$[(\eta^5\text{-}C_5Me_4CH_2R)Ru(\eta^6\text{-arene})]^+$ and $[(\eta^5\text{-}C_5Me_4CH_2R)Ru(CH_3CN)_3]^+$ Compounds Possessing Pendant Arms

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$[(\eta^5\text{-}C_5Me_4CH_2R)Ru(\eta^6\text{-arene})]^+$, $[(\eta^5\text{-}C_5Me_4CH_2R)Ru(CH_3CN)_3]^+$ (R = OH, OR, and NR_1R_2), and related compounds possessing pendant arms are synthesized by the attack of water, alcohol, alkoxide, or amine nucleophiles on the methylenic carbon atoms of the readily available tetramethylfulvene complex $[(\eta^6\text{-}C_5Me_4CH_2)Ru^{II}Cl(\mu\text{-}Cl)]_2$ (**1**) or its simple acetonitrile derivative, $[(\eta^6\text{-}C_5Me_4CH_2)Ru^{II}(CH_3CN)Cl_2]$ (**1a**). The $[(\eta^5\text{-}C_5Me_4CH_2R)Ru(\eta^6\text{-arene})]^+$ compounds can generally be quantitatively converted back into $[(\eta^5\text{-}C_5Me_4CH_2R)Ru(CH_3CN)_3]^+$ species by UV photolysis in CH_3CN.

Introduction

It is well-known that cyclopentadienyl-type ruthenium moieties, $[(\eta^5\text{-}Cp^R)Ru]^+$, display a rich and important chemistry. Half-sandwich compounds of the form $[(\eta^5\text{-}Cp^R)Ru(L)_x]^+$ (L = solvent, olefins, phosphine, halogen, etc.), for example, are efficient catalysts for a range of organic reactions, particularly those involving hydrogen/hydride transfer,[1] the activation of terminal alkynes, or the activation of carbon−carbon multiple bonds.[2] $[(\eta^5\text{-}Cp^R)Ru]^+$ moieties also generally form stable $[(\eta^5\text{-}Cp^R)Ru(\eta^6\text{-arene})]^+$ sandwich compounds,[3] with such species bearing relevance to fields ranging from natural product synthesis,[4] to supramolecular chemistry,[5] to the functionalization of biological compounds.[6] Moreover, $[(\eta^5\text{-}Cp^R)Ru(\eta^6\text{-arene})]^+$ complexes are known to give rise to $[(\eta^5\text{-}Cp^R)Ru(solvent)_3]^+$ catalysts upon UV irradiation in appropriate solvents (e.g., CH_3CN).[7]

Although the chemistry of cyclopentadienyl-type ruthenium moieties is dominated by $[CpRu]^+$ and $[Cp^*Ru]^+$, there has long been interest in the diversification of the cyclopentadienyl-type ligands in these and related $[Cp^RM]^{n+}$ systems. In particular, the incorporation of pendant arms with tailored functionalities has been envisioned and in many cases realized.[8] These arms might interact directly with the metal center to modify catalytic behavior or may serve as synthetic handles or points for attachment (e.g., to surfaces). Recognizing that the more electron-rich, more sterically hindered, permethylated $\eta^5\text{-}C_5Me_4R$ ligands would offer advantages compared to perhaps more readily available C_5H_4R ligands, Maitlis and co-workers have, over a decade ago, extensively explored the synthesis of $[(\eta^5\text{-}C_5Me_4CH_2R)Ru]^+$ half-sandwich compounds possessing a pendant R group (Scheme 1).[9–11] Half-sandwich compounds of $[(\eta^5\text{-}C_5Me_4CH_2R)M]^{n+}$ (M = Ir, Rh, Re, etc.) are also accessible

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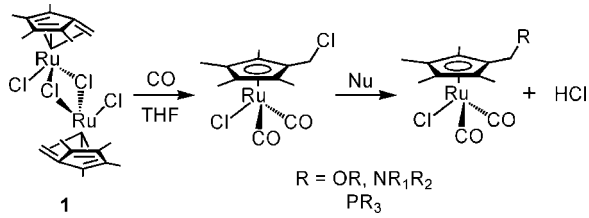
Scheme 1



by similar chemistry.[12] Maitlis' entry into $[(\eta^5\text{-}C_5Me_4CH_2R)Ru]^+$-containing compounds is convenient. Commercially available $[Cp^*Ru^{III}Cl(\mu\text{-}Cl)]_2$ is first simply exposed to air or dioxygen to give the tetramethylfulvene complex $[(\eta^6\text{-}C_5Me_4CH_2)Ru^{II}Cl(\mu\text{-}Cl)]_2$ (**1**) in high yield via oxygen insertion and spontaneous water loss by hydrogen radical abstraction.[9] Reaction of **1** with carbon monoxide gives $[(\eta^5\text{-}C_5Me_4CH_2Cl)Ru(CO)_2Cl]$, from which a variety of $[(\eta^5\text{-}C_5Me_4CH_2R)Ru(CO)_x(L)_yCl_z]$ ($x \geq 1$, L = phosphine, olefin, etc.) half-sandwich compounds can be obtained by nucleophilic substitution of the benzylic chloride.[10] An important element to the versatility of the substitution reactions is the relative inertness of the ruthenium to attack by the nucleophiles due to the protection afforded by the coordinated CO ligands. Unfortunately, the inability to completely remove the substitutively inert CO ligands in a facile manner[13] also presumably limits the range of products that can be obtained, likely prohibiting, for example, the achievement of $[(\eta^5\text{-}C_5Me_4CH_2R)Ru(\eta^6\text{-arene})]^+$ complexes or varieties of potentially catalytic, noncarbonyl-containing species (e.g., $[(\eta^5\text{-}C_5Me_4CH_2R)Ru(CH_3CN)_n]^+$).[2]

In the course of recent work on developing mild and efficient aqueous protocols for the syntheses of $[(\eta^5\text{-Cp*})Ru(\eta^6\text{-arene})]Cl$ compounds by the direct reaction of $[(\eta^5\text{-Cp*})Ru(\mu_3\text{-Cl})]_4$with arenes, we occasionally obtained small amounts (~0–19%) of the previously unknown $[(\eta^5\text{-}C_5Me_4CH_2OH)Ru(\eta^6\text{-arene})]Cl$ compounds as impurities.[14] Similarly, Lindel and co-workers recently observed the formation of $[(\eta^5\text{-}C_5Me_4CH_2OCH_3)Ru(\eta^6\text{-ethylbenzene})][PF_6]$ as an impurity (12%) in their single-step synthesis of $[(\eta^5\text{-Cp*})Ru(\eta^6\text{-ethylbenzene})][PF_6]$.[15] Suspecting that, analogous to Maitlis' chemistry, these compounds arise from the addition of solvents to a **1**-like impurity arising from oxidation/reduction of intermediate $[Cp^*Ru]^+$-containing species, we sought to further explore the chemistry of **1** in the absence of CO, with the goal of intentionally achieving as yet unknown $[(\eta^5\text{-}C_5Me_4CH_2R)Ru(\eta^6\text{-arene})]^+$, $[(\eta^5\text{-}C_5Me_4CH_2R)Ru(CH_3CN)_3]^+$ (R = OH, OR, and NR_1R_2), and related compounds possessing pendant arms. We report here the simple and high-yielding syntheses of more than 20 such new compounds. It is expected that such a facile, diverse, and high-yielding entry to these complexes will serve to expand the scope of $[Cp^RRu]^+$ chemistry, exploiting pendant moieties with tailored functionalities.

Results and Discussion

One-Step Syntheses of $[(\eta^5\text{-}C_5Me_4CH_2OR)Ru(\eta^6\text{-arene})]X$ [X = Cl, PF_6] from 1. Reaction of **1**in a heterogeneous mixture of excess benzene/water (1:1) under reflux (ca. 20 min) results in the clean formation of $[(\eta^5\text{-}C_5Me_4CH_2OH)Ru(\eta^6\text{-}$

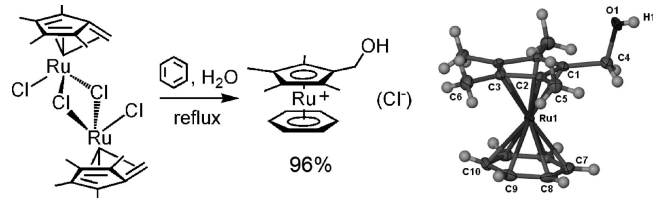


Figure 1. Synthesis of $[\mathbf{2a}]^+$ from **1** and the single crystal structure of $[\mathbf{2a}]^+$. Thermal ellipsoids are shown at 50% probability.

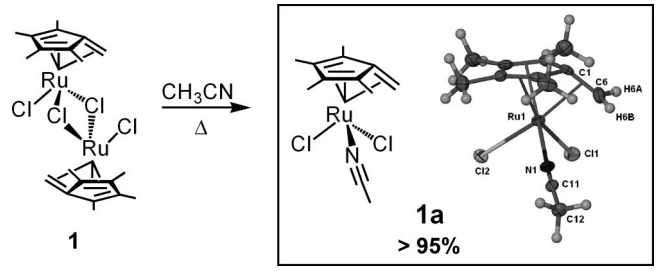


Figure 2. 1a, as derived from **1**, and its single crystal structure. Thermal ellipsoids are shown at 50% probability.

benzene)]Cl, [**2a**]Cl, marked visually by a change from orange to colorless (Figure 1). Workup of the reaction is simple, entailing only removal of solvent and recystallization of [**2a**]Cl from H_2O/dioxane (96% yield). The ^1H NMR of [**2a**]Cl in D_2O gives a singlet at δ 5.88, indicating η^6-coordination of the benzene. The methylenic protons, which appear as a complex set of resonances in **1** (δ 4.6–6.1),[9] are simplified to a single, significantly upfield shifted peak in [**2a**]Cl (δ 4.42), indicative of hydroxyl substitution. The ring methyl substituents give two closely spaced resonances at δ 2.02 and 2.03. Single crystal structure determination of [**2a**]Cl verifies the structure of the cation and is generally unremarkable except for the outwardly directed hydroxyl group and the observed 5.8° dihedral angle between the planes defined by the arene and cyclopentadienyl rings (Figure 1).

Notably, reaction of **1** with only a 2-fold excess of benzene in H_2O was unsuccessful, likely due to the insolubility of **1** in water. To alleviate this problem, dimeric **1** was first dissolved in a minimal amount of CH_3CN, producing the water-amenable monomer $[(\eta^6\text{-}C_5Me_4CH_2)RuCl_2(CH_3CN)]$ (**1a**). The dimethyl sulfoxide and pyridyl (py) analogues of **1a**, $[(\eta^6\text{-}C_5Me_4CH_2)RuCl_2(Me_2SO)]$ and $[(\eta^6\text{-}C_5Me_4CH_2)RuCl_2(py)]$, respectively, have previously been reported.[9a] **1a** in CH_3CN was found to be essentially nonconducting (1.26 Ω^{-1} cm^2 mol^{-1}), supporting the proposed nonionic structure. The X-ray single crystal structure of **1a** shows two coordinated chloride ligands, one CH_3CN ligand, and an η^6-coordinated tetramethylfulvene ligand (Figure 2). The methylenic carbon is found "tucked-in" toward the ruthenium center and is positioned *trans* to one of the two chloride ligands.

Acetonitrile solutions of **1a** were heated (generally at 85 °C) in sealed vessels with arene (2 equiv), excess water, and DMF, when necessary, to give the respective $[(\eta^5\text{-}C_5Me_4CH_2OH)Ru(\eta^6\text{-arene})]^+$ complexes, $[\mathbf{2a}]^+$–$[\mathbf{2g}]^+$ (Scheme 2). Water-insoluble arenes required the use of DMF as an additional cosolvent. In such cases, the HCl generated from the reaction induced hydrolysis of the DMF, which necessitated that the products be isolated by precipitation as their $[PF_6]^-$ salts. The $[(\eta^5\text{-}C_5Me_4CH_2OH)Ru(\eta^6\text{-arene})]X$ (X = Cl^-, $[PF_6]^-$) compounds

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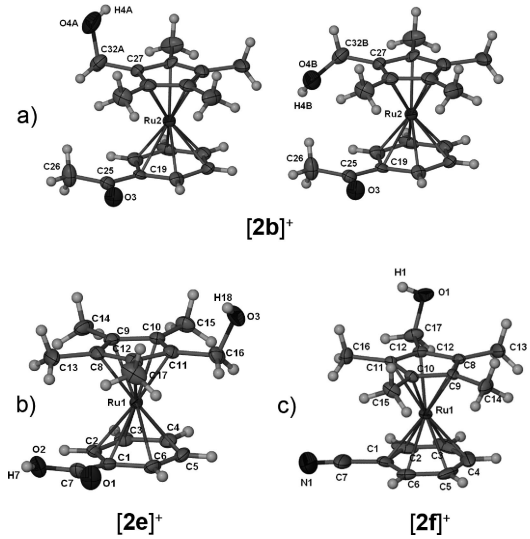

Figure 3. X-ray crystal structures of (a) the two disordered conformations of cations of [**2b**]$^+$, (b) [**2e**]$^+$, and (c) [**2f**]$^+$. Thermal ellipsoids are shown at 50% probability.

Scheme 2

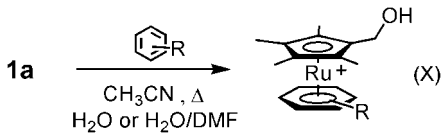

Table 1. Synthesis of Compounds [2a]$^+$−[2g]$^+$ from 1a

complex	R	equiv arene	X^-	solvent	yield (%)
[**2a**]$^+$	H	2	$[PF_6]^-$	CH_3CN/H_2O/DMF	95
[**2b**]$^+$	$COCH_3$	2	$[PF_6]^-$	CH_3CN/H_2O/DMF	90
[**2c**]$^+$	OH	2	Cl^-	CH_3CN/H_2O	98
[**2d**]$^+$	naphthalene	17.5	Cl^-	CH_3CN/H_2O/DMF	89
[**2e**]$^+$	CO_2H	2	Cl^-	CH_3CN/H_2O	92
[**2f**]$^+$	CN	2	Cl^-	CH_3CN/H_2O	94
[**2g**]$^+$	Cl	2	$[PF_6]^-$	CH_3CN/H_2O/DMF	87

were generally obtained in high yields (Table 1) and gave ^{1}H and ^{13}C NMR spectra consistent with their structures (Table 3). Historically, the poor thermal stability of [Cp*Ru]$^+$ complexes of fused arenes has complicated their synthesis.[16] Although the synthesis of [(η^5-$C_5Me_4CH_2OH$)Ru(η^6-naphthalene)]Cl, [**2d**]Cl, required higher arene concentrations under milder reaction conditions (room temperature), the mustard yellow compound was obtained in 89% yield. Single crystals of [**2b**][PF_6], [**2e**]Cl, and [**2f**]Cl were obtained by vapor diffusion of diethyl ether into ethanolic solutions of each compound. The X-ray structures revealed the hydroxyl groups of [**2e**]$^+$ and [**2f**]$^+$ to be outwardly directed. In the crystal structure of [**2b**][PF_6], however, the hydroxyl group of one of the two molecules in the asymmetric unit exhibited disorder between outwardly directed and "tucked-in" conformations (Figure 3).

To explore the possibility of synthesizing ether-substituted [(η^5-$C_5Me_4CH_2OR$)Ru(η^6-arene)]$^+$ complexes, acetonitrile solutions of **1a** were reacted with excess benzene and selected alcohols (i.e., methanol, ethanol, propanol, and 2-propanol, Scheme 3). Thus, [(η^5-$C_5Me_4CH_2OR$)Ru(η^6-benzene)]Cl (R = methyl, ethyl, propyl, isopropyl) compounds, [**3**]Cl−[**6**]Cl, respectively, were obtained in high yields (Table 2) and gave ^{1}H and ^{13}C NMR spectra commensurate with their structures (Table 3). Although, for demonstration purposes, benzene was

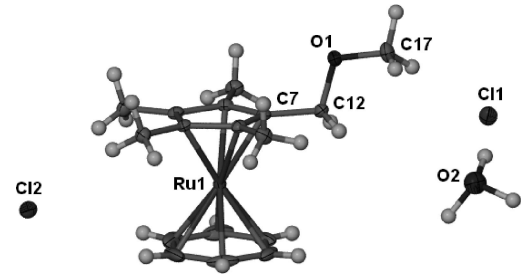

Figure 4. X-ray crystal structure of [**3**]Cl·[H_3O]Cl. Thermal ellipsoids are shown at 50% probability.

Scheme 3. Synthesis of Compounds [3]$^+$−[6]$^+$ from 1a

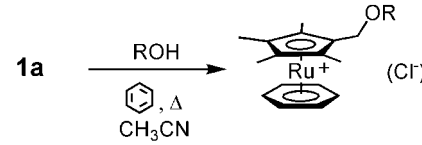

Table 2. Synthesis of Compounds 3–6 from 1a

complex	R	time (h)	yield (%)
[**3**]$^+$	Me	3	98
[**4**]$^+$	Et	5	89
[**5**]$^+$	Pr	10	92
[**6**]$^+$	^{i}Pr	24	94
	^{t}Bu	>72	

subjected to metalation in these reactions, it is clear that a diverse range of arenes could be metalated using this procedure. Moreover, using near stoichiometric amounts of arene should be feasible according to the method described above for complexes [**2a**]$^+$−[**2g**]$^+$. Qualitatively, the rates of product formation, marked visually by a change from orange to colorless, decreased in the order MeOH > EtOH > PrOH > *i*-PrOH, with reactions requiring from 2 to 24 h to reach completion. Notably, the trend in reaction rates appears to correlate more with the ability of the alcoholic solvents to solvate the generated chloride ions than with the relative nucleophilicities of the series. Obviously, the nucleophilicity of the solvent does bear some relevance; reaction with *tert*-butanol was unsuccessful even after 3 days. Single crystals of [**3**]Cl·[H_3O]Cl were grown by vapor diffusion of diethyl ether into the condensed reaction mixture. Interestingly, the crystals contain both reaction products, [**3**]Cl and HCl, the latter in the form of [H_3O]Cl (Figure 4). The structure of [**3**]$^+$ is similar to [**2a**]$^+$, with an outwardly directed methoxy group. Lastly, reactions of **1** or **1a** in bulk amine solvents failed to give the amino-substituted sandwich complexes, presumably due to coordinative saturation of the ruthenium center by amine ligands.

Mechanism. The mechanisms of the reactions described herein deserve comment, as they differ from that reported by Maitlis and co-workers in their synthesis of [($C_5Me_4CH_2Cl$)-Ru($CO)_2$Cl] and related [($C_5Me_4CH_2R$)Ru($CO)_nL_m$] (n = 1–2) complexes. These workers observed, for example, that reaction of CO with **1** results in both CO coordination and a seemingly intramolecular addition of a chloride ligand to the electrophilic methylenic carbon of the tetramethylfulvene ligand to give [($C_5Me_4CH_2Cl$)Ru($CO)_2$Cl] in good yield. Notably, in reactions employing CH_3CN instead of CO, we could uncover no evidence for the existence of intermediate chloro-substituted [(η^5-$C_5Me_4CH_2Cl$)RuCl($CH_3CN)_2$] or [(η^5-$C_5Me_4CH_2Cl$)Ru-($CH_3CN)_3$]Cl complexes. Instead, it was observed by ^{1}H NMR spectroscopy that alcohol/water nucleophiles (Nu) were reversibly adding to **1a** directly, generating HCl, chloride ions, and

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Table 3. ^{1}H NMR Data for New Compounds[a]

complex	C_5Me_4	CH_2Nu	Nu	Arene	CH_2OH
1a	1.53 (6H), 1.78 (6H)	4.97 $C_5Me_4CH_2$			
[**2a**]Cl	2.02 (6H), 2.03 (6H)	4.42		η^6-CH_{ar}, 5.88 (6H)	
[**2b**][PF_6]	2.02 (6H), 2.02 (6H)	4.36 (d, J = 4.8)		$COCH_3$, 2.63 (3H, s) η^6-CH_{ar}, 6.33 (3H, m), 6.65 (2H, m)	4.51 (1H, t,J4.8)
[**2c**]Cl	1.97 (6H), 1.98 (6H)	4.37		η^6-CH_{ar}, 5.61 (1H, t, J = 6.3), 5.71 (2H, d, J = 6.3), 5.78 (2H, t, J = 6.3)	
[**2d**]Cl	1.59 (6H), 1.63 (6H)	4.09		η^6-CH_{ar}, 5.99 (2H, m,), 6.52 (2H, m), 7.49 (2H, m), 7.66 (2H, m)	
[**2e**]Cl	1.95 (6H), 1.97 (6H)	4.35		η^6-CH_{ar}, 6.07 (3H, m), 6.40 (2H, m)	
[**2f**]Cl	2.03 (6H), 2.04 (6H)	4.40		η^6-CH_{ar}, 6.19 (3H, m), 6.42 (2H, m)	
[**2g**][PF_6]	2.08 (6H), 2.09 (6H)	4.43 (d, J = 4.5)	η^6-CH_{ar}, 6.17 (1H, t, J = 5.7), 6.25 (2H, t, J = 5.7), 6.45 (2H, d, J = 5.7)	4.80 (1H, t, J = 4.5)	
[**3**]Cl	2.06 (12H)	4.37	OMe 3.42 (3H, s)	η^6-CH_{ar}, 5.91 (6H, s)	
[**4**]Cl	2.06 (12H)	4.39	OEt, 1.20 (3H, t, J = 7.1), 3.66 (2H, q, J = 7.1)	η^6-CH_{ar}, 5.90 (6H, s)	
[**5**]Cl	2.02 (12H)	4.35	OPr, 0.86 (3H, t, J = 7.2), 1.55 (2H, s, J = 7.2), 3.52 (2H, t, J = 7.2)	η^6-CH_{ar}, 5.87 (6H, s)	
[**6**]Cl	2.03 (12H)	4.35	O^{i}Pr 1.18 (6H, d, J = 6.2), 3.83 (1H, sept, J = 6.2)	η^6-CH_{ar}, 5.88 (6H, s)	
[**7**][PF_6]	1.61 (6H), 1.62 (6H)	4.05	OEt, 1.13 (3H, t, J = 7.0), 3.45 (2H, q, J = 7.0), CH_3CN, 2.33 (9H, bs)		
8	1.57 (6H), 1.60 (6H)	4.19	OEt, 1.14 (3H, t, J = 7.0), 3.47 (2H, q, J = 7.0)		
9	1.59 (12H), 1.77 (12H)	4.38	OEt, 1.13 (6H, t, J = 7.2), 3.42 (4H, q, J = 7.2) μ-OEt, 1.46 (6H, t, J = 7.2), 4.94 (4H, q, J = 7.2)		
[**10**]Cl	2.03 (6H), 2.06 (6H)	3.56	NEtMe, 1.13 (3H, t, J = 7.1), 2.25 (3H, s), 2.66 (2H, t, J = 7.1)	η^6-CH_{ar}, 5.87 (6H, s)	
[**11a**]Cl	2.01 (6H), 2.03 (6H)	3.56	NBu, 0.86 (3H, triplet, J = 7.2), 1.29 (2H, sextet, J = 7.2), 1.43 (2H, quint, J = 7.2), 2.56 (2H, t, J = 7.2)	η^6-CH_{ar}, 5.85 (6H, s)	
[H·**11b**][PF_6]$_3$	2.08 (12H), 2.10 (12H)	3.49	NBu, 0.73 (3H, triplet, J = 7.2), 1.13 (2H, sextet, J = 7.2), 1.38 (2H, quint, J = 7.2), 2.35 (2H, t, J = 7.2)	η^6-CH_{ar}, 6.04 (12H, s)	
[**12**][PF_6]	2.10 (6H), 2.11 (6H)	4.42	OCH_2CH_2CN, 2.81 (2H, t, J = 5.9), 3.80 (2H, t, J = 5.9)	η^6-CH_{ar}, 6.11 (6H, s)	
[**13**][PF_6]$_2$	2.10 (6H), 2.12 (6H)	4.49	$OCH_2CH_2N(CH_3)_2$, 2.89 (6H, s), 3.32 (2H, t, J = 5.1), 3.90 (2H, t, J = 5.1)	η^6-CH_{ar}, 6.10 (6H, s)	
[**14**][PF_6]$_2$	2.12 (6H), 2.13 (6H)	4.55	$CH_2CH_2CH_2N$, 1.93 (4H, bm), NCH_3, 3.07 (3H, s), CHN, 3.29 (1H, m), CH_2N, 3.75 (2H, m), OCH_2CHN, 3.86 and 4.00 (1H, m, 1H, m)	η^6-CH_{ar}, 6.08 (6H, s)	
[**15**][PF_6]	2.09 (6H), 2.16 (6H)	5.03	CH_{ar}, 6.20 (1H, dt, J = 1.3 and 6.7,), 6.38 (1H, ddd, J = 0.7, 1.3, 9.2), 7.39 (1H, ddd, J = 2.1, 6.7, 9.2), 7.57 (1H, ddd, J = 0.7, 2.1 and 6.7)	η^6-CH_{ar}, 6.16 (6H, s)	
[**16**][PF_6]	1.99 (6H), 2.06 (6H)	4.31	OCH_2CH_2, 3.04 (2H, t, J = 6.4), 3.95 (2H, t, J = 6.4), CH_{ar}, 7.19 (1H, dt, J = 4.7 and 8.8), 7.30 (1H, d, J = 7.8), 7.69 (1H, dt, J = 8.8 and 2.1), 8.50 (1H, d, J = 4.6)	η^6-CH_{ar}, 6.03 (6H, s)	
[**17b**][PF_6]	1.48 (6H), 1.72 (6H)	4.18	2.29 (6H, s, CH_3CN), OCH_2CH_2, 3.72 (2H, vbs), 4.05 (2H, t, J = 5.4), η^1-CH_{ar}, 7.25 (1H, dt, J = 7.2 and 1.2), 7.44 (1H, d, J = 7.2), 7.77 (1H, dt, J = 7.2 and 1.2), 8.62 (1H, d, J = 7.2)		

[a] H NMR spectra were taken in D_2O and $(CD_3)_2CO$ for Cl^- and $[PF_6]^-$ salts, respectively; CD_3CN for **1a**; CD_2Cl_2 for **8** and [**17b**][PF_6]; and C_6D_6 for **9**.

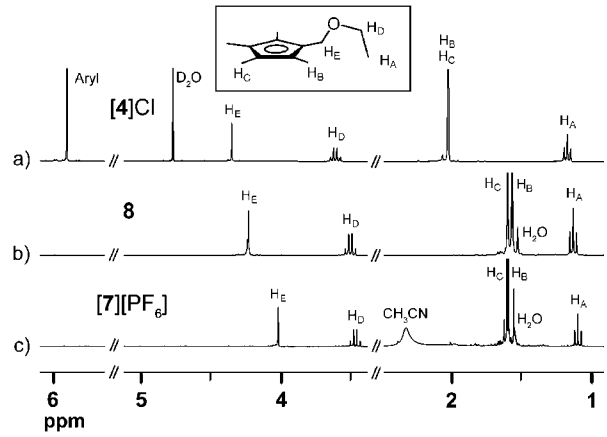
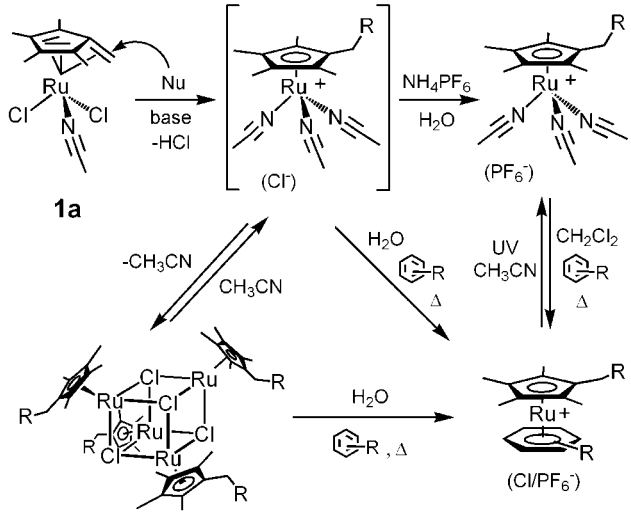


Figure 5. ^{1}H NMR spectra of (a) [**4**]Cl in D_2O, (b) **8** in CD_2Cl_2, and (c) [**7**][PF_6] in CD_2Cl_2.

Scheme 4



[(η^5-$C_5Me_4CH_2Nu$)Ru($CH_3CN)_3$]Cl species in an equilibrium that favored unsubstituted **1a**. In the presence of arenes, however, the functionalized piano-stool [(η^5-$C_5Me_4CH_2$-Nu)Ru($CH_3CN)_3$]$^+$ complexes, being simple analogues of the commonly used metalating agent [(η^5-Cp*)Ru($CH_3CN)_3$]$^+$, readily form [(η^5-$C_5Me_4CH_2Nu$)Ru(η^6-arene)]$^+$ sandwich compounds that, being the thermodynamic sink, push the reaction to completion. As [(η^5-Cp^R)Ru(η^6-arene)]$^+$ sandwich compounds can generally be converted back to [(η^5-Cp^R)Ru-($CH_3CN)_3$]$^+$ species by UV photolysis in CH_3CN, [(η^5-Cp^R)Ru(η^6-arene)]$^+$ compounds can be viewed as a convenient means of isolating and/or "storing" [(η^5-Cp^R)Ru($CH_3CN)_3$]$^+$ in air-stable form. With these concepts in mind, and attempting to demonstrate that the equilibria can be driven toward [(η^5-$C_5Me_4CH_2Nu$)Ru($CH_3CN)_3$]$^+$ complexes, **1a** was reacted with 1 equiv of KOEt (generated *in situ* by the addition of KO^{t}Bu) in ethanol/acetonitrile, and the resulting [(η^5-$C_5Me_4CH_2$-OCH_2CH_3)Ru($CH_3CN)_3$]$^+$ complex was isolated as its yellow [PF_6]$^-$ salt, [**7**][PF_6]. Alternatively, complete removal of the reaction solvent and extraction into pentane results in the isolation of brick red [(η^5-$C_5Me_4CH_2OCH_2CH_3$)RuCl]$_n$ (**8**) after stripping of the pentane. It is important to note that the relationship of monomeric [**7**]Cl to presumably tetrameric **8** (n = 4) is analogous to that of [(η^5-Cp*)Ru($CH_3CN)_3$]Cl to [(η^5-Cp*)Ru(μ_3-Cl)]$_4$.[17] The simple ^{1}H NMR spectrum of **8** is nearly identical to that of [**7**][PF_6] with the exception of the peak corresponding to coordinated CH_3CN (Figure 5). Both [**7**][PF_6] and **8** afford [**4**]$^+$ in near quantitative yield under appropriate conditions for metalation (CH_2Cl_2 and H_2O, respectively). Additionally, [**4**][PF_6] is readily converted back into [**7**][PF_6] upon UV irradiation in acetonitrile. Not surprisingly, it is clear that the transformations exemplified by the [(η^5-$C_5Me_4CH_2$-OCH_2CH_3)Ru]$^+$ and presumably other [(η^5-$C_5Me_4CH_2Nu$)Ru]$^+$ species (Scheme 4) parallel the well-known chemistry of the permethylated [(η^5-Cp*)Ru]$^+$ moiety. Along these lines, treatment of **1a** with excess ethoxide gives rise to what appears by ^{1}H NMR spectroscopy to be the alkoxide dimer [(η^5-C_5Me_4-$CH_2OCH_2CH_3$)Ru(μ-OCH_2CH_3)]$_2$ (**9**), analogous to Koelle's useful [(η^5-Cp*)Ru(μ-OR)]$_2$ compounds.[18] We did not, however, formally isolate pure **9**.

Syntheses of [(η^5-$C_5Me_4CH_2NR_1R_2$)Ru(η^6-arene)]X [X = Cl or PF_6]. The utilization of amine nucleophiles in the synthesis of [(η^5-$C_5Me_4CH_2NR_1R_2$)Ru]$^+$-containing compounds presented some challenges: (i) although they readily add to the electrophilic carbon of **1a** (observable by ^{1}H NMR), excess amines coordinate to the ruthenium center, making isolation of piano-stool complexes of predictable composition difficult; (ii) stoichiometric reactions were sluggish and frequently contained unwanted side products; and, last, (iii) ammonium salts generated from the reaction proved difficult to separate from the products. To circumvent issues i and ii, the isolation of [(η^5-$C_5Me_4CH_2NR_1R_2$)Ru(η^6-benzene)]X (X = Cl^-, $[PF_6]^-$) sandwich compounds was exploited as a convenient means to effectively purify the [(η^5-$C_5Me_4CH_2NR_1R_2$)Ru]$^+$ moieties; this procedure also allowed for the use of greater than stoichiometric amounts of the amine nucleophile. Issue iii is addressed simply by absorbing the generated H^+ with KO^{t}Bu. In certain situations where triethylamine proved superior to KO^{t}Bu,[19] NH_4PF_6 precipitation of the [(η^5-$C_5Me_4CH_2NR_1R_2$)Ru(η^6-benzene)]$^+$ cations avoids ammonium salt contamination of the product (Table 4, Scheme 5).

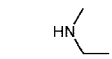
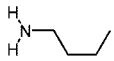
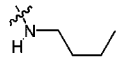
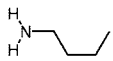
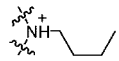
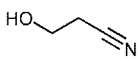
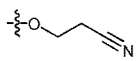
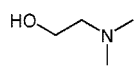
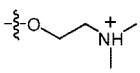
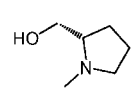
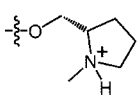
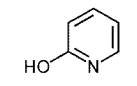
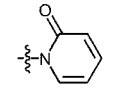
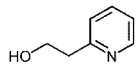
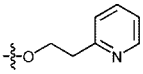
Treatment of an acetonitrile solution of **1a** with *N*-ethylmethylamine and stoichiometric KO^{t}Bu, followed by metalation of benzene in a heated H_2O/benzene mixture, gave [{(η^6-benzene)Ru(η^5-$C_5Me_4CH_2$)}N(CH_3)(CH_2CH_3)]Cl, [**10**]Cl, as a tan solid in 79% yield. The ^{1}H NMR spectrum of [**10**]Cl revealed aryl proton resonances at δ 5.87; $C_5Me_4CH_2R$ methyl resonances at δ 2.03 and 2.06; a singlet for the substituted ring methylene protons at δ 3.56, which is significantly upfield shifted compared to alkoxy-substituted [**3**]$^+$−[**6**]$^+$ ($\delta \approx$ 4.4–4.2); and resonances for the *N*-ethyl (δ 1.13, 2.66) and *N*-methyl protons (δ 2.25) (Table 3). Reactions of **1a** and primary amines were expected to yield a mixture of mono- and disubstituted products.Monosubstituted[{(η^6-benzene)Ru(η^5-$C_5Me_4CH_2$)}NH-($CH_2(CH_2)_2CH_3$)]Cl, [**11a**]Cl, was synthesized by dropwise addition of an acetonitrile solution of **1a** into excess *N*-butylamine and stoichiometric KO^{t}Bu, followed by heat treatment with a H_2O/benzene mixture. [**11a**]Cl was isolated in 89% yield, but the product contained an additional 7%

(17) Fagan, P. J.; Mahoney, W. S.; Calabrese, J. C.; Williams, I. D. *Organometallics* **1990**, *9*, 1843–52.

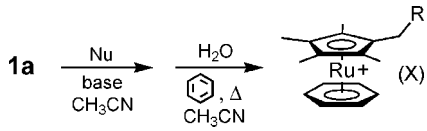
(18) (a) Koelle, H. *Chem. Rev.* **1998**, *98*, 1313–1334. (b) Hornig, A.; Englert, U.; Koelle, U. *J. Organomet. Chem.* **1993**, *453*, 255–261. (c) Koelle, U.; Kossakowski, J. *J. Organomet. Chem.* **1989**, *362*, 383–398. (d) Koelle, U.; Kossakowski, J. *J. Chem. Soc., Chem. Commun.* **1988**, 549–551.

(19) When the nucleophile cannot effectively solvate KO^{t}Bu because of (i) its identity, (ii) its utilization in near-stoichiometric quantities, or (iii) the thermal sensitivity of the nucleophile (which precludes heating), triethylamine was found to be a useful substitute.

Table 4. Synthesis of Compounds $[10]^+$−$[16]^+$ from 1a

	Nu	R	equiv. Nu	base	X	yield (%)
$[10]^+$			5	KO^{t}Bu	Cl^-	79
$[11a]^+$			24	KO^{t}Bu	Cl^-	89
$[H\cdot 11b]^{3+}$			0.5	TEA	$3[PF_6]^-$	74
$[12]^+$			15	TEA	$[PF_6]^-$	79
$[13]^{2+}$			5	KO^{t}Bu	$2[PF_6]^-$	77
$[14]^{2+}$			5	KO^{t}Bu	$2[PF_6]^-$	78
$[15]^+$			5	KO^{t}Bu	$[PF_6]^-$	91
$[16]^+$			5	KO^{t}Bu	$[PF_6]^-$	77

Scheme 5



of the disubstituted $[\{(\eta^6\text{-benzene})Ru(\eta^5\text{-}C_5Me_4CH_2)\}_2N(CH_2(CH_2)_2CH_3)]Cl_2$ compound, $[\mathbf{11b}]Cl_2$. Reaction of 2 equiv of **1a** with 1 equiv of *N*-butylamine and excess triethylamine (TEA)—employed in place of poorly soluble KO^{t}Bu—followed by benzene metalation gave $[\mathbf{11b}]^{2+}$. Because of the presence of triethyl ammonium cations, the complex was easiest isolated (74% yield) by NH_4PF_6 precipitation of the protonated[20] $[H\cdot\mathbf{11b}][PF_6]_3$ compound from aqueous solution. The product also contained an additional 4% of $[H\cdot\mathbf{11a}][PF_6]_2$. Unfortunately, all attempts at separating $[\mathbf{11a}]Cl$ from $[\mathbf{11b}]Cl_2$ or $[H\cdot\mathbf{11a}][PF_6]_2$ from $[H\cdot\mathbf{11b}][PF_6]_3$ via recrystallization failed. Although triethylamine was employed in the synthesis of $[H\cdot\mathbf{11b}][PF_6]_3$, no trace of the quaternary $[(\eta^6\text{-benzene})Ru(\eta^5\text{-}C_5Me_4CH_2N(CH_2CH_3)_3)]^{2+}$ complex appeared in the isolated product. ^1H NMR experiments revealed that the addition of triethylamine to **1a** can occur to some extent, but addition of the tertiary amine is reversible.[21]

Addition of Bifunctional Nucleophiles. Several alcoholic nucleophiles with secondary functionalities potentially capable of interacting with the ruthenium center (containing nitrile, tertiary amino, and pyridyl groups) were also reacted with **1a** (Table 4, Scheme 5). An acetonitrile solution of **1a** was reacted with 3-hydroxypropionitrile in the presence of stoichiometric amounts of TEA. The reaction was then subjected to H_2O/benzene treatment, and the $[(\eta^6\text{-benzene})Ru(\eta^5\text{-}C_5Me_4CH_2OCH_2CH_2CN)]PF_6$, $[\mathbf{12}][PF_6]$ was isolated as a white powder in 79% yield by NH_4PF_6 precipitation from water. In this case, the thermal sensitivity of 3-hydroxypropionitrile in basic solution demanded the use of stoichiometric amounts of TEA in place of the less soluble, more basic KO^{t}Bu. Based on earlier observations concerning the addition of triethylamine (*vide supra*) to **1a**, other tertiary amines and pyridyl compounds were also expected to add reversibly. Consequently, reactions of **1a** with select *N*-tertiary amino alcohols and pyridyl alcohols were expected to afford exclusively ether-linked products. Thus, the reaction of **1a** with tertiary amines *N*,*N*-dimethylethanolamine and (*S*)-2-hydroxymethyl-1-methylpyrrolidine ultimately gave protonated, dicationic products $[(\eta^5\text{-}C_5Me_4CH_2OCH_2CH_2NH(CH_3)_2)Ru(\eta^6\text{-benzene})][PF_6]_2$, $[\mathbf{13}][PF_6]_2$, and (*S*)-$[\eta^5$-{2-((C$_5$Me$_4$CH$_2$O)methyl)-1-methylpyrrolidinium}Ru(η^6-benzene)$][PF_6]_2$, $[\mathbf{14}][PF_6]_2$, in 77% and 78% yields, respectively. Notably, no nitrogen addition products were observed. The X-ray crystal structure of $[\mathbf{14}][PF_6]_2$ reveals the expected dication with its protonated nitrogen (Figure 6). Reactions of **1a** with the series of pyridyl alcohols 2-hydroxypyridine, 2-(hydroxymethyl)-pyridine, and 2-(2-hydroxyethyl)pyridine were not as straightforward. Addition of 2-hydroxypyridine to **1a** occurred at the pyridyl nitrogen atom, giving $[\eta^5$-{1-((C$_5$Me$_4$CH$_2$O)methyl)pyridin-2-one}Ru(η^6-benzene)$]PF_6$, $[\mathbf{15}][PF_6]$, in 91% yield. Under the reaction conditions it is likely that the pyridone tautomer of 2-hydroxypyridine dominates in solution.[22] X-ray structure determination of $[\mathbf{15}][PF_6]\cdot H_2O$ confirmed the identity of the cation. Notably, the carbon−oxygen bond of the pyridone moiety (1.24 Å) shows significant double-bond character. Reaction of **1a** with 2-(hydroxymethyl)pyridine results in oxidation of the nucleophile to 2-pyridinecarbaldehyde via ruthenium-promoted hydride transfer from 2-(hydroxymethyl)pyridine to the methylenic carbon of **1a**, additionally yielding $[(\eta^5\text{-}C_5Me_5)Ru(\eta^6\text{-benzene})]^+$. Both product species were clearly observable via ^1H NMR. Lastly, of the chosen pyridyl alcohols, only 2-(2-hydroxyethyl)pyridine reacted with **1a** to give the desired ether-linked addition product, $[\eta^5$-{2-((C$_5$Me$_4$CH$_2$O)methyl)pyridine}Ru(η^6-benzene)$][PF_6]$, $[\mathbf{16}][PF_6]$, in 77% yield.

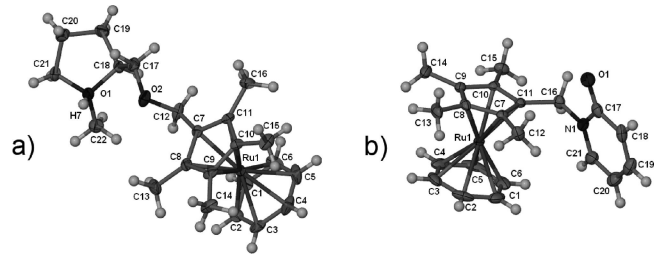


Figure 6. X-ray single crystal structures of (a) $[\mathbf{14}]^{2+}$, and (b) $[\mathbf{15}]^+$. Thermal ellipsoids are shown at 50% probability.

UV Demetalation of $[16]^+$ in CD_3CN. $[\mathbf{16}]^+$ possesses a pendant pyridyl group, which could conceivably interact with the ruthenium center were the arene moiety not present. Moreover, such coordination has the potential to occur in an η^1 or η^6 fashion, either intra- or intermolecularly. UV photolysis

(20) Protonation of the products by NH_4^+ was confirmed by ^1H and ^{19}F NMR, using an internal standard.

(21) The ^1H NMR of a reaction mixture identical to that used in the synthesis of $[H\cdot\mathbf{11b}][PF_6]_3$, but without butylamine and using CD_3CN, showed ca. 25% conversion of **1a** into $[(\eta^5\text{-}C_5Me_4CH_2NEt_3)Ru(CD_3CN)_3]^{2+}$. Subsequent reaction with benzene/H_2O resulted in the isolation of pure $[\mathbf{2a}]PF_6$, indicating that the triethylamine is displaced by water.

(22) Wong, M. W.; Wiberg, K. B.; Frisch, M. J. *J. Am. Chem. Soc.* **1992**, *114*, 1645–1652.

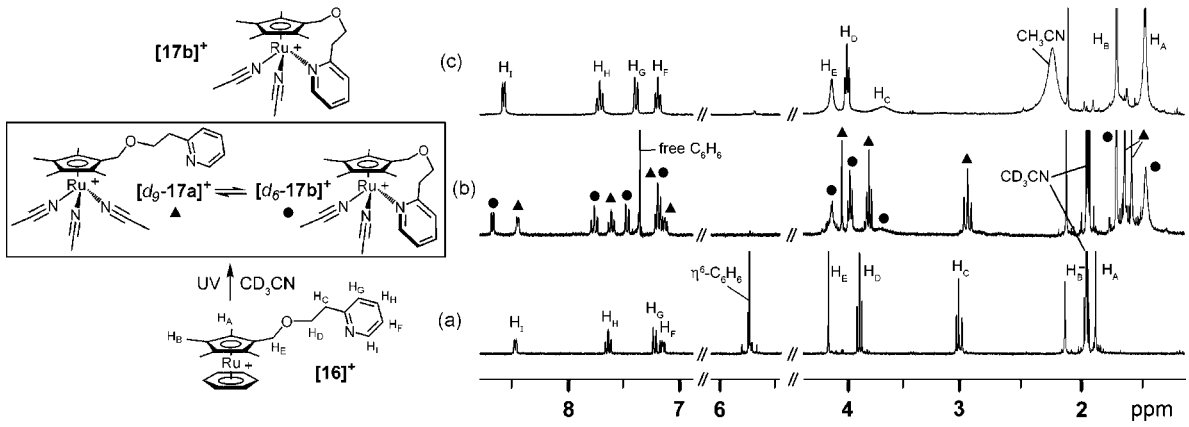


Figure 7. ^{1}H NMR spectra of (a) [**16**]$^+$ in CD_3CN, (b) [d_9-**17a**]$^+$ (▲) and [d_6-**17b**]$^+$ (●) in CD_3CN, and (c) [**17b**]$^+$ in CD_2Cl_2.

of [**16**][PF_6] in a degassed solution of CD_3CN resulted in a distinct color change from colorless to deep orange. The *in situ* ^{1}H NMR spectrum revealed complete liberation of the benzene ligand, marked by a signal for free benzene at δ 7.42. The spectrum also indicated a equilibrium mixture of two species, namely, the tris-solvated [η^5-{2-(($C_5Me_4CH_2O$)ethyl)pyridine}-Ru(CD_3CN)$_3$][PF_6], [d_9-**17a**]$^+$, and the η^1-coordinated pyridyl complex [η^5-{2-((η^5-$C_5Me_4CH_2O$)ethyl)η^1-pyridine}Ru(CD_3-$CN)_2$][PF_6], [d_6-**17b**]$^+$ (Figure 7). In an attempt to drive the equilibrium entirely toward [η^5-{2-((η^5-$C_5Me_4CH_2O$)ethyl)η^1-pyridine}Ru($CH_3CN)_2$][PF_6] [**17b**]$^+$, excess CD_3CN was removed and the residue was briefly exposed to nondeuterated CH_3CN. After an additional drying, the ^{1}H NMR spectrum in CD_2Cl_2 revealed complete conversion to [**17b**]$^+$, with coordinated CH_3CN resonances clearly visible (δ 2.29, 6H). The spectrum of [**17b**]$^+$ additionally consists of pyridyl resonances at δ 7.25, 7.44, 7.77, and 8.62, a slightly broadened methylenic peak at 4.18, one sharp triplet and one very broad peak at δ 4.05 and δ 3.72 corresponding to the distal and proximal ethylenic protons of the pyridyl moiety, and a sharp and broad singlet at δ 1.72 and 1.48 for the ring-methyl protons. The significant peak broadening is clearly indicative of an intramolecularly coordinated cyclic species with limited conformational mobility. Lastly, it is interesting to note that no η^6-pyridyl-coordinated species were observed, even though cyclopentadienyl ruthenium moieties are capable of metalating pyridine in high yield.[14,23]

Conclusions

Described herein is a simple method of modifying ruthenium-coordinated pentamethylcyclopentadienyl moieties to afford [(η^5-$C_5Me_4CH_2R$)Ru(η^6-arene)]$^+$ and [(η^5-$C_5Me_4CH_2R$)Ru-($CH_3CN)_3$]$^+$ (R = OH, OR and NR_1R_2) complexes. The chemistry of these [(η^5-$C_5Me_4CH_2R$)Ru]$^+$ species closely parallels that of the well-known [Cp*Ru]$^+$ moiety. Thus, the [(η^5-$C_5Me_4CH_2R$)Ru($CH_3CN)_3$]$^+$ compounds are expected to similarly function as effective catalysts for a variety of organic transformations, and modification of the pedant arms may provide a means of catalyst optimization. The synthetic approach toward [(η^5-$C_5Me_4CH_2R$)Ru(η^6-arene)]$^+$ and [(η^5-$C_5Me_4CH_2R$)-Ru($CH_3CN)_3$]$^+$ compounds follows the well-developed chemistry of Maitlis and co-workers, but involves use of CH_3CN in place of CO for the activation of **1**. This simple departure allows for direct addition of oxygen- and nitrogen-based nucleophiles to the tetramethylfulvene moiety. Although nucleophiles additionally coordinate to the ruthenium center, they are readily displaced from the metal by reaction with arenes in aqueous media, forming air-stable, easily isolated [(η^5-$C_5Me_4CH_2R$)Ru(η^6-arene)]$^+$ compounds. The [(η^5-$C_5Me_4CH_2R$)Ru(η^6-arene)]$^+$ compounds can generally be quantitatively converted back into [(η^5-$C_5Me_4CH_2R$)Ru($CH_3CN)_3$]$^+$ species by UV photolysis in CH_3CN. In one case, [**17b**]$^+$, it has been demonstrated that the pendant group has the ability to tether itself to the ruthenium center in an intramolecular fashion. Lastly, we have come to view some aspects of this and the related [Cp*Ru]$^+$ chemistry as a form of organometallic "click" chemistry,[24] allowing virtually any sterically accessible arene to be simply conjugated with [(η^5-$C_5Me_4CH_2R$)Ru]$^+$ moieties possessing any number of pendant functional groups (e.g., hydroxyl, pyridyl, tertiary amine, nitrile). Work is currently ongoing in the exploitation of this chemistry for the conjugation of aryl-containing compounds that are costly and/or otherwise difficult to modify (cryptophanes,[5a,14] biomolecules, etc.).

Experimental Section

CH_3CN, DMF, and pentane were obtained from Fisher (Pittsburgh, PA), degassed with nitrogen, and used without further purification. All reagents 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** was prepared according to previously reported literature procedures.[9] All reactions were carried out under nitrogen atmosphere using standard Schlenk and/or glovebox techniques. ^{1}H (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. ^{1}H NMR data for all compounds are given in Table 3. MS data were obtained on a LCQ Classic LCMS ESI mass spectrometer running in positive ion mode. Elemental analyses were carried out on a Perkin-Elmer PE2400 microanalyzer at Georgetown University. Elemental analyses (EA) of at least one member of each chemically similar group of compounds are given. For all compounds lacking EA characterization, ESI mass spectral data are provided. All ^{1}H NMR spectra are given as Supporting Information. Conductance measurements were performed utilizing a VWR 525 conductivity dip cell (Pt) and VWR model 604 conductivity meter (cell constant obtained from a 0.1 M aqueous KCl solution).

Preparation of Complexes. [(η^6-$C_5Me_4CH_2$)$RuCl_2(CH_3CN)$]-(1a). 1 (20 mg, 32.7 μmol) was heated in degassed in CH_3CN or CD_3CN (ca. 10 min, 85 °C), giving **1a** quantitatively via ^{1}H NMR.

(23) (a) Fish, R. H.; Kim, H-S.; Fong, R. H. *Organometallics* **1991**, *10*, 770. (b) Fish, R. H.; Fong, R. H.; Tran, A.; Baralt, E. *Organometallics* **1991**, *10*, 1209.

(24) Kolb, H.; Finn, M. G.; Sharpless, K. B. *Angew. Chem., Int. Ed.* **2001**, *40*, 2004–2021.

Crystals of **1a** were grown by slow evaporation of this solution. Due to partial ligand loss and re-formation of **1** upon CH_3CN removal, however, **1a** was generally prepared *in situ*. ^{13}C NMR (CD_3CN, 75.5 MHz): δ 77.29, 8.50, 7.21. Anal. Calcd (%) for $C_{12}H_{17}Cl_2NRu$: C, 41.51; H, 4.93; N. 4.03. Found: C, 41.43; H, 4.85; N, 3.98.

[(η^6-Benzene)Ru(η^5-$C_5Me_4CH_2OH$)]Cl, [2a]Cl. **1** (250 mg, 0.408 mmol) was placed in 60 mL of degassed H_2O/benzene (1:1). The heterogeneous solution was refluxed under nitrogen with vigorous stirring for ca. 20 min, during which time the solution turned from red-orange to colorless. The solvent was reduced to 5 mL, and [**2a**]Cl was precipitated as a white powder by addition of dioxane (287 mg, 96% yield). *From* **1a** *at 2-fold excess of benzene*: To a solution of **1a** prepared from **1** (30.0 mg, 49.0 μmol, 1 equiv Ru) in 0.5 mL of CH_3CN was added 3 mL of H_2O, 2 mL of DMF, and benzene (15.3 μL, 0.196 mmol, 2 equiv). The vessel was sealed under nitrogen and the solution was reacted overnight (ca. 85 °C). The solution was cooled and the solvent removed under reduced pressure. The resulting solid was dissolved in minimal H_2O and subsequently precipitated with an aqueous solution of NH_4PF_6, resulting in [**2a**][PF_6] as a white powder (44.3 mg, 95% yield). [**2a**]Cl: ^{13}C NMR (D_2O, CH_3OH, 75.5 MHz): δ 98.78, 97.57, 95.40, 87.75, 10.40, 10.10. ESI-MS: (^{102}Ru) 331.1 ($C_{16}H_{21}ORu$ requires 331.1). Anal. Calcd (%) for $C_{16}H_{21}ClORu$: C, 52.53; H, 5.79. Found: C, 52.26; H, 5.72.

[(η^6-Acetophenone)Ru(η^5-$C_5Me_4CH_2OH$)]PF_6, [2b][PF_6]. [**2b**][PF_6] was synthesized and isolated according to the procedure for [**2a**][PF_6] utilizing **1a** prepared from **1** (31.8 mg, 51.2 μmol, 1 equiv of Ru) and acetophenone (24.2 μL, 0.208 mmol, 2 equiv), giving [**2b**][PF_6] as a white powder (48.2 mg, 90% yield). ^{13}C NMR ($(CD_3)_2CO$, 75.5 MHz): δ 197.18, 99.34, 98.80, 95.51, 90.11, 89.16, 87.37, 55.26, 27.34, 10.19, 10.07. ESI-MS: (^{102}Ru) 373.1 ($C_{18}H_{23}O_2Ru$ requires 373.1).

[(η^6-Phenol)Ru(η^5-$C_5Me_4CH_2OH$)]Cl, [2c]Cl. To **1a** prepared from **1** (30.2 mg, 49.3 μmol, 1 equiv of Ru) in 0.5 mL of CH_3CN was added 3 mL of H_2O and phenol (18.2 mg, 0.193 mmol, 2 equiv). The vessel was sealed under nitrogen, and the solution was reacted overnight (ca. 85 °C). The solution was cooled, and the solvent was removed under reduced pressure, resulting in an off-white solid, which was triturated with toluene to produce [**2c**]Cl as a white powder (36.8 mg, 98% yield). ^{13}C NMR (D_2O, CH_3OH, 75.5 MHz): δ 128.86, 96.44, 95.21, 93.08, 85.31, 83.45, 76.26, 53.78, 8.76, 8.50. ESI-MS: (^{102}Ru) 347.1 ($C_{16}H_{21}O_2Ru$ requires 347.1).

[(η^6-Naphthalene)Ru(η^5-$C_5Me_4CH_2OH$)]Cl, [2d]Cl. To **1a** prepared from **1** (150 mg, 0.245 mmol, 1 equiv of Ru) in 2 mL of CH_3CN was added a solution of naphthalene (550 mg, 4.29 mmol, 17.5 equiv) in 7 mL of DMF and 4 mL of H_2O. The orange solution was reacted overnight at room temperature under nitrogen. The solvent was reduced under vacuum (ca. 40 °C) to give a solution of [**2d**]Cl in ca. 4 mL of DMF. The compound was precipitated by addition of diethyl ether, yielding [**2d**]Cl as a mustard yellow powder (181 mg, 89% yield). ^{13}C NMR (D_2O, CH_3OH, 75.5 MHz): δ 131.80, 128.07, 97.57, 95.66, 94.57, 92.03, 88.67, 85.84, 54.77, 9.14, 8.93. ESI-MS: (^{102}Ru) 381.2 ($C_{20}H_{23}ORu$ requires 381.1).

[(η^6-Benzoic acid)Ru(η^5-$C_5Me_4CH_2OH$)]Cl, [2e]Cl. [**2e**]Cl was synthesized and isolated according to the procedure for [**2c**]Cl utilizing **1a** prepared from **1** (33.1 mg, 54.1 μmol, 1 equiv of Ru) in 0.5 mL of CH_3CN and benzoic acid (26.4 mg, 0.216 mmol, 2 equiv). The off-white powder was recrystallized by vapor diffusion of diethyl ether into an ethanolic solution of the crude compounds, resulting in pale yellow crystals (40.8 mg, 92% yield). ^{13}C NMR (D_2O, CH_3OH): 168.90, 99.50, 98.33, 95.93, 90.14, 88.00, 9.80, 9.54. ESI-MS: (^{102}Ru) 375.1 ($C_{17}H_{21}O_3Ru$ requires 375.1).

[(η^6-Benzonitrile)Ru(η^5-$C_5Me_4CH_2OH$)]Cl, [2f]Cl. [**2f**]Cl was synthesized and isolated according to the procedure for [**2c**]Cl utilizing **1a** prepared from **1** (32.7 mg, 54.1 μmol, 1 equiv Ru) in 0.5 mL of CH_3CN and benzonitrile (21.8 μL, 0.214 mmol, 2 equiv), resulting in [**2f**]Cl as a white powder (39.2 mg, 94% yield). ^{13}C NMR (D_2O, CH_3OH, 75.5 MHz): δ 116.22, 101.18, 100.64, 100.09, 97.75, 89.93, 89.29, 88.32, 54.48, 9.86, 9.60. ESI-MS: (^{102}Ru) 356.1 ($C_{17}H_{2o}NORu$ requires 356.1).

[(η^6-Chlorobenzene)Ru(η^5-$C_5Me_4CH_2OH$)][PF_6], [2g][PF_6]. [**2g**][PF_6] was synthesized and isolated according to the procedure for [**2a**][PF_6] utilizing **1a** prepared from **1** (29.2 mg, 47.7 μmol, 1 equiv of Ru) in 0.5 mL of CH_3CN and chlorobenzene (19.4 μL, 0.191 mmol, 2 equiv), resulting in [**2g**][PF_6] as a white powder (42.4 mg, 87% yield). ^{13}C NMR ($(CD_3)_2CO$, 75.5 MHz): δ 93.21, 88.50, 87.98, 87.52, 9.85, 9.59. ESI-MS: (^{102}Ru) 365.1 ($C_{16}H_{20}ClORu$ requires 365.0).

[(η^6-Benzene)Ru(η^5-$C_5Me_4CH_2OCH_3$)]Cl, [3]Cl. **1a** prepared from **1** (30.0 mg, 49.0 μmol) in 0.5 mL of CH_3CN was combined with an excess of benzene (ca. 2 mL) and 6 mL of methanol in a 20 mL glass reaction vessel. The vessel was sealed under nitrogen, and the solution was reacted until colorless (ca. 85 °C). The near colorless solution was cooled, and the solvent was removed under reduced pressure, resulting in [**3**]Cl as an off-white solid (36.5 mg, 98% yield). ^{13}C NMR (D_2O, CH_3OH, 75.5 MHz): δ 98.94, 98.04, 92.76, 87.85, 65.34, 58.45, 10.42, 10.22. ESI-MS: (^{102}Ru) 345.1 ($C_{17}H_{23}ORu$ requires 345.1). Anal. Calcd (%) for $C_{17}H_{23}ClORu$: C, 53.75; H, 6.10. Found: C, 53.88; H, 6.11.

[(η^6-Benzene)Ru(η^5-$C_5Me_4CH_2OCH_2CH_3$)]Cl, [4]Cl. [**4**]Cl was synthesized and isolated according to the procedure for [**3**]Cl utilizing **1a** prepared from **1** (30.0 mg, 49.0 μmol) in 0.5 mL of CH_3CN and 6 mL of ethanol, resulting in [**4**]Cl as an off-white solid (37.3 mg, 97% yield). From **8**: **8** (30.0 mg, 27.6 μmol) was placed in 1 mL of CH_3CN and heated in a sealed vessel (ca. 2 min, 85 °C). To this orange solution was added an excess of benzene (ca. 2 mL) and H_2O (ca. 5 mL). The vessel was sealed under nitrogen, and the solution was reacted for 2 h (ca. 85 °C). The colorless solution was cooled, and the solvent was removed under reduced pressure, resulting in [**4**]Cl as an off-white solid (43.1 mg, 99% yield). ^{13}C NMR (D_2O, CH_3OH, 75.5 MHz): δ 98.45, 97.58, 87.41, 66.78, 62.96, 14.35, 10.00, 9.80. ESI-MS: (^{102}Ru) 359.1 ($C_{18}H_{25}ORu$ requires 359.1). Anal. Calcd (%) for $C_{18}H_{25}ClORu$: C, 54.88; H, 6.40. Found: C, 54.29; H, 6.31.

[(η^6-Benzene)Ru(η^5-$C_5Me_4CH_2OCH_2CH_2CH_3$)]Cl, [5]Cl. [**5**]Cl was synthesized and isolated according to the procedure for [**3**]Cl utilizing **1a** prepared from **1** (30.0 mg, 49.0 μmol) in 0.5 mL of CH_3CN and 6 mL of *n*-propanol, resulting in [**5**]Cl as an off-white solid (38.9 mg, 97% yield). ^{13}C NMR (D_2O, CH_3OH, 75.5 MHz): δ 98.44, 97.61, 92.72, 87.40, 72.81, 63.05, 22.17, 9.98, 9.93, 9.80. ESI-MS: (^{102}Ru) 373.1 ($C_{19}H_{27}ORu$ requires 373.1).

[(η^6-Benzene)Ru(η^5-$C_5Me_4CH_2OCH(CH_3)_2$)]Cl, [6]Cl. [**6**]Cl was synthesized and isolated according to the procedure for [**3**]Cl utilizing **1a** prepared from **1** (30.0 mg, 49.0 μmol) in 0.5 mL of CH_3CN and 6 mL of 2-propanol, resulting in [**6**]Cl as an off-white solid (36.7 mg, 92% yield). ^{13}C NMR (D_2O, CH_3OH, 75.5 MHz): δ 98.40, 97.59, 87.39, 73.18 60.85, 21.31, 10.01, 9.74. ESI-MS: (^{102}Ru) 373.1 ($C_{19}H_{27}ORu$ requires 373.1).

[(η^5-$C_5Me_4CH_2OCH_2CH_3$)Ru(μ_3-Cl)]$_4$, 8. A solution of ethanol (640 μL, 10.96 mmol) and potassium *tert*-butoxide (29.2 mg, 261 μmol) in 1.2 mL of CH_3CN was added dropwise to a solution of **1a** prepared from **1** (80.0 mg, 131 μmol) and 2.5 mL of CH_3CN, during which time the solution changed from dark red to light orange. The solution was stirred for 10 min, and the solvent was removed under reduced pressure. The resulting dark orange oil was triturated with pentane and then filtered to remove unwanted KCl. The pentane was then removed, resulting in **8** as a dark red powder (77.5 mg, 94% yield). ^{13}C NMR (CD_2Cl_2, 75.5 MHz): δ 73.41, 70.50, 67.06, 66.21, 64.33, 15.95, 10.49, 10.41. Anal. Calcd (%) for $C_{48}H_{76}Cl_4O_4Ru_4$: C, 45.64; H, 6.06. Found: C, 44.97; H, 6.12.

[{(η⁶-Benzene)Ru(η⁵-C₅Me₄CH₂)}N(CH₃)(CH₂CH₃)]Cl, [10]Cl. To **1a** prepared from **1** (50.0 mg, 81.5 μmol) in 3 mL of CH_3CN was added *N*,*N*-ethylmethylamine (69.8 μL, 0.815 mmol) in a 20 mL glass reaction vessel, which was sealed, heated (ca. 10 min, 85 °C), and subsequently cooled to room temperature. Potassium *tert*-butoxide (18.3 mg, 0.163 mmol) was then added, and the solution was heated for an additional 30 min. An excess of benzene (ca. 5 mL) and H_2O (ca. 7 mL) were then added to the solution, and the vessel was sealed and reacted until near colorless (ca. 3 h at 85 °C). The aqueous layer was separated, and the organic layer was extracted with H_2O. The combined aqueous layers were evaporated under reduced pressure. The residual crude solid was dissolved in ethanol and filtered to remove unwanted KCl. Additional unwanted byproducts were precipitated with the addition of minimal amounts of diethyl ether and were removed by filtration. The solvent was then removed under reduced pressure, resulting in [**10**]Cl as an oily, tan-colored solid (52.8 mg, 79% yield). ^{13}C NMR (D_2O, CH_3OH, 75.5 MHz): δ 98.72, 97.43, 96.50, 87.57, 51.71, 50.36, 40.33, 10.78, 10.67, 9.99. ESI-MS: (^{102}Ru) 372.1 ($C_{19}H_{28}NRu$ requires 372.1).

[{(η⁶-Benzene)Ru(η⁵-C₅Me₄CH₂)}NH(CH₂(CH₂)₂CH₃)]Cl, [11a]Cl. To a vigorously stirred solution of *N*-butylamine (386.6 μL, 3.91 mmol) in 1 mL of CH_3CN was dropwise added a solution of **1a** prepared from **1** (50.0 mg, 81.5 μmol) in 1.5 mL of CH_3CN. The resulting bright yellow solution was sealed, heated (ca. 2 min, 85 °C), subsequently cooled to room temperature, and then treated with potassium *tert*-butoxide (18.3 mg, 0.163 mmol), resulting in a dark yellow heterogeneous mixture. The resulting solution was reacted with benzene and treated as for [**10**]Cl (excluding diethyl ether precipitation), yielding a brown, oily solid (61.3 mg, 89% yield, containing 7% disubstituted impurity [**11b**]Cl_2 as determined via ^1H NMR). ^{13}C NMR (D_2O, CH_3OH, 75.5 MHz): δ 98.36, 97.29, 97.01, 87.43, 48.11, 42.41, 30.05, 19.86, 13.24, 10.09, 9.99. ESI-MS: (^{102}Ru) 436.1 ($C_{20}H_{30}NRu$ requires 436.1).

[{(η⁶-Benzene)Ru(η⁵-C₅Me₄CH₂)}₂NH(CH₂(CH₂)₂CH₃)][PF₆]₃, [H·11b][PF₆]₃. To a solution of **1a** prepared from **1** (50.0 mg, 81.5 μmol, 2 equiv of Ru) in 1.5 mL of CH_3CN was added *N*-butylamine (8.01 μL, 81.5 μmol, 1equiv). Triethylamine (113.7 μL, 0.816 mmol) was then added, and the solution was sealed and heated for 30 min (ca. 85 °C). The resulting solution was reacted with benzene following the procedure described for [**10**]Cl. The biphasic solution was evaporated under reduced pressure, redissolved in H_2O, and precipitated with NH_4PF_6, giving [H·**11b**][PF_6]$_3$ as a white solid (135.2 mg, 74% yield, containing 4% monosubstituted impurity [H·**11a**][PF_6]$_2$ as determined via ^1H NMR). ^{13}C NMR ($(CD_3)_2CO$, 75.5 MHz): δ 99.08, 98.76, 97.56, 88.93, 53.51, 49.89, 21.27, 14.34, 11.63, 11.07. ESI-MS: ($^{mixed}Ru$) 350.5, 349.7, 349.1 ($C_{36}H_{49}NRu^{2+}$ requires 350.6, 349.6, 349.1). Anal. Calcd (%) for $C_{35}H_{48}F_{18}NP_3Ru_2$: C, 37.54; H, 4.32; N, 1.25. Found: C, 36.98; H, 4.34; N, 1.24.

[(η⁶-Benzene)Ru(η⁵-C₅Me₄CH₂OCH₂CH₂CN)]PF₆, [12][PF₆]. To a solution of **1a** prepared from **1** (50.0 mg, 81.5 μmol, 1 equiv of Ru) in 1.5 mL of CH_3CN were added triethylamine (25.0 μL, 179 μmol, 1.1 equiv) and then, dropwise, 3-hydroxypropionitrile (166.7 μL, 2.43 mmol, 15 equiv). The reaction vessel was sealed and heated for 30 min (ca. 60 °C). The resulting solution was reacted with benzene following the procedure described for [**10**]Cl, and the product was isolated according to the procedure described for [H·**11b**][PF_6]$_3$. The resulting off-white solid was recrystallized from toluene/acetone, giving [**12**][PF_6] as white crystals (68.3 mg, 79% yield). ^{13}C NMR ($(CD_3)_2CO$, 75.5 MHz): δ 119.63, 99.00, 98.52, 95.75, 88.93, 66.68, 64.48, 19.42, 11.01. ESI-MS: (^{102}Ru) 384.1 ($C_{19}H_{24}NORu$ requires 384.1). Anal. Calcd (%) for $C_{19}H_{24}F_6NOPRu$: C, 43.18; H, 4.58; N, 2.65. Found: C, 43.42; H, 4.59; N, 2.68.

[(η⁶-Benzene)Ru(η⁵-C₅Me₄CH₂OCH₂CH₂NH(CH₃)₂)][PF₆]₂, [13][PF₆]₂. A solution of *N*,*N*-dimethylaminoethanol (98.6 μL, 0.980 mmol, 5 equiv) and potassium *tert*-butoxide (22.0 mg, 0.196 mmol, 1 equiv) in 500 μL of CH_3CN was added dropwise to a solution of **1a** prepared from **1** (60.0 mg, 98.0 μmol, 1 equiv of Ru) in 2.0 mL of CH_3CN. The reaction vessel was sealed and heated for 30 min (ca. 85 °C). The resulting solution was reacted with benzene following the procedure described for [**10**]Cl, and the product was isolated according to the procedure described for [H·**11b**][PF_6]$_3$, giving [**13**][PF_6]$_2$ as a white powder (104.4 mg, 77% yield) ^{13}C NMR ($(CD_3)_2CO$, 75.5 MHz): δ 99.13, 98.74, 94.89, 88.95, 66.50, 64.74, 58.75, 44.94, 10.98. ESI-MS: (^{102}Ru) 402.1 ($C_{20}H_{30}NORu$ requires 402.1). Anal. Calcd (%) for $C_{20}H_{31}F_{12}NOP_2Ru$: C, 34.69; H, 4.51; N, 2.02. Found: C, 34.28; H, 4.61; N, 2.08.

(*S*)-[η⁵-{2-(((2,3,4,5-Tetramethylcyclopentadienyl)methoxy)methyl)-1-methylpyrrolidinium}Ru(η⁶-benzene)][PF₆]₂, [14][PF₆]₂. A solution of (*S*)-2-hydroxymethyl-1-methylpyrrolidine (91.9 μL, 0.815 mmol) and potassium *tert*-butoxide (18.3 mg, 0.163 mmol) in 500 μL of CH_3CN was added dropwise to a solution of **1a** prepared from **1** (50.0 mg, 81.5 μmol) in 1.5 mL of CH_3CN. The reaction vessel was sealed and heated with stirring for another 10 min (ca. 85 °C). The resulting orange solution was further reacted with benzene following the procedure described for [**10**]Cl, and the product was isolated according to the procedure described for [H·**11b**][PF_6]$_3$, giving [**14**][PF_6]$_2$ as a white powder (91.2 mg, 78% yield). ^{13}C NMR ($(CD_3)_2CO$, 75.5 MHz): δ 99.21, 98.85, 94.38, 88.96, 69.31, 69.09, 65.07, 58.59, 41.61, 27.68, 23.27, 11.05, 10.98. ESI-MS: (^{102}Ru) 428.1 ($C_{22}H_{32}NORu$ requires 428.2). Anal. Calcd (%) for $C_{22}H_{33}F_{12}NOP_2Ru$: C, 36.78; H, 4.63; N, 1.95. Found: C, 36.66; H, 4.76; N, 2.00.

[η⁵-{1-((2,3,4,5-Tetramethylcyclopentadienyl)methyl)pyridin-2-one}Ru(η⁶-benzene)][PF₆], [15][PF₆]. A solution of 2-hydroxypyridine (77.5 μL, 0.815 mmol) and potassium *tert*-butoxide (18.3 mg, 0.163 mmol) in 500 μL of CH_3CN (heterogeneous mixture) was added dropwise to a solution of **1a** prepared from **1** (50.0 mg, 81.5 μmol) in 1.5 mL of CH_3CN. The reaction vessel was sealed and heated for 10 min (ca. 85 °C). The resulting solution was further reacted with benzene following the procedure described for [**10**]Cl, and the product was isolated according to the procedure described for [H·**11b**][PF_6]$_3$, giving [**15**][PF_6] as a white powder (82.0 mg, 91% yield). ^{13}C NMR ($(CD_3)_2CO$, 75.5 MHz): δ 162.95, 141.302, 139.41, 121.52, 106.86, 99.21, 98.54, 95.13, 89.16, 45.31, 11.75, 11.01. ESI-MS: (^{102}Ru) 407.9 ($C_{21}H_{24}NORu$ requires 408.1). Anal. Calcd (%) for $C_{21}H_{24}F_6NOPRu$: C, 45.66; H, 4.38; N, 2.54. Found: C, 45.78; H, 4.23; N, 2.59.

[η⁵-{2-(((2,3,4,5-Tetramethylcyclopentadienyl)methoxy)ethyl)-pyridine}Ru(η⁶-benzene)][PF₆], [16][PF₆]. A solution of 2-(2-hydroxyethyl)pyridine (91.7 μL, 0.815 mmol) and potassium *tert*-butoxide (18.3 mg, 0.163 mmol) in 500 μL of CH_3CN was added dropwise to a solution of **1a** prepared from **1** (50.0 mg, 81.5 μmol) in 1.5 mL of CH_3CN in a glass reaction vial. The mustard yellow solution was stirred for another ca. 30 min at room temperature. The resulting solution was further reacted with benzene following the procedure described for [**10**]Cl, and the product was isolated according to the procedure described for [H·**11b**][PF_6]$_3$, giving [**16**][PF_6] as an off-white powder (73.3 mg, 77% yield). ^{13}C NMR ($(CD_3)_2CO$, 75.5 MHz): δ 160.55, 150.41, 137.35, 124.56, 122.58, 98.82, 98.44, 96.40, 88.79, 71.03, 64.23, 39.38, 10.97, 10.87. ESI-MS: (^{102}Ru) 436.1 ($C_{23}H_{28}NORu$ requires 436.1). Anal. Calcd (%) for $C_{23}H_{29}F_{12}NOP_2Ru$: C, 47.59; H, 4.86; N, 2.41. Found: C, 47.38; H, 4.88; N, 2.36.

[η⁵-{2-((η⁵-{2-(((2,3,4,5-Tetramethylcyclopentadienyl)methoxy)ethyl)(η¹-pyridine)}Ru(CH₃CN)₂][PF₆], [17b][PF₆]. [**16**][PF_6] (20.0 mg, 34.5 μmol) was dissolved in 1.5 mL of degassed CD_3CN and sealed under N_2 in an NMR tube. The colorless solution was exposed to UV irradiation for ca. 6 h, yielding a deep orange

Table 5. Summary Crystallographic Data

	1a	[**2a**]Cl	[**2b**][PF_6]	[**2e**]Cl
empirical formula	$C_{12}H_{17}NCl_2Ru$	$C_{16}H_{21}ClORu$	$C_{36}H_{46}F_{12}O_4P_2Ru_2$	$C_{17}H_{21}ClO_3Ru$
fw	347.25	365.85	1034.81	409.86
T, K	100(2)	163(2)	100(2)	100(2)
radiation (λ)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
cryst syst	monoclinic	orthorhombic	monoclinic	monoclinic
space group	$P2_1/a$	$Cmc2_1$	$P2_1$	$C2/c$
a, Å	8.6664(8)	9.0438(5)	7.3620(4)	30.227(2)
b, Å	11.8959(11)	13.2365(7)	12.5244(7)	7.0623(6)
c, Å	13.5118(13)	12.6151(7)	21.2886(11)	15.8241(13)
α, deg	90	90	90	90
β, deg	103.525(2)	90	92.9840(10)	104.4030(10)
γ, deg	90	90	90	90
V, Å^3	1354.4(2)	1510.13(14)	1960.25(18)	3271.8(5)
Z	4	4	2	8
D_{calcd}, g·cm^{-3}	1.703	1.609	1.753	1.664
μ, mm^{-1}	1.205	1.205	0.948	1.131
F(000)	696	744	1040	1664
cryst size, mm	0.30 × 0.20 0.08	0.50 × 0.26 × 0.18	0.38 × 0.25 × 0.25	0.40 × 0.30 × 0.30
θ range, deg	2.96–28.20	2.23–28.29	1.89–28.32	2.66–28.31
no. of reflns collected	5654	6711	15670	14400
no. of indep reflns/R_{int}	1987/0.0680	1914/0.0289	8988/0.0389	3948/0.0271
no. of params	161	142	526	213
GOF on F^2	1.93	1.048	1.001	1.108
R1, wR2 [$I > 2\sigma(I)$]	0.0453, 0.1085	0.0196, 0.0466	0.0442, 0.0952	0.0314, 0.0814
R1, wR2 (all data)	0.0821, 0.1153	0.0230, 0.0474	0.0798, 0.1042	0.0367, 0.0832

	[**2f**]Cl	[**3**]Cl·[H_3O]Cl	[**14**][PF_6]$_2$	[**15**][PF_6]·H_2O
empirical formula	$C_{17}H_{20}ClNORu$	$C_{17}H_{26}Cl_2O_2Ru$	$C_{22}H_{33}F_{12}NOP_2Ru$	$C_{21}H_{26}F_6NO_2PRu$
fw	390.86	434.35	718.50	570.47
T, K	100(2)	100(2)	100(2)	100(2)
radiation (λ)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
cryst syst	monoclinic	tetragonal	monoclinic	triclinic
space group	Cc	$P4_2/n$	$P2_1$	P-1
a, Å	17.5733(16)	21.1522(7)	7.1340(6)	6.872(5)
b, Å	8.3436(8)	21.1522(7)	12.2235(10)	10.792(8)
c, Å	13.9530(13)	8.4509(5)	15.9461(12)	14.599(11)
α, deg	90	90	90	97.798(18)
β, deg	126.8710(10)	90	94.3720(10)	95.328(18)
γ, deg	90	90	90	91.472(14)
V, Å^3	1636.7(3)	3781.1(3)	1386.49(19)	1067.3(14)
Z	4	8	2	2
D_{calcd}, g·cm^{-3}	1.586	1.526	1.721	1.775
μ, mm^{-1}	1.119	1.116	0.779	0.881
F(000)	792	1776	724	576
cryst size, mm	0.30 × 0.20 × 0.20	0.20 × 0.20 × 0.20	0.35 × 0.20 × 0.15	0.40 × 0.30 × 0.30
θ range, deg	2.84–28.26	1.93–28.33	2.10–28.29	1.91–28.67
no. of reflns collected	6370	44934	12617	12674
no. of independent reflns/R_{int}	3730/0.0179	4698/0.0583	6421/0.0271	5114/0.0495
no. of params	198	307	361	293
GOF on F^2	1.017	1.083	1.031	1.103
R1, wR2 [$I > 2\sigma(I)$]	0.0275, 0.0663	0.0283, 0.0616	0.0337, 0.0756	0.0491, 0.1119
R1, wR2 (all data)	0.0321, 0.0680	0.0533, 0.0676	0.0411, 0.0784	0.0688, 0.1161

solution. The quantitative conversion of [**16**][PF_6] to [d_9-**17a**][PF_6] and [d_6-**17b**][PF_6] was apparent by ^{1}H NMR (see Figure 7). The solvent was removed under reduced pressure, and the resulting oil was exposed to CH_3CN. The solvent was removed again, and the resulting orange oily solid was dissolved in CD_2Cl_2. The ^{1}H NMR spectrum indicated only the presence of [**17b**][PF_6]. ^{13}C NMR (CD_2Cl_2, 75.5 MHz): δ 165.63, 153.20, 137.25, 125.13, 122.83, 87.33, 75.91, 74.63, 41.03, 30.83, 9.38, 3.18.

X-ray Crystallography. Single crystals of **1a** were obtained by slow evaporation of an acetonitrile solution of **1**. Single crystals of [**2a**]Cl were obtained by vapor diffusion of THF into an aqueous solution of [**2a**]Cl. Crystals of [**2b**]PF_6, [**2e**]Cl, [**2f**]Cl, [**3**]Cl·[H_3O]Cl, and [**15**][PF_6]·H_2O were obtained by vapor diffusion of Et_2O into ethanolic solutions of each compound. Crystals of [**14**][PF_6]$_2$ were obtained by slow evaporation of an ethanolic solution of the compound. Experimental parameters pertaining to single crystal X-ray analyses are given in Table 5. Data were collected on a Siemens SMART 1000 CCD platform diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The data were integrated using the SAINT suite of software and corrected for the effects of absorption using SADABS, except for **1a**. Crystals of **1a** were habitually twinned, with two major components of roughly equal contribution. Reflections of both components were integrated simultaneously using a two-component orientation matrix file. Data were treated with TWINABS. The refinement was based upon HKLF 5 format data from both components. All structures were solved by direct methods and refined iteratively via full-matrix least-squares and difference Fourier analysis using the SHELX-97-2 suite of software[25] and with the assistance of X-Seed.[26] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were generally either located in the difference Fourier map and refined upon or placed in calculated positions and refined with a riding model. Absolute structure (Flack) parameters:[27] [**2a**]Cl = −0.01(4), [**2b**]PF_6= 0.49(3), [**2f**]Cl = −0.06(3),

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and [**14**][PF_6]$_2$ = −0.02(2). CCDC 634127, 664329–664334, and 665191 contain the supplementary crystallographic data. These data can be obtained online free of charge (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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Supporting Information Available: ^{1}H NMR spectra of all compounds and crystallographic data in the form of CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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