Synthesis and Atropo-diastereoselective Ring Cleavage of a [Cp*Ru]-Complexed Biaryl Lactone: Experimental and Computational Investigations†

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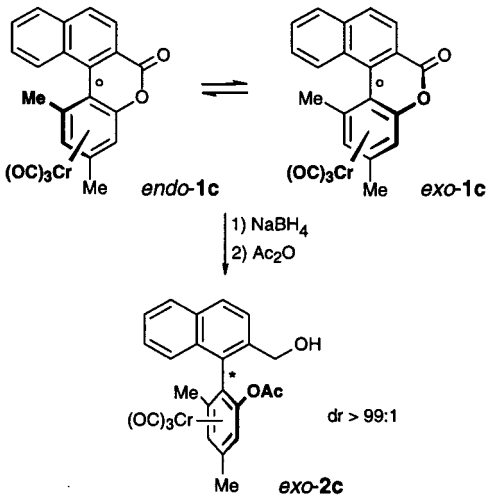
The planar-chiral biaryl lactone complex **5b** is cleaved highly atropo-diastereoselectively by simple O-nucleophiles. Toward H-nucleophiles, it shows a different reactivity behavior consistent with DF calculations using the Fukui function.

Introduction

Axially chiral biaryls are gaining increasing significance as chiral auxiliaries in asymmetric synthesis[1] and as bioactive natural products.[2] A highly efficient approach to enantiopure biaryls is provided by the synthesis and atroposelective cleavage of helically distorted, but configurationally unstable biaryl lactones.[3] An interesting variant of this synthetic methodology is the effective steric shielding of one of the two diastereotopic faces by an η^6-coordinated transition metal fragment and diastereoselective ring opening of the resulting planar-chiral benzonaphthopyranones (e.g., **1c**; cf. Scheme 1) to give configurationally stable biaryl compounds. Thus reduction of the rapidly interconverting chromium complexes *endo*-**1c**/*exo*-**1c** with $NaBH_4$ leads to *exo*-**2c** as the only atropo-diastereomer.[4,5]

The value of this remarkably stereocontrolled ring cleavage reaction is, however, diminished by the unsatisfactory yields obtained in the preparation of the chromium complexes of type **1c** (36%) and their low chemical stability. In this paper, we report on the more efficient preparation of related, but cationic (still racemic) ruthenium complexes **5**[6] and their highly diastereoselective ring cleavage.

Scheme 1. Stereoselective Reductive Ring Opening of the Chromium Complexes *endo*-1c ⇌ *exo*-1c To Give *exo*-2c as the Only Atropo-diastereomer



Results and Discussion

As a η^6-ruthenium fragment, the sterically demanding Cp*Ru group was chosen, for an optimum stereodifferentiation exerted by the additional element of planar chirality of the complexes **5**. Thus, reaction of the free lactones **3** with the corresponding acetonitrile complex **4**[7] (see Scheme 2) gave the corresponding ruthenium complexes **5** in distinctly better yields than for the related chromium complexes (see above). Other than in the chromium complex **1c** and independent of the size

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(1) Examples of biaryl reagents: (a) Shibasaki, M.; Sasai, H.; Arai, T. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1236. (b) Bringmann, G.; Breuning, M. *Tetrahedron: Asymmetry* **1998**, *9*, 667.

(2) (a) Asano, J.; Chiba, K.; Tada, M.; Yoshii, T. *Phytochemistry* **1996**, *42*, 713. (b) Bringmann, G.; François, G.; Aké Assi, L.; Schlauer, J. *Chimia* **1998**, *52*, 18.

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(4) Bringmann, G.; Göbel, L.; Peters, K.; Peters, E.-M.; von Schnering, H. G. *Inorg. Chim. Acta* **1994**, *222*, 255.

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(6) For other stereoselective reactions using chiral ruthenium or chromium complexes, see: (a) Pearson, A. J.; Bignan, G.; Zhang, P.; Chelliah, M. *J. Org. Chem.* **1996**, *61*, 3940. (b) Kündig, E. P.; Saudan, C. M.; Bernardinelli, G. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 1220. (c) Kündig, E. P.; Leresche, J. *Tetrahedron* **1993**, *49*, 5599. (d) Blystone, S. L. *Chem. Rev.* **1989**, *89*, 1663. (e) Schenk, W. A.; Kümmel, M.; Reuther, I.; Burzlaff, N.; Wuzik, A.; Schupp, O.; Bringmann, G. *Eur. J. Inorg. Chem.* **1979**, 1745.

(7) Fagan, P. J.; Ward, M. D.; Calabrese, J. C. *J. Am. Chem. Soc.* **1989**, *111*, 1698.

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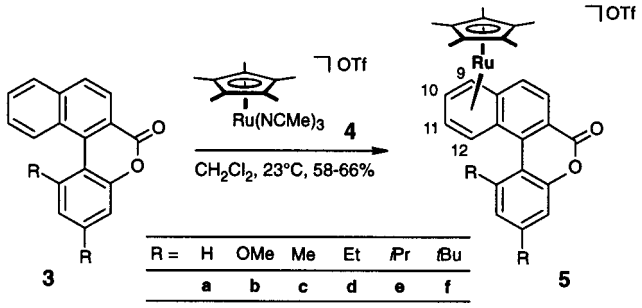
Scheme 2. Synthesis of the Ruthenium Sandwich Complexes 5

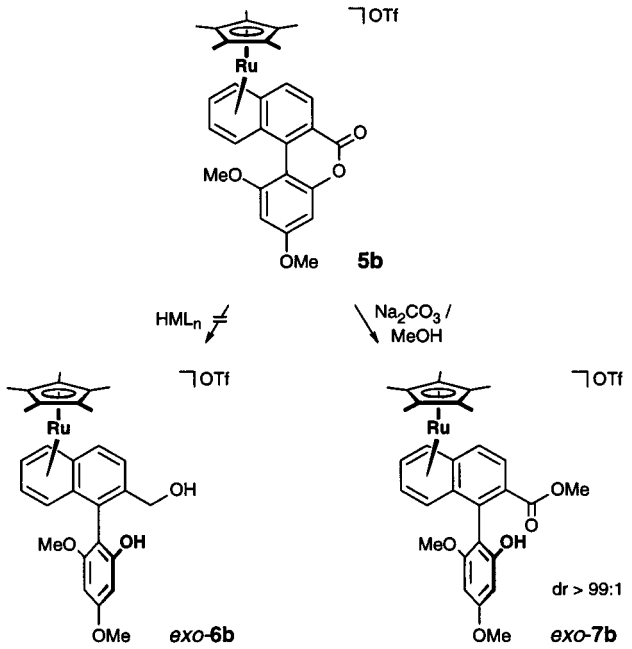


of R, the coordination of the Cp*Ru fragment occurs on the distal naphthalene ring, exclusively. This is evident from the ^{1}H NMR signals of the protons at C9 to C12, which, compared to the corresponding protons of the metal-free lactone precursor **3**,[8] are shifted to significantly higher field. For the chromium complexes of type **1**, a complexation to that distal ring had been found only in the case of the highly sterically hindered representatives (e.g., starting from **3f**), whereas in other cases, the chromium was found to be complexed to the phenol-derived "southern" ring as in **1c**.

First experiments on the atroposelective ring cleavage of the complexes **5** were exemplarily carried out with the dimethoxy-substituted derivative **5b**. This complex[9] showed a surprising differentiation in its behavior toward nucleophiles: The attack of $NaBH_4$ and other H-nucleophiles did not lead to the expected stereoselective lactone ring cleavage to give product **6b**, which would easily have been identified, after decomplexation, as the well-known[10] metal-free alcohol. In situ NMR investigations rather indicated an attack on the ruthenium activated distal ring, yielding an unstable product, which upon attempted isolation by chromatography on silica immediately decomposed back to **5b** and then to the uncomplexed benzonaphthopyranone **3b**. Such addition reactions are known for cationic arene complexes.[11] No attack on the Cp* fragment or on the metal was found in any case, in accordance with the Davies−Green−Mingos rules.[12] The reaction with simple O-nucleophiles such as MeOH/Na_2CO_3 by contrast, proceeded smoothly, resulting in the expected ring-opening product *exo*-**7b** as the only atropisomer[13] in good yields.

Density functional (DF) calculations are excellently suited to describe energetic and structural properties of transition metal activated biaryl lactones (such as **1**[14]) precisely. This is already evident from the good agreement of the calculated structure of **5b** with the experimental one, as determined by X-ray crystallography, the only major difference being the (not so important) orientation of the 3-methoxy group, which may be due to packing effects.

Scheme 3. Divergent Ring-Opening Behavior of the [Cp*Ru]-Complexed Biaryl Lactone 5b



This encouraged us to investigate whether the Fukui function within the DF theory is capable of describing the interesting reactivity differentiation detected for complex **5b**, although this is a relatively large molecule for ab initio studies. In the case of a nucleophilic attack, the Fukui function,[15] which is defined as the variation of the chemical potential of a system with respect to the external potential $f(r) = (\delta\mu/\delta V)_N$ (with the number of particles kept constant), can be approximated by $(\rho_{N+1} - \rho_N)_V$ (ρ, electron density, N, electron number), after transformation to $(\delta\rho(r)/\delta N)_V$. As a result, one obtains molecular areas of local softness.[15] The Fukui function has so far been used mainly for the calculation of small organic molecules.[16] For transition metal complexes, there is, to the best of our knowledge, as yet only one study in which the Fukui function has been used for the calculation of $XPtCl_3$ and $XPt(NH_3)_3$ model complexes.[17]

The results of the calculation of the Fukui function presented here are illustrated in Figure 2 as a contour plot.[18] In the upper part, green areas indicate large values of the Fukui function as reactive areas of high local softness; in the lower part, these areas are indicated by arrows.

(8) Bringmann, G.; Hartung, T.; Göbel, L.; Schupp, O.; Ewers, C. L. J.; Schöner, B.; Zagst, R.; Peters, K.; von Schnering, H. G.; Burschka, C. *Liebigs Ann. Chem.* **1992**, 225.

(9) For the investigations on *diastereoselective* ring cleavage reactions described here, it was sufficient to prepare the complex **5b** in a racemic form.

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(18) The use of the older Gaussian 92 program package, by contrast, showed only large values of the Fukui function in the region of the metal center and the Michael acceptor and phenylogous Michael acceptor positions.

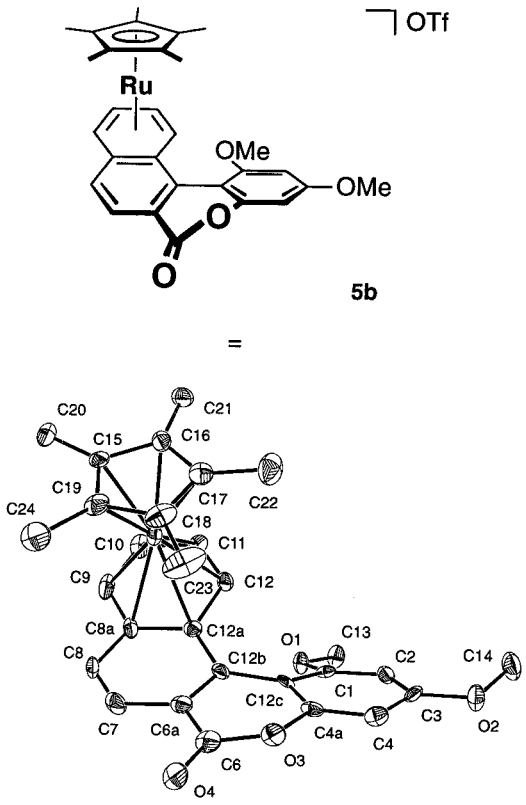

Figure 1. (top) Formula structure; (middle) crystal structure; (bottom) match plot of crystal structure (dark) and calculated structure (light). Selected bond lengths [Å] of the crystal structure: RuC(Cp*, average), 2.18(6); RuC(η^6-C, average), 2.23(6); C(1)O(1), 1.36(6); C(3)O(2), 1.36(7); C(6)O(3), 1.37(7); C(6)O(4), 1.22(7); C(1)O(2), 1.38(7); C(4a)O(3), 1.40(6); C(6)C(6a), 1.47(9); C(7)C(8), 1.34(9); C(8a)C(12a), 1.43(8); C(9)C(10), 1.40(9); C(12b)C(12c), 1.45(7). The hydrogen atoms and the triflate counterion are omitted for clarity.

These results make the above-described experimental findings understandable: Hydrides, which may be classified as soft according to the HSAB concept,[19] should react mainly at the metal center as the position of the highest Fukui value in the complex **5b**. For a coordinatively saturated 18-electron complex such a hydride addition would, however, be thermodynamically disfavored and, in the present case, also sterically inhibited

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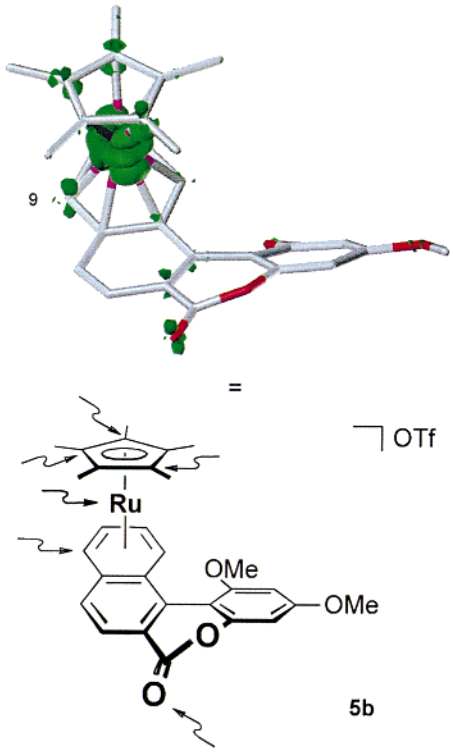

Figure 2. Calculated Fukui function $f^{Nu}(r)$: (top) shown as a contour plot (function value 0.007); green regions indicate areas of high local softness; (bottom) additional indication of these areas by arrows.

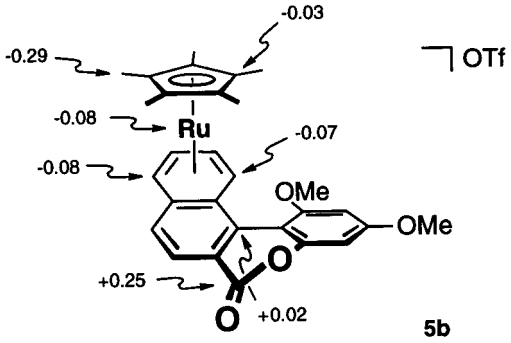

Figure 3. Selected charges of **5b** calculated by the method of Loewdin (for further values, see the table in the Supporting Information).

by the bulky Cp* and arene ligands. Hydrides may, in principle, also attack the Cp* ring system, which, however, was not observed, as mentioned before (see above). Since no reaction can take place at the carbonyl oxygen due to its high electronegativity, C9 in the benzonaphthopyranone system remains the position most likely to be attacked, which supports our discussions described before. Hard nucleophiles, by contrast, should react charge controlled at hard positions of the molecule, i.e., at places of high positive partial charges. According to the calculations, complex **5b** has the largest calculated positive charge on the lactone carbonyl C atom (cf. Figure 3). Thus the reaction of MeOH/Na_2CO_3—in contrast to that of the soft hydrides—led to the desired stereoselective ring opening. As a consequence, hard nucleophiles can be recommended for ring cleavage reactions on this type of molecules, resulting in good chemo- (and stereo-) selectivities.

As exemplarily shown here for **5b**, such ruthenium

complexes are most rewarding substrates for highly atroposelective cleavage reactions and, simultaneously, interesting objects of useful reactivity studies by means of DF calculations involving the Fukui function, leading to good agreements with the experimental results.

Experimental Section

The experiments were performed under an argon atmosphere with dried and distilled solvents using Schlenk techniques. [Cp*Ru(NCMe)$_3$]OTf (**4**)[7] and the lactones **3**[8] were synthesized according to literature procedures. NMR spectra were recorded with a Bruker AM 250 and a Bruker DMX 600 spectrometer at the Institut für Organische Chemie, Universität Würzburg. Elemental analyses were carried out by the microanalytical laboratory of the Institut für Anorganische Chemie, Universität Würzburg.

General Procedure for the Synthesis of the Ruthenium Complexes 5. To a solution of 1 equiv of lactone **3** in CH_2Cl_2 (20 mL/mmol) was added 1 equiv of [Cp*Ru(CH_3CN)$_3$]-OTf. After 24 h stirring at room temperature and separation of the precipitate, the reaction solution was diluted with 30 mL of Et_2O to give complex **5**. Recrystallization of the crude product from CH_2Cl_2/Et_2O (1:1) yielded the product in an analytically pure form.

Preparation of 5a. According to the general procedure described above, 500 mg (2.03 mmol) lactone **3a** and 1.03 g (2.03 mmol) of [Cp*Ru(NCMe)$_3$]OTf (**4**) gave 850 mg (66%) of **5a**. Mp: 232 °C. ^{1}H NMR (CD_2Cl_2): δ = 8.43 (m, 1 H), 8.30 (d, J = 8.6 Hz, 1 H), 8.12 (d, J = 8.6 Hz, 1 H), 7.33−7.55 (m, 3 H), 6.97 (m, 1 H), 6.79 (m, 1 H), 6.59−6.70 (m, 2 H), 1.50 (s, 15 H). ^{13}C NMR (CD_2Cl_2): δ = 161.0 (−COO−), 154.3 (CH), 136.5 (CH), 134.8 (CH), 131.5 (CH), 131.4 (CH), 128.9 (CH), 128.3 (CH), 127.8 (CH), 126.5 (CH), 123.3 (CH), 118.2 (CF), 112.7 (CH), 97.27 (CH), 95.33 ((*C*Me)$_5$), 93.72 (CH), 91.23 (CH), 87.12 (CH), 83.56 (CH), 9.52 ((C*Me*)$_5$). IR (KBr): ν (cm^{-1}) = 1700 (s), 1590 (m), 1040 (s). MS (DCI, 70 eV): m/z (%) = 482 (1) [M$^+$], 246 (100) [M$^+$ − Ru(CMe)$_5$], 218 (67) [M$^+$ − CO], 126 (14) [$C_{10}H_6^+$], 94 (19) [$C_6H_6O^+$]. Anal. Calcd for $C_{28}H_{25}F_3O_7$-SRu: C, 53.24; H, 3.99; S, 5.08. Found: C, 52.87; H, 3.71; S, 4.88.

Preparation of 5b. According to the general procedure, 301 mg (0.98 mmol) of lactone **3b** and 500 mg (0.98 mmol) of [Cp*Ru(NCMe)$_3$]OTf (**4**) gave 420 mg (62%) of **5b**. Mp: 218 °C. ^{1}H NMR ($CDCl_3$): δ = 8.16 (d, J = 8.9 Hz, 1 H), 7.54 (d, J = 8.9 Hz, 1 H), 6.66 (m, 1 H), 6.62 (m, 1 H), 6.60 (d, J = 2.2 Hz, 1 H), 6.55 (d, J = 2.2 Hz, 1 H), 6.49 (t, J = 5.8 Hz, 1 H), 6.32 (t, J = 5.8 Hz, 1 H), 3.94 (s, 3 H), 3.92 (s, 3 H), 1.52 (s, 15 H). ^{13}C NMR ($CDCl_3$): δ = 164.10 (−COO−), 160.3 (CH), 157.6 (C−OMe), 154.4 (C−OMe), 138.1 (CH), 127.4 (CH), 126.1 (CH), 120.7 (CH), 118.7 (CH), 101.2 (CH), 97.80 (CH), 96.73 (CH), 96.14 (CH), 94.93 ((*C*Me)$_5$), 94.43 (CH), 91.03 (CH), 88.06 (CH), 85.89 (CH), 85.16 (CH), 56.28 (OMe), 56.12 (OMe), 9.51 ((C*Me*)$_5$). IR (KBr): ν (cm^{-1}) = 1720 (s), 1600 (m), 1030 (m). MS (DCI, 70 eV): m/z (%) = 542 (11) [M$^+$], 306 (100) [M$^+$ − Ru(CMe)$_5$], 291 (11) [306 − Me], 262 (11) [306 − CO_2]. Anal. Calcd for $C_{30}H_{29}F_3O_7SRu$: C, 52.09; H, 4.23; S, 4.64. Found: C, 51.63; H, 4.20; S, 4.74.

Preparation of 5c. According to the general procedure, 280 mg (1.02 mmol) of lactone **3c** and 520 mg (1.02 mmol) of [Cp*Ru(NCMe)$_3$]OTf (**4**) gave 417 mg (62%) of **5c**. Mp: 216 °C. ^{1}H NMR ($CDCl_3$): δ = 8.27 (d, J = 9.0 Hz, 1 H), 7.71 (d, J = 9.0 Hz, 1 H), 7.19 (s, 1 H), 7.14 (s, 1 H), 6.81 (d, J = 6.0 Hz, 1 H), 6.54 (m, 3 H), 2.50 (s, 3 H), 2.40 (s, 3 H), 1.51 (s, 15 H). ^{13}C NMR ($CDCl_3$): δ = 170.9 (−COO−), 159.9 (CH), 151.9 (CH), 143.0 (CH), 138.1 (CH), 137.3 (CH), 136.2 (CH), 130.3 (CH), 128.6 (CH), 114.7 (CH), 97.41 (CH), 96.00 (CH), 95.13 ((*C*Me)$_5$), 91.44 (CH), 88.31 (CH), 85.43 (CH), 83.89 (CH), 23.72 (CH), 21.4 (CH), 9.04 ((C*Me*)$_5$). IR (KBr): ν (cm^{-1}) = 1720 (s), 1600 (m), 1025 (s). MS (DCI, 70 eV): m/z (%) = 510 (1) [M$^+$], 274 (100) [M$^+$ − $C_{19}H_{14}O_2^+$]. Anal. Calcd for $C_{30}H_{29}F_3O_5SRu$: C, 54.62; H, 4.43; S, 4.86 Found: C, 53.57; H, 4.54; S, 4.84.

Preparation of 5d. According to the general procedure, 500 mg (1.65 mmol) of lactone **3d** and 841 mg (1.65 mmol) of [Cp*Ru(NCMe)$_3$]OTf (**4**) gave 682 mg (60%) of **5d**. Mp: 247 °C. ^{1}H NMR (CD_2Cl_2): δ = 8.26 (d, J = 8.6 Hz, 1 H), 8.03 (d, J = 8.6 Hz, 1 H), 7.29−7.59 (m, 2 H), 6.93 (m, 1 H), 6.81 (m, 1 H), 6.49−6.62 (m, 2 H), 2.83−2.90 (m, 1 H), 2.77 (m, J = 7.5 Hz, 2 H), 2.52−2.61 (m, 1 H), 1.53 (s, 15 H), 1.29 (t, J = 7.4 Hz, 3 H), 0.91 (t, J = 7.4 Hz, 3 H). ^{13}C NMR (CD_2Cl_2): δ = 163.4 (−COO−), 156.8 (CH), 135.2 (CH), 132.5 (CH), 131.4 (CH), 130.4 (CH), 129.3 (CH), 127.3 (CH), 126.8 (CH), 125.9 (CH), 120.5 (CH), 116.8 (CF), 111.5 (CH), 96.55 (CH), 93.74 ((*C*Me)$_5$), 89.11 (CH), 85.82 (CH), 84.90 (CH), 84.23 (CH), 28.90 (CH), 28.27 (CH), 15.73 (CH), 14.62 (CH), 9.31 ((C*Me*)$_5$). IR (KBr): ν (cm^{-1}) = 1700 (s), 1590 (m), 1030 (s). MS (DCI, 70 eV): m/z (%) = 538 (1) [M$^+$], 302 (100) [M$^+$ − Ru(CMe)$_5$], 287 (49) [M$^+$ − Me], 259 (8) [287 − CO]. Anal. Calcd for $C_{32}H_{33}F_3O_5$-SRu: C, 55.87; H, 4.84; S, 4.66. Found: C, 55.39; H, 4.60; S, 4.39.

Preparation of 5e. Following the general procedure, 500 mg (1.51 mmol) of lactone **3e** and 770 mg (1.51 mmol) of [Cp*Ru(NCMe)$_3$]OTf (**4**) gave 628 mg (58%) of **5e**. Mp: 249 °C. ^{1}H NMR (CD_2Cl_2): δ = 8.30 (d, J = 8.7 Hz, 1 H), 8.08 (d, J = 8.7 Hz, 1 H), 7.33−7.61 (m, 2 H), 6.99 (m, 1 H), 6.87 (m, 1 H), 6.51−6.63 (m, 2 H), 3.11 (sept, J = 6.8 Hz, 1 H), 2.99 (m, J = 6.8 Hz, 1 H), 1.59 (d, J = 6.8 Hz, 3 H), 1.48 (s, 15 H), 1.38 (d, J = 6.6 Hz, 3 H), 1.36 (d, J = 6.8 Hz, 3 H), 0.71 (d, J = 6.6 Hz, 3 H). ^{13}C NMR (CD_2Cl_2): δ = 162.9 (−COO−), 155.3 (CH), 135.2 (CH), 132.8 (CH), 131.2 (CH), 129.6 (CH), 128.5 (CH), 125.8 (CH), 124.8 (CH), 121.8 (CH), 120.8 (CH), 115.8 (CF), 112.3 (CH), 99.34 (CH), 94.55 ((*C*Me)$_5$), 91.33 (CH), 88.56 (CH), 85.43 (CH), 83.93 (CH), 33.26 (CH), 30.93 (CH), 26.86 (CH), 22.91 (CH), 22.34 (CH), 19.52 (CH), 9.44 ((C*Me*)$_5$). IR (KBr): ν (cm^{-1}) = 1700 (s), 1580 (m), 1020 (s). MS (DCI, 70 eV): m/z (%) = 566 (1) [M$^+$], 330 (100) [M$^+$ − Ru(CMe)$_5$], 315 (36) [M$^+$ − Me], 273 (58) [M$^+$ − C_4H_9]. Anal. Calcd for $C_{34}H_{37}F_3O_5SRu$: C, 57.05; H, 5.21; S, 4.48. Found: C, 56.72; H, 5.02; S, 4.21.

Preparation of 5f. According to the general procedure, 120 mg (240 μmol) of lactone **3f** and 86.0 mg (240 μmol) of [Cp*Ru-(NCMe)$_3$]OTf (**4**) yielded 111 mg (63%) of **5d**. Mp: 256 °C. ^{1}H NMR ($CDCl_3$): δ = 8.19 (d, J = 9.0 Hz, 1 H), 7.71 (d, J = 2.0 Hz, 1 H), 7.68 (d, J = 9.0 Hz, 1 H), 7.27 (d, J = 2.0 Hz, 1 H), 6.82 (d, J = 6.0 Hz, 1 H), 6.64 (m, 1 H), 6.35−6.47 (m, 2 H), 1.43 (s, 15 H), 1.42 (s, 9 H), 1.15 (s, 9 H). ^{13}C NMR ($CDCl_3$): δ = 160.0 (−COO−), 156.0 (CH), 151.9 (CH), 139.8 (CH), 127.5 (CH), 126.4 (CH), 125.8 (CH), 125.2 (CH), 124.7 (CH), 123.2 (CH), 122.9 (CH), 122.7 (CH), 121.6 (CH), 120.1 (CH), 115.1 (CF), 111.0 (CH), 110.7 (CH), 98.23 (CH), 95.39 ((*C*Me)$_5$), 94.45 (CH), 93.69 (CH), 89.51 (CH), 87.84 (CH), 40.12 (CH), 35.62 (CH), 33.66 (CH), 31.25 (CH), 9.35 ((C*Me*)$_5$). IR (KBr): ν (cm^{-1}) = 1720 (s), 1580 (m), 1020 (s). MS (DCI, 70 eV): m/z (%) = 595 (1) [M$^+$], 358 (100) [M$^+$ − Ru(CMe)$_5$], 343 (77) [M$^+$ − Me], 329 (53) [343 − Me]. Anal. Calcd for $C_{36}H_{41}F_3O_5SRu$: C, 58.13; H, 5.56; S, 4.31. Found: C, 57.86; H, 5.29; S, 4.29.

Ring Cleavage of Complex 5b with MeOH/Na_2CO_3. To a solution of 100 mg (0.14 mmol) of **5b** in 15.0 mL of CH_2Cl_2 was added a suspension of 30.7 mg (0.28 mmol) of Na_2CO_3 in 11.7 mL of methanol. The solution was stirred for 3 h at room temperature, filtered, and diluted with 20 mL of Et_2O to give complex **7b**. Recrystallization from CH_2Cl_2/Et_2O (1:1) yielded 70.1 mg (67%) of **5** as a yellow to orange-colored solid. Mp: 168 °C. ^{1}H NMR ($CDCl_3$): δ = 8.62 (br s, 1 H), 7.93 (d, J = 9.0 Hz, 1 H), 7.46 (d, J = 9.0 Hz, 1 H), 6.59 (d, J = 2.0 Hz, 1 H), 6.44 (d, J = 6.0 Hz, 1 H), 6.13 (m, 2 H), 5.96 (t, J = 6.0 Hz, 2 H), 5.76 (t, J = 6.0 Hz, 2 H), 3.84 (s, 3 H), 3.73 (s, 3 H), 3.51 (s, 3 H), 1.68 (s, 15 H). ^{13}C NMR ($CDCl_3$): δ = 167.52 (−COO−), 162.35 (CH), 157.92 (C−OMe), 156.34 (C−OMe), 136.31 (CH), 133.98 (CH), 130.69 (CH), 125.49 (CH), 103.50 (CH), 99.41 (CH), 96.36 (CH), 94.98 ((*C*Me)$_5$), 94.20 (CH), 91.29 (CH), 88.20 (CH), 84.91 (CH), 84.06 (CH), 77.22 (OCO*Me*), 55.52

(OMe), 52.78 (OMe), 9.69 ((C*Me*)$_5$). IR (KBr): ν (cm^{-1}) = 3400 (m, br), 1680 (s), 1590 (m), 1010 (m). MS (CI, 70 eV): *m*/*z* (%) = 574 (1) [M$^+$], 515 (100) [M$^+$ − $C_2H_3O_2$], 338 (1) [M$^+$ − Ru(CMe)$_5$]. Anal. Calcd for $C_{31}H_{33}F_3O_8SRu$: C, 51.59; H, 4.60; S, 4.43. Found: C, 51.29; H, 4.73; S, 4.51.

Crystal Structure of 5b. $C_{30}H_{29}F_3O_7RuS$, M = 691.66, crystal size: 0.4 × 0.3 × 0.1 mm^3, triclinic, $P\bar{1}$, unit cell dimensions a = 7.375(4) Å, b = 11.802(5) Å, c = 16.827(8) Å, α = 80.54(3)°, β = 82.50(3)°, γ = 75.60(4)°, V = 1393(2) Å^3, Z = 2, D_c = 1.649 Mg m^{-3}, F(000) = 704, λ = 0.71073 Å, T = 133(2) K, μ = 0.706 mm^{-1}; total number of reflections measured 4301, unique 3634 (R_{int} = 0.047). Final R indices: $R1(F > 2\sigma(F))$ = 0.044, w$R2$ = 0.103 on all data, largest difference peak and hole 925 and −588 e nm^{-3}. Data were collected from a shock-cooled crystal on an Enraf Nonius CAD4 four-circle diffractometer (graphite-monochromated Mo Kα radiation, λ = 71.073 pm) equipped with a low-temperature device.[20] The structure was solved by direct methods using SHELXS-97[21] and refined against F^2 on all data by full-matrix least-squares with SHELXL-97.[22] Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101332. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [fax (internat.) +44(1223)336-033; e-mail deposit@ccdc.com.ac.uk].

Theoretical Calculations. The structure of **5b** was minimized on a CRAY computer YMP/8-128 by means of the standard optimization algorithm, as implemented in the program DGAUSS 3.0.[23] As the functional/basis set combination, BLYP/DZVP was applied. The electron density was fitted by a triple-Z A1 set. Electron densities ρ_{N+1} and ρ_N at fixed nucleus positions were calculated on an SGI INDIGO R4400 workstation by means of the program package Gaussian 94 (UHF/LANL1DZ).[24] The subtraction of the electron densities was performed by the tool CUBMAN, as implemented in Gaussian 94. For the visualization of the Fukui function, the SYBYL molecular modeling package was used.[25] Charges were calculated by the method of Loewdin by means of the program DGAUSS 3.0.[23]

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Supporting Information Available: Table with the calculated charges of **5b**. Text giving details of the X-ray crystal structure studies and tables of crystal structure determination data, atomic coordinates, anisotropic thermal parameters, and bond length and angles for compound **5b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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