

Supporting information for *Org. Lett.*

Rhodium(II,II) Dimer as an Efficient Catalyst for Aziridination of Sulfonamides and Amidation of Steroids

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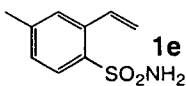
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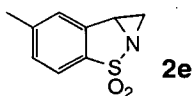
Part I: Experimental Section

General: $\text{PhI}(\text{OAc})_2$, NH_2Ts (Aldrich), NH_2Ns , cholesteryl acetate, 4-X-benzenesulfonyl chloride, (X = H, Methyl or Chloro: Acros), $\text{Rh}_2(\text{OAc})_4$, Doyle's catalyst $\text{Rh}_2(4\text{S-MEOX})_4$ (Aldrich) were used as received. Solvents were purified according to standard procedures. Al_2O_3 (pH = 7.4, Merck) was dried to constant weight at 250 °C for 12 h before use. Complexes $\text{Rh}_2(\text{R-BNP})_4$,¹ $\text{Rh}_2(\text{R-ODACA})_4$,² unsaturated sulfonamides **1**, **3–11**³, $\text{PhI}=\text{NTs}$ ⁴ were prepared from respective literatures. ^1H and ^{13}C NMR spectra were measured on a Bruker DPX 400 or DPX-300 spectrometer with CDCl_3 as the solvent (the chemical shifts are relative to tetramethylsilane). Mass spectra were obtained on a Finnigan MAT 95 mass spectrometer. HPLC measurements were carried out on a HP 1050 Series HPLC.

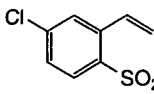
Typical procedure for intramolecular aziridination of unsaturated sulfonamides catalyzed by rhodium dimer complexes: Dichloromethane (1.5 mL) was added through syringe into a Schlenk flask containing unsaturated sulfonamides (0.2 mmol), $\text{PhI}(\text{OAc})_2$ (0.3 mmol), catalyst (0.004 mmol), Al_2O_3 (0.5 mmol), and molecular sieves (4 Å, 50 mg) under an argon atmosphere. The mixture was stirred at 40 °C for 3 h, diluted with dichloromethane (5 mL) after cooling to room temperature, and filtered through Celite. The residue on the Celite was washed with dichloromethane (2 × 5 mL). Evaporation of the combined filtrates under reduced pressure followed by chromatography on silica gel column with CH_2Cl_2 as eluent afforded the cyclic sulfonamides as white solids.

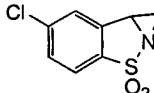
Spectral data of some unsaturated sulfonamides and the respective aziridination products:

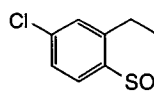
 **1e** ^1H NMR (CDCl_3 , 400 MHz): δ = 7.85 (d, J = 8.1 Hz, 1H), 7.49 (m, 1H), 7.39 (s, 1H), 7.17 (d, J = 8.0 Hz, 1H), 5.72 (d, J = 17.3 Hz, 1H), 5.49 (d, J = 11.0 Hz, 1H), 4.98 (s, 2H), 2.42 (s, 3H); ^{13}C NMR (CDCl_3 , 100 MHz): δ = 143.6, 136.7, 133.7, 129.6, 128.9, 128.3, 127.8, 119.5, 21.4. HRMS (EI) calcd. for $\text{C}_9\text{H}_{11}\text{NO}_2\text{S}$: 197.0511, found: 197.0504.

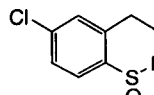
 **2e** ^1H NMR (CDCl_3 , 400 MHz): δ = 7.58 (d, J = 8.4 Hz, 1H), 7.34 (m, 2H), 4.06 (t, J = 4.4 Hz, 1H), 2.84 (d, J = 3.9 Hz, 1H), 2.47 (s, 3H)(m, 1H), 2.34

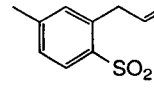
(d, $J = 2.7$ Hz, 1H); ^{13}C NMR (CDCl_3 , 100 MHz): $\delta = 144.5, 137.4, 131.2, 128.7, 125.7, 123.3, 43.9, 42.7, 21.6$; HRMS (EI) calcd. for $\text{C}_9\text{H}_9\text{NO}_2\text{S}$: 195.0354, found: 195.0350.

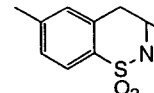
 **1f** ^1H NMR (CDCl_3 , 400 MHz): $\delta = 7.95$ (d, $J = 8.4$ Hz, 1H), 7.58 (s, 1H), 7.47 (m, 1H), 7.37 (d, $J = 8.2$ Hz, 1H), 5.78 (d, $J = 17.3$ Hz, 1H), 5.59 (d, $J = 11.0$ Hz, 1H), 4.85 (s, 2H); ^{13}C NMR (CDCl_3 , 100 MHz): $\delta = 139.3, 138.6, 132.7, 129.3, 129.0, 128.3, 127.8, 121.0$. HRMS (EI) calcd. for $\text{C}_8\text{H}_8\text{ClNO}_2\text{S}$: 216.9964, found: 216.9927.

 **2f** ^1H NMR (CDCl_3 , 300 MHz): $\delta = 7.64$ (d, $J = 8.3$ Hz, 1H), 7.54 (m, 2H), 4.09 (t, $J = 4.4$ Hz, 1H), 2.89 (d, $J = 3.8$ Hz, 1H), 2.39 (d, $J = 2.6$ Hz, 1H); ^{13}C NMR (CDCl_3 , 75 MHz): $\delta = 140.0, 138.9, 130.9, 128.9, 125.8, 124.8, 43.9, 42.2$; HRMS (EI) calcd. for $\text{C}_8\text{H}_6\text{ClNO}_2\text{S}$: 214.9808, found: 214.9814.

 **1h** ^1H NMR (CDCl_3 , 400 MHz): $\delta = 7.96$ (d, $J = 8.5$ Hz, 1H), 7.35 (m, 2H), 6.00 (m, 1H), 5.21 (m, 2H), 4.97 (s, 2H), 3.84 (d, $J = 6.3$ Hz, 2H); ^{13}C NMR (CDCl_3 , 100 MHz): $\delta = 140.4, 139.2, 138.4, 135.7, 131.8, 129.9, 126.9, 118.0, 36.8$; HRMS (EI) calcd. for $\text{C}_9\text{H}_{10}\text{ClNO}_2\text{S}$: 231.0121, found: 231.0120.

 **2h** ^1H NMR (CDCl_3 , 400 MHz): $\delta = 7.81$ (d, $J = 8.4$ Hz, 1H), 7.49 (m, 1H), 7.29 (m, 1H), 3.58 (m, 1H), 3.23 (m, 1H), 2.51 (m, 1H), 1.92 (m, 1H); ^{13}C NMR (CDCl_3 , 100 MHz): $\delta = 140.0, 133.0, 129.5, 129.3, 129.2, 127.8, 36.6, 29.8, 25.7$; HRMS (EI) calcd. for $\text{C}_9\text{H}_8\text{ClNO}_2\text{S}$: 228.9964, found: 228.9953.

 **1i** ^1H NMR (CDCl_3 , 300 MHz): $\delta = 7.91$ (d, $J = 8.0$ Hz, 1H), 7.14 (m, 2H), 6.02 (m, 1H), 5.15 (m, 2H), 4.87 (s, 2H), 3.84 (d, $J = 6.3$ Hz, 2H), 2.39 (s, 3H); ^{13}C NMR (CDCl_3 , 75 MHz): $\delta = 147.4, 143.7, 138.1, 137.0, 132.7, 128.6, 127.4, 117.1, 37.0, 21.3$; HRMS (EI) calcd. for $\text{C}_{10}\text{H}_{13}\text{NO}_2\text{S}$: 211.0667, found: 211.0662.

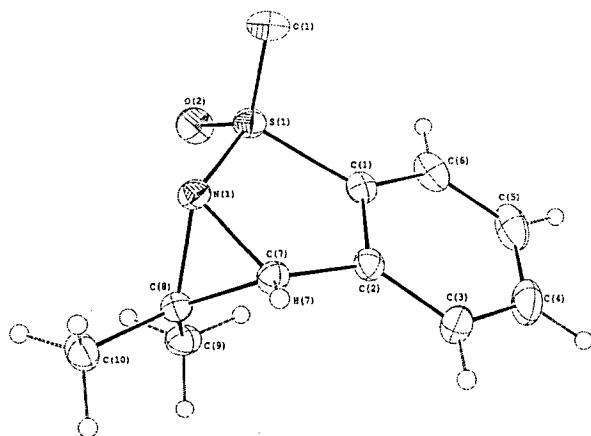
 **2i** ^1H NMR (CDCl_3 , 300 MHz): $\delta = 7.74$ (d, $J = 8.0$ Hz, 1H), 7.29 (d, $J = 8.0$ Hz, 1H), 7.07 (s, 1H), 3.56 (m, 1H), 3.20 (m, 2H), 2.45 (m, 1H), 2.41 (s, 3H), 1.89 (m, 1H); ^{13}C NMR (CDCl_3 , 75 MHz): $\delta = 144.7, 131.1, 129.6, 129.5, 128.1, 126.2, 36.7, 29.7, 25.7, 21.6$; HRMS (EI) calcd. for $\text{C}_{10}\text{H}_{11}\text{NO}_2\text{S}$: 209.0511, found: 209.0502.

References

- (a) McCarthy, N.; McKerver, M. A.; Ye, T.; McCann, M.; Murphy, E.; Doyle, M. P. *Tetrahedron Lett.* **1992**, 33, 5983. (b) Pirrung, M. C.; Zhang, J. *Tetrahedron Lett.* **1992**, 33, 5987.
- Pierson, N.; Fernandez-Garcia, C.; McKerver, M. A. *Tetrahedron Lett.* **1997**, 38, 4705.
- Dauban, P.; Dodd, R. H. *Org. Lett.* **2000**, 2, 2327

4. Yamada, Y.; Yamamoto, T.; Okawara, M. *Chem. Lett.* **1975**, 361.

Part II: X-ray structure data of Aziridine 2j



ORTEP drawing for **2j** crystallized from a racemic sample (only the structure of one enantiomer is shown).

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Rm. 301A

Crystal data: $[C_{10}H_{11}NO_2S]$; formula weight = 209.26, Monoclinic, $P2_1/n$, $a = 6.6410(13) \text{ \AA}$, $b = 10.961(2) \text{ \AA}$, $c = 14.039(3) \text{ \AA}$, $\beta = 94.40(3)^\circ$, $V = 1018.9(4) \text{ \AA}^3$, $Z = 4$, $D_c = 1.364 \text{ g cm}^{-3}$, $\mu(\text{Mo-K}\alpha) = 0.290 \text{ mm}^{-1}$, $F(000) = 440$, $T = 253 \text{ K}$.

Data collection: A crystal of dimensions $0.50 \times 0.45 \times 0.30 \text{ mm}$ mounted in a glass capillary was used for data collection at -20°C on a MAR diffractometer with a 300 mm image plate detector using graphite monochromatized Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). Data collection was made with 4° oscillation step of ϕ , 480 seconds exposure time and scanner distance at 120 mm. 45 images were collected.

Data reduction: The images were interpreted and intensities integrated using program DENZO¹.

Structure solution: The structure was solved by direct methods employing SHELXS-97 program² on PC. Most of non-H atoms were located according to the direct methods. The positions of the other non-hydrogen atoms were found after successful refinement by full-matrix least-squares using program SHELXL-97³ on PC.

Structure refinement: According to the SHELXL-97 program³, all 1850 independent reflections (R_{int} ⁴ equal to 0.0226, 1653 reflections larger than $4\sigma(F_o)$) from a total 4824 reflections were participated in the full-matrix least-square refinement against F^2 . These reflections were in the range $-7 \leq h \leq 7$, $-13 \leq k \leq 13$, $-16 \leq l \leq 17$ with $2\theta_{\text{max}}$ equal to 51.24° .

One crystallographic asymmetric unit consists of one formula unit. In the final stage of least-squares refinement, all non-H atoms were refined anisotropically. The positions of H atoms were calculated based on riding mode with thermal parameters equal to 1.2 times that of the associated C atoms, and participated in the calculation of final R-indices⁵.

Convergence ($(\Delta/\sigma)_{\text{max}} = 0.001$, av. 0.001) for 129 variable parameters by full-matrix least-squares refinement on F^2 reaches to $R_1 = 0.0426$ and $wR_2 = 0.1174$ with a goodness-of-fit of 1.167, the parameters a and b for weighting scheme are 0.0683 and 0.2038. The final difference Fourier map shows maximum rest peaks and holes of 0.244 and $-0.628 \text{ e \AA}^{-3}$ respectively.

Drawing: The ORTEP⁶ drawing of the molecule was made with thermal ellipsoids at the 30 % probability level. Screen drawing is provided for reference. The drawing with high quality can be provided upon request.

Tables: Table (1) of Crystallographic and refinement data, table (3) of full bond lengths and bond angles and this report⁷ are provided. The other supplementary materials, such as table of atomic coordinates with thermal parameters, table of anisotropic displacement parameters, table of hydrogen coordinates and/or other tables and/or CIF, RES-files, can be provided under request by notifying the identification code.

¹ Otwinowski, Z. and Minor, W., "Processing of X-ray Diffraction Data Collected in Oscillation Mode", Methods in Enzymology, Volume 276: Macromolecular Crystallography, part A, p. 307-326, 1997. Carter C. W., Sweet Jr. & R. M., Eds., Academic Press.

² SHELXS97, Sheldrick, G. M. (1997). SHELX97: Programs for Crystal Structure Analysis (Release 97-2). University of Goettingen, Germany.

³ SHELXL97, Sheldrick, G. M. (1997). SHELX97. Programs for Crystal Structure Analysis (Release 97-2). University of Goettingen, Germany.

⁴ $R_{\text{int}} = \sum [F_o^2 - F_o^2(\text{mean})] / \sum [F_o^2]$

⁵ Since the structure refinements are against F^2 , R-indices based on F^2 are larger than (more than double) those based on F. For comparison with older refinements based on F and an OMIT threshold, a conventional index R_1 based on observed F values larger than $4\sigma(F_o)$ is also given (corresponding to $\text{Intensity} \geq 2\sigma(I)$). $wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$. $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$. The Goodness of Fit is always based on F^2 : $\text{Goof} = S = \{ \sum [w(F_o^2 - F_c^2)^2] / (n - p) \}^{1/2}$, where n is the number of reflections and p is the total number of parameters refined. The weighting scheme is: $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where P is $[2F_c^2 + \text{Max}(F_o^2, 0)]/3$.

⁶ ORTEP3 for Windows - Farrugia, L. J. (1997) J. Appl. Cryst. 30, 565.

⁷ The crystallographic data summarized in this reported are abstracted from the previous tables and the experiment record.

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Table 1. Crystal data and structure refinement for mar656.

Identification code	mar656	
Empirical formula	C ₁₀ H ₁₁ N O ₂ S	
Formula weight	209.26	
Temperature	253(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 2 ₁ /n	
Unit cell dimensions	a = 6.6410(13) Å	α = 90°.
	b = 10.961(2) Å	β = 94.40(3)°.
	c = 14.039(3) Å	γ = 90°.
Volume	1018.9(4) Å ³	
Z	4	
Density (calculated)	1.364 Mg/m ³	
Absorption coefficient	0.290 mm ⁻¹	
F(000)	440	
Crystal size	0.50 x 0.45 x 0.30 mm ³	
Theta range for data collection	2.36 to 25.62°.	
Index ranges	-7<=h<=7, -13<=k<=13, -16<=l<=17	
Reflections collected	4824	
Independent reflections	1850 [R(int) = 0.0226]	
Completeness to theta = 25.62°	96.4 %	
Absorption correction	None	
Max. and min. transmission	0.9181 and 0.8686	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	1850 / 0 / 129	
Goodness-of-fit on F ²	1.167	
Final R indices [I>2sigma(I)]	R1 = 0.0426, wR2 = 0.1174	
R indices (all data)	R1 = 0.0462, wR2 = 0.1195	
Largest diff. peak and hole	0.244 and -0.628 e.Å ⁻³	

Table 3. Bond lengths [Å] and angles [°] for mar656.

S(1)-O(1)	1.4312(14)	C(7)-N(1)-C(8)	59.19(11)
S(1)-O(2)	1.4346(15)	C(7)-N(1)-S(1)	108.98(11)
S(1)-N(1)	1.6609(16)	C(8)-N(1)-S(1)	119.89(12)
S(1)-C(1)	1.752(2)	C(2)-C(1)-C(6)	122.6(2)
N(1)-C(7)	1.507(2)	C(2)-C(1)-S(1)	109.52(14)
N(1)-C(8)	1.515(2)	C(6)-C(1)-S(1)	127.91(17)
C(1)-C(2)	1.385(3)	C(3)-C(2)-C(1)	119.24(19)
C(1)-C(6)	1.391(3)	C(3)-C(2)-C(7)	127.34(18)
C(2)-C(3)	1.381(3)	C(1)-C(2)-C(7)	113.39(16)
C(2)-C(7)	1.487(3)	C(2)-C(3)-C(4)	118.6(2)
C(3)-C(4)	1.386(3)	C(3)-C(4)-C(5)	121.4(2)
C(4)-C(5)	1.386(4)	C(6)-C(5)-C(4)	120.8(2)
C(5)-C(6)	1.373(3)	C(5)-C(6)-C(1)	117.4(2)
C(7)-C(8)	1.493(2)	C(2)-C(7)-C(8)	117.95(15)
C(8)-C(9)	1.498(3)	C(2)-C(7)-N(1)	110.36(15)
C(8)-C(10)	1.507(3)	C(8)-C(7)-N(1)	60.69(11)
		C(7)-C(8)-C(9)	122.36(16)
O(1)-S(1)-O(2)	117.17(9)	C(7)-C(8)-C(10)	116.98(17)
O(1)-S(1)-N(1)	106.71(8)	C(9)-C(8)-C(10)	114.10(17)
O(2)-S(1)-N(1)	111.13(8)	C(7)-C(8)-N(1)	60.12(11)
O(1)-S(1)-C(1)	109.64(9)	C(9)-C(8)-N(1)	122.25(15)
O(2)-S(1)-C(1)	112.85(9)	C(10)-C(8)-N(1)	110.08(16)
N(1)-S(1)-C(1)	97.40(8)		

Symmetry transformations used to generate equivalent atoms: