ORGANOMETALLICS
Article

Organometallics **2009,** *28,* 3869–3875 3869
DOI: 10.1021/om900178w

Synthesis of Polycyclic Cyclohexadienyl Ruthenium(II) Complexes from η^6-Arene Precursors via Phosphine-Promoted Intramolecular Nucleophilic Aromatic Addition

F. Christopher Pigge,* R. Dhanya, and Dale C. Swenson

Department of Chemistry, University of Iowa, Iowa City, Iowa 52242

Received March 6, 2009

An experimentally straightforward procedure for the synthesis of structurally elaborate cyclohexadienyl ruthenium(II) complexes has been developed along the lines of the Morita−Baylis−Hillman reaction. Coordination of (cyclopentadienyl)Ru(II) fragments to *N*-benzyl and *N*-phenethyl acrylamides was found to facilitate conversion to stable cyclohexadienyl complexes via Bu_3P-mediated intramolecular cyclization. An *ipso* cyclization was observed in all but one case, resulting in formation of five- or six-membered spirolactams at C6 positions of cyclohexadienyl ligands. Acrylamides prepared from dihydroindene and tetrahydronaphthalene precursors were suitable substrates for this transformation, affording access to novel tricyclic cyclohexadienyl complexes. One such complex was characterized by X-ray crystallography.

Introduction

Arene metal complexes have proven to be versatile organometallic intermediates that are widely used in organic synthesis and materials chemistry.[1,2] In particular, various arene complexes of Cr(0), Mn(I), Fe(II), and Ru(II) are easily prepared and possess excellent air and moisture stability.[3] The utility of these complexes is due in large part to the enhanced electrophilicity exhibited by the coordinated arene ligand.[4] Consequently, arene functionalization can be accomplished via normally unfavorable reaction manifolds such as nucleophilic aromatic substitution. This enhanced arene reactivity also facilitates nucleophilic aromatic addition to produce (η^5-cyclohexadienyl)metal derivatives. In contrast to their (η^6-arene) progenitors, however, the chemistry and synthetic utility of cyclohexadienyl adducts have not been extensively investigated.[5,6]

For the past several years we have been developing Ru-mediated dearomatization reaction sequences that lead to generation of 2-azaspiro[4.5]decanes starting from various (η^6-*N*-benzylamide) complexes.[7,8] A particularly straightforward procedure utilizing simple benzyl acrylamides is illustrated in Scheme 1.[9] Conversion of **1** to **2** is envisioned to proceed via Michael-type addition of a phosphine promoter to the acrylamide side chain. Regioselective nucleophilic aromatic addition to the *ipso* position followed by base-mediated elimination of phosphine affords cyclohexadienyl complexes **2** as stable and isolable products. The presence of an electron-releasing substituent at the cyclohexadienyl C3 position (R = OMe in Scheme 1) then allows oxidative demetalation of **2** to proceed with preservation of the spirocyclic linkage.

An interesting observation in the context of the chemistry shown in Scheme 1 concerns the compatibility of *N*-phenethyl acrylamide complexes with the spirocyclization manifold (i.e., **1**, $n = 1$).[9] These substrates reacted smoothly in the presence of Bu_3P to deliver 6,6-spirofused products in good yield, whereas closely related complexes possessing alternative

*Corresponding author. E-mail: chris-pigge@uiowa.edu.

(1) (a) Lavy, S.; Pérez-Luna, A.; Kündig, E. P. *Synlett* **2008**, 2621. (b) Rosillo, M.; Domínguez, G.; Pérez-Castells, J. *Chem. Soc. Rev.* **2007**, *36*, 1589. (c) Pearson, A. J.; Paramahamsan, H.; Dudones, J. D. *Org. Lett.* **2004**, *6*, 2121. (d) Bolm, C.; Muñiz, K. *Chem. Soc. Rev.* **1999**, *28*, 51.

(2) (a) Astruc, D.; Ornelas, C.; Ruiz, J. *Acc. Chem. Res.* **2008**, *41*, 841. (b) Park, K. H.; Jang, K.; Cho, Y.; Chun, J.; Kim, H. J.; Sweigart, D. A.; Son, S. U. *Adv. Mater.* **2007**, *19*, 2547. (c) Rigby, J. H.; Kondratenko, M. A. *Org. Lett.* **2001**, *3*, 3683.

(3) Kündig, E. P. *Top. Organomet. Chem.* **2004**, *7*, 3.

(4) Recent examples: (a) Pearson, A. J.; Ciurea, D. V.; Velankar, A. *Tetrahedron Lett.* **2008**, *49*, 1922. (b) Storm, J. P.; Andersson, C.-M. *J. Org. Chem.* **2000**, *65*, 5264. Reviews: (c) Semmelhack, M. F.; Chlenov, A. *Top. Organomet. Chem.* **2004**, *7*, 43. (d) Abd-El-Aziz, A. S.; Bernardin, S. *Coord. Chem. Rev.* **2000**, *203*, 219. (e) Pike, R. D.; Sweigart, D. A. *Coord. Chem. Rev.* **1999**, *187*, 183.

(5) For examples, see: (a) Eloi, A.; Rose-Munch, F.; Rose, E.; Chavarot-Kerlidou, M.; Gérard, H. *Organometallics* **2009**, *28*, 925, and references therein. (b) Kirss, R. U.; Henriksen, A.; Forsyth, D. A.; Feighery, W. *Inorg. Chim. Acta* **2006**, *359*, 4393. (c) Older, C. M.; Stryker, J. M. *J. Am. Chem. Soc.* **2000**, *122*, 2784. (d) Bhambri, S.; Bishop, A.; Kaltsoyannis, N.; Tocher, D. A. *J. Chem. Soc., Dalton Trans.* **1998**, 3379. (e) Shirin, Z.; Pramanik, A.; Ghosh, P.; Mukherjee, R. *Inorg. Chem.* **1996**, *35*, 3431. (f) Djukic, J.-P.; Rose-Munch, F.; Rose, E.; Dromzee, Y. *J. Am. Chem. Soc.* **1993**, *115*, 6434. (g) Sutherland, R. G.; Chowdhury, R. L.; Piórko, A.; Lee, C. C. *J. Organomet. Chem.* **1987**, *319*, 379. (h) Vol'kenau, N. A.; Bolesova, L. N.; Shul'pina, L. S.; Kitaigorodskii, A. N. *J. Organomet. Chem.* **1984**, *267*, 313. (i) Robertson, D. R.; Robertson, I. W.; Stephenson, T. A. *J. Organomet. Chem.* **1980**, *202*, 309.

(6) (η^5-Cyclohexadienyl)$Fe(CO)_3$ cations have been extensively used in synthesis; however these materials are typically prepared from iron diene precursors. For example, see: Owen, D. A.; Malkov, A. V.; Palotai, I. M.; Roe, C.; Sandoe, E. J.; Stephenson, G. R. *Chem.—Eur. J.* **2007**, *13*, 4293, and references therein.

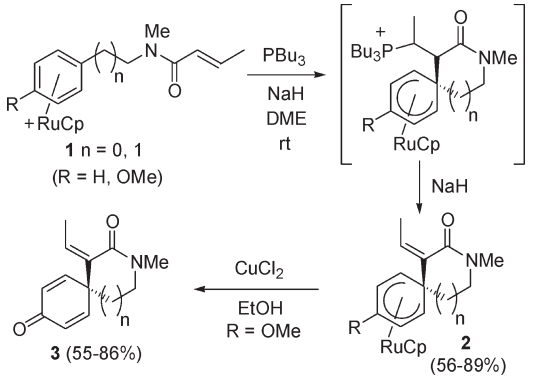
(7) (a) Pigge, F. C.; Dalvi, R. *Tetrahedron* **2008**, *64*, 10123. (b) Pigge, F. C.; Coniglio, J. J.; Dalvi, R. *J. Am. Chem. Soc.* **2006**, *128*, 3498. (c) Pigge, F. C.; Coniglio, J. J.; Rath, N. P. *J. Org. Chem.* **2004**, *69*, 1161. (d) Pigge, F. C.; Coniglio, J. J.; Fang, S. *Organometallics* **2002**, *21*, 4505.

(8) For a review of metal-mediated dearomatization, see: (a) Pape, A. R.; Kaliappan, K. P.; Kündig, E. P. *Chem. Rev.* **2000**, *100*, 2917. (b) Keane, J. M.; Harman, W. D. *Organometallics* **2005**, *24*, 1786.

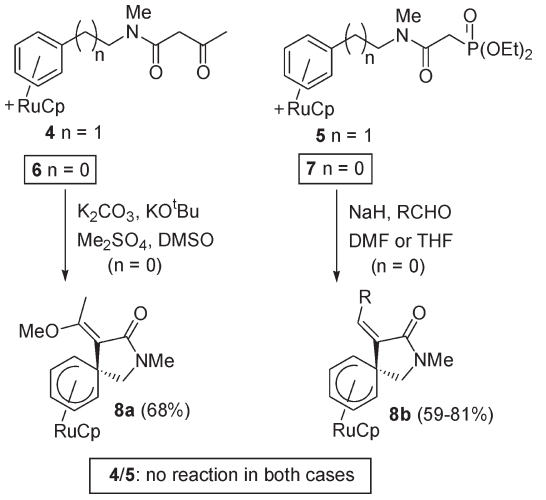
(9) Pigge, F. C.; Dhanya, R.; Hoefgen, E. R. *Angew. Chem., Int. Ed.* **2007**, *46*, 2887.

Published on Web 05/19/2009

Scheme 1



Scheme 2

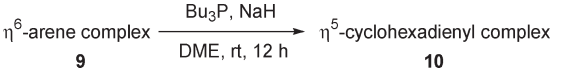


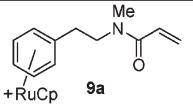
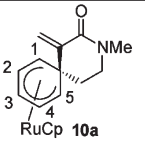
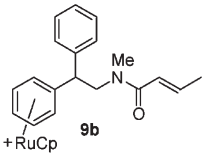
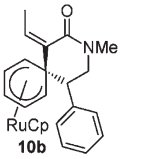
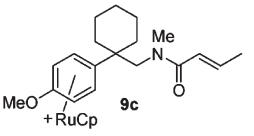
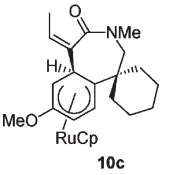
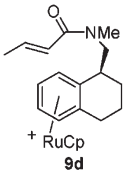
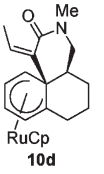
pronucleophilic side-chain functionality (acetoacetamide **4** and β-amidophosphonate **5**) failed to undergo similar transformations (Scheme 2). Notably, however, the *N*-benzyl analogues **6** and **7** (with $n = 0$) have been efficiently converted to spirolactam cyclohexadienyl complexes **8**.[7] On the basis of these initial observations we became interested in testing the limits of phosphine-promoted nucleophilic aromatic addition as a means to construct unique and structurally elaborate cyclohexadienyl ruthenium(II) complexes. We now report the successful application of this method for the preparation of several bicyclic (azaspiro[5.5]undecane) and tricyclic cyclohexadienyl complexes. One example from this latter family of compounds has been structurally characterized by X-ray crystallography.

Results and Discussion

The first set of substrates examined in this study all featured arene ligands with a two-carbon linker between the arene ring and the acrylamide group. Introduction of the cyclopentadienyl (Cp) ruthenium fragment was achieved in high yields (70−98%) upon exposure of the arene ligands to $[(CH_3CN)_3RuCp][PF_6]$ in warm dichloroethane.[10] In this manner (η^6-arene) complexes **9a**−**9d** were obtained (Table 1). It is notable that selective metalation of a single phenyl ring in **9b** occurred in the presence of 1 equiv of the Ru-tris(acetonitrile) salt. Complex **9d** can potentially exist as a mixture of *exo* and *endo* diastereomers. The *exo* complex has been assigned primarily on the basis of subsequent reactivity (*vide infra*), as the presence of amide bond rotamers resulted in a complicated NMR spectrum that precluded definitive determination of stereochemistry.

Table 1. Phosphine-Promoted Transformations of Phenethylamine-Based Arene Complexes



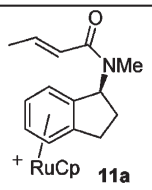
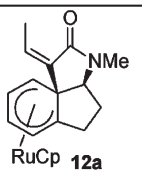
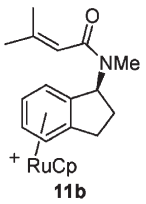
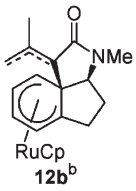
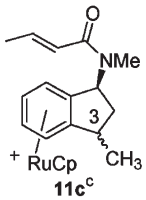
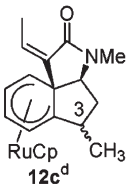
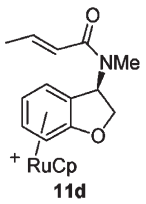
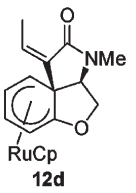
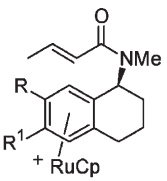
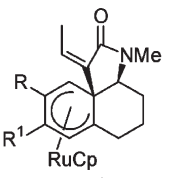
entry	substrate **9**[a]	product **10**	% yield
1	 **9a**	 **10a**	89
2	 **9b**	 **10b**	48
3	 **9c**	 **10c**	75
4	 **9d**	 **10d**	50

[a] Counterion is PF_6 in all cases.

As indicated in Table 1, **9a**, **9b**, and **9d** were all converted to the corresponding spirocyclic cyclohexadienyl products **10a**, **10b**, and **10d** in good yield upon treatment with Bu_3P and NaH in DME at room temperature. The ^1H NMR spectra clearly reveal transformation of the bound arenes into cyclohexadienyl ligands. Diagnostic signals include a triplet at ~5.5 ppm (C3 hydrogen, see **10a** for numbering), triplet(s) at ~4.5 ppm (C2 and C4), and upfield doublet(s) at ~2−3 ppm (C1 and C5). Additionally, the signal for the Cp hydrogens experiences an upfield shift from ~5.5 ppm in arene complexes **9** to ~4.8 ppm in **10**. The stereochemistry at the newly generated C−C bond is envisioned to arise from *exo* addition of the nucleophilic side chain to the coordinated arene, a result consistent with the well-known reactivity profile of arene metal complexes and our own observations in closely related systems.[4,7,8a] Thus, the successful construction of sterically congested and structurally intriguing tricyclic spirolactam **10d** seemingly confirms the stereochemical assignment of **9d**. Substrate **9c**, featuring a benzylic quaternary center, exhibits a different reactivity. Intramolecular nucleophilic aromatic addition was found to give a cyclohexadienyl product exhibiting a doublet at 5.67 ppm corresponding to a C3 cyclohexadienyl hydrogen and a doublet at 4.46 ppm (integrating to one hydrogen) corresponding to a C2 cyclohexadienyl hydrogen. Since the spirocyclic product would possess two

(10) (a) Gill, T. P.; Mann, K. R. *Organometallics* **1982**, *1*, 485. (b) Kündig, E. P.; Monnier, F. R. *Adv. Synth. Catal.* **2004**, *346*, 901.

Table 2. Synthesis of Spirotricyclic Cyclohexadienyl Ru(II) Complexes

entry	substrate **11**[a]	product **12**	% yield
1	 **11a**	 **12a**	59
2	 **11b**	 **12b**[b]	54
3	 **11c**[c]	 **12c**[d]	53
4	 **11d**	 **12d**	59
5	 **11e** (R,R^1=H)	 **12e** (R,R^1=H)	58
6	**11f** (R=OMe, R^1=H)	**12f** (R=OMe, R^1=H)	62
7	**11g** (R=H, R^1=OMe)	**12g** (R=H, R^1=OMe)	58

[a] Counterion is PF_6. [b] 1:1 mixture of alkene isomers. [c] ~5:1 mixture of C3 diastereomers. [d] ~2:1 mixture of C3 diastereomers.

hydrogens at the C2/C4 positions and no C3 hydrogen, the product of this reaction must result from cyclization to an *ortho* position, affording fused bicyclic cyclohexadienyl complex **10c**. This regioselectivity may arise from an electronic effect exerted by the methoxy substituent, as Semmelhack has shown that methoxy groups in (arene)$Cr(CO)_3$ complexes direct nucleophilic aromatic addition to occur at *meta* positions.[4c,11] However, a simpler analogue of **9c** also possessing a *para* methoxy group but lacking a benzylic substituent (**1**, see Scheme 1) was found to exhibit regioselective *ipso* cyclization under the same reaction conditions.[9] Consequently, we attribute the behavior of **9c** primarily to steric effects emanating from the benzylic cyclohexyl substituent.

The successful elaboration of **9d** into tricyclic cyclohexadienyl **10d** seemed to indicate that structurally more complicated arene ruthenium complexes may be amenable to phosphine-promoted spirocyclization. To test the generality of the process, several acrylamide arene ruthenium complexes were prepared from indanone and tetralone precursors. Each of these materials was then subjected to our standard intramolecular cyclization conditions (see Table 1), and the results are tabulated in Table 2. As shown in entry 1, a dihydroindene acrylamide complex (**11a**) was smoothly converted to cyclohexadienyl product **12a** in 59% isolated yield. As with **9d**, isolation of the *exo* diastereomer of **11a** upon coordination of the CpRu(II) fragment is inferred from subsequent reactivity and an X-ray crystal structure analysis of **12a** (*vide infra*). The stereochemistry of the other (η^6-arene) complexes shown in Table 2 was assigned by analogy to **11a**. Complex **11b** features a β,β-disubstituted acrylamide unit. Nonetheless, cyclization was found to proceed smoothly, and **12b** was isolated in 54% yield as a separable ~1:1 mixture of α,β- and β,γ-unsaturated spirolactams. The reaction was found to be compatible with additional substitution on the dihydroindene framework (**11c**) as well as the presence of an oxygen heteroatom (**11d**). Tetrahydronaphthalene derivatives **11e**−**11g** also gave the reaction to afford the 6,6,5-fused tricycles **12e**−**12g** with isolated yields of ~60% in each case.

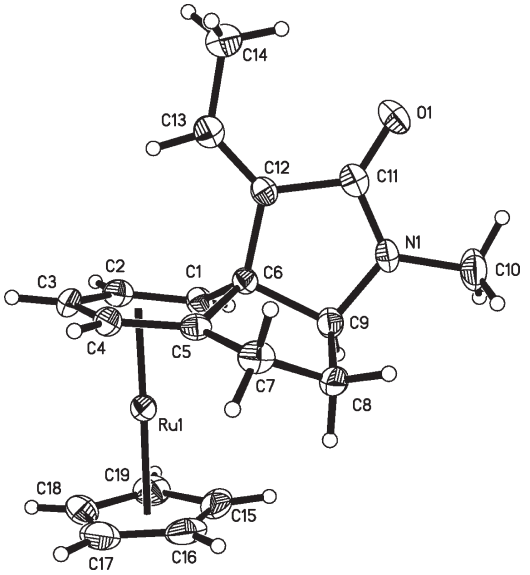


Figure 1. Molecular structure of **12a**. Selected bond distances (Å): Ru−C1, 2.178; Ru−C2, 2.164; Ru−C3, 2.171; Ru−C4, 2.180; Ru−C5, 2.210; Ru−C15, 2.181; Ru−C16, 2.202; Ru−C17, 2.245; Ru−C18, 2.231; Ru−C19, 2.178.

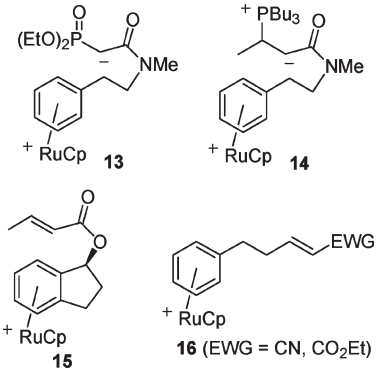
Crystals of **12a** suitable for X-ray diffraction were obtained from slow evaporation of an EtOAc solution, and the molecular structure is shown in Figure 1.[12] The *exo* orientation of the spirolactam ring with respect to the CpRu(II) fragment is clearly evident. The CpRu(II) fragment is located on a line between the centroids of the Cp ring and cyclohexadienyl ligand (centroid−Ru−centroid angle ~178°). The average Ru−carbon bond lengths to the cyclohexadienyl and Cp ligands are 2.181 and 2.207 Å, respectively, indicative of

(11) (a) Semmelhack, M. F.; Harrison, J. J.; Thebtaranonth, Y. *J. Org. Chem.* **1979**, *44*, 3275. (b) Semmelhack, M. F.; Yamashita, A. *J. Am. Chem. Soc.* **1980**, *102*, 5924.

(12) Crystal data: fw = 380.44, orthorhombic, $P2_12_12_1$, a = 7.9074 (9) Å, b = 8.1560(9) Å, c = 24.107(3) Å, V = 1554.7(3)Å^3, Z = 4, D_{calc} = 1.625 g cm^{-3}, μ = 1.010 mm^{-1}, T (K) = 190(2), reflections = 37452, unique reflections = 3572, reflections $I > 2\sigma(I)$ = 3348, parameters = 201, R_1 [$I > 2\sigma(I)$] = 0.0247, wR_2 = 0.0541. This structure has been deposited with the Cambridge Crystallographic Database (CCDC #722760).

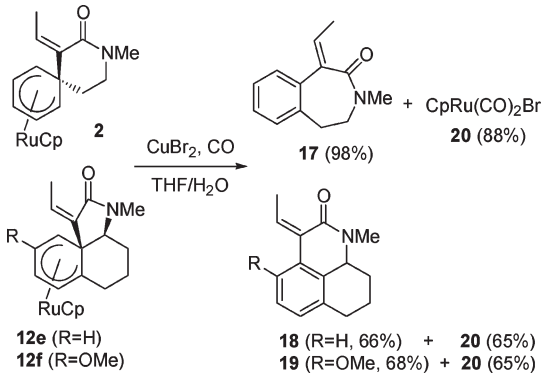
slightly stronger bonding to the cyclohexadienyl ligand.[13] In the solid state both the Cp and cyclohexadienyl ligands are slightly tilted such that the Ru−carbon bonds distal from the fused ring substituent (Ru−C2, Ru−C3, Ru−C15, and Ru−C19) are slightly shorter than the remaining Ru−carbon linkages. Carbon−carbon distances within the η^5-cyclohexadienyl ligand are all comparable and range from 1.409 to 1.419 Å.

From the results described above we conclude that phosphine-promoted intramolecular nucleophilic aromatic addition of acrylamide-functionalized arene ruthenium complexes provides a relatively straightforward means of constructing substituted and stable cyclohexadienyl ruthenium complexes. The basis for the enhanced reactivity exhibited by the acrylamide/phosphine reagent combination compared to β-amido phosphonate anions derived from complexes such as **5** (n = 1) is attributed to differences in reactivity of the anion intermediates. While our previous success in manipulating *N*-benzyl β-amido phosphonate complexes (see Scheme 2) demonstrates that stabilized phosphoryl anions (**13**) are suitable partners for nucleophilic aromatic additions,[7a,7b] the wider substrate scope evident in phosphine-promoted reactions of acrylamide complexes presumably reflects enhanced reactivity (greater nucleophilicity) of zwitterion **14**. Additionally, the zwitterionic intermediate **14** may adopt a more ordered conformation conducive to intramolecular nucleophilic addition as compared to the nominally more flexible phosphonate anion **13**. Evidence supporting the importance of side-chain conformational effects in these types of reactions is provided by the failure of **15** and **16** (complexes in which the amide group has been replaced with an ester or alkyl linkage, respectively) to afford cyclohexadienyl ruthenium derivatives upon treatment with Bu_3P/NaH.

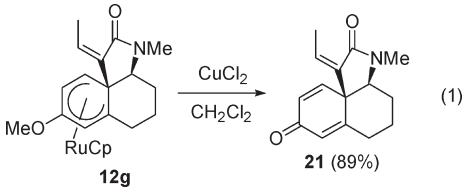


As mentioned previously, the chemistry of discrete cyclohexadienyl metal complexes (especially ruthenium complexes) derived from (η^6-arene) precursors has not been extensively developed.[5] The preparative route to structurally elaborate cyclohexadienyl complexes described above has proven to be straightforward and reasonably broad in scope, features that may spur additional investigations into the reactivity of these materials. In this context we have briefly examined oxidative demetalation of selected substrates with the aim of obtaining heterocyclic synthetic building blocks. As shown in Scheme 3, exposure of complexes **2** and **12e**,**f** to previously established oxidative demetalation reaction conditions afforded rearomatized products arising from cleavage of the spirolactam and

Scheme 3



migration of the vinyl group.[7,9] No evidence for the addition of H_2O to a cyclohexadienyl terminal position was detected, although this type of transformation has been observed in closely related substrates. It should be noted that application of a CO atmosphere resulted in recovery of the CpRu(II) fragment. The 3-benzazepine product **17** was obtained in excellent isolated yield, while the tetrahydroisoquinolinone derivatives **18** and **19** were formed slightly less efficiently. The NMR spectra of these latter two compounds are fully consistent with the illustrated structures; however, rapid decomposition prevented further characterization. Cyclohexadienyl complex **12g** was also subjected to oxidative demetalation reaction conditions. In this case the spirocyclic linkage was preserved in the metal-free product due to the presence of the C3 methoxy substituent and **21** was isolated in good yield (eq 1).



Conclusions

In summary, the conversion of easily prepared cationic arene ruthenium complexes bearing acrylamide side chains into neutral spirocyclic cyclohexadienyl derivatives has been achieved in the presence of Bu_3P and NaH. These mild reaction conditions were found to be compatible with a range of acrylamide substrates, and a variety of structurally intriguing (cyclohexadienyl)RuCp products have been successfully prepared and characterized. Superficially these transformations resemble the well-known Morita−Baylis−Hillman reaction.[14] It is noteworthy that while the compounds examined in this study are all racemic, enantiomerically pure analogues of ligands found in arene complexes **11** should be easily accessible.[15] Coupled with the high stereoselectivity exhibited in the arene complexation and nucleophilic aromatic addition reactions described above, the use of such optically enriched ligands would provide entry to enantiomerically pure cyclohexadienyl complexes.

(13) These bond distances are similar to other structurally characterized cyclohexadienyl ruthenium complexes. See refs 5c−5e and: Pigge, F. C.; Coniglio, J. J.; Rath, N. P. *Organometallics* **2005**, *24*, 5424.

(14) Basavaiah, D.; Rao, A. J.; Satyanarayana, T. *Chem. Rev.* **2003**, *103*, 811.

(15) For example both antipodes of enantiomerically enriched 1-aminoindane and 1-aminotetraline are commercially available (Aldrich).

Experimental Section

All reactions were performed in oven-dried glassware under a blanket of dry argon unless otherwise noted. Reagents purchased from commercial sources were used as received. Solvents were distilled from appropriate drying agents. ^{1}H and ^{13}C NMR spectra were obtained at 300 and 75 MHz, respectively. Chemical shifts (δ) are reported relative to TMS. IR spectra were recorded on an FT-IR spectrophotometer equipped with an ATR attachment. Melting points were determined using a capillary melting point apparatus and are uncorrected. High-resolution mass spectra were obtained using electron impact ionization (EI). All arene ligands were prepared from commercially available starting materials using routine functional group transformations. $[CpRu(CH_3CN)_3][PF_6]$ was prepared according to literature procedures.[10]

General Procedure for the Preparation of (η^6-Arene)ruthenium complexes. The preparation of **9a** is representative. The arene ligand (189 mg, 1.0 mmol) and $[CpRu(CH_3CN)_3][PF_6]$ (477 mg, 1.1 mmol) were combined in 20 mL of 1,2-dichloroethane. The solution was heated to 70 °C for 36 h. After cooling to rt the solvent was evaporated and the residue was dissolved in acetone and passed through a short column of neutral alumina. The filtrate was concentrated, then redissolved in a minimum amount of acetone. Slow addition of anhydrous ether resulted in precipitation of **9a** as a colorless solid that was collected by filtration and dried under vacuum. Yield: 350 mg (70%). Mp: 172−173 °C. ^{1}H NMR (acetone-d_6, mixture of rotamers): δ 2.75−2.88 (m, 3.2H), 3.08 (s, 1.8H), 3.70 (t, 1.5H, J = 7.4 Hz), 3.77−3.82 (m, 0.5H), 5.63 (s, 5H), 5.65 (dd, 1H, J_1 = 10.4 Hz, J_2 = 2.5 Hz), 6.14 (dd, 1H, J_1 = 12.0 Hz, J_2 = 4.4 Hz), 6.23−6.63 (m, 5H), 6.60−6.81 (m, 1H). ^{13}C NMR (acetone-d_6): δ 31.9, 35.2, 48.7, 80.8, 80.9, 85.2, 85.4, 85.8, 85.9, 87.1, 87.5, 104.2, 127.0, 128.4, 165.7. Anal. Calcd for $C_{17}H_{20}NORuPF_6$: C, 40.81; H, 4.03; N, 2.80. Found: C, 40.89, H, 4.05, N, 2.87.

Arene Complex 9b. White solid, 74%, mp 165−167 °C. ^{1}H NMR (acetone-d_6, mixture of rotamers): δ 1.71 (d, 0.5H, J = 6.7 Hz), 1.84 (d, 2.5H, J = 6.8 Hz), 2.75 (s, 1.2H), 2.88 (s, 1.8H), 3.74 (t, 1H, J = 7.3 Hz), 4.17−4.21 (m, 1H), 4.36−4.42 (m, 1H), 5.55 (s, 5H), 6.26−6.29 (m, 5H), 6.54 (br s, 1H), 6.80 (m, 1H), 7.34−7.49 (m, 5H). ^{13}C NMR (acetone-d_6): δ 18.0, 37.2, 48.4, 54.0, 81.7, 85.9, 86.0, 87.2, 109.1, 122.7, 128.7, 129.2, 129.8, 141.8, 142.0, 166.8. Anal. Calcd for $C_{24}H_{26}NORuPF_6$: C, 48.82; H, 4.44; N, 2.37. Found: C, 48.56, H, 4.49, N, 2.32.

Arene Complex 9c. White solid, 98%, mp 203−205 °C. ^{1}H NMR (acetone-d_6, mixture of rotamers): δ 1.25−1.30 (m, 3H), 1.31−1.88 (m, 8H), 2.06−2.21 (m, 2H), 2.85 (s, 2.8H), 2.95 (s, 0.2H), 3.77 (s, 2H), 3.86 (s, 3H), 5.51 (s, 5H), 6.28−6.23 (m, 5H), 6.54−6.63 (m, 1H). ^{13}C NMR (acetone-d_6): δ 18.0, 22.6, 26.1, 34.3, 39.4, 40.9, 55.1, 57.6, 73.7, 80.8, 83.5, 115.0, 123.3, 134.9, 141.4, 167.7. Anal. Calcd for $C_{24}H_{32}NO_2RuPF_6$: C, 47.06; H, 5.27; N, 2.29. Found: C, 47.08; H, 5.40; N, 2.23.

Arene Complex 9d. White solid, 82%, mp 210−212 °C. ^{1}H NMR (acetone-d_6, mixture of rotamers): δ 1.66−2.00 (m, 6H), 2.79−3.02 (m, 5H), 3.11−3.23 (m, 2H), 3.36−3.62 (m, 1H), 3.76−3.94 (m, 1H), 5.49 (s, 2.5 H), 5.58 (s, 2.5H), 6.15−6.37 (m, 4H), 6.49−6.55 (m, 1H), 6.75−6.89 (m, 1H). ^{13}C NMR (acetone-d_6): δ 18.0, 19.9, 25.5, 32.5, 36.0, 52.8, 54.0, 80.6, 81.1, 81.2, 81.3, 84.3, 84.5, 85.1, 104.2, 107.4, 141.5, 167.6. Anal. Calcd for $C_{21}H_{26}NORuPF_6$: C, 45.66; H, 4.38; N, 2.54. Found: C, 45.46; H, 4.80; N, 2.66.

Arene Complex 11a. White solid, 87%, mp 145−147 °C. ^{1}H NMR (acetone-d_6, mixture of rotamers): δ 1.87 (dd, 3H, J_1 = 1.6 Hz, J_2 = 6.8 Hz), 2.14−2.23 (m, 1H), 2.81 (s, 3H), 3.02−3.08 (m, 3H), 3.34−3.46 (m, 1H), 5.58 (s, 5H), 5.77 (d, 1H, J = 8.1 Hz), 6.19−6.24 (m, 2H), 6.41−6.57 (m, 2H), 6.78−6.87 (m, 1H). ^{13}C NMR (acetone-d_6): δ 19.9, 33.5, 34.3, 62.1, 83.5, 83.9, 85.5, 85.8, 85.9, 87.5, 87.6, 112.2, 124.8, 144.3, 168.2. Anal. Calcd for $C_{19}H_{22}NORuPF_6$: C, 43.35; H, 4.21; N, 2.66. Found: C, 43.31, H, 4.23, N, 2.68.

Arene Complex 11b. White solid, 83%, mp 135−137 °C. ^{1}H NMR (acetone-d_6, mixture of rotamers): δ 1.83 (s, 2.5H), 1.89 (s, 0.5H), 1.91 (s, 2.5H), 2.04 (s, 0.5H), 2.12−2.25 (m, 1H), 2.56−2.27 (m, 1H), 2.88 (s, 2.5H), 2.96−2.99 (m, 1H), 3.04 (s, 0.5H), 3.31−3.43 (m, 1H), 5.52 (s, 5H), 5.76−5.80 (m, 1H), 5.93 (s, 0.8H), 6.08 (s, 0.2H), 6.18−6.24 (m, 2H), 6.47−6.49 (m, 1H), 6.55−6.57 (m, 1H). ^{13}C NMR (acetone-d_6): δ 19.5, 19.7, 25.7, 31.0, 32.2, 54.7, 58.7, 65.4, 81.0, 81.4, 82.8, 83.0, 83.2, 83.5, 83.9, 85.0, 86.3, 106.1, 109.6, 118.0, 147.8, 167.7. Anal. Calcd for $C_{20}H_{24}NORuPF_6$: C, 44.45; H, 4.48; N, 2.59. Found: C, 44.27, H, 4.49, N, 2.66.

Arene Complex 11c. White solid, 83%, ∼5:1 mixture of inseparable diastereomers. ^{1}H NMR (acetone-d_6, mixture of rotamers): δ 1.36 (dd, 0.5H, J_1 = 2.1 Hz, J_2 = 6.6 Hz), 1.44 (d, 2.5H, J = 7.2 Hz), 1.77−1.84 (m, 1H), 1.87 (dd, 3H, J_1 = 1.2 Hz, J_2 = 6.9 Hz), 2.83 (s, 0.5H), 2.85 (s, 2.5H), 2.99−3.04 (m, 1.6H), 3.12−3.13 (m, 0.4H), 3.52−3.59 (m, 1H), 5.48 (s, 4.18H), 5.62 (s, 0.82H), 5.93−5.95 (m, 1H), 6.18−6.23 (m, 2H), 6.46−6.48 (m, 1H), 6.49−6.66 (m, 1H), 6.80−6.87 (m, 1H). ^{13}C NMR (acetone-d_6): δ 18.2, 21.3, 33.5, 37.9, 60.8, 81.5, 82.3, 82.5, 83.4, 85.03, 85.05, 85.2, 85.4, 108.5, 108.6, 113.3, 122.9, 123.1, 142.6, 142.8, 166.9, 167.0. Anal. Calcd for $C_{20}H_{24}NORuPF_6$: C, 44.45; H, 4.48; N, 2.59. Found: C, 44.36; H, 4.41; N, 2.55.

Arene Complex 11d. White solid, 78%, mp 177−179 °C. ^{1}H NMR (acetone-d_6, mixture of rotamers): δ 1.86 (dd, 3H, J_1 = 1.6 Hz, J_2 = 6.9 Hz), 2.86 (br s, 1.5H), 2.96 (br s, 2.5H), 4.75−4.82 (m, 2H), 5.57 (s, 5H), 5.94−5.96 (m, 1H), 6.05−6.11 (m, 1H), 6.22−6.33 (m, 1H), 6.45−6.56 (m, 2H), 6.80−6.87 (m, 1H). ^{13}C NMR (acetone-d_6): 18.0, 56.8, 72.8, 76.7, 81.1, 81.6, 82.5, 83.3, 84.7, 86.9, 122.5, 143.2, 158.8, 167.1. Anal. Calcd for $C_{18}H_{20}NO_2RuPF_6$: C, 40.92; H, 3.82; N, 2.65. Found: C, 41.09; H, 3.75; N, 2.28.

Arene Complex 11e. White solid, 88%, mp 203−206 °C. ^{1}H NMR (acetone-d_6, mixture of rotamers): δ 1.88 (dd, 3H, J_1 = 1.6 Hz, J_2 = 6.9 Hz), 1.98−2.00 (m, 2H), 2.11−2.12 (m, 1H), 2.68−2.77 (m, 1H), 2.95−3.00 (m, 1H), 3.03 (s, 3H), 5.53 (s, 5H), 5.55−5.63 (m, 2H), 6.17−6.26 (m, 3H), 6.29−6.33 (m, 1H), 6.48 (d, 1H, J = 14.7 Hz), 6.79−6.89 (m, 1H). ^{13}C NMR (acetone-d_6): δ 17.4, 21.7, 25.9, 31.8, 53.7, 81.3, 81.5, 81.6, 85.0, 85.4, 102.8, 104.7, 122.2, 142.1, 166.3. Anal. Calcd for $C_{20}H_{24}NORuPF_6$: C, 44.45; H, 4.48; N, 2.59. Found: C, 44.88; H, 4.52; N, 2.76.

Arene Complex 11f. White solid, 99%, mp 218−220 °C. ^{1}H NMR (acetone-d_6, mixture of rotamers): δ 1.86−1.98 (m, 5H), 2.06−2.10 (m, 2H), 2.64−2.70 (m, 1H), 3.00 (s, 2.5H), 3.22 (s, 0.5H), 3.79−3.84 (m, 4H), 5.51 (s, 5H), 5.57 (s, 1H), 6.22−6.31 (m, 3H), 6.47 (d, 1H, J = 14.1 Hz), 6.79−6.90 (m, 1H). ^{13}C NMR (acetone-d_6): δ 17.4, 21.8, 25.9, 26.4, 32.0, 54.0, 57.0, 72.8, 73.2, 80.4, 80.5, 81.0, 81.1, 81.3, 83.4, 86.3, 101.4, 101.7, 122.3, 133.9, 142.0, 166.3. Anal. Calcd for $C_{21}H_{26}NO_2RuPF_6$: C, 44.21; H, 4.59; N, 2.46. Found: C, 43.95; H, 4.53; N, 2.35.

Arene Complex 11g. White solid, 90%, mp 170−172 °C. ^{1}H NMR (acetone-d_6, mixture of rotamers): δ 1.90 (dd, 3H, J_1 = 1.7 Hz, J_2 = 6.9 Hz), 1.93−1.97 (m, 3H), 2.06−2.11 (m, 1H), 2.69−2.79 (m, 2H), 2.90 (s, 3H), 3.84 (s, 3H), 3.86−3.88 (m, 1H), 5.53 (s, 5H), 5.57 (s, 1H), 6.13 (d, 1H, J = 6.4 Hz), 6.31 (d, 1H, J = 6.4 Hz), 6.49 (d, 1H, J = 15.0 Hz), 6.85−6.91 (m, 1H). ^{13}C NMR (acetone-d_6): δ 17.4, 21.8, 26.0, 31.8, 53.4, 57.0, 73.4, 73.9, 80.5, 81.0, 81.2, 82.4, 99.8, 103.1, 133.9, 142.0, 166.2. Anal. Calcd for $C_{21}H_{26}NO_2RuPF_6$: C, 44.21; H, 4.59; N, 2.46. Found: C, 43.76; H, 4.50; N, 2.41.

General Procedure for Preparation of (η^5-Cyclohexadienyl) ruthenium Complexes. The procedure used for the synthesis of **10a** is representative. A solution of **9a** (200 mg, 0.4 mmol), Bu_3P (80 mg, 0.4 mmol), and NaH (60%, 32 mg, 0.8 mmol) in 1,2-dimethoxyethane (DME, 10 mL) was stirred at rt for 12 h. The solvent was evaporated, and the residue was partitioned between CH_2Cl_2 and brine. The organic phase was separated, dried over anhydrous Na_2SO_4, filtered, and concentrated. The residue was purified by flash column chromatography (SiO_2, 1:1 hexanes/EtOAc) to afford **10a** (126 mg, 89%) as a yellow solid. Mp: 181−183 °C. ^{1}H NMR ($CDCl_3$): δ 2.15 (t, 2H, J = 6.4 Hz), 2.63 (d, 2H, J = 6.4 Hz), 2.93 (s, 3H), 3.40 (t, 2H, J = 6.4 Hz), 4.51 (t, 2H, J = 5.6 Hz), 4.72 (s, 5H), 4.95 (d, 1H, J = 2.2 Hz), 5.70 (t, 1H, J = 4.8 Hz), 5.82 (d, 1H, J = 2.2 Hz). ^{13}C NMR ($CDCl_3$): δ 34.6, 35.0, 36.8, 43.8, 45.80, 75.6, 76.8, 80.4, 119.5, 148.2, 164.1. IR (neat): ν (cm^{-1}) 1651. HRMS (EI): calcd for $C_{17}H_{19}NORu$ 354.0437 $[M]^+$, found 354.0432.

Cyclohexadienyl Complex 10b. Yellow solid, 48%, mp 222−224 °C. ^{1}H NMR ($CDCl_3$): δ 1.87 (d, 3H, J = 7.1 Hz), 2.21 (d, 1H, J = 7.5 Hz), 2.94 (s, 3H), 2.95 (d, 1H, J = 7.5 Hz), 3.34 (d, 1H, J = 13.0 Hz), 3.80 (d, 1H, J = 7.2 Hz), 3.90−3.96 (m, 1H), 4.39 (t, 1H, J = 5.5 Hz), 4.52 (t, 1H, J = 5.5 Hz), 4.84 (s, 5H), 5.60 (q, 1H, J = 7.1 Hz), 5.62 (t, 1H, J = 4.8 Hz), 7.01−7.04 (m, 2H), 7.22−7.26 (m, 3H). ^{13}C NMR ($CDCl_3$): δ 15.3, 32.3, 34.2, 36.8, 49.9, 50.6, 52.7, 65.8, 75.7, 80.6, 127.0, 128.0, 129.2, 134.1, 138.1, 142.4, 165.4. IR (neat): ν (cm^{-1}) 1661. HRMS (EI): calcd for $C_{24}H_{25}NORu$ 444.0907 $[M]^+$, found 444.0901.

Cyclohexadienyl Complex 10c. Yellow solid, 75%, mp 142−144 °C. ^{1}H NMR ($CDCl_3$): δ 0.88−1.77 (m, 10H), 1.76 (d, 3H, J = 5.0 Hz), 2.03 (d, 1H, J = 14.0 Hz), 2.93 (s, 3H), 3.25 (d, 1H, J = 14.0 Hz), 3.29 (s, 3H), 3.46 (br s, 2H), 4.45 (d, 1H, J = 4.5 Hz), 4.73 (s, 5H), 5.64 (d, 1H, J = 4.5 Hz) 5.70 (q, 1H, J = 5.0 Hz). ^{13}C NMR ($CDCl_3$): δ 14.2, 22.1, 22.6, 23.6, 26.6, 28.3, 37.2, 38.9, 40.4, 40.8, 53.25, 53.31, 54.7, 66.1, 71.9, 75.9, 127.5, 128.4, 147.3, 172.6. IR (neat): ν (cm^{-1}) 1655. HRMS (EI): calcd for $C_{24}H_{30}NO_2Ru$ 466.1320 $[M - H]^+$, found 466.1328.

Cyclohexadienyl Complex 10d. Yellow solid, 50%, mp 156−158 °C. ^{1}H NMR ($CDCl_3$): δ 1.58−1.62 (m, 4H), 1.87 (d, 3H, J = 7.1 Hz), 1.89−1.96 (m, 3H), 2.85 (d, 1H, J = 6.4 Hz), 2.88 (s, 3H), 3.09 (d, 1H, J = 13.1 Hz), 3.38 (d, 1H, J = 13.2 Hz), 4.45 (t, 1H, J = 5.6 Hz), 4.58 (d, 1H, J = 4.7 Hz), 4.81 (s, 5H), 5.43 (q, 1H, J = 7.1 Hz), 5.66 (t, 1H, J = 4.8 Hz). ^{13}C NMR ($CDCl_3$): δ 15.5, 26.0, 29.2, 31.1, 34.1, 38.0, 43.1, 49.5, 52.4, 75.7, 75.5, 76.0, 78.1, 78.5, 134.3, 135.6. IR (neat): ν (cm^{-1}) 1646. HRMS (EI): calcd for $C_{21}H_{25}NORu$ 409.0978 $[M]^+$, found 409.0980.

Cyclohexadienyl Complex 12a. Yellow solid, 59%, mp 167−169 °C. ^{1}H NMR ($CDCl_3$): δ 1.53−1.74 (m, 1H), 1.80−1.89 (m, 2H), 2.02 (d, 3H, J = 7.2 Hz), 2.27−2.33 (m, 1H), 2.83 (d, 1H, J = 6.0 Hz), 2.86 (s, 3H), 3.80 (d, 1H, J = 7.5 Hz), 4.35 (t, 1H, J = 2.7 Hz), 4.58 (d, 1H, J = 4.5 Hz), 4.71 (s, 5H), 5.61 (t, 1H, J = 4.7 Hz), 5.70 (q, 1H, J = 7.4 Hz). ^{13}C NMR ($CDCl_3$): δ 12.7, 27.9, 30.3, 31.0, 33.7, 52.7, 59.2, 70.8, 71.6, 73.5, 76.0, 133.6, 140.9, 167.7. IR (neat): ν (cm^{-1}) 1679. Anal. Calcd for $C_{19}H_{21}NORu$: C, 59.98; H, 5.56; N, 3.68. Found: C, 59.59; H, 5.43; N, 3.89.

Cyclohexadienyl Complex 12b. Obtained as a separable mixture of alkene isomers. **α,β-isomer:** Yellow solid, 27%, mp 162−164 °C. ^{1}H NMR ($CDCl_3$): δ 1.51−1.60 (m, 2H), 1.69 (s, 3H), 2.02 (d, 2H, J = 7.2 Hz), 2.14 (s, 3H), 2.85−2.90 (m, 1H), 2.91 (s, 3H), 4.23 (dd, 1H, J_1 = 3.3 Hz, J_2 = 8.9 Hz), 4.35 (t, 1H, J = 5.4 Hz), 4.71 (s, 5H), 4.78 (d, 1H, J = 4.5 Hz), 5.66 (t, 1H, J = 4.7 Hz). ^{13}C NMR ($CDCl_3$): δ 13.3, 22.6, 25.1, 29.0, 30.0, 31.6, 34.3, 39.7, 55.6, 60.9, 76.2, 75.4, 75.7, 75.5, 76.3, 133.0, 134.2, 168.9. IR (neat): ν (cm^{-1}) 1679. Anal. Calcd for $C_{20}H_{23}NORu$: C, 60.90; H, 5.88; N, 3.55. Found: C, 60.97; H, 5.89; N, 3.58. **β,γ-isomer:** Pale yellow solid, 27%, mp 174−176 °C. ^{1}H NMR ($CDCl_3$): δ 1.59 (s, 3H), 1.61−1.71 (m, 2H), 1.82−2.05 (m, 2H), 2.15 (s, 1H), 2.17−2.65 (m, 1H), 2.66 (d, 1H, J = 6.0 Hz), 2.83 (s, 3H), 3.88 (d, 1H, J = 6.5 Hz), 4.36 (t, 1H, J = 5.7 Hz), 4.61 (s, 1H), 4.67 (s, 5H), 4.93 (s, 1H), 5.46 (t, 1H, J = 4.8 Hz). ^{13}C NMR ($CDCl_3$): δ 19.6, 21.0, 22.5, 25.8, 28.3, 30.8, 31.5, 53.0, 55.6, 65.5, 71.5, 71.8, 75.4, 76.4, 77.6, 116.9, 118.3, 141.2, 173.9. IR (neat): ν (cm^{-1}) 1667. Anal. Calcd for $C_{20}H_{23}NORu$: C, 60.90; H, 5.88; N, 3.55. Found: C, 60.89; H, 5.91; N, 3.65.

Cyclohexadienyl Complex 12c. Pale yellow oil, 53%, ∼2:1 mixture of inseparable diasteromers. ^{1}H NMR ($CDCl_3$): δ 0.76 (d, 1.5H, J = 5.7 Hz), 0.89 (d, 3H, J = 7.5 Hz), 1.52 (d, 1H, J = 13.2 Hz), 1.82−1.88 (m, 2H), 2.02 (d, 4.5H, J = 7.5 Hz), 2.17−2.22 (m, 1H), 2.46−2.53 (m, 1H), 2.82−2.85 (m, 2.5H), 2.89 (s, 3H), 3.67 (d, 0.5H, J = 6.9 Hz), 3.84 (d, 1H, J = 6.6 Hz), 4.28−4.32 (m, 1.5H), 4.42 (d, 0.5H, J = 4.5 Hz), 4.62 (d, 1H, J = 4.5 Hz), 4.61 (s, 5H), 4.63 (s, 2.5H), 5.62−5.75 (m, 3H). ^{13}C NMR ($CDCl_3$): δ 13.3, 14.8, 24.0, 28.03, 28.05, 29.9, 34.3, 34.8, 35.3, 37.9, 39.8, 42.3, 53.3, 54.0, 63.6, 67.8, 69.9, 71.3, 71.9, 72.3, 72.9, 73.7, 133.8, 133.9, 142.1, 143.5, 167.8, 168.4. IR (neat): ν (cm^{-1}) 1647, 1673. HRMS (EI): calcd for $C_{20}H_{23}NORu$ 395.0827 $[M]^+$, found 395.0823.

Cyclohexadienyl Complex 12d. Yellow solid, 59%, mp 177−179 °C. ^{1}H NMR ($CDCl_3$): δ 2.01 (d, 3H, J = 7.2 Hz), 2.87 (s, 3H), 3.15 (d, 1H, J = 6.0 Hz), 3.82−3.87 (m, 1H), 3.96−4.03 (m, 2H), 4.22 (t, 1H, J = 2.9 Hz), 4.80 (s, 5H), 4.81 (d, 1H, J = 1.8 Hz), 5.42 (t, 1H, J = 4.7 Hz), 5.75 (d, 1H, J = 7.5 Hz). ^{13}C NMR ($CDCl_3$): δ 13.1, 28.6, 36.3, 55.6, 62.6, 69.3, 71.8, 72.5, 73.9, 76.0, 97.3, 135.9, 139.9, 167.6. IR (neat): ν (cm^{-1}) 1676. HRMS (EI): calcd for $C_{18}H_{19}NO_2Ru$ 381.0458 $[M]^+$, found 381.0443.

Cyclohexadienyl Complex 12e. Yellow solid, 58%, mp 152−154 °C. ^{1}H NMR ($CDCl_3$): δ 1.57−1.75 (m, 5H), 1.96 (d, 3H, J = 7.2 Hz), 2.09−2.13 (m, 1H), 2.67 (d, 1H, J = 6.0 Hz), 2.87 (s, 3H), 3.29−3.38 (m, 1H), 4.12 (t, 1H, J = 5.3 Hz), 4.57 (d, 1H, J = 4.5 Hz), 4.77 (s, 5H), 5.35 (q, 1H, J = 7.4 Hz), 5.60 (t, 1H, J = 4.7 Hz). ^{13}C NMR ($CDCl_3$): δ 13.8, 14.7, 24.5, 28.7, 30.4, 31.9, 40.0, 47.8, 50.7, 68.4, 75.4, 78.9, 131.0, 138.3, 168.2. IR (neat): ν (cm^{-1}) 1676. Anal. Calcd for $C_{20}H_{23}NORu$: C, 60.90; H, 5.88; N, 3.55. Found: C, 61.37; H, 6.39; N, 3.24.

Cyclohexadienyl Complex 12f. Yellow solid, 62%, mp 148−150 °C. ^{1}H NMR ($CDCl_3$): δ 1.26−1.78 (m, 5H), 1.98 (d, 3H, J = 7.5 Hz), 2.06−2.15 (m, 1H), 2.92 (s, 3H), 3.02 (s, 1H), 3.23 (s, 3H), 3.39−3.45 (m, 1H), 4.56 (d, 1H, J = 5.1 Hz), 4.78 (s, 5H), 5.39 (q, 1H, J = 7.2 Hz), 5.72 (d, 1H, J = 4.8 Hz). ^{13}C NMR ($CDCl_3$): δ 13.1, 23.8, 28.0, 29.6, 30.1, 30.5, 46.8, 52.2, 55.1, 67.1, 67.7, 73.7, 75.7, 127.7, 130.7, 136.9, 167.5. IR (neat): ν (cm^{-1}) 1666. Anal. Calcd for $C_{21}H_{25}NO_2Ru$: C, 59.42; H, 5.94; N, 3.30. Found: C, 59.50; H, 5.99; N, 3.21.

Cyclohexadienyl Complex 12g. Yellow solid, 58%, mp 177−179 °C. ^{1}H NMR ($CDCl_3$): δ 1.22−1.72 (m, 6H), 1.97 (d, 3H, J = 7.2 Hz), 2.07−2.13 (m, 1H), 2.46 (d, 1H, J = 6.0 Hz), 2.88 (s, 3H), 3.27−3.38 (m, 1H), 3.63 (s, 3H), 4.32 (d, 1H, J = 6.0 Hz), 4.81 (s, 5H), 5.44 (q, 1H, J = 7.2 Hz). ^{13}C NMR ($CDCl_3$): δ 13.8, 24.4, 28.7, 30.3, 31.8, 34.6, 42.1, 58.1, 64.1, 67.8, 69.5, 77.3, 131.0, 132.2, 138.0, 168.2. IR (neat): ν (cm^{-1}) 1666. Anal. Calcd for $C_{21}H_{25}NO_2Ru$: C, 59.42; H, 5.94; N, 3.30. Found: C, 59.46; H, 6.06; N, 3.40.

3-Benzazepine 17. A solution of cyclohexadienyl complex **2**[9] (78 mg, 0.21 mmol) in ∼3 mL of THF was placed under a CO atmosphere (balloon). Copper(II) bromide (135 mg, 0.60 mmol) in ∼1 mL of H_2O was added slowly via syringe. The resulting dark reaction mixture was maintained at rt for 3 h. The solvent was removed *in vacuo*, and the residue was dissolved in CH_2Cl_2, washed with brine, dried over anhydrous $MgSO_4$, filtered, and concentrated to afford a yellow residue. Purification by flash column chromatography (SiO_2, EtOAc) gave 55 mg (88%) of $CpRu(CO)_2Br$[16] **20** (eluting first) along with 42 mg (98%) of benzazepine **17** as a white solid. Mp: 116−118 °C. ^{1}H NMR ($CDCl_3$): δ 2.05 (d, 3H, J = 7.0 Hz), 3.01−3.13 (m, 5H), 3.62−3.67 (m, 2H), 6.07 (q, 1H, J = 7.0 Hz). 7.22−7.38 (m, 4H). ^{13}C NMR ($CDCl_3$): δ 13.9, 32.1, 33.1, 47.8, 126.8, 127.8, 130.0, 130.1, 130.7, 135.0, 135.6, 139.9, 170.9. IR (neat): ν (cm^{-1}) 1658. Anal. Calcd for $C_{13}H_{15}NO$: C, 77.58; H, 7.51; N, 6.96. Found: C, 77.53; H, 7.53; N, 6.98.

Tetrahydroisoquinolinone 18. This material was prepared in 66% isolated yield from complex **12e** using the procedure given above. Mp: 130−132 °C. ^{1}H NMR ($CDCl_3$): δ 1.93−1.95 (m, 1H), 2.18 (d, 3H, 7.4 Hz), 2.33−2.34 (m, 2H), 2.41−2.46 (m, 2H), 2.99 (d, 1H, J = 3.8 Hz), 3.06 (s, 3H), 3.91 (m, 1H, 3.9 Hz), 5.74 (q, 1H, J = 7.3 Hz), 6.24 (dd, 1H, J_1 = 1.8 Hz, J_2 = 9.8 Hz), 6.83−6.88 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 13.4, 24.3, 27.9, 32.1, 47.1, 60.0, 125.3, 127.9, 129.7, 137.9, 148.8, 149.7, 168.7. IR (neat): ν (cm^{-1}) 1687. Satisfactory HRMS data could not be obtained as the compound was observed to decompose within several hours after isolation.

Tetrahydroisoquinoline 19. Isolated as an oil in 68% yield from **12f** using the procedure given above. ^{1}H NMR ($CDCl_3$): δ 1.68−1.73 (m, 1H), 2.11−2.12 (m, 2H), 2.26 (d, 3H, J = 7.1 Hz), 2.53−2.86 (m, 3H), 2.88 (s, 3H), 3.91 (s, 3H), 4.62 (dd, 1H, J_1 = 4.5 Hz, J_2 = 12.3 Hz), 6.80 (q, 1H, J = 7.4 Hz), 7.01 (d, 1H, J = 8.8 Hz), 7.80 (d, 1H, J = 8.8 Hz). ^{13}C NMR ($CDCl_3$): δ 14.0, 16.5, 28.4, 28.9, 36.7, 54.6, 56.2, 111.3, 123.3, 123.4, 125.1, 128.1, 139.9, 140.0, 160.0. IR (neat): ν (cm^{-1}) 1682. Satisfactory HRMS data could not be obtained as the compound was observed to decompose within several hours after isolation.

Tricyclic Spirolactam 21. Solid $CuCl_2$ (46 mg, 0.35 mmol) was added to a solution of **12g** (60 mg, 0.14 mmol) in ∼3 mL of CH_2Cl_2. The mixture was stirred at rt for 30 min. The dark-colored precipitate was removed by filtration, and the filtrate was concentrated.

(16) Haines, R. J.; du Preez, A. L. *J. Chem. Soc., Dalton Trans.* **1972**, 944.

Purification of the residue by flash column chromatography (SiO_2, EtOAc) afforded **21** (28 mg, 89%) as a white solid. Mp: 140−142 °C. ^{1}H NMR ($CDCl_3$): δ 1.60−1.73 (m, 4H), 2.19 (d, 3H, J = 7.4 Hz), 2.20−2.49 (m, 1H), 2.95 (s, 3H), 3.61−3.64 (m, 1H), 5.69 (q, 1H, J = 7.4 Hz), 6.15 (d, 1H, J = 9.8 Hz), 6.28 (s, 1H), 6.80 (d, 1H, J = 9.8 Hz). ^{13}C NMR ($CDCl_3$): δ 14.3, 18.5, 26.8, 28.9, 31.0, 50.3, 63.5, 126.4, 129.4, 131.0, 136.2, 151.8, 161.4, 167.7, 187.1. IR (neat): ν (cm^{-1}) 1655, 1685. Anal. Calcd for $C_{15}H_{17}NO_2$: C, 74.05; H, 7.04; N, 5.76. Found: C, 73.28; H, 7.00; N, 5.72.

Acknowledgment. We thank the U.S. National Science Foundation for financial support (CHE-0544572), and Dr. Venu R. Vangala for assistance with X-ray crystallography.

Supporting Information Available: X-ray crystallographic details for **12a** (cif). Copies of NMR spectra for compounds **10a**−**d**, **12a**, **12c**−**e**, **18**, **19**, and **21**. This material is available free of charge via the Internet at http://pubs.acs.org.