O, δ 4.79; ^{13}C NMR, CH_3OH in D_2O, δ 49.5). IR measurements were performed on a Perkin-Elmer Spectrum One FT-IR spectrometer fitted with a Pike Technologies MIRacle Single Reflection ATR adapter for solid sample analysis. ESI-MS data was obtained on a JEOL AccuTOF instrument at the University of Maryland. Elemental analyses were carried out on a Perkin-Elmer PE2400 microanalyzer at Georgetown University.

Synthetic Methods. Complete synthetic and spectroscopic details for all compounds can be found in the Supporting Information. Reported herein are the general protocols for methods I−III, along with one specific example for each method.

Method I: Microwave Reaction of 1 with Arenes (8:1 Arene−Ru). Arene (0.88 mmol, 8 equiv), **1** (30 mg, 28 μmol, 1 equiv of Ru), and 8 mL of H_2O were combined in a 10 mL glass microwave reaction vessel fitted with a stir bar. The vessel was sealed and reacted at 50 W until the desired temperature was reached and was thereafter maintained automatically via wattage regulation (usually ca. 130 °C and 10 min). The resulting solution was evaporated under reduced pressure, extracted/triturated with toluene or appropriate solvent, and subsequently dried to give the desired $[Cp^*Ru(\eta^6\text{-arene})]Cl$ product.

$[Cp^*Ru(\eta^6\text{-ethylbenzene})]Cl$ (3). Ethylbenzene (110.0 μL, 0.896 mmol, 8 equiv) and **1** (30.4 mg, 28.0 μmol, 1 equiv of Ru) were reacted according to method I. The colorless, clear solution was evaporated under reduced pressure. The oily solid was then triturated with hexane, yielding **3** as a white powder (42.1 mg, 99% yield). IR (ATR, cm^{-1}): 3422, 2952, 1615, 1523, 1450, 1038, 821, 503. ^1H NMR (D_2O, 300 MHz): δ 1.21 (3H, triplet, J 7.6, η^6-$C_{ar}CCH_3$), 1.93 (15H, singlet, η^5-CCH_3), 2.40 (2H, quartet, J 7.6, η^6-$C_{ar}CH_2$), 5.74 (5H, multiplet, η^6-CH_{ar}). ^{13}C NMR (D_2O, CH_3OH, 75.5 MHz): δ 107.12, 97.32, 88.48, 88.25, 87.55, 27.21, 15.68, 10.54. ESI-MS (^{102}Ru, *m/z*): 343.101 ($C_{18}H_{25}Ru$ requires 343.100).

Thermal Reaction of 1 with Arenes (8:1 Arene−Ru). Arene (0.88 mmol, 8 equiv), **1** (30 mg, 28 μmol, 1 equiv of Ru), and 10 mL of H_2O and were combined in a Schlenk tube fitted with a stir bar under nitrogen. The heterogeneous solution was subsequently heated in an oil bath (ca. 115 °C) with intermittent sonication for 1−3 days (reaction completion determined by change from red to colorless, correlating with the consumption of **1**). *Warning! Contents under pressure.* The reaction vessel was cooled (ca. 25 °C), and the resulting $[Cp^*Ru(\eta^6\text{-arene})]Cl$ compounds were isolated using the procedures outlined in method I.

Method II: General Microwave Reaction of 1 with Arenes (1:1 Arene−Ru). Arene (0.11 mmol, 1 equiv), **1** (30 mg, 28 μmol, 1 equiv of Ru), 3 mL of H_2O, and 1.5 mL THF were combined, reacted (*ca.* 15 min), and isolated using the procedures outlined in method I.

$[Cp^*Ru(\eta^6\text{-benzoic acid})]Cl$ (11). Benzoic acid (12.9 mg, 0.106 mmol, 1 equiv) and **1** (28.7 mg, 26.5 μmol, 1 equiv of Ru) were reacted according to method II. The clear solution was cooled to room temperature, and the solvent was removed under reduced pressure. The resulting solid was triturated with toluene to yield **11** as a pale green powder (41.3 mg, 99% yield). IR (ATR, cm^{-1}): 3377, 3074, 2571, 1718, 1632, 1381, 1220, 1039, 601. ^1H NMR (D_2O, 300 MHz): δ 1.90 (15H, singlet, η^5-CCH_3), 6.00 (3H, multiplet, η^6-CH_{ar}), 6.32 (2H, multiplet, η^6-CH_{ar}). ^{13}C NMR (D_2O, CH_3OH, 75.5 MHz): δ 126.14, 100.21, 98.18, 88.78, 88.35, 87.82, 9.85. ESI-MS (^{102}Ru, *m/z*): 359.066 ($C_{17}H_{21}O_2Ru$ requires 359.059).

Method III: General Room-Temperature Reaction of 1 with Arenes (1:1). A solution of **1** (30 mg, 0.11 mmol, 1 equiv) in 500 μL of CH_3CN was heated until transparent and subsequently cooled to ca. 25 °C. To this, a solution of arene (0.11 mmol, 1 equiv) in 8 mL of H_2O was added and reacted overnight (ca. 25 °C). The resulting $[Cp^*Ru(\eta^6\text{-arene})]Cl$ compounds were isolated using the procedures outlined in method I.

$[Cp^*Ru(\eta^6\text{-phenol})]Cl$ (7). Phenol (10.4 mg, 0.110 mmol, 1 equiv) and **1** (30.0 mg, 27.5 μmol, 1 equiv of Ru) were reacted according to method III, above. The solvent was removed under reduced pressure, giving **7** as an off-white powder (40.0 mg, 99%

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[27] Canceill, J.; Collet, A. *J. Chem. Soc., Chem. Commun*. **1988**, 582−584.

yield). IR (ATR, cm^{-1}): 3387, 1651, 1437, 1260, 1240, 1040, 530. ^{1}H NMR (D_2O, 300 MHz): δ 1.93 (15H, singlet, η^5-CCH_3), 5.53 (1H, triplet, $J = 5.7$ Hz, η^6-CH_{ar}), 5.61 (2H, doublet, $J = 5.7$ Hz, η^6-CH_{ar}), 5.70 (2H, triplet, J 5.7, η^6-CH_{ar}). ^{13}C NMR (D_2O, CH_3OH, 75.5 MHz): δ 129.62, 96.21, 86.33, 84.57, 77.39, 10.13. ESI-MS (^{102}Ru, *m*/*z*): 331.059 ($C_{16}H_{21}ORu$ requires 331.064).

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Supporting Information Available: Text, figures, and tables giving complete experimental details, including individual syntheses, spectroscopic data, and crystallographic data, and CIF files giving crystallographic data for **12b**·H_2O and **8**·H_2O. This material is available free of charge via the Internet at http://pubs.acs.org.

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