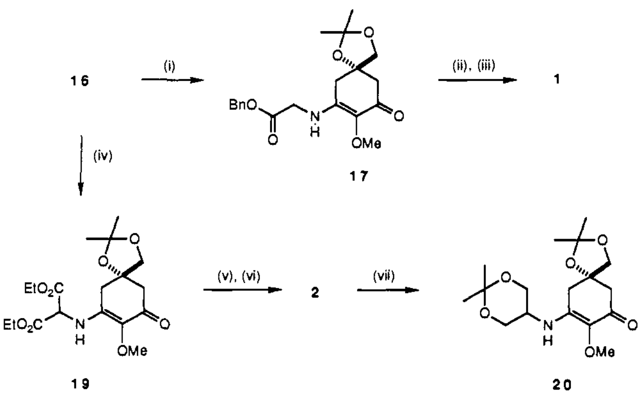
Scheme II[a]



[a] Reagents and conditions: (i) $PhCH_2O_2CCHO$ (25 equiv), THF, 25 °C, 7 h, then $NaBH_3CN$, MeOH, 25 °C, 57%; (ii) 50% aqueous TFA–$CHCl_3$ (3:10), 0 °C, 20 min; (iii) H_2, 10% Pd/C, 58% from **17**; (iv) EtO_2CCOCO_2Et (5 equiv), Et_2O, reflux, 2 h, then $NaBH_3CN$, MeOH, 25 °C, 1 h, 73%; (v) $NaBH_4$, MeOH–H_2O (5:1), 0 °C, 3 h; (vi) 50% aqueous TFA, 0 °C, 20 min, 59% from **19**; (vii) $(MeO)_2CMe_2$, pyridinium *p*-toluenesulfonate, acetone, 25 °C, 3 days, 44%.

to prepare iminomycosporins by condensation of **1** with various amines have been unsuccessful.

Acknowledgment. We are grateful to Dr. Noël Arpin, Université de Lyon, France, for a sample of natural mycosporin I and to Professor Shosuke Ito, Fujita-Gakuen Health University, Toyoake, Japan, for UV, IR, and ^1H NMR spectra of **18**. Financial support was provided by the National Science Foundation (CHE-8619029).

Supplementary Material Available: Spectroscopic data (IR, ^1H NMR, ^{13}C NMR, MS), optical rotations ($[\alpha]_D$), and analytical data for **1**, **2**, and **6–20** (4 pages). Ordering information is given on any current masthead page.

Regioselective and Diastereoselective Addition of Methyl Anion to Chiral (Pentadienyl)ruthenium Complexes[1]

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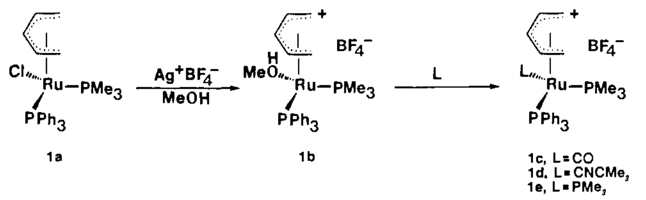
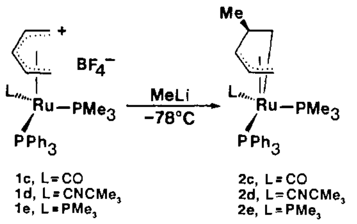
During the past two decades, there has been considerable interest in the reactions of acyclic pentadienyl ligands with nucleophiles.[2] Virtually all of these studies have involved complexes in which the pentadienyl ligand is bonded to an electron-poor $Fe(CO)_3^+$ moiety and have, with few exceptions, resulted in nucleophilic attack at the pentadienyl termini (C1/C5).

Scheme I



Scheme II



We are interested in promoting nucleophilic attack at the *internal* carbons (C2/C4) of pentadienyl ligands in order to produce (pentenediyl)metal complexes, a relatively unexplored compound class[3] with potential applications to organic synthesis. Following the thesis of Davies, Green, and Mingos,[4] who assert that electron-rich ML_n moieties will promote nucleophilic attack at the even-numbered carbon atoms of odd open polyenyl ligands (i.e., C2/C4 in pentadienyl ligands), we have synthesized a family of electron-rich (pentadienyl)ruthenium complexes. We report herein the regio- and diastereoselective nucleophilic addition of methyl anion to the C2 position of the pentadienyl ligands in these complexes.[5]

As shown in Scheme I, treatment of (η^5-pentadienyl)Ru(PMe_3)(PPh_3)(Cl) (**1a**)[1a] with $Ag^+BF_4^-$ in methanol produces $[(\eta^5\text{-pentadienyl})Ru(PMe_3)(PPh_3)(MeOH)]^+BF_4^-$ (**1b**). The weakly coordinated methanol ligand in **1b** is readily displaced by a series of 2e ligands, including carbon monoxide, *tert*-butyl isocyanide, and trimethylphosphine, producing a family of complexes of formula $[(\eta^5\text{-pentadienyl})Ru(PMe_3)(PPh_3)(L)]^+BF_4^-$ (L = CO, **1c**; L = $CNCMe_3$, **1d**; L = PMe_3, **1e**).[6] Each of these complexes exists in solution as a *single detectable rotamer*,[7] in which the smaller phosphine ligand, PMe_3, resides under the open pentadienyl "mouth", while PPh_3 and L reside under the pentadienyl "edges". Furthermore, the *barrier* to pentadienyl ligand rotation is quite high. For example, line-shape simulations of the variable-temperature $^{31}P\{^1H\}$ NMR spectra of **1e** yield a $\Delta G^{\ddagger}$ for rotation of >18 kcal/mol. Finally, each of the complexes (**1c–e**) is *chiral* with a stereogenic center at ruthenium.[8]

Treatment of **1c–e** with methyllithium at −78 °C leads cleanly to the production of the (2-methyl-1,3,4,5-η-pentenediyl)Ru(PMe_3)(PPh_3)(L) complexes (**2c–e**)[9] (see Scheme II). In each

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[1] Pentadienyl–Metal–Phosphine Chemistry. 19. For recent papers in this series, see: (a) Bleeke, J. R.; Rauscher, D. J. *Organometallics* **1988**, *7*, 2328. (b) Bleeke, J. R.; Earl, P. L. *Ibid.*, in press.

[2] (a) Maglio, G.; Musco, A.; Palumbo, R. *J. Organomet. Chem.* **1971**, *32*, 127. (b) Maglio, G.; Palumbo, R. *Ibid.* **1974**, *76*, 367. (c) Bonner, T. G.; Holder, K. A.; Powell, P. *Ibid.* **1974**, *77*, C37. (d) Birch, A. J.; Pearson, A. J. *J. Chem. Soc., Perkin Trans. 1* **1976**, 954. (e) Whitesides, T. H.; Neilan, J. P. *J. Am. Chem. Soc.* **1976**, *98*, 63. (f) Bayoud, R. S.; Biehl, E. R.; Reeves, P. C. *J. Organomet. Chem.* **1978**, *150*, 75. (g) Bayoud, R. S.; Biehl, E. R.; Reeves, P. C. *Ibid.* **1979**, *174*, 297. (h) Powell, P. *Ibid.* **1979**, *165*, C43. (i) Pearson, A. J.; Roy, T. *Tetrahedron* **1985**, *41*, 5765. (j) Gree, R.; Laabassi, M.; Mosset, P.; Carrie, R. *Tetrahedron Lett.* **1985**, *26*, 2317. (k) Uemura, M.; Minami, T.; Yamashita, Y.; Hiyoshi, K.; Hayashi, Y. *Ibid.* **1987**, *28*, 641. (l) Semmelhack, M. F.; Park, J. *J. Am. Chem. Soc.* **1987**, *109*, 935. (m) Bleeke, J. R.; Hays, M. K. *Organometallics* **1987**, *6*, 1367. (n) Donaldson, W. A.; Ramaswamy, M. *Tetrahedron Lett.* **1988**, *29*, 1343. (o) Donaldson, W. A.; Ramaswamy, M. *Ibid.* **1989**, *30*, 1339. (p) Donaldson, W. A.; Ramaswamy, M. *Ibid.* **1989**, *30*, 1343. (q) Pinsard, P.; Lellouche, J.-P.; Beaucourt, J.-P.; Toupet, L.; Schio, L.; Gree, R. *J. Organomet. Chem.* **1989**, *371*, 219.

[3] (a) The first (pentenediyl)metal complexes were obtained by Aumann via metal-centered vinylcyclopropane ring opening: Aumann, R. *J. Organomet. Chem.* **1973**, *47*, C29. Aumann, R. *J. Am. Chem. Soc.* **1974**, *96*, 2631. (b) See ref 2e,m,p,q for other examples of (pentenediyl)metal complexes.

[4] (a) Davies, S. G.; Green, M. L. H.; Mingos, D. M. P. *Tetrahedron* **1978**, *34*, 3047. (b) These rules are particularly applicable to nucleophilic additions involving hard nucleophiles where charge control is anticipated.

[5] Pearson has previously reported nucleophilic attack at C2 of the dienyl moiety in $[(\eta^5\text{-cycloheptadienyl})Fe(CO)_2(L)]^+$ (L = PPh_3 and $P(OPh)_3$) complexes. See: Pearson, A. J.; Kole, S. L.; Ray, T. *J. Am. Chem. Soc.* **1984**, *106*, 6060.

[6] Representative Synthesis of **1c**. Carbon monoxide was bubbled rapidly through a 75-mL solution of compound **1b** (0.63 g, 1.0×10^{-3} mol) in methanol for 5 min. The solution volume was reduced in vacuo to approximately 10 mL and then cooled to −30 °C, to yield pale yellow crystals of **1c** overnight (0.42 g, 67%).

[7] If other rotamers are present, they must represent <1% of the mixture.

[8] The two PMe_3 ligands in **1e** are different by virtue of their orientation with respect to the pentadienyl ligand.

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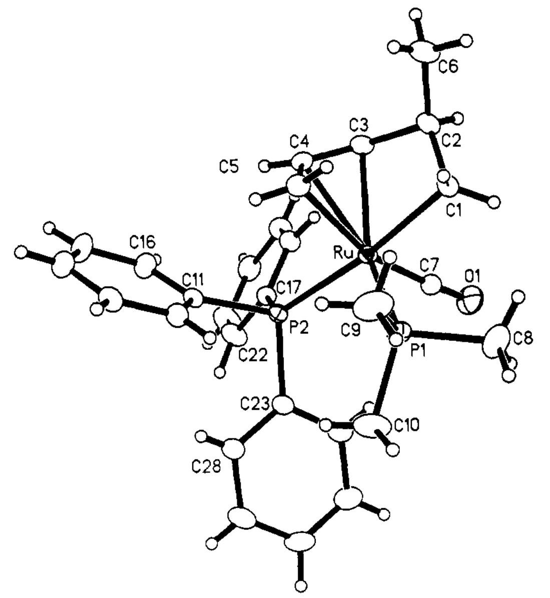

Figure 1. ORTEP drawing of (2-methyl-1,3,4,5-η-pentenediyl)Ru(PMe_3)(PPh_3)(CO) (**2c**). Selected bond distances and angles: Ru–C1, 2.167 (5) Å; Ru–C3, 2.290 (6) Å; Ru–C4, 2.223 (5) Å; Ru–C5, 2.237 (4) Å; C1–C2, 1.530 (10) Å; C2–C3, 1.520 (8) Å; C2–C6, 1.522 (8) Å; C3–C4, 1.383 (7) Å; C4–C5, 1.410 (9) Å; Ru–C1–C2, 97.5 (4)°; C1–C2–C6, 115.5 (6)°; C1–C2–C3, 103.8 (4)°; C3–C2–C6, 113.9 (5)°; C2–C3–C4, 123.8 (5)°; C3–C4–C5, 123.7 (5)°; C4–C5–Ru, 71.0 (2)°; C1–Ru–C5, 81.0 (2)°.

case, attack occurs with ≥95% diastereoselectivity on the "L-side" of the pentadienyl ligand, i.e., at the internal pentadienyl carbon which resides above ligand L and opposite the bulky PPh_3 ligand. It is interesting to note that even when L is electron-withdrawing (e.g., CO or $CNCMe_3$) and the pentadienyl carbons trans to it (C4 and C5) are therefore relatively electron-poor,[10] "L-side" attack (at C2) is still observed. Hence in this system, the site of nucleophilic attack is determined by steric factors, not by small electronic differences between the two sides of the pentadienyl ligand.

The solid-state structure of **2c**, derived from a single-crystal X-ray diffraction study, is shown in Figure 1.[11] As expected, attack occurs exo to the $[Ru(PMe_3)(PPh_3)(CO)]^+$ fragment, displacing the attacked carbon, C2, 0.73 Å out of the C1/C3/C4/C5 plane; C2 resides 2.81 Å from the ruthenium atom. The dihedral angle between plane C1/C3/C4/C5 and plane C1/C2/C3 is 50.8 (4)°. Within the 1,3,4,5-η-pentenediyl ligand, carbon–carbon bonds C1–C2 and C2–C3 exhibit normal single-bond lengths, while C3–C4 and C4–C5 exhibit typical allylic bond distances (see caption to Figure 1).

The site of nucleophilic attack in compounds **2c** and **2d** can be unambiguously determined from their NMR spectra. Particularly diagnostic is the strong P-C coupling exhibited by pentenediyl carbon C1. This strong coupling (50 Hz in **2c** and 55 Hz in **2d**) indicates that C1 residues trans to a phosphine ligand, which, in turn, requires that nucleophilic attack must be "L-side". Interpretation of **2e**'s NMR spectra is less straightforward because, in this case, C1 resides trans to a phosphine ligand regardless of the site of attack. However, a preliminary X-ray diffraction study of **2e** has confirmed "L-side" attack.[12]

In summary, we have demonstrated that electron-rich (pentadienyl)ruthenium cations undergo regioselective nucleophilic attack at internal carbon C2 of the pentadienyl ligand. The $[Ru(PMe_3)(PPh_3)(L)]^+$ fragment serves as an effective chiral auxiliary, directing diastereoselective addition to the less hindered side of the pentadienyl ligand. Work currently in progress is directed toward (a) obtaining optically pure ruthenium cations and (b) effecting further transformations of the pentenediyl ligand. Results of these studies will be reported in the future.

Acknowledgment. Support from the National Science Foundation (Grant CHE-8520680) is gratefully acknowledged. Washington University's X-Ray Crystallography Facility was funded by the National Science Foundation's Chemical Instrumentation Program (Grant CHE-8811456).

Supplementary Material Available: Detailed descriptions of the syntheses and spectra of compounds **1b–e** and **2c–e** and tables of structure determination summaries, final atomic coordinates, thermal parameters, bond lengths, bond angles, and significant least-squares planes for **2c** (17 pages); listing of observed and calculated structure factor amplitudes for **2c** (22 pages). Ordering information is given on any current masthead page.

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(9) Representative Synthesis of **2c**. Methyllithium (0.50 mL, 1.4 M in diethyl ether, 7.0×10^{-4} mol) was added to a stirred slurry of **1c** (0.39 g, 6.2×10^{-4} mol) in 50 mL of cold (−78 °C) tetrahydrofuran. The mixture was warmed to room temperature, stirred for 1 h, and filtered. The tetrahydrofuran solvent was reduced in vacuo to yield an orange oil. The oil was dissolved in 50 mL of diethyl ether, filtered, reduced in vacuo to approximately 10 mL, and then cooled to −30 °C, to precipitate **2c** as yellow-orange crystals (0.16 g, 47%).

(10) In the ^{13}C NMR of $[(\eta^5\text{-pentadienyl})Ru(PMe_3)(PPh_3)(CO)]^+BF_4^-$ (**1c**), for example, C2 and C4 resonate at δ 99.1 and δ 112.7, respectively, indicating greater positive charge on C4.

(11) Crystal data for **2c**: monoclinic, space group $P2_1/n$, $a = 15.980$ (4) Å, $b = 10.945$ (3) Å, $c = 16.541$ (5) Å, $\beta = 113.62$ (2)°, $V = 2650.7$ (13) Å^3, $Z = 4$, $d_{calcd} = 1.377$ g/cm^3, $\mu = 7.15$ cm^{-1}; Nicolet P3 diffractometer, Mo Kα radiation, 22 °C; 6090 unique reflections with $4° < 2\theta < 55°$ collected, 3945 reflections with $I > 3\sigma(I)$ used in refinement; empirical absorption correction (ψ scans); $R = 0.0352$, $R_w = 0.0381$, GOF = 1.73.

(12) Bleeke, J. R.; Rauscher, D. J., unpublished results.

Nucleophile-Assisted Cleavage of Silane Cation Radicals

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Nucleophilic addition to π organic cation radicals is commonly observed in many one-electron oxidation reactions.[1] In contrast, the nucleophilic cleavage of cation radical σ bonds is much less common.[2] This latter process is of considerable mechanistic

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(1) For reviews see: (a) Mattes, S. L.; Farid, S. In *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker: New York, 1983; Vol. 6, p 233. (b) Julliard, M.; Chanon, M. *Chem. Rev.* **1983**, *83*, 425. (c) Kavarnos, G. J.; Turro, N. J. *Chem. Rev.* **1986**, *86*, 401. (d) Fox, M. A. In *Advances in Photochemistry*; Volman, D. H., Gollnick, K., Hammond, G. S., Eds.; Wiley: New York, 1986; Vol. 13, p 237. (e) Lewis, F. D. In *Photoinduced Electron Transfer Part C. Photoinduced Electron Transfer Reactions: Organic Substrates*; Fox, M. A., Chanon, M., Eds.; Elsevier: Amsterdam, 1988; p 1. (f) Mattay, J. *Synthesis* **1989**, 233. (g) Hammerich, O.; Parker, V. D. *Adv. Phys. Org. Chem.* **1984**, *20*, 55.

(2) The photooxidative ring-opening reactions of several strained-ring compounds may involve the nucleophilic cleavage of one-electron σ bonds.[2a–g] Also, the deprotonation of cation radicals may be viewed as the nucleophilic cleavage of a σ bond. (a) Rao, V. R.; Hixson, S. S. *J. Am. Chem. Soc.* **1979**, *101*, 6458. (b) Mizuno, K.; Ogawa, J.; Kagano, H.; Otsuji, Y. *Chem. Lett.* **1981**, 437. (c) Mizuno, K.; Ogawa, J.; Otsuji, Y. *Chem. Lett.* **1981**, 741. (d) Gassman, P. G.; Olson, K. D.; Walter, L.; Yamaguchi, R. *J. Am. Chem. Soc.* **1981**, *103*, 4977. (e) Gassman, P. G.; Olson, K. D. *J. Am. Chem. Soc.* **1982**, *104*, 3740. (f) Mazzocchi, P. H.; Somich, C.; Edwards, M.; Morgan, T.; Ammon, H. L. *J. Am. Chem. Soc.* **1986**, *108*, 6828. (g) Mazzocchi, P. H.; Somich, C. *Tetrahedron Lett.* **1988**, *29*, 513.

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