Spirocyclic and Bicyclic Cyclohexadienyl Complexes from Intramolecular Nucleophilic Addition Reactions in Dicationic Arene Complexes

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The dicationic arene complexes [(*p*-cymene)Ru($PhCH_2CH_2[CH_2]_nOH$)][$OTf]_2$ and [Cp*Ir-($PhCH_2CH_2[CH_2]_nOH$)][$OTf]_2$ (n = 1−2) react with K_2CO_3 to cleanly generate spirocyclic cyclohexadienyl complexes through intramolecular nucleophilic addition of the alkoxide at the ipso carbon of the arene ligand. When the internal nucleophile is the bulkier benzenesulfonamide group, cyclohexadienyl complexes derived from both ipso and ortho intramolecular nucleophilic addition are formed.

Introduction

Coordination of an aromatic compound to a metal is well known to activate the arene toward nucleophilic attack; nucleophilic addition reactions at π-coordinated arene ligands have been extensively employed in organic synthesis.[1] Carrying out the nucleophilic addition reaction intramolecularly, with a nucleophile that is attached to the arene ligand through a side chain, has been used as an efficient means of synthesizing bicyclic and spirocyclic compounds. Semmelhack and co-workers were the first to utilize this methodology, employing intramolecular nucleophilic addition at (arene)$Cr(CO)_3$ as the key step in the synthesis of the spirocyclic natural products acorenone and acorenone B.[2,3] Wulff later combined intramolecular nucleophilic addition with benzannulation to provide a convenient synthesis of the tetracyclic ring system of anthracyclines.[4] Pigge and co-workers have recently reported the first successful isolation and characterization of the organometallic products of an intramolecular nucleophilic addition at an arene ligand, spirocyclic cyclohexadienyl complexes generated through the addition of enolates to [CpRu-(arene)]$^+$ complexes.[5,6]

Research efforts in our laboratory have focused on exploiting the substantial electrophilic activation of the arene ligands in dicationic arene complexes of ruthenium and iridium for organic synthesis applications.[7,8] Several characteristics of these complexes make them attractive substrates for the continued development of intramolecular nucleophilic addition reactions. The ability of dicationic arene complexes to react with a wide range of nucleophiles[9,10] may dramatically expand the scope of this methodology by providing access to more types of spirocyclic and bicyclic ring systems. The cationic nature of cyclohexadienyl complexes formed by nucleophilic addition at dicationic arene complexes should provide for additional elaboration of the spirocyclic and bicyclic ring systems. We report here the successful synthesis, isolation, and characterization of spirocyclic and bicyclic cyclohexadienyl complexes formed through intramolecular nucleophilic addition reactions in dicationic arene complexes of ruthenium and iridium.

Results and Discussion

We initially investigated the intramolecular addition of *alkoxide* nucleophiles because alkoxides will add to the arene ligands of dicationic arene complexes (but not (arene)$Cr(CO)_3$ complexes) to give stable cyclohexadienyl complexes.[11,12] Reaction of the commercially available phenylalkyl alcohols, $PhCH_2CH_2[CH_2]_nOH$ (n = 1−2), with either [(*p*-cymene)$Ru(OTf)_2$] or [Cp*$Ir(OTf)_2$] (OTf = O_3SCF_3)[13] in nitromethane[7] generates the air- and water-stable dicationic arene complexes **1**−**4** in good to excellent yield (Scheme 1). Allowing **1**−**4** to react with excess K_2CO_3 in CH_3CN leads to the exclusive formation of spirocyclic cyclohexadienyl complexes, **5**−**8**, through intramolecular nucleophilic addition of alkoxide at the ipso carbon of the arene ligand (Scheme 1). The identity of **5**−**8** as spirocyclic cyclohexadienyl complexes was confirmed by NMR spectroscopy; their ^1H and ^{13}C NMR spectra all contain proton and carbon resonances diagnostic for cyclohexadienyl ligands.[5,14] Monitoring the

(1) Semmelhack, M. F. In *Comprehensive Organometallic Chemistry II*; Abel, E. D., Stone, F. G. A., Wilkinson, G., Eds.; Elsevier: Oxford, UK, 1995; Vol. 12, Chapter 9.1.
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(13) Ganja, E. A.; Rauchfuss, T. B.; Stern, C. L. *Organometallics* **1991**, *10*, 270.
(14) The stereochemistry of **5**−**8** is almost certainly that obtained by exo addition of the nucleophile, but this has not yet been definitively verified.

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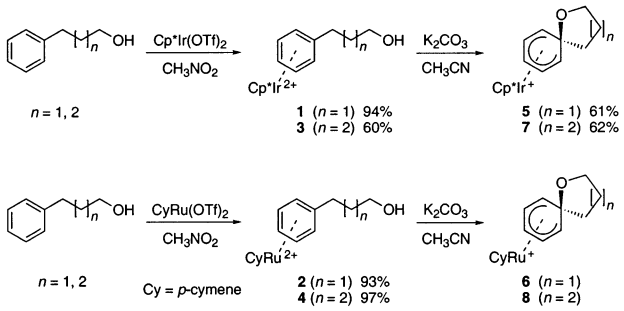
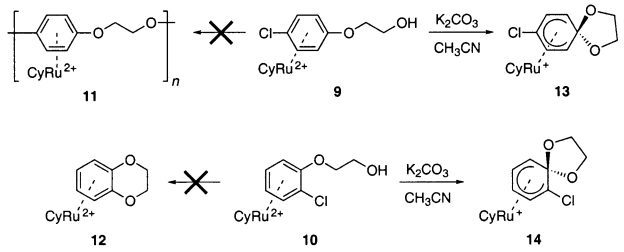
Scheme 1



Scheme 2

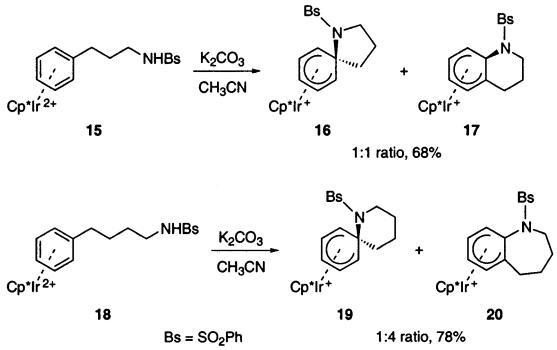


reaction of **1**−**4** with K_2CO_3 by NMR spectroscopy in CD_3CN revealed that the formation of **5**−**8** is essentially quantitative. The spirocyclic cyclohexadienyl complexes can be handled and even synthesized in the presence of both water and oxygen, which bodes well for their use in future synthetic applications.

The iridium cyclohexadienyl complexes **5** and **7** could be isolated as analytically pure solids in reasonable (ca. 60%) yield by extraction of the reaction mixture with CH_2Cl_2. However, because the analogous ruthenium complexes **6** and **8** are not stable in CH_2Cl_2 solution, we have not yet been able to separate them completely from the excess K_2CO_3 and the KOTf produced in the reaction. Attempts to synthesize spirocyclic cyclohexadienyl complexes via intramolecular addition of alkoxides that require the formation of either smaller four-membered or larger seven-membered rings gave complex mixtures of cyclohexadienyl products arising from nonselective, *intermolecular* nucleophilic addition.[3,15]

We have also found that intramolecular nucleophilic addition can be the favored reaction for dicationic arene complexes even in situations for which nucleophilic *substitution* might be expected. The ruthenium arene complexes, **9** and **10**, which contain a chloride substituent on an arene ligand, were synthesized in moderate yield by the same procedure used for **1**−**4** (Scheme 2). Even though alcohols have been shown to readily displace chloride in other dicationic arene complexes,[16−18] conversion of **9** and **10** into products derived from nucleophilic substitution of the chloride substituent (**11** and **12**) does not occur (Scheme 2), even on long standing for several days.[19] The absence of nucleophilic substitution for **9** can be attributed to the fact that it

Scheme 3



requires an *intermolecular* reaction between two dicationic species; however, the inability of **10** to undergo *intramolecular* nucleophilic substitution (to form **12**) is somewhat surprising.[17] As was the case with **1**−**4**, deprotonation of the −OH groups in **9** and **10** with K_2CO_3 in CH_3CN results in intramolecular nucleophilic addition of alkoxide at the ipso carbon to give the spirocyclic cyclohexadienyl complexes **13** and **14** (Scheme 2). These complexes are apparently unable to undergo subsequent nucleophilic substitution of chloride—they are recovered unchanged even after heating for extended periods. Pigge and co-workers have recently reported a similar instance of intramolecular nucleophilic addition being favored over nucleophilic substitution for a series of $[CpRu(arene)]^+$ complexes.[5,6]

Given our success with alkoxide nucleophiles, we extended our investigations of intramolecular nucleophilic addition reactions to include nitrogen-based nucleophiles. Because the presence of $-NH_2$ groups interferes with the synthesis of the dicationic arene complexes,[16,20,21] we employed benzenesulfonamide as the internal nucleophile. The reaction of the iridium arene complex, **15**, with K_2CO_3 in CH_3CN generates a 1:1 mixture of the expected spirocyclic cyclohexadienyl complex, **16**, and the bicyclic cyclohexadienyl complex, **17**, formed through ortho addition of the nucleophile (Scheme 3). It has not proved possible to separate **16** and **17**, but the isolated mixture of these two compounds could be completely characterized by NMR spectroscopy. The presence of five proton resonances and six ^{13}C resonances assignable to an unsymmetrical cyclohexadienyl ligand in the NMR spectra of the **16**:**17** mixture confirmed the ortho addition of the sulfonamide group in **17**. The relative amounts of **16** and **17** do not change on long standing in solution, even at elevated temperatures. Preliminary reactions examining the deprotonation of **15** with different bases or at different temperatures also generate the same 1:1 ratio of **16** and **17**.

Deprotonation of the benzenesulfonamide group in **18** also gives a mixture of spirocyclic (**19**) and bicyclic (**20**) cyclohexadienyl complexes, although in this case the two complexes are generated in a 1:4 ratio (Scheme 3). Remarkably, the presence of the longer butyl chain in **18** favors ortho addition of the sulfonamide nucleophile to give **20**, despite the fact that this requires the formation of a *seven*-membered ring. Although bicyclic

(15) Semmelhack, M. F.; Harrison, J. J.; Young, D. C.; Gutiérrez, A.; Rafii, S.; Clardy, J. *J. Am. Chem. Soc.* **1985**, *107*, 7508.
(16) Bennett, M. A.; Matheson, T. W. *J. Organomet. Chem.* **1979**, *175*, 87.
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(18) Goryunov, L. I.; Shteingarts, V. D. *Zh. Org. Khim.* **1991**, *27*, 1144.
(19) We have independently synthesized **12** in high yield by reacting $[(p\text{-cymene})Ru(OTf)_2]$ with excess benzodioxan in CH_3NO_2.
(20) Chen, S.; Carperos, V.; Noll, B.; Swope, R. J.; DuBois, M. R. *Organometallics* **1995**, *14*, 1221.
(21) Wolff, J. M.; Sheldrick, W. S. *J. Organomet. Chem.* **1997**, *531*, 141.

organic products consistent with ortho addition have been isolated from intramolecular nucleophilic addition reactions in (arene)$Cr(CO)_3$ complexes,[3,4] **17** and **20** are the first cyclohexadienyl complexes derived from an intramolecular ortho nucleophilic addition to be isolated and definitively characterized.

A probable explanation for the change in regioselectivity for the intramolecular additions on going from alkoxide to benzenesulfonamide is the larger steric bulk of the latter species. Because ipso addition for **15** and **18** requires the bulky $-SO_2Ph$ group to occupy a more crowded position directly over the face of the cyclohexadienyl ligand in **16** and **19**, ortho addition of the sulfonamide becomes a competitive reaction pathway. Greater steric hindrance between the $-SO_2Ph$ group and the cyclohexadienyl ligand in **19** as compared to **16,** caused by the larger six-membered ring in the former complex, might also explain why ipso addition is less favorable with **18** than with **15**.

In conclusion, we have demonstrated that dicationic ruthenium and iridium arene complexes can participate in intramolecular nucleophilic addition reactions to give isolable spirocyclic and bicyclic cyclohexadienyl complexes. The greater electrophilicity of the arene ligands in the dicationic arene complexes allows for the use of new types of internal nucleophiles (alkoxides, sulfonamides) in intramolecular addition reactions, potentially providing access to a wider range of spirocyclic and bicyclic ring systems from this methodology. We are currently extending our efforts in this area to include other types of nucleophiles (enolates, amides, carboxylates). We are also investigating the reactivity of the spirocyclic and bicyclic cyclohexadienyl complexes, with the goal of developing high-yield routes for the selective removal of the spirocyclic and bicyclic ligands from the metal.

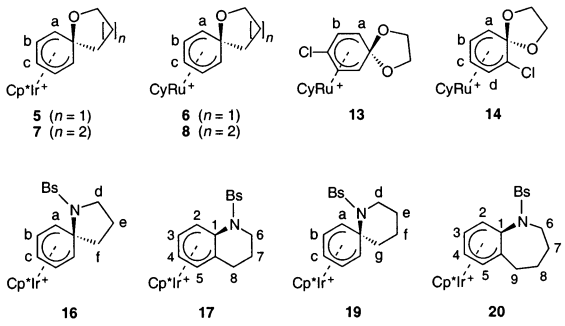
Experimental Section

General. [(*p*-cymene)$Ru(OTf)_2$] and [Cp*$Ir(OTf)_2$] (OTf = O_3SCF_3) were synthesized by a literature procedure.[13] *N*-(3-Phenylpropyl)benzenesulfonamide and *N*-(4-phenylbutyl)-benzenesulfonamide were synthesized by reacting the corresponding phenylalkylamines with benzenesulfonyl chloride in pyridine.[22] Diethyl ether was distilled under nitrogen from sodium benzophenone ketyl. Dichloromethane was distilled under nitrogen from CaH_2. Nitromethane was degassed with argon, passed twice through activated neutral alumina, and stored over 3A molecular sieves in the dark.

^1H NMR spectra were referenced to the residual proton resonances of CD_3NO_2 (4.33 ppm) and CD_3CN (1.94 ppm); ^{13}C NMR spectra were referenced to the $^{13}CD_3$ resonances of CD_3NO_2 (60.5 ppm) and CD_3CN (1.39 ppm). In the NMR spectral assignments, "Ar" refers to an arene ring bound to ruthenium or iridium. Atom labels used in the NMR assignments of **5**−**8**, **13**, **14**, **16**, **17**, **19**, and **20** are indicated in Chart 1. Infrared spectra were recorded as Nujol mulls between NaCl plates; only characteristic and/or strong signals are reported. Elemental analyses were performed by NuMega Resonance Labs, Inc., San Diego, CA.

Preparation of Dicationic Arene Complexes. The preparation of [(*p*-cymene)$Ru(C_6H_5CH_2CH_2CH_2OH)][OTf]_2$ (**2**) is described in detail below. The other dicationic arene complexes were synthesized by similar procedures. Complexes **9** and **10** were isolated under anhydrous conditions to prevent hydrolysis of the chloride substituent on the arene ligand; workup and isolation of the remaining complexes were performed in air.

Chart 1



Preparation of 2. In the drybox, a 50-mL flask equipped with a Teflon stopper was charged with [(*p*-cymene)$Ru(OTf)_2$] (0.12 g, 0.225 mmol) and CH_3NO_2 (15 mL). The flask was sealed, taken outside the box, and attached to a Schlenk line. 3-Phenyl-1-propanol (91 μL, 0.68 mmol) was added to the flask with a syringe under argon and the flask was placed in an oil bath set at 60 °C for 30 min. The solution was then transferred to an Erlenmeyer flask and carefully layered with CH_2Cl_2 (2 mL) and Et_2O (5 mL). On standing overnight at −20 °C, yellow crystals precipitated from solution; the filtrate was removed and the crystals were washed with CH_2Cl_2 (2 mL) and Et_2O (2 mL) and dried under vacuum to give **2** in 93% yield (0.14 g). Anal. Calcd for $C_{21}H_{26}RuO_7F_6S_2$: C, 37.67; H, 3.91. Found: C, 37.54; H, 4.03. ^1H NMR (CD_3CN): δ 6.77−6.85 (overlapping m, 9H, *p*-cymene Ar*H*, *o*-Ar*H*, *m*-Ar*H*, and *p*-Ar*H*), 3.58 (dt, J = 5.5, 5.0 Hz, 2H, $-CH_2OH$), 2.95 (septet, J = 7.0 Hz, 1H, $-CH(CH_3)_2$), 2.89 (t, J = 5.0 Hz, 1H, $-OH$), 2.75 (t, J = 7.5 Hz, 2H, $-CH_2Ar$), 2.44 (s, 3H, $-CH_3$), 1.84 (m, 2H, $-CH_2-$), 1.29 (d, J = 7.0 Hz, 6H, $-CH(CH_3)_2$). ^{13}C NMR (CD_3CN): δ 123.3 (Ar*C*-*i*Pr), 114.0 (Ar*C*-Me), 95.9 (Ar*C*H), 95.60 (Ar*C*H), 95.59 (Ar*C*H), 94.4 (Ar*C*H), 93.3 (Ar*C*H), 61.2 ($-CH_2OH$), 34.2 ($-CH_2-$), 32.8 ($-CH(CH_3)_2$), 31.4 ($-CH_2Ar$), 22.8 ($-CH(CH_3)_2$), 19.8 ($-CH_3$); the Ar*C*-CH_2 resonance is obscured by the CD_3CN peak. IR (cm^{-1}): 3412 (m, O−H), 1263 (vs, S−O, free OTf).

Characterization data for the remaining dicationic arene complexes are given below.

[Cp*Ir($C_6H_5CH_2CH_2CH_2OH$)][OTf]$_2$ (1): Isolated in 94% yield (0.24 g) as a white solid from the reaction of [Cp*$Ir(OTf)_2$] (0.21 g, 0.34 mmol) and 3-phenyl-1-propanol (88 μL, 0.66 mmol). Anal. Calcd for $C_{21}H_{27}IrO_7F_6S_2$: C, 33.11; H, 3.57. Found: C, 31.96; H, 2.97. ^1H NMR (CD_3CN): δ 7.21−7.24 (overlapping m, 5H, *o*-Ar*H*, *m*-Ar*H*, and *p*-Ar*H*), 3.61 (dt, J = 5.5, 5.0 Hz, 2H, $-CH_2OH$), 2.89 (t, J = 5.0 Hz, 1H, $-OH$), 2.77 (t, J = 7.0 Hz, 2H, $-CH_2Ar$), 2.29 (s, 15H, Cp*CH_3), 1.90 (m, 2H, $-CH_2-$). ^{13}C NMR (CD_3CN): δ 119.8 (Ar*C*-CH_2), 106.8 (Cp*CCH_3), 99.1 (Ar*C*H), 98.9 (Ar*C*H), 98.3 (Ar*C*H), 61.2 ($-CH_2OH$), 33.6 ($-CH_2-$), 30.1 ($-CH_2Ar$), 10.6 (Cp*CH_3). IR (cm^{-1}): 3455 (m, O−H), 1260 (vs, S−O, free OTf).

[Cp*Ir($C_6H_4CH_2CH_2CH_2CH_2OH$)][OTf]$_2$ (3): Isolated in 60% yield (0.10 g) as a pale yellow solid from the reaction of [Cp*$Ir(OTf)_2$] (0.135 g, 0.22 mmol) and 4-phenyl-1-butanol (67 μL, 0.44 mmol). Anal. Calcd for $C_{22}H_{29}IrO_7F_6S_2$: C, 34.06; H, 3.77. Found: C, 33.86; H, 3.66. ^1H NMR (CD_3CN): δ 7.23−7.25 (overlapping m, 5H, *o*-Ar*H*, *m*-Ar*H*, and *p*-Ar*H*), 3.55 (dt, J = 5.0, 6.0 Hz, 2H, $-CH_2OH$), 2.74 (t, J = 5.0 Hz, 1H, $-OH$), 2.70 (t, J = 8.0 Hz, 2H, $-CH_2Ar$), 2.29 (s, 15H, Cp*CH_3), 1.76 (m, 2H, $-CH_2-$), 1.60 (m, 2H, $-CH_2-$). ^{13}C NMR (CD_3CN): δ 119.4 (Ar*C*-CH_2), 106.9 (Cp*CCH_3), 99.3 (Ar*C*H), 98.8 (Ar*C*H), 98.3 (Ar*C*H), 61.8 ($-CH_2OH$), 32.5 ($-CH_2Ar$), 32.45 ($-CH_2-$), 28.0 ($-CH_2-$), 10.6 (Cp*CH_3). IR (cm^{-1}): 3483 (m, O−H), 1260 (vs, S−O, free OTf)

[(*p*-cymene)Ru($C_6H_5CH_2CH_2CH_2CH_2OH$)][OTf]$_2$ (4): Isolated in 97% yield (0.18 g) as a sticky, yellow oil from the reaction of [(*p*-cymene)$Ru(OTf)_2$] (0.145 g, 0.27 mmol) and

(22) Anderson, K. K. In *Comprehensive Organic Chemistry*; Jones, D. N., Ed.; Pergamon Press: Oxford, UK, 1979; Vol. 3, p 345.

4-phenyl-1-butanol (63 μL, 0.41 mmol). Anal. Calcd for $C_{22}H_{28}RuO_7F_6S_2$: C, 38.65; H, 4.13. Found: C, 38.11; H, 4.14. ^{1}H NMR (CD_3NO_2): δ 6.98−7.05 (overlapping m, 9H, *p*-cymene Ar*H*, *o*-Ar*H*, *m*-Ar*H*, and *p*-Ar*H*), 3.63 (t, *J* = 6.0 Hz, 2H, −C*H*$_2$OH), 3.07 (septet, *J* = 7.0 Hz, 1H, −C*H*(CH$_3$)$_2$), 2.82 (t, *J* = 7.5 Hz, 2H, −C*H*$_2$Ar), 2.57 (s, 3H, −C*H*$_3$), 2.38 (br s, 1H, −O*H*), 1.86 (m, 2H, −C*H*$_2$−), 1.66 (m, 2H, −C*H*$_2$−), 1.38 (d, *J* = 7.0 Hz, 6H, −CH(C*H*$_3$)$_2$). ^{13}C NMR (CD_3CN): δ 123.4 (Ar*C*-*i*Pr), 114.1 (Ar*C*-Me), 95.8 (Ar*C*H), 95.7 (Ar*C*H), 95.6 (Ar*C*H), 94.4 (Ar*C*H), 93.3 (Ar*C*H), 61.8 (−*C*H$_2$OH), 33.9 (−*C*H$_2$−), 32.8 (−*C*H(CH$_3$)$_2$), 32.5 (−*C*H$_2$Ar), 28.5 (−*C*H$_2$−), 22.8 (−CH(*C*H$_3$)$_2$), 19.8 (−*C*H$_3$); the Ar*C*-CH$_2$ resonance is obscured by the CD_3CN peak. IR (cm^{-1}): 3505 (m, O−H), 1275 (vs, S−O, free OTf).

[(*p*-cymene)Ru(4-ClC$_6$H$_4$OCH$_2$CH$_2$OH)][OTf]$_2$ (9): Isolated in 57% yield (0.36 g) as a yellow oily residue from the reaction of [(*p*-cymene)Ru(OTf)$_2$] (0.48 g, 0.90 mmol) and 2-(4-chlorophenoxy)ethanol (0.47 g, 2.70 mmol). Anal. Calcd for $C_{20}H_{23}RuO_8F_6S_2Cl$: C, 34.02; H, 3.28. Found: C, 33.71; H, 3.18. ^{1}H NMR (CD_3CN): δ 7.11 (app d, *J* = 7.0 Hz, 2H, Ar*H*), 6.90 (app d, *J* = 7.0 Hz, 2H, Ar*H*), 6.87 (app d, *J* = 6.5 Hz, 2H, *p*-cymene Ar*H*), 6.84 (app d, *J* = 6.5 Hz, 2H, *p*-cymene Ar*H*), 4.37 (t, *J* = 4.5 Hz, 2H, −C*H*$_2$OAr), 3.85 (dt, *J* = 5.5, 5.5 Hz, 2H, −C*H*$_2$OH), 3.55 (t, *J* = 5.0 Hz, 1H, −O*H*), 2.88 (septet, *J* = 7.0 Hz, 1H, −C*H*(CH$_3$)$_2$), 2.37 (s, 3H, −C*H*$_3$), 1.30 (d, *J* = 7.0 Hz, 6H, −CH(C*H*$_3$)$_2$). ^{13}C NMR (CD_3CN): δ 142.6 (Ar*C*-OCH$_2$), 123.1 (Ar*C*-*i*Pr), 114.1 (Ar*C*-Me), 110.5 (Ar*C*-Cl), 96.4 (Ar*C*H), 95.4 (Ar*C*H), 94.1 (Ar*C*H), 82.0 (Ar*C*H), 76.3 (−*C*H$_2$-OAr), 60.6 (−*C*H$_2$OH), 32.1 (−*C*H(CH$_3$)$_2$), 22.4 (−CH(*C*H$_3$)$_2$), 18.7 (−*C*H$_3$). IR (cm^{-1}): 3428 (m, O−H), 1260 (vs, S−O, free OTf).

[(*p*-cymene)Ru(2-ClC$_6$H$_4$OCH$_2$CH$_2$OH)][OTf]$_2$ (10): Isolated in 68% yield (27 mg) as a yellow oily residue from the reaction of [(*p*-cymene)Ru(OTf)$_2$] (30 mg, 0.056 mmol) and 2-(2-chlorophenoxy)ethanol (10 μL, 0.17 mmol). Anal. Calcd for $C_{20}H_{23}RuO_8F_6S_2Cl$: C, 34.02; H, 3.28. Found: C, 33.31; H, 3.32. ^{1}H NMR (CD_3CN): δ 7.23−7.27 (overlapping m, 2H, Ar*H*), 6.82−6.86 (overlapping m, 3H, *p*-cymene Ar*H*), 6.78 (app d, *J* = 6.5 Hz, 1H, *p*-cymene), 6.66−6.70 (overlapping m, 2H, Ar*H*), 4.53 (t, *J* = 5.0 Hz, 2H, −C*H*$_2$OAr), 3.93 (dt, *J* = 5.0, 5.0 Hz, 2H, −C*H*$_2$OH), 3.84 (t, *J* = 5.0 Hz, 1H, −O*H*), 2.91 (septet, *J* = 7.0 Hz, 1H, −C*H*(CH$_3$)$_2$), 2.36 (s, 3H, −C*H*$_3$), 1.30 (d, *J* = 7.0 Hz, 3H, −CH(C*H*$_3$)$_2$), 1.27 (d, *J* = 7.0 Hz, 3H, −CH(C*H*$_3$)$_2$). ^{13}C NMR (CD_3NO_2): δ 140.6 (Ar*C*-OCH$_2$), 122.9 (Ar*C*-*i*Pr), 114.1 (Ar*C*-Me), 103.6 (Ar*C*-Cl), 96.4 (Ar*C*H), 96.11 (Ar*C*H), 96.06 (Ar*C*H), 94.6 (Ar*C*H), 93.8 (Ar*C*H), 93.6 (Ar*C*H), 90.7 (Ar*C*H), 82.4 (Ar*C*H), 77.0 (−*C*H$_2$OAr), 60.7 (−*C*H$_2$OH), 32.3 (−*C*H(CH$_3$)$_2$), 22.7 (−CH(*C*H$_3$)$_2$), 22.4 (−CH(*C*H$_3$)$_2$), 18.7 (−*C*H$_3$). IR (cm^{-1}): 3428 (m, O−H), 1260 (vs, S−O, free OTf).

[(*p*-cymene)Ru(benzodioxan)][OTf]$_2$ (12): Isolated in 82% yield (38 mg) as a pale yellow powder from the reaction of [(*p*-cymene)Ru(OTf)$_2$] (37 mg, 0.069 mmol) and benzodioxan (25 μL, 0.21 mmol). Anal. Calcd for $C_{20}H_{22}RuO_8F_6S_2$: C, 35.88; H, 3.31. Found: C, 35.66; H, 3.11. ^{1}H NMR (CD_3CN): δ 6.80 (s, 4H, *p*-cymene Ar*H*), 6.75 (m, 2H, Ar*H*), 6.49 (m, 2H, Ar*H*), 4.65 (m, 2H, −OCH*H*), 4.46 (m, 2H, −OC*H*H), 2.95 (septet, *J* = 7.0 Hz, 1H, −C*H*(CH$_3$)$_2$), 2.43 (s, 3H, −C*H*$_3$), 1.29 (d, *J* = 7.0 Hz, 6H, −CH(C*H*$_3$)$_2$). ^{13}C NMR (CD_3CN): δ 128.7 (Ar*C*-OCH$_2$), 121.9 (Ar*C*-*i*Pr), 112.5 (Ar*C*-Me), 95.0 (Ar*C*H), 92.6 (Ar*C*H), 90.2 (Ar*C*H), 83.6 (Ar*C*H), 67.7 (−O*C*H$_2$), 32.9 (−*C*H-(CH$_3$)$_2$), 22.8 (−CH(*C*H$_3$)$_2$), 19.5 (−*C*H$_3$). IR (cm^{-1}): 1277 (vs, S−O, free OTf).

[Cp*Ir(C$_6$H$_5$CH$_2$CH$_2$CH$_2$NHSO$_2$Ph)][OTf]$_2$ (15): Isolated in 61% yield (0.15 g) as a yellow residue from the reaction of [Cp*Ir(OTf)$_2$] (0.17 g, 0.27 mmol) and *N*-(3-phenylpropyl)-benzenesulfonamide (0.15 g, 0.55 mmol). Anal. Calcd for $C_{27}H_{32}IrNO_8F_6S_3$: C, 35.00; H, 3.58; N, 1.55. Found: C, 34.88; H, 3.55; N, 1.87. ^{1}H NMR (CD_3NO_2): δ 7.84 (m, 2H, *o*-Bs*H*), 7.68 (m, 1H, *p*-Bs*H*), 7.62 (m, 2H, *m*-Bs*H*), 7.40 (br s, 5H, *o*-Ar*H*, *m*-Ar*H*, and *p*-Ar*H*), 5.61 (t, *J* = 6.0 Hz, 1H, −N*H*), 3.07 (dt, *J* = 6.5, 6.0 Hz, 2H, −C*H*$_2$NH), 2.91 (t, *J* = 7.5 Hz, 2H, −C*H*$_2$Ar), 2.44 (s, 15H, Cp*C*H$_3$), 2.03 (m, 2H, −C*H*$_2$−). ^{13}C NMR (CD_3NO_2): δ 138.9 (*C*-SO$_2$), 132.0 (Bs*C*H), 128.4 (Bs*C*H), 125.9 (Bs*C*H), 116.9 (Ar*C*-CH$_2$), 105.5 (Cp**C*CH$_3$), 97.4 (Ar*C*H), 97.1 (Ar*C*H), 96.5 (Ar*C*H), 41.1 (−*C*H$_2$NH), 29.1 (−*C*H$_2$Ar), 28.5 (−*C*H$_2$−), 8.2 (Cp**C*H$_3$). IR (cm^{-1}): 3197 (m, N−H), 1259 (vs, S−O, free OTf).

[Cp*Ir(C$_6$H$_5$CH$_2$CH$_2$CH$_2$CH$_2$NHSO$_2$Ph)][OTf]$_2$ (18): Isolated in 48% yield (42 mg) as a yellow residue from the reaction of [Cp*Ir(OTf)$_2$] (60 mg, 0.096 mmol) and *N*-(4-phenylbutyl)-benzenesulfonamide (56 mg, 0.19 mmol). Anal. Calcd for $C_{28}H_{34}IrNO_8F_6S_3$: C, 36.76; H, 3.75; N, 1.53. Found: C, 36.24; H, 3.58; N, 1.97. ^{1}H NMR (CD_3CN): δ 7.82 (m, 2H, *o*-Bs*H*), 7.64 (m, 1H, *p*-Bs*H*), 7.58 (m, 2H, *m*-Bs*H*), 7.18−7.25 (overlapping m, 5H, *o*-Ar*H*, *m*-Ar*H*, and *p*-Ar*H*), 5.73 (t, *J* = 6.0 Hz, 1H, −N*H*), 2.89 (dt, *J* = 6.5, 6.0 Hz, 2H, −C*H*$_2$NH), 2.63 (t, *J* = 7.5 Hz, 2H, −C*H*$_2$Ar), 2.28 (s, 15H, Cp*C*H$_3$), 1.70 (m, 2H, −C*H*$_2$−), 1.57 (m, 2H, −C*H*$_2$−). ^{13}C NMR (CD_3CN): δ 141.5 (*C*-SO$_2$), 133.7 (Bs*C*H), 130.3 (Bs*C*H), 127.8 (Bs*C*H), 119.0 (Ar*C*-CH$_2$), 106.9 (Cp**C*CH$_3$), 99.4 (Ar*C*H), 98.8 (Ar*C*H), 98.4 (Ar*C*H), 43.2 (−*C*H$_2$NH), 32.1 (−*C*H$_2$Ar), 29.5 (−*C*H$_2$−), 28.3 (−*C*H$_2$−), 10.6 (Cp**C*H$_3$). IR (cm^{-1}): 3212 (m, N−H), 1259 (vs, S−O, free OTf).

Preparation of Cyclohexadienyl Complexes. The preparation of **5** is described in detail below. The remaining iridium cyclohexadienyl complexes were synthesized and isolated by using the same procedure. The ruthenium cyclohexadienyl complexes (**6**, **8**, **13**, **14**) were synthesized in an analogous manner; however, the instability of these complexes in CH_2Cl_2 has so far prevented the isolation of analytically pure samples of these complexes free of KOTf and K_2CO_3. Monitoring the reaction mixtures for these reactions by NMR spectroscopy confirmed that the cyclohexadienyl complexes were generated in essentially quantitative yield from the corresponding dicationic arene complexes.

Preparation of 5. An Erlenmeyer flask was charged with **1** (80 mg, 0.11 mmol) and K_2CO_3 (56 mg, 0.22 mmol); CH_3CN (10 mL) was added and the mixture was stirred at room temperature for 2 h. The CH_3CN was then removed under vacuum and the residue extracted with 10 mL of CH_2Cl_2. The solution was filtered through Celite; Et_2O (10 mL) was then added and a white solid precipitated out of solution. The filtrate was removed and the precipitate was dried under vacuum to give **5** as a white powder in 61% yield (39 mg). Anal. Calcd for $C_{20}H_{26}IrO_4F_3S$: C, 39.27; H, 4.28. Found: C, 38.94; H, 3.93. ^{1}H NMR (CD_3CN) δ 6.34 (app tt, *J* = 4.5, 1.0 Hz, 1H, H_c), 5.29 (m, 2H, H_b), 4.07 (app dd, 2H, *J* = 6.0, 1.0 Hz, H_a), 3.65 (t, *J* = 6.5 Hz, 2H, −OC*H*$_2$), 2.15 (s, 15H, Cp*C*H$_3$), 2.02 (t, *J* = 7.5 Hz, 2H, −CC*H*$_2$), 1.94 (m, 2H, −C*H*$_2$−). ^{13}C NMR (CD_3CN): δ 97.1 (Cp**C*CH$_3$), 86.7 (*C*H$_b$), 85.7 (*C*H$_c$), 75.0 (spiro-*C*), 67.9 (−O*C*H$_2$), 53.7 (*C*H$_a$), 37.4 (−C*C*H$_2$), 25.0 (−*C*H$_2$−), 9.1 (Cp**C*H$_3$).

Characterization data for the remaining cyclohexadienyl complexes are given below.

Spectroscopic data for 6: ^{1}H NMR (CD_3CN) δ 6.18 (app d, *J* = 6.5 Hz, 2H, *p*-cymene Ar*H*), 6.10 (app d, *J* = 6.5 Hz, 2H, *p*-cymene Ar*H*), 6.06 (app tt, *J* = 5.0, 1.0 Hz, 2H, H_c), 5.10 (m, 2H, H_b), 3.95 (app dd, 2H, *J* = 6.0, 1.0 Hz, H_a), 3.60 (t, *J* = 6.5 Hz, 2H, −OC*H*$_2$), 2.65 (septet, *J* = 7.0 Hz, 1H, −C*H*(CH$_3$)$_2$), 2.31 (s, 3H, −C*H*$_3$), 2.02 (t, *J* = 7.5 Hz, 2H, −CC*H*$_2$), 1.88 (tt, *J* = 7.5, 6.5 Hz, 2H, −C*H*$_2$−), 1.18 (d, *J* = 7.0 Hz, 6H, −CH(C*H*$_3$)$_2$). ^{13}C NMR (CD_3CN): δ 121.0 (Ar*C*-*i*Pr), 106.7 (Ar*C*-Me), 90.7 (*p*-cymene *C*H), 88.9 (*p*-cymene *C*H), 87.9 (*C*H$_b$), 86.1 (*C*H$_c$), 76.7 (spiro-*C*), 69.2 (−O*C*H$_2$), 58.9 (*C*H$_a$), 39.6 (−C*C*H$_2$), 32.6 (−*C*H(CH$_3$)$_2$), 26.6 (−*C*H$_2$−), 23.4 (−CH(*C*H$_3$)$_2$), 20.0 (−*C*H$_3$).

Characterization data for 7: Isolated in 62% yield (15 mg) as a white solid from the reaction of **3** (30 mg, 0.039 mmol) and excess K_2CO_3. Anal. Calcd for $C_{21}H_{28}IrO_4F_3S$: C, 40.31; H, 4.51. Found: C, 40.94; H, 4.23. ^{1}H NMR (CD_3CN): δ 6.44 (app tt, *J* = 5.0, 1.0 Hz, 1H, H_c), 5.24 (m, 2H, H_b), 4.09 (app dd, *J* = 6.5, 1.0 Hz, 2H, H_a), 3.23 (t, *J* = 5.5 Hz, 2H, −OC*H*$_2$), 2.14 (s, 15H, Cp*C*H$_3$), 1.76−1.79 (overlapping m, 4H, −CC*H*$_2$

and $-CH_2-$), 1.42 (tt, J = 5.5, 1.0 Hz, 2H, $-CH_2-$). ^{13}C NMR (CD_3CN): δ 98.7 (Cp*CCH$_3$), 86.6 (CH$_c$), 87.3 (CH$_b$), 70.0 (spiro-C), 59.5 ($-OCH_2$), 51.0 (CH$_a$), 34.2 ($-CCH_2$), 26.2 ($-CH_2-$), 20.6 ($-CH_2-$), 10.4 (Cp*CH$_3$).

Spectroscopic data for 8: ^1H NMR (CD_3CN) δ 6.20 (app d, J = 6.5 Hz, 2H, *p*-cymene ArH), 6.16 (app tt, J = 5.0, 1.0 Hz, 2H, H_c), 6.13 (app d, J = 6.0 Hz, 2H, *p*-cymene ArH), 5.09 (m, 2H, H_b), 3.96 (app dd, 2H, J = 7.0, 1.0 Hz, H_a), 3.22 (t, J = 5.5 Hz, 2H, $-OCH_2$), 2.65 (septet, J = 7.0 Hz, 1H, $-CH(CH_3)_2$), 2.28 (s, 3H, $-CH_3$), 1.81 (t, J = 7.5 Hz, 2H, $-CCH_2$), 1.70 (m, 2H, $-CH_2-$), 1.37 (m, 2H, $-CH_2-$), 1.18 (d, J = 7.0 Hz, 6H, $-CH(CH_3)_2$). ^{13}C NMR (CD_3CN): δ 117.6 (ArC-*i*Pr), 107.1 (ArC-Me), 91.1 (*p*-cymene CH), 89.4 (*p*-cymene CH), 87.6 (CH$_c$), 87.2 (CH$_b$), 69.6 (spiro-C), 59.2 ($-OCH_2$), 55.0 (CH$_a$), 34.9 ($-CCH_2$), 32.6 ($-CH(CH_3)_2$), 26.3 ($-CH_2-$), 23.3 ($-CH(CH_3)_2$), 20.6 ($-CH_2-$), 19.9 ($-CH_3$).

Spectroscopic data for 13: ^1H NMR (CD_3CN) δ 6.21 (app d, J = 6.5 Hz, 2H, *p*-cymene ArH), 6.15 (app d, J = 6.5 Hz, 2H, *p*-cymene ArH), 5.61 (app d, J = 5.6 Hz, 2H, H_b), 4.05 (app d, J = 5.4 Hz, 2H, H_a), 3.86 (m, 2H, $-OCH_2$), 3.75 (m, 2H, $-OCH_2$), 2.85 (septet, J = 7.0 Hz, 1H, $-CH(CH_3)_2$), 2.29 (s, 3H, $-CH_3$), 1.28 (d, J = 7.0 Hz, 6H, $-CH(CH_3)_2$). ^{13}C NMR (CD_3CN): δ 119.2 (ArC-*i*Pr), 109.1 (ArC-Me), 105.9 (C-Cl), 102.8 (spiro-C), 92.8 (*p*-cymene CH), 90.6 (*p*-cymene CH), 89.3 (CH$_b$), 66.4 ($-OCH_2$), 65.6 ($-OCH_2$), 55.3 (CH$_a$), 32.5 ($-CH(CH_3)_2$), 22.9 ($-CH(CH_3)_2$), 18.9 ($-CH_3$).

Spectroscopic data for 14: ^1H NMR (CD_3CN) δ 6.24 (dd, J = 6.2, 1.1 Hz, 1H, *p*-cymene ArH), 6.15 (dd, J = 6.2, 1.1 Hz, 1H, *p*-cymene ArH), 6.05 (overlapping m, 2H, *p*-cymene ArH), 6.00 (ddd, J = 5.1, 5.1, 1.1 Hz, 1H, H_c), 5.67 (dd, J = 5.4, 1.2 Hz, 1H, H_d), 5.22 (ddd, J = 6.7, 5.0, 1.1 Hz, 1H, H_b), 4.34 (dd, 1H, J = 6.8, 1.1 Hz, H_a), 4.05 (m, 1H, $-OCHH$), 3.99 (m, 1H, $-OCHH$), 3.85 (app t, 6.2 Hz, 2H, two $-OCHH$), 2.75 (septet, J = 7.0 Hz, 1H, $-CH(CH_3)_2$), 2.38 (s, 3H, $-CH_3$), 1.25 (d, J = 7.0 Hz, 3H, $-CH(CH_3)_2$), 1.23 (d, J = 7.0 Hz, 3H, $-CH(CH_3)_2$). ^{13}C NMR (CD_3CN): δ 119.7 (ArC-*i*Pr), 109.4 (ArC-Me), 105.3 (spiro-C), 93.9 (*p*-cymene CH), 92.9 (*p*-cymene CH), 91.0 (*p*-cymene CH), 90.4 (*p*-cymene CH), 89.0 (CH$_d$), 87.9 (CH$_b$), 84.1 (CH$_c$), 80.5 (C-Cl), 67.9 ($-OCH_2$), 66.6 ($-OCH_2$), 61.0 (CH$_a$), 32.3 ($-CH(CH_3)_2$), 23.4 ($-CH(CH_3)_2$), 23.0 ($-CH(CH_3)_2$), 19.1 ($-CH_3$).

Characterization data for 16 and 17: Isolated as a 1:1 mixture in 68% overall yield (27 mg, 0.036 mmol) as a yellow, semicrystalline residue from the reaction of **15** (48 mg, 0.053 mmol) and excess K_2CO_3. Anal. Calcd for $C_{26}H_{31}IrNO_5F_3S_2$: C, 41.59; H, 4.16; N, 1.87. Found: C, 40.98; H, 4.05; N, 1.77. NMR data for the **16**:**17** mixture: ^1H NMR (CD_3CN): δ 7.71−7.74 (overlapping m, 5H, BsH), 7.62−7.66 (overlapping m, 3H, BsH), 7.56 (m, 2H, BsH), 6.44 (t, J = 6.0 Hz, 1H, H_4), 6.30 (t, J = 5.5 Hz, 1H, H_c), 5.48 (t, J = 6.0 Hz, 1H, H_3), 5.27 (dt, J = 6.0, 1.5 Hz, 2H, H_b), 5.18 (d, J = 5.0 Hz, 1H, H_5), 4.24 (t, J = 6.0 Hz, 1H, H_2), 3.93 (d, J = 7.0 Hz, 2H, H_a), 3.62 (dt, J = 12, 3.5 Hz, 1H, H_6), 3.59 (d, J = 6.0 Hz, 1H, H_1), 3.54 (t, J = 6.5 Hz, 2H, H_d), 2.41 (td, J = 12, 3.5 Hz, 1H, H_6'), 2.21 (m, 2H, H_f), 2.09 (br s, 30H, 2 Cp*CH_3), 2.05 (m, 1H, H_7'), 1.94 (m, 1H, H_8), 1.89 (m, 1H, H_e), 1.75 (m, 1H, H_7), 1.63 (m, 1H, H_8'). ^{13}C NMR (CD_3CN): δ 142.9 (C-SO_2), 137.4 (C-SO_2), 134.4 (BsCH), 133.7 (BsCH), 130.5 (BsCH), 130.2 (BsCH), 128.8 (BsCH), 128.1 (BsCH), 98.7 (Cp*CCH$_3$), 98.6 (Cp*CCH$_3$), 89.0 (C_b), 87.7 (C_3), 86.8 (C_4), 86.5 (C_5), 86.3 (C_c), 63.4 (spiro-C, **16**), 59.0 (C_1), 57.6 (ipso-C, **17**), 54.7 (C_a), 52.9 (C_d), 48.5 (C_6), 47.4 (C_2), 45.7 (C_f), 30.6 (C_8), 27.8 (C_7), 22.5 (C_e), 10.4 (Cp*CH$_3$), 10.2 (Cp*CH$_3$).

Characterization data for 19 and 20: Isolated as a 1:4 mixture (**20** as the major product) in 78% overall yield (19 mg, 0.025 mmol) as a yellow, semicrystalline residue from the reaction of **18** (29 mg, 0.032 mmol) and excess K_2CO_3. Anal. Calcd for $C_{27}H_{33}IrNO_5F_3S_2$: C, 42.40; H, 4.35; N, 1.83. Found: C, 42.31; H, 4.55; N, 1.97. NMR data for **19**: ^1H NMR (CD_3CN): δ 7.85 (m, 2H, *o*-BsH), 5.87 (t, J = 5.0 Hz, 1H, H_c), 4.91 (t, J = 5.8 Hz, 2H, H_b), 4.07 (dd, J = 6.5, 1.0 Hz, 2H, H_a), 3.22 (m, 2H, H_d), 2.08 (s, 15H, Cp*CH_3), 1.86 (m, 2H, H_g), 1.51 (m, 2H, H_e), 1.50 (m, 2H, H_f), the remaining BsH resonances were obscured by resonances for **20**. ^{13}C NMR (CD_3CN): δ 133.5 (BsCH), 130.0 (BsCH), 127.8 (BsCH), 99.1 (Cp*CCH$_3$), 88.9 (C_c), 86.3 (C_b), 58.6 (spiro-C), 45.7 (C_a), 42.0 (C_d), 35.8 (C_g), 26.3 (C_f), 20.7 (C_e), 10.3 (Cp*CH$_3$), the C-SO_2 resonance was not observed. NMR data for **20**: ^1H NMR (CD_3CN): δ 7.81 (m, 2H, *o*-BsH), 7.67 (m, 1H, *p*-BsH), 7.60 (m, 2H, *m*-BsH), 6.40 (td, J = 6.0, 1.0 Hz, 1H, H_4), 5.35 (d, J = 5.0 Hz, 1H, H_5), 5.23 (td, J = 6.0, 1.0 Hz, 1H, H_3), 4.47 (td, J = 6.5, 1.0 Hz, 1H, H_2), 4.28 (d, J = 5.5 Hz, 1H, H_1), 3.38 (dd, J = 12, 7.0 Hz, 1H, H_6), 2.52 (dd, J = 16, 10 Hz, 1H, H_6'), 2.19 (s, 15H, Cp*CH_3), 2.00 (m, 1H, H_9), 1.76 (m, 1H, H_8'), 1.52 (m, 1H, H_7'), 1.49 (m, 1H, H_9'), 1.24 (m, 1H, H_8), 0.62 (m, 1H, H_7). ^{13}C NMR (CD_3CN): δ 141.2 (C-SO_2), 134.0 (BsCH), 130.5 (BsCH), 128.2 (BsCH), 98.9 (Cp*CCH$_3$), 88.1 (C_4), 87.6 (C_5), 86.1 (C_3), 56.7 (C_1), 53.7 (ipso-C), 48.5 (C_2), 47.6 (C_6), 36.3 (C_9), 30.4 (C_8), 27.7 (C_7), 10.1 (Cp*CH$_3$).

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Supporting Information Available: Figures showing the 2D gCOSY NMR spectra of the isolated **16**:**17** and **19**:**20** mixtures. This material is available free of charge via the Internet at http://pubs.acs.org.

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