Ruthenium-Coordinated Spirolactams via Intramolecular Nucleophilic Addition to η^6-Arene Metal Complexes

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Cyclohexadienyl ruthenium(II) complexes incorporating an azaspirocyclic ring system have been prepared from (η^6-*N*-benzyl acetoacetamide)CpRu(II) precursors via an intramolecular nucleophilic aromatic addition/enolate trapping reaction sequence. The spirocyclization process was found to be applicable to a variety of alkyl-, alkoxy-, and chloro-substituted *N*-benzyl acetoacetamide ligands, and isolated yields of the cyclohexadienyl products ranged from 44% to 86%. In contrast, related arene ruthenium complexes prepared from benzyl acetoacetate and phenethyl acetoacetamide failed to undergo spirocyclization, but were found to participate in intramolecular S_NAr reactions (leading to formation of tetralone and benzazepinone ring systems, respectively). Thus, the conformational mobility of the side chain linking the nucleophilic center to the coordinated arene ring appears to be important in governing the regioselectivity of aromatic addition in these reactions. Several spirolactam complexes were reduced with $LiAlH_4$ to the corresponding Ru-coordinated spirocyclic amines; however, attempts to remove the cyclohexadienyl moiety from the CpRu(II) center via ligand protonation were unsuccessful.

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Introduction

η^6-Arene metal complexes are well-characterized organometallic derivatives that are widely utilized in organic synthesis. In particular, (arene)$Cr(CO)_3$ complexes have emerged as versatile synthetic intermediates that are amenable to stereocontrolled side-chain functionalization and nucleophilic aromatic addition/substitution (S_NAr) processes.[1] In addition to chromium, isoelectronic arene−metal complexes of $(CO)_3Mn(I)$ and cyclopentadienyl (Cp) Fe(II) also have been frequently employed in the context of complex molecule construction.[2,3] In contrast, the chemistry of related (η^6-arene)-CpRu(II) derivatives has not been extensively developed.[4] Importantly, however, the CpRu(II) fragment offers several distinct advantages as an arene activating organometallic moiety in that arene ruthenium complexes can be prepared in high yield using exceedingly mild reaction conditions and coordination of the CpRu group is compatible with a wide range of preexisting arene ligand functionality. To date, the most significant synthetic applications of stoichiometric (arene)Ru complexes have been reported by Pearson[5] and Rich[6] in connection with efforts aimed at the total synthesis of peptide-based antibiotics incorporating a biaryl ether linkage.[7]

As part of a larger effort aimed at further defining and expanding the synthetic utility of (arene)Ru(II) derivatives, a previous report from this laboratory described the preparation and characterization of several novel spirocyclic cyclohexadienyl cyclopentadienyl ruthenium complexes **3** (Scheme 1).[8] While it was originally envisioned that the stabilized anion generated from **1a** would be capable of participating in a Ru-

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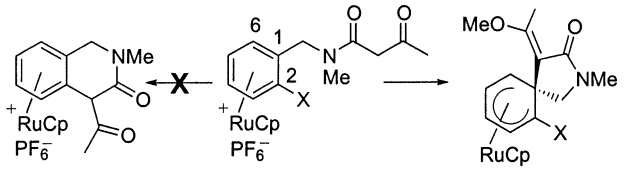
Scheme 1

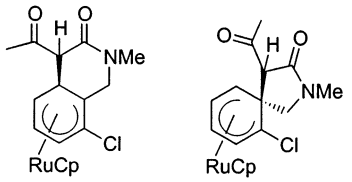


mediated intramolecular S_NAr reaction to deliver tetrahydroisoquinolinone **2**, the stereo- and regioselective aromatic addition leading to **3** appears to be the favored reaction pathway. It is interesting to note that spirocyclization effected via intramolecular nucleophilic addition to an arene−metal complex is a rarely observed reaction manifold, and the only other significant examples of such a process involve chromium complexes as first reported by Semmelhack.[9,10]

The presence of spirocyclic linkages in a variety of biologically active natural products[11] coupled with the importance accorded to the development of new methods for the stereocontrolled construction of quaternary spirocyclic centers[12] provided the impetus for continued work in this area with the goal of defining the scope of the Ru-mediated process illustrated in Scheme 1. In this paper we report the results of these studies. In addition, the underlying factors responsible for controlling the regioselectivity of intramolecular nucleophilic addition in complexes such as **1** are also discussed. Finally, the outcome of initial efforts aimed at liberating the structurally intriguing spirocyclic lactam ligand present in **3** from the CpRu(II) fragment is described.

Results and Discussion

Discovery and Optimization of Ru-Promoted Spirocyclization. As alluded to in the preceding section, we originally sought an entry into the synthetically versatile tetrahydroisoquinolinone ring system via intramolecular S_NAr. After numerous failed attempts at effecting the conversion of **1a** to **2**, however, we directed our attention toward developing a means to trap any intermediate species generated by nucleophilic addition to the activated arene ring. It is well known that reaction of a stabilized enolate nucleophile with an (η^6-arene)metal complex is reversible, and the kinetically preferred site of nucleophilic addition is typically at an unsubstituted aryl carbon.[1] In the case at hand, such an event would produce the neutral cyclohexadienyl species **4** via nucleophilic addition to C-6. Alternatively, initial nucleophilic addition to the *ipso* position (C-1) would afford **5**.



Provided that putative intermediates **4** and/or **5** are susceptible to equilibration, under thermodynamic reaction conditions, one would expect eventual nucleophilic addition to the chlorine-bearing aromatic carbon. Given that successful S_NAr was never observed even under conditions chosen so as to promote equilibration of any initially formed adducts (e.g., KOH/H_2O/DMSO, 25 °C; KO^{t}Bu/^{t}BuOH, 25 °C and reflux; sodium 2,6-di-*tert*-butylphenoxide/DMSO, 70 °C; TFA/THF, 25 °C and reflux), we were forced to consider the possibility that reaction at either C-6 or C-1 represented the kinetically and thermodynamically preferred site of attack.

We reasoned that if **4** and/or **5** were generated in significant amounts during the course of attempted cyclizations, then further deprotonation of the activated methine carbon should be feasible in the presence of excess base. It may then be possible to trap the resulting exocyclic enolate ion via O-alkylation, thereby "locking-in" fused- or spiro-ring products. Gratifyingly, treatment of **1a** with 2 equiv each of KO^{t}Bu and 18-crown-6 (18-C-6) in refluxing THF followed by addition of methyl tosylate (MeOTs) afforded spirocyclic lactam **3a** in 37% isolated yield as a single stereoisomer. The structural assignment was made on the basis of extensive 1D and 2D NMR experiments as well as single-crystal X-ray diffractometry.[8] Lactam **3a** is clearly formed via the intermediacy of **5**; thus, the C-1 position must be the preferred site of nucleophilic addition by the stabilized anion generated from the starting *N*-benzyl acetoacetamide complex.

With this initial success in hand, efforts were next directed toward improving the efficiency of the spirocyclization process. For these experiments, either the chloro-substituted complex **1a** or the parent *N*-benzyl acetoacetamide complex **1b** was employed. (η^6-Arene)-CpRu(II) complexes exist as monocations and so are sparingly soluble in common organic solvents (including THF). Consequently, it was felt that switching to a more polar solvent so as to obtain homogeneous reaction mixtures would be beneficial. Solvents screened in the course of this study included MeCN, DMF, and DMSO, with DMSO ultimately providing the best results. In addition, the use of water-soluble Me_2SO_4 as an electrophile in place of MeOTs simplified product isolation.

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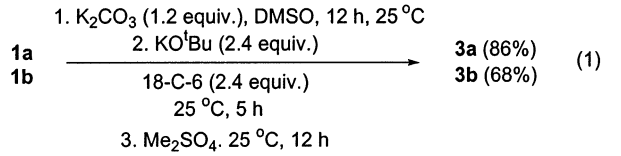
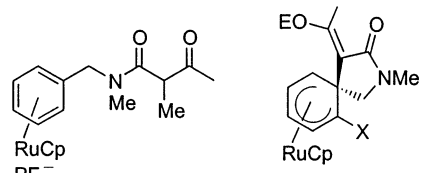
Eventually, the conditions shown in eq 1 were found to



deliver spirocyclic products **3** cleanly and in reproducible yields. Other deprotonating agents examined included KHMDS, NaH, and DBU, but the combination of K_2CO_3/KO^{t}Bu was found to be superior. Initial treatment of **1** with the nonnucleophilic base K_2CO_3 proved to be an important first step in the spirocyclization process, and omitting this step in the case of **1a** resulted in isolation of **3a** in only 59% yield (vs 86% yield in eq 1). We speculate that the K_2CO_3 treatment may be important in promoting the formation of **5** prior to a second deprotonation upon addition of KO^{t}Bu. The use of 18-C-6 to facilitate O-alkylation of the enolate generated from **5** also was found to be an important reaction parameter. Conversion of **1b** to **3b** in the absence of crown ether (DMSO solvent) occurred with ~10−15% diminution in isolated yield, while treatment of a THF suspension of **1b** with KO^{t}Bu/MeOTs produced only a small amount (24%) of C-alkylated η^6-arene complex **6**.

Several alternative O-alkylating agents (in place of Me_2SO_4) were examined in the course of reaction optimization studies as well. Among these, only Ac_2O was effective and enol acetate **7** was isolated from **1b** in 64% yield. Allyl tosylate gave **8** in substantially lower yield (27%), while the use of triflic anhydride failed to provide an isolable cyclohexadienyl complex. One attempt was made to prepare a silyl enol ether from **1a**. In the event, treatment of **1a** with KO^{t}Bu and 18-C-6 in THF followed by addition of TBDMS−Cl did indeed afford **9**, albeit in modest 15% yield.

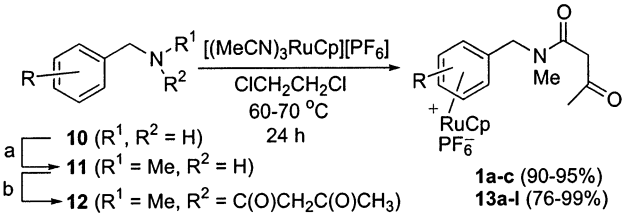


6

7 (E = Ac, X = H)
8 (E = $CH_2CH{=}CH_2$, X = H)
9 (E = TBDMS, X = Cl)

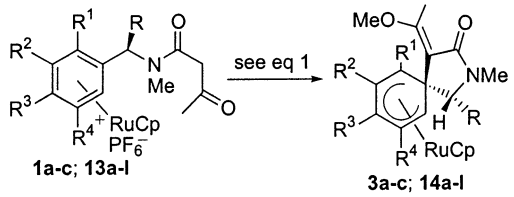
Scope of Ruthenium-Mediated Spirocyclization. The spirocyclization reaction manifold illustrated in Scheme 1 potentially offers concise and stereocontrolled access to synthetically versatile azaspiro[4.5]decane frameworks. Consequently, the generality of the process was examined for a series of substituted *N*-benzyl acetoacetamide complexes. The (η^6-arene)Ru(II) substrates utilized in this study were generally prepared using the sequence of reactions indicated in Scheme 2. Commercially available benzylamines were converted to their *N*-methyl analogues using a two-step formylation/reduction protocol.[13] Introduction of the acetoacetamide moiety was accomplished by simply heating amines **11** in neat methyl acetoacetate. Coordination of the CpRu(II) fragment was then effected using standard procedures[14] that entail stirring an approximately equimolar solution of the arene ligand and [CpRu(MeCN)$_3$][PF_6][15] in 1,2-dichloroethane at slightly elevated temperature. As can be seen in Scheme 2, isolated yields for the desired arene complexes were uniformly good to excellent. Moreover, the presence of the potentially competitive β-dicarbonyl ligating group was found to be completely compatible with η^6-coordination.[16]

Scheme 2[a]



[a] Conditions: (a) (i) EtOCHO (neat), 12 h, 25 °C (65%−99%); (ii) $LiAlH_4$, Et_2O, 25 °C (73%−97%). (b) $MeO_2CCH_2C(O)CH_3$, 120 °C (32%−85%).

Table 1. Spirocyclization of (Arene)Ru(II) Complexes 1 and 13



1a-c; 13a-l **3a-c; 14a-l**

entry	substrate	R	R^1	R^2	R^3	R^4	% isolated yield
1	**1a**	H	Cl	H	H	H	86 (**3a**)
2	**1b**	H	H	H	H	H	68 (**3b**)
3	**1c**	H	OMe	H	H	H	67 (**3c**)
4	**13a**	H	Me	H	H	H	45 (**14a**)
5	**13b**	H	H	Me	H	H	54 (**14b**)
6	**13c**	H	H	OMe	H	H	58 (**14c**)
7	**13d**	H	H	Cl	H	H	66 (**14d**)
8	**13e**	H	H	H	Me	H	64 (**14e**)
9	**13f**	H	H	H	OMe	H	60 (**14f**)
10	**13g**	H	H	H	Cl	H	59 (**14g**)
11	**13h**	Me	H	H	H	H	62 (**14h**)
12	**13i**	H	OMe	OMe	H	H	51 (**14i**)
13	**13j**	H	OMe	H	OMe	H	64 (**14j**)
14	**13k**	H	OMe	H	H	OMe	48 (**14k**)
15	**13l**	H	H	OMe	OMe	H	44 (**14l**)

The results of spirocyclization experiments performed on substrates **1a**−**c** and **13a**−**l** are presented in Table 1. The conditions employed for these reactions are those depicted in eq 1. As is evident from entries 1−10, *ortho*-, *meta*-, and *para*-substituted *N*-benzyl acetoacetamide complexes are converted to the corresponding cyclohexadienyl lactams **3a**−**c** and **14a**−**g** in good yield (45%−86%). The arene substituent was varied from a strongly activating methoxy group to a weakly deactivating chlorine with no obvious decrease in efficiency.

(13) In the sequence involving 2-chlorobenzylamine, MeO_2CCl was used in place of EtOCHO. 2,5-Dimethoxy- and 3,4-dimethoxy-*N*-methylbenzylamines were prepared from the corresponding aldehydes and $MeNH_2$ according to the procedure of Neidigh, K. A.; Avery, M. A.; Williamson, J. S.; Bhattacharyya, S. *J. Chem. Soc., Perkin Trans. 1* **1998**, 2527.

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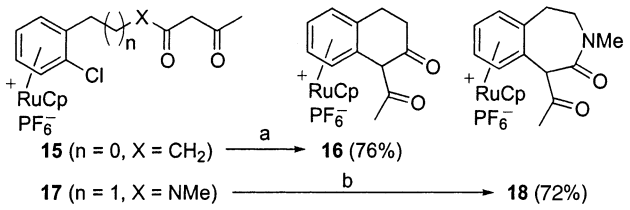
It thus appears that the regioselectivity of intramolecular nucleophilic addition in these substrates is not subject to electronic directing effects.[17] Arene ruthenium complex **13h** (prepared from (*S*)-(−)-α-methylbenzylamine) afforded chiral spirocycle **14h** in reasonable yield (entry 11) and demonstrates the ability to access a fully substituted five-membered lactam ring via this process. The final four entries in Table 1 illustrate the successful preparation of spirocyclic materials from electron-rich trisubstituted arene precursors. The observation that dimethoxy-substituted complexes participate in the reaction serves as a testament to the arene activating ability of the CpRu(II) fragment. Additionally, the isolation of heavily functionalized derivatives **14i**−**l** augurs well for future synthetic applications.

Cyclohexadienyl ruthenium complexes **3** and **14** are both air- and moisture-stable crystalline solids that can be purified by silica gel chromatography (although this was normally unnecessary). Each spirocycle was isolated as a single stereoisomer formed via approach of the pendant nucleophile from the face opposite the CpRu(II) fragment. Additionally, O-alkylation of the putative exocyclic enolate intermediates results in generation of *E*-enol ether products exclusively. Spectroscopic evidence for spirocyclization is provided by a dramatic change in the chemical shifts of the aromatic hydrogens. For example, the aromatic hydrogens present in **1b** appear as a multiplet ∼1 ppm upfield (6.2−6.4 ppm) of the normal chemical shift range for substituted benzenes (as is typically observed in arene−metal complexes). Upon conversion to **3b**, these hydrogens are now part of the cyclohexadienyl ligand and appear as three well-defined signals at 2.59 ppm (d, 2H), 4.50 ppm (dd, 2H), and 5.75 ppm (d, 1H). The Cp ring hydrogens also resonate at higher field in **3**/**14** relative to their position in the ^{1}H NMR spectra of the starting arene complexes (∼4.7 vs ∼5.5 ppm). The geometry of the exocyclic olefin was established in each case by 2D NOESY experiments, which revealed NOE cross-peaks between the methoxy hydrogens and the cyclohexadienyl ring protons.

Origin of Regioselectivity in Intramolecular Nucleophilic Additions to *N*-Benzyl Acetoacetamide Ruthenium Complexes. The results accumulated to date indicate a preference for intramolecular nucleophilic addition in complexes **1** and **13** to occur at the C-1 (*ipso*) position. That five-membered ring formation would be favored on kinetic grounds is not surprising. Indeed, similar azaspiro[4.5]decane ring systems have been prepared from *N*-benzyl acetamide derivatives via electrophilic aromatic alkylation and radical addition processes.[18,19] However, the apparent thermodynamic preference for spirolactam formation in the current context was unexpected. As there are no obvious electronic effects responsible for the observed reactivity (vide supra), it was speculated that conformational constraints present in the benzyl acetoacetamide side chain exert a major influence upon the regioselectivity of nucleophilic addition performed under conditions of thermodynamic control.

Scheme 3[a]



[a] Conditions: (a) sodium 2,6-di-*tert*-butylphenoxide (5 equiv), DMSO, 70 °C, 12 h. (b) NaH (1.1 equiv), DMF, 70 °C, 24 h.

The previously described behavior of benzyl acetoacetate complex **15** appears to support this postulate (Scheme 3).[20] Specifically, unlike **1a**, exposure of **15** to the conditions given in eq 1 failed to produce the corresponding carbocyclic spiro[4.5]decane ring system. In contrast, treatment of **15** with sodium 2,6-di-*tert*-butylphenoxide in warm DMSO resulted in smooth S_NAr to afford 2-tetralone complex **16**.[21] We attribute the different reactivity exhibited by these two complexes to the greater conformational flexibility of the carbon side chain in **15** as compared to the benzyl amide linkage in **1a**. Further evidence pointing to the importance of conformational mobility in determining the regioselectivity of intramolecular nucleophilic addition is provided by the effect of increasing the distance between the acetamide moiety and the coordinated arene, as indicated in **17**. As with **15**, exposure of **17** to the conditions given in eq 1 failed to produce a spirocyclic derivative. Simply heating a DMF solution of **17** and NaH, however, afforded the 3-benzazepine complex **18** in quite respectable 72% isolated yield.

Attempted Demetalation of Spirocyclic Cyclohexadienyl Complexes. An important issue relating to the use of Ru-mediated spirocyclization as a means of constructing spirolactam ring systems concerns the development of methods suitable for liberating the cyclohexadienyl ligand from the CpRu(II) fragment. In contrast to η^6-arene complexes (which can be demetalated under mild photochemical conditions[14]), the cyclohexadienyl ligand present in **3** and **14** is not a tractable organic moiety; hence, some type of chemical transformation involving this group must occur concomitant with ruthenium cleavage in order to obtain isolable spirolactam products. While direct literature precedents for accomplishing such transformations are unavailable, the reactivity of "open" pentadienyl and bis(cyclohexadienyl) ruthenium(II) complexes has been examined.[22,23] In these systems, protonation of the complexes leads to formation of agostic Ru−H derivatives, which can then engage in ligand exchange processes to afford metal-free dienes.

It was initially envisioned that application of the general demetalation protocol described above to a complex such as **3b** may generate the corresponding

(17) With respect to nucleophilic aromatic addition, electron-donating substituents present on an arene−metal complex function as *meta*-directors. For general discussions concerning substituent effects operative in arene−metal complexes, see ref 1.

(18) Rishton, G. M.; Schwartz, M. A. *Tetrahedron Lett.* **1988**, *29*, 2643.

(19) Boivin, J.; Yousfi, M.; Zard, S. Z. *Tetrahedron Lett.* **1997**, *38*, 5985.

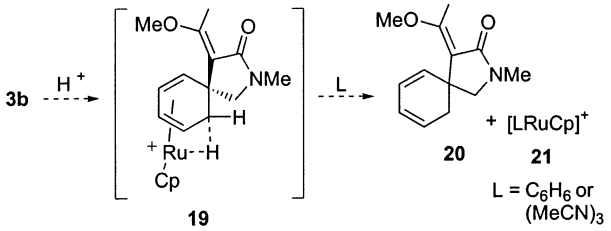
(20) Pigge, F. C.; Fang, S. *Tetrahedron Lett.* **2001**, *42*, 17.

(21) Exposure of **1b** to these reaction conditions returned unchanged starting material.

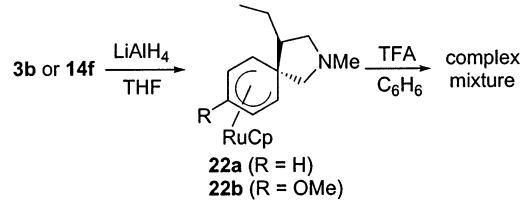
(22) (a) Gleiter, R.; Hyla-Kryspin, I.; Ziegler, M. L.; Sergeson, G.; Green, J. C.; Stahl, L.; Ernst, R. D. *Organometallics* **1989**, *8*, 298. (b) Cox, D. N.; Roulet, R. *J. Chem. Soc., Chem. Commun.* **1989**, 175. (c) Trakarnpruk, W.; Hyla-Kryspin, I.; Arif, A. M.; Gleiter, R.; Ernst, R. D. *Inorg. Chim. Acta* **1997**, *259*, 197.

(23) Dimauro, P. T.; Wolczanski, P. T. *Polyhedron* **1995**, *14*, 149.

Scheme 4



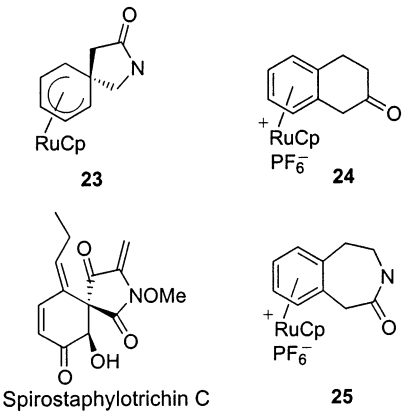
Scheme 5



agostic intermediate **19** (Scheme 4), which, in the presence of donor solvents such as MeCN or benzene, may ultimately provide diene **20** and CpRu(II) derivative **21**. Unfortunately, attempts to effect the transformation illustrated in Scheme 4 starting from **3b** or **14g** using various protic acids (TFA, HBF_4) and solvents (C_6H_6, MeCN, CH_2Cl_2/MeCN) returned complex multicomponent mixtures. In some instances, the presence of the arene complex **1b** or **13g** was detected by ^{1}H NMR. Concerned that the acid lability of the enol ether functionality was complicating the demetalation process, we attempted to reduce the exocyclic olefin using standard hydrogenation conditions (1 or 3.5 atm H_2, Pd/C or PtO_2) and via electron transfer processes (Mg^0, SmI_2/HMPA)[24] with no success (only unreacted starting material was recovered). The olefin also proved unreactive toward oxidizing agents such as OsO_4 and $KMnO_4$ (presumably a consequence of steric hindrance about the tetrasubstituted alkene). Complete reduction of the lactam ring could be effected in good yield, however, by treatment with $LiAlH_4$ (Scheme 5). Disappointingly, attempted demetalation of **22a** and **22b** under protic conditions (5 equiv of TFA) also resulted in generation of complex mixtures.

Conclusions

In conclusion, we have uncovered a general reaction manifold available to η^6-ruthenium complexes of *N*-benzyl acetoacetamide derivatives that delivers Ru-coordinated cyclohexadienyl azaspiro[4.5]decane products in good yield and with complete stereoselectivity. Noteworthy features of the reaction include compatibility with electron-donating and inductively electron-withdrawing arene substituents, as well as substitution at the benzylic position. It is postulated that conformational constraints inherent in the benzyl amide linkage are responsible for dictating the regioselectivity of intramolecular nucleophilic addition in favor of spirocyclization. Increasing the flexibility of the tether connecting the stabilized pronucleophile to the arene ring (as in **15** and **17**) affords products of S_NAr reactions (i.e., tetralones and benzazapinones, respectively) at the expense of spirocyclization pathways. Thus, Ru-promoted nucleophilic aromatic addition/substitution provides rapid access to the basic polycyclic ring systems **23**−**25**



in synthetically useful yields from easily prepared starting materials. It is envisioned that further manipulation of these products, either prior to or after removal of the CpRu(II) fragment, will result in concise and stereocontrolled construction of numerous hetero- and carbocyclic materials of medicinal/pharmaceutical interest (e.g., spirostapylotrichin C).[25] Moreover, synthetic approaches predicated upon the use of planar chiral nonracemic arene ruthenium complexes may provide an asymmetric entry into these important ring systems. Toward this end, we have attempted to convert (albeit unsuccessfully) several cyclohexadienyl-Ru complexes to the corresponding metal-free azaspirocycles under acidic conditions. Despite these initial frustrations, work aimed at achieving controlled ligand demetalation continues and results will be reported in due course.

Experimental Section[26]

General Procedure for the Preparation of [(η^6-Arene)-CpRu][PF_6] Complexes 1 and 13. The procedure used for the preparation of **1a** is representative. *N*-(2-Chlorobenzyl)-*N*-methyl acetoacetamide (0.87 g, 3.63 mmol) and [$(MeCN)_3$-RuCp][PF_6][14] (1.43 g, 3.30 mmol) were combined in ∼30 mL of deoxygenated 1,2-dichloroethane. The resulting red solution was stirred in a 60 °C oil bath for 36 h. Evaporation of the solvent gave a brown residue that was then dissolved in acetone and filtered through a short column of neutral alumina. The filtrate was concentrated and the solid residue was redissolved in a minimum amount of acetone. Addition of anhydrous diethyl ether resulted in precipitation of **1a** as a white solid, which was isolated by vacuum filtration (1.70 g, 94%). Mp: 184−186 °C. ^{1}H NMR (500 MHz, acetone-d_6): δ 2.29 (s, 3H), 3.23 (s, 3H), 3.81 (d, J = 16.9 Hz, 1H), 3.96 (d, J = 16.9 Hz, 1H), 4.49 (d, J = 16.6 Hz, 1H), 5.12 (d, J = 16.6 Hz, 1H), 5.59 (s, 5H), 6.35 (t, J = 5.8 Hz, 1H), 6.41 (t, J = 5.8 Hz, 1H), 6.63 (d, J = 5.8 Hz, 1H), 6.82 (d, J = 5.8 Hz, 1H). ^{13}C NMR (125 MHz, acetone-d_6): δ 30.3, 36.6, 47.9, 49.2, 82.6, 83.6, 84.5, 85.3, 87.3, 100.4, 103.9, 168.1, 203.4. IR (thin film): ν

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(25) Walser-Volken, P.; Tamm, Ch. In *Progress in the Chemistry of Organic Natural Products*; Herz, W., Kirby, G. W., Moore, R. E., Steglich, W., Tamm, Ch., Eds.; Springer: New York, 1996; Vol. 67, pp 125−165, and references therein.

(26) For general experimental details, see the Supporting Information.

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(cm^{-1}) 1718, 1644, 838. Anal. Calcd for $C_{17}H_{19}ClNO_2RuPF_6$: C 37.07, H 3,48, N 2.54. Found: C 37.23, 3.52, 2.58.

Complex 1b: 94%, mp 120−121 °C. ^{1}H NMR (300 MHz, acetone-d_6): δ 2.24 (s, 3H), 3.15 (s, 3H), 3.79 (s, 2H), 4.58 (s, 2H), 5.50 (s, 5H), 6.23−6.43 (m, 5H). ^{13}C NMR (75 MHz, acetone-d_6): δ 30.8, 37.5, 50.4, 50.5, 82.3, 86.5, 86.59, 86.61, 103.4, 169.5, 204.0. IR (thin film): ν (cm^{-1}) 1714, 1650, 838. Anal. Calcd for $C_{17}H_{20}NO_2RuPF_6$: C 39.54, H 3.90, N 2.71. Found: C 39.76, H 3.90, N 2.83.

Complex 1c: 95%, mp 110−112 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ 2.20 (s, 3H), 3.03 (s, 3H), 3.79 (s, 2H), 3.84 (s, 3H), 4.33 (d, J = 16.1 Hz, 1H), 4.56 (d, J = 16.1 Hz, 1H), 5.43 (s, 5H), 6.02 (t, J = 5.7 Hz, 1H), 6.14 (t, J = 5.7 Hz, 1H), 6.28 (d, J = 5.7 Hz, 1H), 6.46 (d, J = 5.7 Hz, 1H). ^{13}C NMR (75 MHz, DMSO-d_6): δ 30.3, 36.7, 46.0, 49.2, 57.5, 71.1, 80.2, 81.8, 83.2, 83.6, 91.8, 131.9, 168.2, 203.6. IR (thin film): ν (cm^{-1}) 1715, 1643, 839. Anal. Calcd for $C_{18}H_{22}NO_3RuPF_6$: C 39.57, H 4.06, N 2.56. Found: C 39.83, H 4.02, N 2.68.

Complex 13a: 86%, mp 126 °C. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 2.28 (s, 3H), 2.37 (s, 3H), 3.06 (s, 3H), 3.67 (d, J = 17.0 Hz, 1H), 3.81 (d, J = 17.0 Hz, 1H), 4.22 (d, J = 16.5 Hz, 1H), 4.91 (d, J = 16.5 Hz, 1H), 5.29 (s, 5H), 6.00−6.33 (m, 4H). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 18.9, 30.9, 37.3, 48.6, 50.1, 81.9, 83.9, 84.5, 85.2, 88.1, 100.8, 101.5, 168.5, 203.4. IR (thin film): ν (cm^{-1}) 1715.9, 1650, 839. HRMS (FAB$^+$, NBA): calcd for $C_{18}H_{22}NO_2Ru$ 386.0693 [M − PF_6]$^+$, found 386.0694. Anal. Calcd for $C_{18}H_{22}NO_2RuPF_6$: C 40.76, H 4.18, N 2.64. Found: C 41.03, H, 4.22, N 2.73.

Complex 13b: 88%, mp 93−95 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ 2.20 (s, 3H), 2.31 (s, 3H), 3.01 (s, 3H), 3.73 (s, 2H), 4.42 (s, 2H), 5.41 (s, 5H), 6.12−6.36 (m, 4H). ^{13}C NMR (75 MHz, DMSO-d_6): δ 20.0, 30.2, 36.3, 48.8, 49.2, 80.9, 83.6, 85.0, 86.1, 86.2, 100.5, 101.2, 168.0, 203.5. IR (thin film): ν (cm^{-1}) 1717, 1644, 837. HRMS (FAB$^+$, NBA): calcd for $C_{18}H_{22}NO_2Ru$ 386.0693 [M − PF_6]$^+$, found 386.0693. Anal. Calcd for $C_{18}H_{22}NO_2RuPF_6$: C 40.76, H 4.18, N 2.64. Found: C 40.75, H 4.20, N 2.84.

Complex 13c: 87%, mp 107−108 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ 2.20 (s, 3H), 3.02 (s, 3H), 3.33 (s, 2H), 3.78 (s, 3H), 4.42 (d, J = 15.7 Hz, 1H), 4.49 (d, J = 15.7 Hz, 1H), 5.45 (s, 5H), 6.09 (d, J = 6.0 Hz, 1H), 6.20 (t, J = 6.0 Hz, 1H), 6.33 (dd, J = 6.0, 1.6 Hz, 1H), 6.47 (s, 1H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 30.2, 36.3, 48.6, 49.2, 57.2, 73.5, 73.8, 80.3, 82.0, 83.3, 100.0, 133.5, 168.1, 203.6. IR (thin film): ν (cm^{-1}) 1716, 1643, 837. HRMS (FAB$^+$, NBA): calcd for $C_{18}H_{22}NO_3Ru$ 402.0643 [M − PF_6]$^+$, found 402.0645. Anal. Calcd for $C_{18}H_{22}NO_3RuPF_6$: C 39.57, H 4.06, N 2.56. Found: C 39.81, H 4.04, N 2.57.

Complex 13d: 96%, oily semisolid. ^{1}H NMR (300 MHz, DMSO-d_6, mixture of rotamers/tautomers): δ 1.94 (s, 0.3H), 2.19 (s, 0.4H), 2.20 (s, 2.3H), 2.89 (s, 0.3H), 3.03 (s, 2.5H), 3.10 (s, 0.2H), 3.76 (s, 0.2H), 3.79 (s, 1.6H), 4.46 (d, J = 15.9 Hz, 1H), 4.54 (d, J = 15.9 Hz, 1H), 5.42 (s, 0.1H), 5.56 (s, 4.1H), 5.59 (s, 0.9H), 6.30 (d, J = 5.8 Hz, 1H), 6.40 (t, J = 5.8 Hz, 1H), 6.78 (d, J = 5.8 Hz, 1H), 6.90 (s, 1H), 14.55 (s, 0.1H). ^{13}C NMR (75 MHz, DMSO-d_6, mixture of rotamers/tautomers): δ 21.5, 30.2, 30.4, 33.3, 36.4, 48.5, 49.2, 50.8, 82.7, 84.3, 85.0, 86.3, 86.7, 101.6, 104.3, 168.3, 203.6. IR (thin film): ν (cm^{-1}) 1717 1643, 839. HRMS (FAB$^+$, NBA): calcd for $C_{17}H_{19}ClNO_2Ru$ 406.0147 [M − PF_6]$^+$, found 406.0147.

Complex 13e: 90%, mp 94−96 °C. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 2.25 (s, 3H), 2.30 (s, 3H), 3.03 (s, 3H), 3.66 (s, 2H), 4.43 (s, 2H), 5.29 (s, 5H), 6.08 (d, J = 6.3 Hz, 2H), 6.21 (d, J = 6.3 Hz, 2H). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 20.8, 30.9, 37.3, 49.7, 50.1, 81.8, 84.9, 86.8, 101.0, 102.3, 168.2, 202.9. IR (thin film) ν (cm^{-1}) 1715, 1650, 838. HRMS (FAB$^+$, NBA): calcd for $C_{18}H_{22}NO_2Ru$ 386.0693 [M − PF_6]$^+$, found 386.0692. Anal. Calcd for $C_{18}H_{22}NO_2RuPF_6$: C 40.76, H 4.18, N 2.64. Found: C 41.06, H 4.25, N 2.86.

Complex 13f: 95%, mp 128−130 °C. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 2.86 (s, 3H), 3.04 (s, 3H), 3.66 (s, 2H), 3.75 (s, 3H), 4.41 (s, 2H), 5.33 (s, 5H), 6.12 (d, J = 6.6 Hz, 2H), 6.21 (d, J = 6.6 Hz, 2H). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 30.9, 37.2, 49.5, 50.0, 57.7, 73.9, 81.2, 83.9, 99.1, 134.8, 168.2, 202.9. IR (KBr): ν (cm^{-1}) 1715, 1637, 841. HRMS (FAB$^+$, NBA): calcd for $C_{18}H_{22}NO_3Ru$ 402.0643 [M − PF_6]$^+$, found 402.0645. Anal. Calcd for $C_{18}H_{22}NO_3RuPF_6$: C 39.57, H 4.06, N 2.56. Found: C 39.56, H 4.01, N 2.82.

Complex 13g: 83%, oily semisolid. ^{1}H NMR (300 MHz, acetone-d_6, mixture of tautomers): δ 1.94 (s, 0.5H), 2.25 (s, 2.5H), 3.14 (s, 2.7H), 3.17 (s, 0.3H), 3.80 (s, 2H), 4.58 (s, 2H), 5.63 (s, 5H), 6.57 (d, J = 6.3 Hz, 2H), 6.80 (d, J = 6.3 Hz, 2H), 14.54 (s, 0.1H). ^{13}C NMR (75 MHz, acetone-d_6, mixture of tautomers): δ 30.4, 37.1, 49.5, 50.0, 84.1, 85.9, 87.8, 102.8, 105.8, 169.1, 203.6. IR (thin film): ν (cm^{-1}) 1708, 1646, 838. HRMS (FAB$^+$, NBA): calcd for $C_{17}H_{19}ClNO_2Ru$ 406.0147 [M − PF_6]$^+$, found 406.0148.

Complex 13h: 96%, mp 86−89 °C. $[\alpha]_D$ +2.0 (*c* 1.69, CH_2Cl_2). ^{1}H NMR (300 MHz, acetone-d_6, mixture of rotamers/tautomers): 1.56 δ (d, J = 7.0 Hz, 2.4H), 1.62 (d, J = 7.0 Hz, 0.6H), 1.93 (s, 0.6H), 2.23 (s, 2.4H), 2.69 (s, 0.6H), 2.94 (s, 2.4H), 3.67 (d, J = 16.7 Hz, 0.8H), 3.83 (d, J = 16.7 Hz, 0.8H), 5.46 (s, 0.2H), 5.51 (s, 4H), 5.53 (s, 1H), 5.69 (quartet, J = 7.2 Hz, 1H), 6.23−6.36 (m, 4H), 6.49 (d, J = 5.7 Hz, 1H), 14.7 (s, 0.2H). ^{13}C NMR (75 MHz, acetone-d_6, mixture of rotamers/tautomers): δ 16.4, 17.1, 21.9, 27.7, 30.4, 31.3, 50.4, 51.1, 81.9, 82.1, 85.2, 86.1, 86.1, 86.2, 86.9, 87.0, 107.2, 168.9, 203.6. IR (thin film): ν (cm^{-1}) 1716, 1634, 839. HRMS (FAB$^+$ NBA): calcd for $C_{18}H_{22}NO_4Ru$ 386.0693 [M − PF_6]$^+$, found 386.0697. Anal. Calcd for $C_{18}H_{22}NO_2RuPF_6$: C 40.76, H 4.18, N 2.64. Found: C 40.49, H 4.10, N 2.78.

Complex 13i: 99%, mp 189 °C. ^{1}H NMR (300 MHz, DMSO-d_6, mixture of rotamers): δ 2.17 (s, 0.5H), 2.19 (s, 2.5H), 2.86 (s, 0.4H), 3.01 (s, 2.6H), 3.77 (s, 2H), 3.84 (s, 3H), 3.86 (s, 3H), 4.28 (d, J = 16.6 Hz, 0.1H), 4.39 (d, J = 16.0 Hz, 0.9H), 4.57 (d, J = 16.0 Hz, 0.9H), 4.68 (d, J = 16.6 Hz, 0.1H), 5.52 (s, 4.4H), 5.57 (s, 0.6H), 5.96−6.04 (m, 2H), 6.36−6.44 (m, 1H). ^{13}C NMR (75 MHz, DMSO-d_6, mixture of rotamers): δ 30.2, 36.6, 45.9, 49.2, 57.9, 65.3, 71.0, 79.9, 80.1, 80.3, 97.0, 123.5, 127.5, 168.1, 203.5. IR (KBr): ν (cm^{-1}) 1721, 1638, 836. HRMS (FAB$^+$, NBA): calcd for $C_{19}H_{24}NO_4Ru$ 432.0748 [M − PF_6]$^+$, found 432.0742. Anal. Calcd for $C_{19}H_{24}NO_4RuPF_6$: C 39.59, H 4.20, N 2.43. Found: C 39.78, H 4.18, N 2.50.

Complex 13j: 95%, mp 147−148 °C. ^{1}H NMR (300 MHz, acetone-d_6): δ 2.25 (s, 3H), 3.15 (s, 3H), 3.74 (d, J = 15.3 Hz, 1H), 3.83 (d, J = 15.3 Hz, 1H), 3.88 (s, 3H), 4.01 (s, 3H), 4.23 (d, J = 16.0 Hz, 1H), 4.77 (d, J = 16.0 Hz, 1H), 5.48 (s, 5H), 6.17 (dd, J = 6.2, 1.4 Hz, 1H), 6.39 (d, J = 6.2 Hz, 1H), 6.63 (d, J = 1.4 Hz, 1H). ^{13}C NMR (75 MHz, acetone-d_6): δ 30.4, 37.4, 46.9, 50.1, 58.2, 58.4, 63.3, 71.2, 81.1, 82.7, 90.8, 132.7, 134.2, 169.1, 203.6. IR (thin film): ν (cm^{-1}) 1717, 1644, 838. HRMS (FAB$^+$, NBA): calcd for $C_{19}H_{24}NO_4Ru$ 432.0748 [M − PF_6]$^+$, found 432.0752. Anal. Calcd for $C_{19}H_{24}NO_4RuPF_6$: C 39.59, H 4.20, N 2.43. Found: C 39.72, H 4.11, N 2.62.

Complex 13k: 76%, mp 141 °C. ^{1}H NMR (300 MHz, acetone-d_6, mixture of rotamers): δ 2.21 (s, 0.2H), 2.29 (s, 2.8H), 2.96 (s, 0.2H), 3.18 (s, 2.8H), 3.82 (d, J = 17.1 Hz, 1H), 3.86 (s, 3H), 3.93 (s, 3H), 3.94 (d, J = 17.1 Hz, 1H), 4.32 (d, J = 16.3 Hz, 1H), 4.84 (d, J = 16.3 Hz, 1H), 5.50 (s, 4.6H), 5.56 (s, 0.4H), 6.24 (dd, J = 6.6, 2.0 Hz, 1H), 6.43 (d, J = 6.6 Hz, 1H), 6.57 (d, J = 2.0 Hz, 1H). ^{13}C NMR (75 MHz, acetone-d_6, mixture of rotamers): δ 30.2, 37.4, 47.2, 50.3, 58.2, 58.4, 70.0, 72.3, 73.3, 81.5, 91.8, 130.9, 132.2, 169.1, 204.3. IR (thin film): ν (cm^{-1}) 1722, 1645, 839. HRMS (FAB$^+$, NBA): calcd for $C_{19}H_{24}NO_4Ru$ 432.0748 [M − PF_6]$^+$, found 432.0750. Anal. Calcd for $C_{19}H_{24}NO_4RuPF_6$: C 39.59 H 4.20, N 2.43. Found: C 40.06, H 4.33, N 2.56.

Complex 13l: 99%, mp 154−156 °C. ^{1}H NMR (300 MHz, acetone-d_6, mixture of rotamers): δ 1.93 (s, 0.3H), 2.26 (s, 2.7H), 2.94 (s, 0.2H), 3.13 (s, 2.8H), 3.81 (s, 2H), 3.91−3.96 (m, 6H), 4.52 (s, 2H), 5.47 (s, 5H), 6.07 (d, J = 6.2 Hz, 1H), 6.48 (d, J = 6.2 Hz, 1H), 6.65 (s, 1H). ^{13}C NMR (75 MHz,

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acetone-d_6, mixture of rotamers): δ 30.4, 37.0, 49.5, 50.1, 58.3, 58.3, 72.0, 72.5, 80.3, 81.1, 97.4, 126.8, 126.9, 168.9, 204.0. IR (KBr): ν (cm^{-1}) 1723, 1650, 855. HRMS (FAB$^+$, NBA): calcd for $C_{19}H_{24}NO_4Ru$ 432.0748 $[M - PF_6]^+$, found 432.0746. Anal. Calcd for $C_{19}H_{24}NO_4RuPF_6$: C 39.59, H 4.20, N 2.43. Found: C 39.88, H 4.25, N 2.42.

General Procedure for the Preparation of Spirocyclic Cyclohexadienyl Complexes 3 and 14. The preparation of **3a** is representative. Arene complex **1a** (0.63 g, 1.14 mmol) and K_2CO_3 (0.19 g, 1.37 mmol) were combined in ~12 mL of dry deoxygenated DMSO. The resulting solution was stirred at room temperature for 12 h. Next, KO^{t}Bu (0.32 g, 2.85 mmol) and 18-C-6 (0.61 g, 2.31 mmol) were added to the reaction, and stirring was maintained for 5 h. Finally, Me_2SO_4 (0.36 g, 0.27 mL, 2.85 mmol) was added via syringe, and the reaction was maintained at room temperature an additional 12 h. The reaction was quenched with H_2O, and the solvents were removed in vacuo. The resulting residue was combined with diethyl ether, and the insoluble material was removed by filtration. The filtrate was washed sequentially with saturated aqueous KCl solution, H_2O, and brine and dried over anhydrous $MgSO_4$. Filtration and evaporation of the solvent afforded **3a** (0.41 g, 86%) as a yellow solid. Mp: 192−194 °C. R_f = 0.63 (EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.35 (s, 3H), 2.89 (s, 3H), 2.99 (dd, J = 6.1, 1.1 Hz, 1H), 3.33 (d, J = 9.9 Hz, 1H), 3.59 (s, 3H), 4.15 (d, J = 9.9 Hz, 1H), 4.49 (ddd, J = 6.1, 4.8, 0.8 Hz, 1H), 4.82 (s, 5H), 4.97 (dd, J = 4.8, 0.8 Hz, 1H), 5.67 (dt, J = 4.8, 1.1 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 12.8, 29.5, 45.5, 53.3, 54.2, 64.3, 69.6, 76.9, 77.7, 77.7, 79.0, 115.7, 165.0, 169.4. IR (thin film): ν (cm^{-1}) 1666. Anal. Calcd for $C_{18}H_{20}ClNO_2Ru$: C 51.61, H 4.81, N 3.34. Found: C 51.84, H 4.71, N 3.40.

Complex 3b: 68%, mp 142−143 °C, R_f = 0.74 (EtOAc). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.32 (s, 3H), 2.59 (d, J = 6.2 Hz, 2H), 2.86 (s, 3H), 3.36 (s, 2H), 3.59 (s, 3H), 4.50 (dd, J = 6.2, 5.0 Hz, 2H), 4.76 (s, 5H), 5.75 (t, J = 5.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 12.9, 29.8, 40.2, 45.7, 53.4, 67.7, 74.9, 75.5, 77.8, 119.6, 164.1, 169.86. IR (thin film): ν (cm^{-1}) 1665. Anal. Calcd for $C_{18}H_{21}NO_2Ru$: C 56.23, H 5.51, N 3.64. Found: C 56.19, H 5.47, N 3.67.

Complex 3c: 67%, mp 172−175 °C, R_f = 0.50 (EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.33 (s, 3H), 2.77 (d, J = 5.1 Hz, 1H), 2.89 (s, 3H), 3.20 (d, J = 9.1 Hz, 1H), 3.21 (s, 3H), 3.56 (s, 3H), 4.13 (d, J = 9.1 Hz, 1H), 4.30 (t, J = 5.1 Hz, 1H), 4.55 (d, J = 5.1 Hz, 1H), 4.74 (s, 5H), 5.44 (t, J = 5.1 Hz, 1H). ^{13}C NMR (500 MHz, $CDCl_3$): δ 12.8, 29.7, 43.9, 50.7, 53.3, 55.2, 62.3, 65.0, 71.7, 74.3, 74.9, 96.4, 117.1, 163.9, 169.6. IR (thin film): ν (cm^{-1}) 1666. Anal. Calcd for $C_{19}H_{23}NO_3Ru$: C 55.06, H 5.59, N 3.38. Found: C 54.79, H 5.56, N 3.32.

Complex 14a: 45%, mp 154 °C, R_f = 0.43 (EtOAc). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.28 (s, 3H), 2.32 (s, 3H), 2.53 (d, J = 5.5 Hz, 1H), 2.88 (s, 3H), 3.16 (d, J = 9.9 Hz, 1H), 3.57 (s, 3H), 3.92 (d, J = 9.9 Hz, 1H), 4.31 (d, J = 5.5 Hz, 1H), 4.50 (t, J = 5.5 Hz, 1H), 4.68 (s, 5H), 5.65 (t, J = 5.5 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.0, 20.6, 29.5, 39.7, 50.0, 51.0, 53.4, 64.0, 75.4, 76.7, 77.6, 80.5, 117.3, 164.0, 170.4. IR (thin film): ν (cm^{-1}) 1666. HRMS (EI): calcd for $C_{19}H_{23}NO_2Ru$ 399.0772 $[M]^+$, found 399.0775. Anal. Calcd for $C_{19}H_{23}NO_2Ru$: C 57.27, H 5.82, N 3.52. Found: C 57.02, H 5.68, N 3.44.

Complex 14b: 54%, mp 145 °C, R_f = 0.61 (EtOAc). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.81 (s, 3H), 2.31 (s, 3H), 2.55 (dd, J = 6.2, 1.8 Hz, 1H), 2.66 (s, 1H), 2.87 (s, 3H), 3.34 (d, J = 9.6 Hz, 1H), 3.42 (d, J = 9.6 Hz, 1H), 3.58 (s, 3H), 4.43 (dd, J = 6.2, 4.8 Hz, 1H), 4.68 (s, 5H), 5.74 (dd, J = 4.8, 1.8 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 12.9, 23.2, 29.8, 39.9, 41.6, 46.8, 53.5, 67.3, 75.2, 76.3, 78.8, 93.5, 119.6, 163.6, 169.8. IR (thin film): ν (cm^{-1}) 1666. HRMS (EI): calcd for $C_{19}H_{23}NO_2Ru$ 399.0772 $[M]^+$, found 399.0772. Anal. Calcd for $C_{19}H_{23}NO_2Ru$: C 57.27, H 5.82, N 3.52. Found: C 57.42, H 5.85, N 3.50.

Complex 14c: 58%, mp 156 °C, R_f = 0.52 (EtOAc). ^{1}H NMR (300 MHz, acetone-d_6): δ 2.26 (s, 3H), 2.48 (dd, J = 6.2, 1.6 Hz, 1H), 2.76 (s, 3H), 2.86 (t, J = 1.6 Hz, 1H), 3.34 (s, 3H), 3.39 (d, J = 9.6 Hz, 1H), 3.45 (d, J = 9.6 Hz, 1H), 3.56 (s, 3H), 4.40 (dd, J = 6.1, 5.0 Hz, 1H), 4.76 (s, 5H), 5.87 (dd, J = 5.0, 1.6 Hz, 1H). ^{13}C NMR (75 MHz, acetone-d_6): 12.7, 29.6, 31.4, 40.8, 49.2, 53.6, 55.4, 67.0, 67.1, 73.6, 75.2, 119.8, 131.5, 163.8, 169.2. IR (thin film): ν (cm^{-1}) 1666. HRMS (EI) calcd for $C_{19}H_{23}NO_3Ru$ 415.0721 $[M]^+$, found 415.0716. Anal. Calcd for $C_{19}H_{23}NO_3Ru$: C 55.06, H 5.59, N 3.38. Found: C 55.22, H 5.64, N 3.36.

Complex 14d: 66%, mp 183 °C, R_f = 0.61 (EtOAc). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.32 (s, 3H), 2.58 (dd, J = 6.1, 1.1 Hz, 1H), 2.86 (s, 3H), 3.04 (s, 1H), 3.36 (d, J = 9.7 Hz, 1H), 3.42 (d, J = 9.7 Hz, 1H), 3.64 (s, 3H), 4.48 (dd, J = 6.1, 4.6 Hz, 1H), 4.82 (s, 5H), 6.11 (dd, J = 4.6, 1.1 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): 12.8, 29.8, 39.9, 41.1, 49.3, 53.76, 66.4, 75.5, 77.4, 79.0, 101.7, 118.4, 164.5, 169.4. IR (thin film): ν (cm^{-1}) 1666. HRMS (EI): calcd for $C_{18}H_{20}ClNO_2Ru$ 419.0226 $[M]^+$, found 419.0230. Anal. Calcd for $C_{18}H_{20}ClNO_2Ru$: C 51.61, H 4.81, N 3.34. Found: C 51.70, H 4.95, N 3.30.

Complex 14e: 64%, mp 175 °C, R_f = 0.49 (EtOAc). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.32 (s, 3H), 2.36 (s, 3H), 2.50 (d, J = 6.3 Hz, 2H), 2.84 (s, 3H), 3.31 (s, 2H), 3.60 (s, 3H), 4.54 (d, J = 6.3 Hz, 2H), 4.69 (s, 5H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.0, 21.7, 29.8, 39.0, 46.0, 53.9, 67.3, 75.3, 79.3, 93.2, 119.4, 164.1, 169.8. IR (thin film): ν (cm^{-1}) 1660. HRMS (EI): calcd for $C_{19}H_{23}NO_2Ru$ 399.0772 $[M]^+$, found 399.0776. Anal. Calcd for $C_{19}H_{23}NO_2Ru$: C 57.27, H 5.82, N 3.52. Found: C 57.21, H 5.73, N 3.41.

Complex 14f: 60%, mp 171 °C, R_f = 0.62 (EtOAc). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.32 (d, J = 6.4 Hz, 2H), 2.33 (s, 3H), 2.84 (s, 3H), 3.32 (s, 2H), 3.62 (s, 3H), 3.67 (s, 3H), 4.66 (d, J = 6.4 Hz, 2H), 4.81 (s, 5H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 12.9, 29.8, 34.1, 46.9, 53.7, 57.3, 66.5, 66.8, 75.5, 118.9, 132.6, 164.4, 169.7. IR (thin film): ν (cm^{-1}) 1665. HRMS (EI): calcd for $C_{19}H_{23}NO_3Ru$ 415.0721 $[M]^+$, found 415.0719. Anal. Calcd for $C_{19}H_{23}NO_3Ru$: C 55.06, H 5.59, N 3.38. Found: C 54.99, H 5.61, N 3.42.

Complex 14g: 59%, mp 202 °C, R_f = 0.69 (EtOAc). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.34 (s, 3H), 2.50 (d, J = 6.5 Hz, 2H), 2.83 (s, 3H), 3.27 (s, 2H), 3.69 (s, 3H), 4.82 (s, 5H), 4.94 (d, J = 6.5 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 12.8, 29.7, 37.9, 45.8, 54.0, 66.6, 76.9, 79.7, 102.7, 118.4, 165.1, 169.5. IR (thin film): ν (cm^{-1}) 1660. HRMS (EI): calcd for $C_{18}H_{20}ClNO_2Ru$ 419.0226 $[M]^+$, found 419.0226. Anal. Calcd for $C_{18}H_{20}ClNO_2Ru$: C 51.61, H 4.81, N 3.34. Found: C 51.56, H 4.94, N 3.34.

Complex 14h: 62%, mp >215 °C; R_f = 0.67 (EtOAc), $[\alpha]_D$ −11.9 (c 1.58, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.11 (d, J = 6.4 Hz, 3H), 2.27 (s, 3H), 2.63 (dd, J = 6.5, 1.8 Hz, 1H), 2.69 (dd, J = 6.5, 1.8 Hz, 1H), 2.87 (s, 3H), 3.52 (quartet, J = 6.4 Hz, 1H), 3.54 (s, 3H), 4.31 (t, J = 6.5 Hz, 1H), 4.71 (t, J = 6.5 Hz, 1H), 4.75 (s, 5H), 5.72 (t, J = 6.5 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.2, 14.2, 28.4, 33.9, 42.3, 50.0, 53.8, 69.4, 75.1, 76.4, 78.2, 79.7, 118.6, 163.2, 168.6. IR (thin film): ν (cm^{-1}) 1662. HRMS (EI): calcd for $C_{19}H_{23}NO_2Ru$ 399.0772 $[M]^+$, found 399.0770. Anal. Calcd for $C_{19}H_{23}NO_2Ru$: C 57.27, H 5.82, N 3.52. Found: C 57.25, H 5.82, N 3.62.

Complex 14i: 51%, mp 145−146 °C, R_f = 0.33 (EtOAc). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.31 (s, 3H), 2.73 (d, J = 5.9 Hz, 1H), 2.89 (s, 3H), 3.26 (d, J = 9.6 Hz, 1H), 3.35 (s, 3H), 3.57 (s, 3H), 3.62 (s, 3H), 4.02 (d, J = 9.6 Hz, 1H), 4.14 (dd, J = 5.9, 4.9 Hz, 1H), 4.80 (s, 5H), 5.05 (d, J = 4.9 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 12.8, 29.8, 44.3, 53.0, 53.4, 56.5, 61.1, 61.4, 61.6, 70.0, 75.3, 86.4, 116.9, 124.0, 163.5, 169.4. IR (thin film): ν (cm^{-1}) 1664. HRMS (EI): calcd for $C_{20}H_{25}NO_4Ru$ 445.0826 $[M]^+$, found 445.0819. Anal. Calcd for $C_{20}H_{25}NO_4Ru$: C 54.04, H 5.67, N 3.15. Found: C 53.98, H 5.79, N 3.03.

Complex 14j: 64%, mp 171 °C, R_f = 0.20 (EtOAc). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.34 (s, 3H), 2.52 (d, J = 6.2 Hz, 1H), 2.88 (s, 3H), 3.17 (d, J = 9.6 Hz, 1H), 3.22 (s, 3H), 3.60 (s, 3H), 3.68 (s, 3H), 4.07 (d, J = 9.6 Hz, 1H), 4.48 (dd, J = 6.2, 0.91 Hz, 1H), 4.80 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 12.9,

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29.8, 37.6, 51.6, 53.7, 55.5, 56.9, 57.6, 61.3, 63.0, 75.6, 90.9, 116.5, 127.8, 164.2, 169.7. IR (thin film): ν (cm^{-1}) 1655. HRMS (EI): calcd for $C_{20}H_{25}NO_4Ru$ 445.0826 $[M]^+$, found 445.0833. Anal. Calcd for $C_{20}H_{25}NO_4Ru$: C 54.04, H 5.67, N 3.15. Found: C 54.16, H 5.56, N 3.11.

Complex 14k: 48%, mp 181−182 °C, R_f = 0.45 (EtOAc). ^1H NMR (300 MHz, $CDCl_3$): δ 2.33 (s, 3H), 2.89 (s, 3H), 3.07 (d, J = 1.3 Hz, 1H), 3.18 (s, 3H), 3.26 (d, J = 9.6 Hz, 1H), 3.33 (s, 3H), 3.57 (s, 3H), 4.10 (d, J = 9.6 Hz, 1H), 4.42 (d, J = 5.3 Hz, 1H), 4.73 (s, 5H), 5.49 (dd, J = 5.2, 1.3 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 12.9, 30.0, 34.7, 52.5, 53.5, 55.5, 55.7, 60.0, 60.4, 62.2, 74.7, 96.5, 116.8, 128.3, 164.0, 169.6. IR (thin film): ν (cm^{-1}) 1666. HRMS (EI): calcd for $C_{20}H_{25}NO_4Ru$ 445.0826 $[M]^+$, found 445.0829. Anal. Calcd for $C_{20}H_{25}NO_4Ru$: C 54.04, H 5.67, N 3.15. Found: C 53.97, H 5.68, N 3.20.

Complex 14l: 44%, mp 136 °C, R_f = 0.44 (EtOAc). ^1H NMR (500 MHz, $CDCl_3$): δ 2.19 (dd, J = 6.3, 1.8 Hz, 1H), 2.30 (s, 3H), 2.68 (d, J = 1.8 Hz, 1H), 2.84 (s, 3H), 3.30 (s, 3H), 3.34 (d, J = 9.7 Hz, 1H), 3.36 (d, J = 9.7 Hz, 1H), 3.62 (s, 3H), 3.80 (s, 3H), 4.59 (d, J = 6.3 Hz, 1H), 4.83 (s, 5H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 12.9, 24.6, 29.8, 33.4, 49.5, 54.0, 56.4, 58.4, 61.6, 66.1, 75.5, 118.4, 123.3, 124.7, 164.5, 169.7. IR (thin film): ν (cm^{-1}) 1669. HRMS (FAB^+, NBA + CsI): calcd for $C_{20}H_{25}NO_4RuCs$ 577.9887 $[M + Cs]^+$, found 577.9882. Anal. Calcd for $C_{20}H_{25}NO_4Ru$: C 54.04, H 5.67, N 3.15. Found: C 53.99, H 5.75, N 3.14.

[(η^6-1-Acetyl-2-tetralone)RuCp][PF_6] (16). Sodium hydride (60%, 0.13 g, 3.2 mmol) and 2,6-di-*tert*-butylphenol (0.83 g, 4.0 mmol) were combined in a dry round-bottom flask and cooled to 0 °C. Anhydrous DMSO (15 mL) was added via syringe, and the resulting solution was allowed to warm to room temperature while stirring over 1 h. A solution of complex **15** (0.43 g, 0.80 mmol) in 15 mL of DMSO was added via syringe, and the reaction mixture was warmed in a 70 °C oil bath for 12 h. After cooling to room temperature, the reaction was quenched with H_2O and concentrated in vacuo. The residue was partitioned between 5% aqueous NH_4PF_6 solution and CH_2Cl_2. The layers were separated, and the organic phase was washed with H_2O and brine and dried over anhydrous $MgSO_4$. Filtration and evaporation of the solvent afforded a yellow residue that was redissolved in a minimum amount of CH_2Cl_2. Addition of anhydrous diethyl ether resulted in precipitation of **16** as a microcrystalline yellow solid. Yield: 0.30 g (76%), mp 145−160 °C (dec). ^1H NMR (500 MHz, acetone-d_6, enol tautomer): δ 2.49 (s, 3H), 2.69−2.79 (m, 3H), 2.90−2.94 (m, 1H), 5.50 (s, 5H), 6.19 (dt, J = 5.7, 0.6 Hz, 1H), 6.33 (dt, J = 5.9, 0.6 Hz, 1H), 6.43 (d, J = 5.7 Hz, 1H), 6.60 (d, J = 5.9 Hz, 1H). ^{13}C NMR (125 MHz, acetone-d_6): δ 24.6, 26.2, 36.1, 82.0, 82.7, 84.7, 84.8, 86.5, 100.3, 103.6, 106.7, 191.0, 198.1. IR (thin film): ν (cm^{-1}) 1709, 836. Anal. Calcd for $C_{17}H_{17}O_2RuPF_6$: C 40.89, H 3.43. Found: C 41.16, H 3.37.

[(η^6-1-Acetyl-3-methyl-2-oxo-3-benzazepine)RuCp][PF_6] (18). Sodium hydride (60%, 20 mg, 0.49 mmol) and **17** (252 mg, 0.45 mmol) were combined in a dry round-bottom flask and flushed with argon. Deoxygenated DMF (~5 mL) was added by syringe, and the resulting solution was stirred for 24 h in a 70 °C oil bath. After cooling to room temperature, the reaction was quenched with 10% aqueous HCl solution and the solvent was removed in vacuo. The residue was partitioned between a 5% aqueous NH_4PF_6 solution and CH_2Cl_2. The layers were separated, and the organic phase was dried over anhydrous $MgSO_4$. Filtration and evaporation of the solvent yielded a brown oil, which was then dissolved in acetone and filtered through a short column of neutral alumina. The filtrate was concentrated in vacuo to afford **18** (170 mg, 72%) as a light brown semisolid. ^1H NMR (500 MHz, acetone-d_6, mixture of tautomers): δ 2.14 (s, 0.9H), 2.36 (s, 2.1H), 2.60 (s, 0.7H), 3.14 (s, 2.3H), 3.11−3.16 (m, 1H), 3.36 (ddd, J = 10.1, 8.0, 2.7 Hz, 1H), 3.46 (ddd, J = 10.1, 2.7, 1.8 Hz, 1H), 3.70 (ddd, J = 10.1, 8.0, 1.8 Hz, 1H), 4.77 (s, 0.9H), 5.38 (s, 0.6 H), 5.42 (s, 4.4H), 6.24−6.41 (m, 4H), 15.26 (s, 0.1H). ^{13}C NMR (125 MHz, acetone-d_6, mixture of tautomers): δ 23.3, 28.0, 30.7, 30.9, 35.1, 35.1, 45.3, 45.8, 55.5, 70.1, 81.4, 82.5, 82.8, 83.8, 86.6, 86.7, 88.0, 89.9, 95.6, 98.3, 102.0, 104.0, 167.7, 169.8, 201.8, 209.9. IR (thin film): ν (cm^{-1}) 1716, 1658, 839. HRMS (FAB^+, NBA): calcd for $C_{18}H_{20}NO_2Ru$ 384.0537 $[M - PF_6]^+$, found 384.0541.

Complex 22a. A solution of **3b** (0.56 g, 1.5 mmol) in 20 mL of THF was added to solid $LiAlH_4$ (0.14 g, 3.7 mmol) at −78 °C. The reaction was allowed to warm to room temperature, resulting in generation of a bright red mixture. After 40 h at room temperature, the reaction mixture acquired a mossy green color. At this time the reaction was quenched by sequential addition of 0.14 mL of H_2O, 0.14 mL of 15% aqueous NaOH solution, and 0.42 mL of H_2O. Inorganic salts were removed by filtration, and the filtrate was concentrated in vacuo. The residue was dissolved in CH_2Cl_2, washed with brine, and dried over anhydrous $MgSO_4$. Filtration and evaporation of the solvent afforded an oil that was purified by flash column chromatography (SiO_2, 2:1 MeOH/EtOAc). Complex **22a** was isolated as a yellow oil that solidified on standing (0.69 g, 47%). R_f = 0.26 (2:1 MeOH/EtOAc). ^1H NMR (300 MHz, acetone-d_6): δ 0.66 (dd, J = 7.9, 6.1 Hz, 3H), 0.70−0.79 (m, 2H), 1.22−1.30 (m, 1H), 1.72 (dd, J = 8.9, 6.9 Hz, 1H), 2.16 (s, 3H), 2.28 (d, J = 8.8 Hz, 1H), 2.43 (ddd, J = 6.2, 0.8, 0.8 Hz, 1H), 2.70 (dd, J = 8.8, 6.9 Hz, 1H), 2.81 (ddd, J = 6.2, 0.8, 0.8 Hz, 1H), 2.90 (d, J = 8.8 Hz, 1H), 4.29 (ddd, J = 6.2, 4.7, 0.8 Hz, 1H), 4.55 (ddd, J = 6.2, 4.7, 0.8 Hz, 1H), 4.76 (s, 5H), 5.63 (tt, J = 4.7, 0.8 Hz, 1H). ^{13}C NMR (75 MHz, acetone-d_6): δ 13.0, 24.0, 35.2, 41.7, 43.0, 52.3, 57.7, 63.7, 74.6, 75.9, 76.4, 78.0, 79.8. HRMS (EI): calcd for $C_{17}H_{23}NRu$ 343.0873 $[M]^+$, found 343.0874. Anal. Calcd for $C_{17}H_{23}NRu$: C 59.63, H 6.77, N 4.09. Found: C 59.89, H 6.92, N 4.10.

Complex 22b. Using the procedure described above, treatment of **14f** (0.2 g, 0.5 mmol) with $LiAlH_4$ (0.05 g, 1.2 mmol) gave **22b** (0.10 g, 54%) as an oily semisolid after purification by flash column chromatography (SiO_2, 2:1 MeOH/EtOAc). R_f = 0.21 (2:1 MeOH/EtOAc). ^1H NMR (500 MHz, $CDCl_3$): δ 0.69 (t, J = 7.1 Hz, 3H), 0.79−0.86 (m, 2H), 1.26−1.31 (m, 1H), 1.81 (t, J = 7.8 Hz, 1H), 2.18 (dd, J = 6.4, 1.9 Hz, 1H), 2.27 (s, 3H), 2.32 (d, J = 8.8 Hz, 1H), 2.59 (dd, J = 6.4, 1.9 Hz, 1H), 2.82 (t, J = 7.8 Hz, 1H), 2.95 (d, J = 8.8 Hz, 1H), 3.63 (s, 3H), 4.49 (dd, J = 6.4, 1.5 Hz, 1H), 4.72 (dd, J = 6.4, 1.5 Hz, 1H), 4.80 (s, 5H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 12.8, 23.4, 28.7, 34.9, 43.1, 53.1, 56.2, 57.7, 63.1, 65.46, 67.3, 73.1, 75.9, 132.9. HRMS (EI): calcd for $C_{18}H_{25}NORu$ 373.0979 $[M]^+$, found 373.0969. Anal. Calcd for $C_{18}H_{25}NORu$: C 58.04, H 6.77, N 3.76. Found: C 57.84, H 6.69, N 3.72.

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Supporting Information Available: Experimental procedures and compound characterization data for **6**−**9**, **11**, **12**, **15**, and **17**. ^1H NMR spectra of **13d**, **13g**, **15**, **17**, and **18**. This material is available free of charge via the Internet at http://pubs.acs.org.

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