Transformations of strained-ring thioethers by metal cluster complexes. Nature of the ring opening of a bridging 3,3-dimethylthietane ligand in a triosmium cluster complex

Richard D. Adams, and Michael P. Pompeo

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Transformations of Strained-Ring Thioethers by Metal Cluster Complexes. The Nature of the Ring Opening of a Bridging 3,3-Dimethylthietane Ligand in a Triosmium Cluster Complex

Richard D. Adams* and Michael P. Pompeo

Department of Chemistry, University of South Carolina, Columbia, South Carolina 29208

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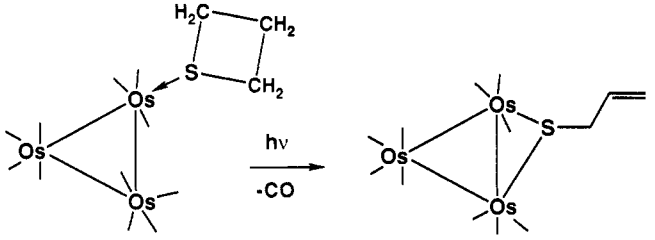
Summary: The complex $Os_3(CO)_{10}[\mu\text{-}SCH_2CMe_2CH_2]$ (**3**) was synthesized in 41% yield by the reaction of $Os_3(CO)_{10}(NCMe)_2$ with $SCH_2CMe_2CH_2$ (DMT). The three new compounds $Os_3(CO)_9(\mu_3\text{-}SCH_2CMe_2CH)(\mu\text{-}H)$ (**4**; 21%), $Os_2(CO)_6[\mu\text{-}S(CH_2)_3CMe](\mu\text{-}H)$ (**5**; 18%), and $Os_4(CO)_{12}(\mu\text{-}Co)(\mu\text{-}SCH_2CMe_2CH_2)$ (**6**; 12%) were formed when the compound **3** was heated to 97 °C. The DMT ligand in **3** was transformed by a C–S bond cleavage and a CH activation on the methylene group to yield **4**. The sulfur atom bridges one edge of the cluster, and an alkylidene carbon bridges a different edge. Compound **5** was formed from **4** by loss of a "$Os(CO)_3$" grouping, a return of hydride to the alkylidene carbon, and a CH activation on one of the methyl groups. Compound **6** contains a butterfly tetrahedral cluster of four osmium atoms with a DMT ligand bridging the two wingtip metal atoms.

The ring-opening reaction of cyclic thioethers is believed to be a key step in the hydrodesulfurization of fossil fuels.[1] Metal complexes have been shown to produce ring opening of cyclic thioethers.[2] Ring opening of cyclic thioethers also occurs readily on certain metal surfaces.[3,4] Small-ring thioethers, such as thiiranes and thietanes, possess a greater tendency to undergo ring opening as a result of their intrinsic ring strain.[3,4] In order to examine the nature of this ring opening at multinuclear metal sites, we have begun investigations of the reactions of thietanes with metal carbonyl cluster complexes. Recently, we have shown that the thietane cluster complex $Os_3(CO)_{11}[S(CH_2)_3]$ (**1**) undergoes a photochemical, ring-opening, de-



1 **2**

carbonylation reaction to yield the allenethiolato cluster complex $Os_3(CO)_{10}[\mu\text{-}SCH_2CH{=}CH_2](\mu\text{-}H)$ (**2**) by the cleavage of one C–S bond and one C–H bond at the 3-position in the thietane molecule.[5] In order to examine the C–S bond cleavage in the absence of CH activation at the 3-position, we have prepared and studied the ring opening of the 3,3-dimethylthietane ligand in the cluster complex $Os_3(CO)_{10}[\mu\text{-}SCH_2CMe_2CH_2]$ (**3**).

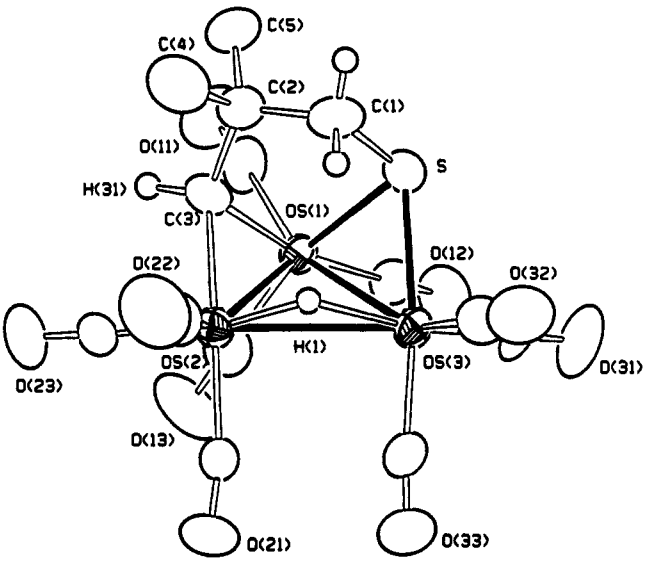


Figure 1. ORTEP diagram of $Os_3(CO)_9(\mu_3\text{-}SCH_2CMe_2CH)(\mu\text{-}H)$ (**4**). Selected intramolecular distances (Å) are as follows: Os(1)–Os(2) = 2.8301(7), Os(1)–Os(3) = 2.8233 (8), Os(2)–Os(3) = 3.0006 (8), Os(1)–S = 2.429 (3), Os(3)–S = 2.404 (3), S–C(1) = 1.83 (1), Os(2)–C(3) = 2.12 (1), Os(1)–C(3) = 2.23 (1).

Complex **3** was obtained in 41% yield from the reaction of $Os_3(CO)_{10}(NCMe)_2$ with 3,3-dimethylthietane[6] (DMT) in CH_2Cl_2 solvent at 25 °C.[7] The complex was characterized structurally by a single-crystal X-ray diffraction analysis and was found to contain a DMT ligand bridging the edge of the triangular cluster by using both lone pairs of electrons on the sulfur atom.[8,9] The DMT ligand is slightly nonplanar, the C–S–C, C–C–C dihedral angle being 28.5°, but it shows no unusual distortions.

Three products, $Os_3(CO)_9(\mu_3\text{-}SCH_2CMe_2CH)(\mu\text{-}H)$ (**4**; 21% yield), $Os_2(CO)_6[\mu\text{-}S(CH_2)_3CMe](\mu\text{-}H)$ (**5**; 18% yield), and $Os_4(CO)_{12}(\mu\text{-}CO)[\mu\text{-}S(CH_2)_2CMe_2]$ (**6**; 12% yield), were

(1) (a) Markel, E. J.; Schrader, G. L.; Sauer, N. N.; Angelici, R. J. *J. Catal.* **1989**, *116*, 11. (b) Sauer, N. N.; Markel, E. J.; Schrader, G. L.; Angelici, R. J. *J. Catal.* **1989**, *117*, 295. (c) Kwart, H.; Schuit, G. C. A.; Gates, B. C. *J. Catal.* **1980**, *61*, 128. (d) Curtis, M. D.; Penner-Hahn, J. E.; Schwank, J.; Beralt, O.; McCabe, D. J.; Thompson, L.; Waldo, G. *Polyhedron* **1988**, *7*, 2411. (e) Prins, R.; De Beer, V. H. J.; Somorjai, G. A. *Catal. Rev.—Sci. Eng.* **1989**, *31*, 1.

(2) (a) Angelici, R. J. *Acc. Chem. Res.* **1988**, *21*, 387. (b) Hachgenei, J. W.; Angelici, R. J. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 909. (c) Chen, J.; Daniels, L. M.; Angelici, R. J. *J. Am. Chem. Soc.* **1990**, *112*, 199. (d) Ogilvy, A. E.; Draganjac, M.; Rauchfuss, T. B.; Wilson, S. R. *Organometallics* **1988**, *7*, 1171.

(3) (a) Friend, C. M.; Roberts, J. T. *Acc. Chem. Res.* **1988**, *21*, 394 and references therein. (b) Roberts, J. T.; Friend, C. M. *J. Am. Chem. Soc.* **1986**, *108*, 7204.

(4) Roberts, J. T.; Friend, C. M. *J. Am. Chem. Soc.* **1987**, *109*, 3872.

(5) Adams, R. D.; Pompeo, M. P. *Organometallics* **1990**, *9*, 1718.

(6) Johnson, P. Y.; Bergman, M. *J. Org. Chem.* **1975**, *40*, 3050.

(7) 3,3-Dimethylthietane (16 μL, approximately 1 equiv) was allowed to react with 115 mg (0.123 mmol) of $Os_3(CO)_{10}(NCMe)_2$ in 25 mL of CH_2Cl_2 at 25 °C for 2 h. Compound **3** was isolated by TLC on silica gel; yield 48 mg, 41%. IR (ν(CO), cm^{-1}; in hexane): 2095 (m), 2038 (sh), 2035 (vs), 2020 (s), 1988 (s), 1969 (m). ^1H NMR (δ; in $CDCl_3$): 4.04 (s, 2 H), 3.76 (s, 2 H), 1.58 (s, 6 H).

(8) Crystal data for **3**: space group $P2_1/c$, a = 14.075 (3) Å, b = 22.143 (4) Å, c = 14.778 (3) Å, β = 108.37 (2)°, Z = 8. The structure was refined (3227 reflections) to the final residuals R = 0.046 and R_w = 0.049. Selected bond distances (Å) for **3** are as follows: Os(1)–Os(2) = 2.764 (2), Os(1)–Os(3) = 2.896 (2), Os(2)–Os(3) = 2.871 (2), Os(1)–S(1) = 2.320 (6), Os(2)–S(1) = 2.322 (7), S(1)–C(1) = 1.87 (2), S(1)–C(3) = 1.82 (3).

(9) Diffraction measurements were made on a Rigaku AFC6S diffractometer using Mo Kα radiation. Calculations were performed by using the TEXSAN structure solving program library (version 5.0) obtained from the Molecular Structure Corp., The Woodlands, TX. Absorption corrections were applied in each structural analysis.

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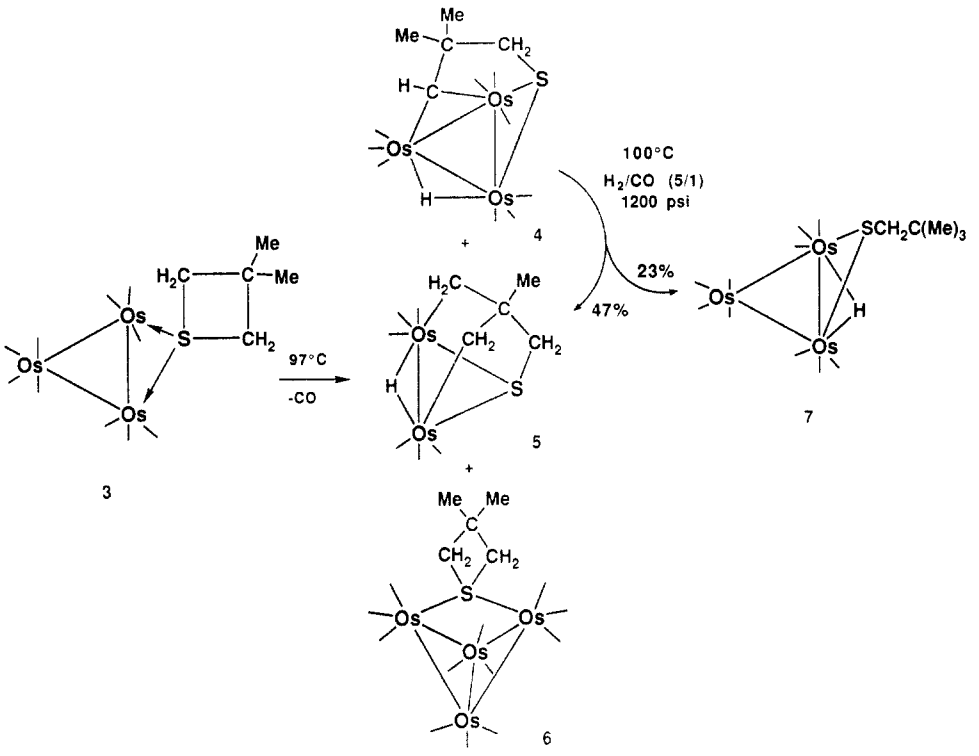
Scheme I



obtained when compound **3** was heated to reflux in heptane solvent for 1 h.[10] All three products were characterized by single-crystal X-ray diffraction analyses.[9,11] An ORTEP drawing of the molecular structure of **4** is shown in Figure 1. The molecule contains a closed triangular cluster of three metal atoms with a SCH_2CMe_2CH ligand bridging the face of the cluster. The sulfur atom bridges the Os(1)–Os(3) edge of the cluster, and the alkylidene center, C(3), bridges the Os(1)–Os(2) edge of the cluster. A hydride ligand (located crystallographically) bridges the Os(2)–Os(3) edge of the cluster (δ = −17.46 ppm). The formation of **4** has involved a decarbonylation of **3** that was accompanied by C–S and C–H bond cleavages at one of the CH_2 groups of the DMT ligand. It is not yet known which step occurs first, but it probably takes place at the $Os(CO)_4$ group in **3** after decarbonylation (see Scheme I).

An ORTEP drawing of **5** is shown in Figure 2.[12] This molecule contains two metal atoms and has a crystallographically imposed reflection plane passing through the atoms S(1), C(1), C(2), C(4), and H. The sulfur atom S(1) and the hydride ligand H (δ = −17.45 ppm) bridge the metal–metal bond; Os(1)–Os(1) = 2.9576 (9) Å. There is a CH_2 group bonded to each metal atom and the sulfur atom. All three CH_2 groups are bonded to the CMe grouping. The formation of **5** has involved cleavage of a C–S bond of the DMT ligand in **3**, a CH activation on one of the methyl groups, and a fragmentation of the cluster. Mechanistically, this may have involved **4** as an intermediate. We have found that **5** can be obtained from **4** in 47% yield together with the hydrogenation product $Os_3(CO)_{10}(\mu\text{-}SCH_2Bu^t)(\mu\text{-}H)$ (**7**; 23% yield) when heated to 100 °C under a mixture of CO and hydrogen.[13] The formation of **5** from **4** results in the loss of an $Os(CO)_3$ grouping. The fate of this group has not yet been ascertained in this latter reaction, but in the original reaction, it appears to have been captured by a molecule of **3** to yield **6**. Compound

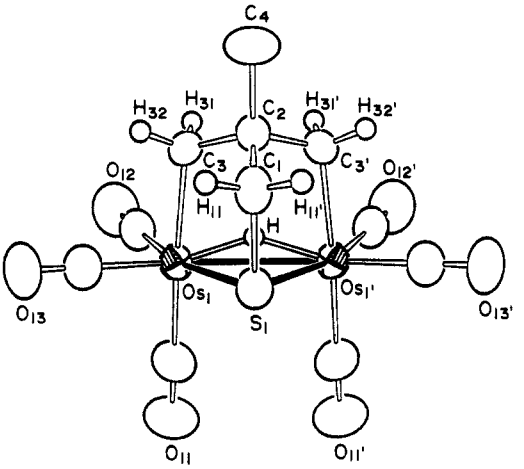


Figure 2. ORTEP diagram of $Os_2(CO)_6[\mu\text{-}S(CH_2)_3CMe](\mu\text{-}H)$ (**5**). Selected intramolecular distances (Å) are as follows: Os(1)–Os(1′) = 2.9576 (9), Os(1)–S(1) = 2.410 (3), Os(1)–C(3) = 2.18 (1), S(1)–C(1) = 1.81 (2), Os(1)–H = 1.55 (4).

(10) **3** (40 mg, 0.042 mmol) in 40 mL of heptane was heated to reflux for 1 h. The products were separated by TLC on silica gel to yield 5.0 mg of colorless $Os_2(CO)_6(\mu\text{-}S(CH_2)_3CMe)(\mu\text{-}H)$ (**5**; 18%), 8.0 mg of orange $Os_3(CO)_9(\mu_3\text{-}SCH_2CMe_2CH)(\mu\text{-}H)$ (**4**; 21%), and 6.0 mg or red $Os_4(CO)_{12}(\mu\text{-}CO)[\mu\text{-}S(CH_2)_2CMe_2]$ (**6**; 12%). IR (ν(CO), cm^{-1}; in hexane): for **4**, 2099 (m), 2070 (vs), 2050 (s), 2017 (sh), 2013 (s), 2003 (s), 1986 (m), 1975 (w); for **5**, 2100 (s), 2081 (vs) 2019 (s), 2014 (s), 2002 (s), 1977 (w); for **6**, 2088 (w), 2050 (vs), 2040 (s), 2027 (m), 1997 (m), 1976 (w). ^{1}H NMR (δ; in $CDCl_3$): for **4**, 3.02 (d, 1 H, J_{H-H} = 11.3 Hz, J_{H-H} = 1.7 Hz), 2.11 (d, 1 H, J_{H-H} = 11.3 Hz), 1.50 (s, 3 H), 1.31 (s, 3 H), −17.47 (d, 1 H, J_{H-H} = 1.7 Hz); for **6**, 4.42 (s, 4 H), 1.64 (s, 6 H). Satisfactory elemental analyses (C, H) have been obtained for **4**, **5**, and **6**.

(11) Crystal data for **4**: space group $P\bar{1}$, a = 9.330 (2) Å, b = 14.352 (2) Å, c = 8.656 (2) Å, α = 93.73 (2)°, β = 117.58 (1)°, γ = 101.09 (2)°, Z = 2. The structure was refined (1977 reflections) to the final residuals R = 0.023 and R_w = 0.025.

(12) Crystal data for **5**: space group $P2_1/m$, a = 6.3804 (8) Å, b = 14.149 (2) Å, c = 8.649 (1) Å, β = 96.70 (1)°, Z = 2. The structure was refined (1019 reflections) to the final residuals R = 0.036 and R_w = 0.043.

(13) **4** (27 mg, 0.029 mmol) in 15 mL of heptane was placed in a 50-mL Parr reaction vessel, pressurized to 1200 psi with 1000 psi of H_2 and 200 psi of CO, and heated to 100 °C for 8 h. The products of **5** (7.0 mg) and **7** (5.0 mg) were separated from **4** (6.0 mg) by TLC. ^{1}H NMR for **7** (δ; in $CDCl_3$): 2.29 (s, 2 H), 1.06 (s, 9 H), −17.38 (s, 1 H). The mass spectrum showed the parent ion and ions corresponding to the loss of the neopentyl group and 10 CO ligands.

6 consists of a butterfly tetrahedral cluster of four osmium atoms bridged at the wingtips by an untransformed DMT ligand.[9,14]

We believe that the bridging coordination of the DMT ligand in 3 may play an important role in the ring-opening process.[15] Curiously, the metallacycle formation, as observed in the formation of 4, contrasts with the decomposition of thietane on molybdenum surfaces, where the principal product, cyclopropane, is believed to be formed without the formation of a metallacyclic intermediate.[4]

Acknowledgment. These studies were supported by the Office of Basic Energy Sciences of the U.S. Department of Energy.

Supplementary Material Available: An ORTEP diagram of 3 and tables of crystal data, positional and thermal parameters, and bond distances and angles for the structural analyses of 3–6 (35 pages); tables of structure factor amplitudes for 3–6 (62 pages). Ordering information is given on any current masthead page.

(14) The structure was refined (2678 reflections) to the final residuals $R = 0.029$ and $R_w = 0.030$.

(15) Calhorda, M. J.: Hoffmann, R.; Friend, C. M. *J. Am. Chem. Soc.* **1990**, *112*, 50.

New Electron-Rich Chiral Phosphines for Asymmetric Catalysis†

Mark J. Burk,* John E. Feaster, and Richard L. Harlow

Central Research & Development Department, E. I. du Pont de Nemours & Company, Experimental Station, Wilmington, Delaware 19880-0328

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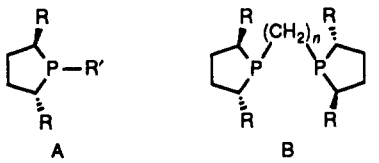
Summary: We describe a new series of chiral mono- and bidentate 2,5-disubstituted phospholanes and demonstrate their use as ligands in asymmetric catalysis. Rhodium complexes bearing the new phosphine ligands were prepared and characterized by X-ray crystallography. These complexes act as efficient catalyst precursors for the enantioselective hydrogenation of unsaturated substrates.

The synthesis of new chiral ligands for transition metals is an essential component for the development of novel catalytic systems exhibiting unique reactivity and high enantioselectivity. In general, some of the most successful chiral ligands used for asymmetric catalysis are chelating phosphines possessing a C_2 symmetry axis.[1] Noteworthy in this regard are the recently described BINAP ligands used by Noyori and co-workers to prepare Rh and Ru catalysts exhibiting very high enantioselectivities in hydrogenation and isomerization reactions.[2] The synthesis of optically pure asymmetric phosphines often involves tedious routes that are limited to only one antipode or require a resolution step. In addition, most chiral phosphines to date bear at least two aryl substituents on phosphorus, rendering that center relatively electron-poor.[3] In fact, the mechanism of asymmetric induction with these phosphines has been intimately linked to the proper conformational relationship between the phenyl rings on the phosphorus centers.[1] Our primary objective has been the development of efficient routes to new, chiral electron-rich phospholanes (A and B) analogous to known C_2-symmetric heterocycles, which are well-documented to provide high



levels of absolute stereocontrol in both stoichiometric and catalytic transformations.[4] We report a versatile route to these asymmetric phosphines, as well as the preparation and characterization of several rhodium complexes that act as efficient catalyst precursors for the asymmetric hydrogenation of unsaturated substrates.

Masamune and co-workers recently reported[5] the use of baker's yeast for the reduction of 2,5-hexanedione to the (*S,S*)-diol **1a** (R = CH_3), followed by reaction with MsCl and closure ultimately to afford (2*R*,5*R*)-2,5-dimethylpyrrolidine. Our initial studies utilized this same approach to prepare the corresponding bis(mesylate), which upon treatment with Li_2PPh provided (2*R*,5*R*)-2,5-dimethyl-1-phenylphospholane[6] ((*R,R*)-**2a**) in 76% isolated yield. Enzymatic reductions, however, generally provide only one enantiomer of a desired product and often suffer from inherent limitations such as high substrate specificity, low product yields, and involved isolation procedures.[7] We have developed a new three-step process that affords large quantities of either antipode of a series of chiral 2,5-disubstituted diols **1** (Scheme I). The first step introduces the desired chirality and utilized Noyori's Ru(BINAP) catalysts[8] for the asymmetric reduction of β-keto esters to

†Contribution No. 5476.

(1) Reviews: (a) Knowles, W. S. *Acc. Chem. Res.* **1983**, *16*, 106. (b) Kagan, H. B. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic Press: New York, 1985; Vol. 5, Chapter 1. (c) Brunner, H. *J. Organomet. Chem.* **1986**, *300*, 39. (d) Koenig, K. E. In *Asymmetric Synthesis*; Morrison, J. D., Eds.; Academic Press: New York, 1985; Vol, 5, Chapter 3. (e) Riley, D. P.; Shumate, R. E. *J. Org. Chem.* **1980**, *45*, 5187 and references therein.

(2) Noyori, R. *Chem. Soc. Rev.* **1989**, *18*, 187.

(3) For recent reports dealing with electron-rich asymmetric phosphines: (a) Tani, K.; Suwa, K.; Tanigawa, E.; Ise, T.; Yamagata, T.; Tatsuno, Y.; Otsuka, S. *J. Organomet. Chem.* **1989**, *370*, 203. (b) Miyashita, A.; Karino, H.; Shimamura, J.; Chiba, T.; Nagano, K.; Nohira, H.; Takaya, H. *Chem. Lett.* **1989**, 1849. (c) Brunner, H.; Sievi, R. *J. Organomet. Chem.* **1987**, *328*, 71.

(4) For a recent review, see: Whitesell, J. K. *Chem. Rev.* **1989**, *89*, 1581 and references therein.

(5) Short, R. P.; Kennedy, R. M.; Masamune, S. *J. Org. Chem.* **1989**, *54*, 1755.

(6) For a recent report describing the use of yeast reduction in the preparation of (*R,R*)-**2a** by a route of limited scope and yield, see: Wilson, S. R.; Pasternak, A. *Synlett* **1990**, 199.

(7) (a) Servi, S. *Synthesis* **1990**, 1. (b) Jones, J. B. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic Press: New York, 1985; Vol. 5, Chapter 9. (c) Simon, H.; Bader, J.; Gunther, H.; Neumann, S.; Thanos, J. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 539.

(8) (a) Noyori, R.; Ohkuma, T.; Kitamura, M.; Takaya, H.; Sayo, N.; Kumobayashi, H.; Akutagawa, S. *J. Am. Chem. Soc.* **1987**, *109*, 5856. (b) Kitamura, M.; Ohkuma, T.; Inoue, S.; Sayo, N.; Kumobayashi, H.; Akutagawa, S.; Ohata, T.; Takaya, H.; Noyori, R. *J. Am. Chem. Soc.* **1988**, *110*, 629.

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