A mechanism shown in Scheme I involves a rapid ligand exchange of **1** with halides and thereby formation of vinyliodonium halides **3** as intermediates. It was established by ^{1}H NMR that **3** (R = n-C_8H_{17}, X = Cl) is produced instantaneously by the addition of **1a** to a solution of n-Bu_4NCl in $CDCl_3$ at room temperature.[15,16] Furthermore, this compound **3** in CH_2Cl_2 at room temperature decomposed to a 45:55 mixture of (Z)-**2a** (X = Cl) and 1-decyne quantitatively. Attack of another halide to **3** will produce (Z)-**2**, although the mechanism is unknown. Alternatively, intramolecular cis-β-proton abstraction[9] by the ligand X of **3** gives 1-alkynes. Thus, the relative ratios of the substitution to the alkyne-forming reaction depend on the concentration of halide ions, which is compatible with the results shown in Figure 1.

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(15) The authentic **3** (R = n-C_8H_{17}, X = Cl) was prepared quantitatively by the reaction of **1a** with NaCl.

(16) On the other hand, **1a** did not undergo the ligand exchange with fluoride ion. This fact could be interpreted by the hard and soft acids and bases principle and may be the reason for the preferential α-elimination of **1a** with n-Bu_4NF.

Small-Ring Organometallic Systems. Ring Strain and Quantum Yields of Formation in CpMn(CO)(η^2-P-P) Complexes

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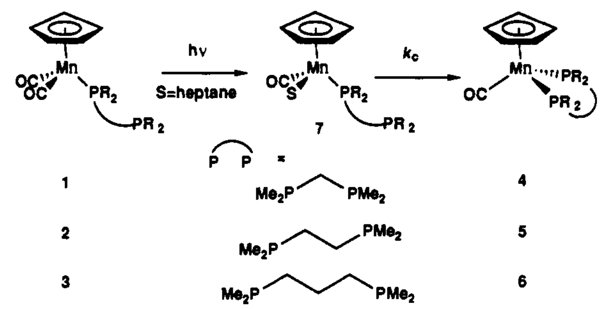
Four-, five-, and six-membered rings abound in organometallic chemistry as proposed catalytic and reactive intermediates and as stable complexes. In light of their role as intermediates in olefin metathesis reactions, four-membered rings are of particular interest. Marks[1] and Puddephatt[2] respectively have determined the strain in thoracyclobutanes and platinacyclobutanes to be 16 and 10-13 kcal/mol while a study of Whitesides[3] suggests that the strain in platinacyclobutanes is less than 5 kcal/mol. From the heat of norbornadiene substitution from (NBD)Mo(CO)$_4$ by bidentate phosphine ligands, Hoff[4] has determined ring strain in four-membered rings containing the P-Mo-P moiety to be 8 kcal/mol. Although it is clear that there is some strain in these systems, the magnitude of the strain is still in some dispute. Studies on classical coordination complexes reveal a dependence of ring strain on chelate ring size.[5] None of these studies have addressed the strain in four-membered metallacycles containing first-row transition elements. We now report the determination of the strain in four-membered rings containing Mn and P atoms by measurement of the enthalpy of cyclization as a function of ring size. The determination of the quantum yield for the ring-closure reactions is also reported.

The reaction of photochemically generated CpMn(CO)$_2$THF with a roughly 2-fold excess of the appropriate bis(dimethylphosphino)alkane ligand dmpm, dmpe, or dmpp (P-P) gives the corresponding CpMn(CO)$_2$(η^1-P-P) complex (**1**, **2**, **3**) in ~70% yield.[6] Only small amounts of the dinuclear (CpMn(CO)$_2$)$_2$(μ-P-P) complexes are formed under these conditions. Recrystallization of the crude η^1-**1** and η^1-**2** complexes from hexanes removed the dinuclear impurity. The η^1-**3** complex was difficult to crystallize and was purified by air-free column chromatography (silica-60/hexanes/THF (100:1)). In benzene-d_6 solution at room temperature, the η^1 complexes did not undergo thermal CO loss or ring closure.

Scheme I



Photolysis of the η^1-bis(dimethylphosphino)alkane complexes **1**, **2**, or **3** with a medium-pressure Hg lamp in heptane solution results in CO dissociation and ring closure to form the corresponding four-, five-, and six-membered rings (**4**, **5**, **6**) in quantitative yield.[7] Photolysis of η^1-**1**, -**2**, or -**3** in heptane solution under 600 Torr of CO leads only to the cyclized products with no evidence for loss of the phosphine ligand. This result is in agreement with CO loss as the only significant photochemical step.[8] Complex **4** has been previously reported by King and RaghuVeer.[9] The quantum yields at 337.1 nm for the cyclization reactions were directly determined to be 0.62 and 0.60 for η^1-**1** and η^1-**2**, respectively.[10] The quantum yield for the ring closure

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(1) Bruno, J. W.; Marks, T. J.; Morss, J. R. *J. Am. Chem. Soc.* **1983**, *105*, 6824-6832.

(2) Puddephatt, R. J. *Coord. Chem. Rev.* **1980**, *33*, 149-194.

(3) Moore, S. S.; DiCosimo, R.; Sowinski, A. F.; Whitesides, G. M. *J. Am. Chem. Soc.* **1981**, *103*, 948-949.

(4) Mukerjee, S. L.; Nolan, S. P.; Hoff, C. D.; Lopez de la Vega, R. *Inorg. Chem.* **1988**, *27*, 81-85.

(5) (a) Hancock, R. D.; Wade, P. W.; Ngwenya, M. P.; de Sousa, A. S.; Damu, K. V. *Inorg. Chem.* **1990**, *29*, 1968-1974. (b) Hancock, R. D.; Martell, A. E. *Chem. Rev.* **1989**, *89*, 1875-1914. (c) Smith, R. M.; Martell, A. E. *Critical Stability Constants*; Plenum: New York, 1975; Vol. 2.

(6) Data for **1**: ^{1}H NMR (benzene-d_6) δ 4.17 (d, 5 H, C_5H_5, J_{P-H} = 2.0 Hz), 1.40 (dd, 2 H, CH_2, J_{P-H} = 2.2, 8.1 Hz), 1.15 (d, 6 H, MnPMe_2, J_{P-H} = 8.3 Hz), 0.74 (d, 6 H, free PMe_2, J_{P-H} = 3.6 Hz). $^{13}C\{^1H\}$ NMR (benzene-d_6) δ 81.27 (s, C_5H_5), 39.54 (dd, CH_2, J_{P-C} = 30.8, 20.7 Hz), 20.76 (dd, MnPMe_2, J_{P-C} = 27.7, 7.6 Hz), 16.38 (dd, free PMe_2, J_{P-C} = 14.9, 5.9 Hz). ^{31}P NMR (benzene-d_6) δ 56.7 (br, MnP), -57.0 (d, free P, J_{P-P} = 40.9 Hz). IR (THF) ν_{CO} 1927, 1861 cm^{-1}. Anal. Calcd for $C_{11}H_{19}OMnP_2$: C, 46.17; H, 6.13. Found: C, 46.46, H, 6.23. Data for **2**: ^{1}H NMR (benzene-d_6) δ 4.08 (d, 5 H, C_5H_5, J_{P-H} = 1.9 Hz), 1.35 (m, 4 H, CH_2CH_2), 0.93 (d, 6 H, MnPMe_2, J_{P-H} = 8.3 Hz), 0.81 (d, 6 H, free PMe_2, J_{P-H} = 2.7 Hz). $^{13}C\{^1H\}$ NMR (benzene-d_6) δ 81.0 (s, C_5H_5), 31.91 (dd, MnPCH_2, J_{P-C} = 22.4, 13.1 Hz), 26.14 (dd, MnPCH_2CH_2, J_{P-C} = 13.7, 2.0 Hz), 19.00 (d, MnPMe_2, J_{P-C} = 26.5 Hz), 13.79 (d, free PMe_2, J_{P-C} = 15.4 Hz). ^{31}P NMR (benzene-d_6) δ 59.8 (br, MnP), -47.1 (d, free P, J_{P-P} = 28.1 Hz). IR (THF) ν_{CO} 1927, 1861 cm^{-1}. Data for **3**: ^{1}H NMR (benzene-d_6) δ 4.12 (d, 5 H, C_5H_5, J_{P-H} = 2.0 Hz), 1.4 (m, 4 H), 1.1 (m, 2 H), 0.95 (d, 6 H, MnPMe_2, J_{P-H} = 8.5 Hz), 0.84 (d, 6 H, free PMe_2, J_{P-H} = 2.6 Hz). $^{13}C\{^1H\}$ NMR (benzene-d_6) δ 81.01 (s, C_5H_5), 37.29 (dd, MnPCH_2, J_{P-C} = 24.1, 10.8 Hz), 34.10 (t, MnPCH_2CH_2, J_{P-C} = 11.7 Hz), 20.86 (dd, MnP$CH_2CH_2CH_2$, J_{P-C} = 14.5, 0.7 Hz), 19.18 (d, MnPMe_2, J_{P-C} = 26.7 Hz), 14.04 (d, free PMe_2, J_{P-C} = 14.6 Hz). ^{31}P NMR (benzene-d_6) δ 56.0 (br, MnP), -53.6 (s, free P). IR (THF) ν_{CO} 1926, 1861 cm^{-1}.

(7) Data for **4**: ^{1}H NMR (benzene-d_6) δ 4.08 (t, 5 H, C_5H_5, J_{P-H} = 2.0 Hz), 2.8 (m, 2 H, CH^aCH^b), 1.29 (t, 6 H, Me^a, J_{P-H} = 4.6 Hz), 1.08 (t, 6 H, Me^b, J_{P-H} = 4.4 Hz). $^{13}C\{^1H\}$ NMR (benzene-d_6) δ 75.82 (s, C_5H_5), 54.95 (t, CH_2, J_{P-C} = 16.7 Hz), 22.45 (t, Me^a, J_{P-C} = 13.7 Hz), 21.51 (t, Me^b, J_{P-C} = 4.3 Hz). ^{31}P NMR (benzene-d_6) δ 34.78 (br). IR (heptane) ν_{CO} 1844 cm^{-1}. Data for **5**: ^{1}H NMR (benzene-d_6) δ 3.98 (t, 5 H, C_5H_5, J_{P-H} = 2.1 Hz), 1.34 (m, 6 H, Me^a), 1.22 (m, 2 H, CH^aCH^b), 1.08 (m, 2 H, CH^aCH^b), 0.88 (m, 6 H, Me^b). $^{13}C\{^1H\}$ NMR (benzene-d_6) δ 76.53 (s, C_5H_5), 31.55 (m, CH_2), 22.16 (m, Me^a), 20.87 (m, Me^b). ^{31}P NMR (benzene-d_6) δ 90.6 (br). IR (THF) ν_{CO} 1827 cm^{-1}. Anal. Calcd for $C_{12}H_{21}OMnP_2$: C, 48.34, H. 7.10. Found: C, 48.41, H, 6.89. Data for **6**: ^{1}H NMR (benzene-d_6) δ 3.98 (t, 5 H, C_5H_5, J_{P-H} = 2.1 Hz), 1.7 (m, 2 H, PCH_2CH_2), 1.35 (m, 4 H, PCH_2), 1.14 (t, 6 H, P$Me^a{}_2$, J_{P-H} = 4.1 Hz), 0.93 (t, 6 H, P$Me^b{}_2$), J_{P-H} = 3.7 Hz). $^{13}C\{^1H\}$ NMR (benzene-d_6) δ 77.79 (s, C_5H_5) 32.57 (dd, CH_2, J_{P-C} = 14.6, 15.5 Hz), 24.72 (dd, CH_2, J_{P-C} = 13.2, 14.1 Hz), 20.84 (dd, Me^a, J_{P-C} = 5.6, 6.3 Hz), 20.15 (t, Me^b, J_{P-C} = 1.3 Hz). ^{31}P NMR (benzene-d_6) δ 55.9 (br). IR (THF) ν_{CO} 1822 cm^{-1}. Anal. Calcd for $C_{13}H_{23}OMnP_2$: C, 50.03, H, 7.43. Found: C, 50.35, H, 7.50.

(8) Teixeira, G.; Avilẽs, T.; Dias, A. R.; Pina, F. *J. Organomet. Chem.* **1988**, *353*, 83-91.

(9) King, R. B.; RaghuVeer, K. S. *Inorg. Chem.* **1984**, *23*, 2482-2491.

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Table I. Quantum Yields (Φ), Thermal Yield (q), Enthalpies of Reaction (ΔH_{rxn}) and Strain Energy for the Photochemical Cyclizations of $CpMn(CO)_2(\eta^1\text{-}P\text{–}P)$ in Heptane Solution

	Φ^a	$q^{b,c}$	ΔH_{rxn},^{c,d} kcal/mol	strain
Mn–dmpm (**1**)	0.62	0.90	+13.9 ± 1.3	11.8 ± 2.3
Mn–dmpe (**2**)	0.60	0.98	+2.7 ± 1.9	~0
Mn–dmpp (**3**)	0.60	0.99	+1.6 ± 1.3	~0

[a] Errors in Φ are estimated to be ±10% for the cyclizations of **1** and **2**, and ±15% for the cyclization of **3**. [b] q is the fraction of absorbed photochemical energy which is returned as heat. Errors are nominally ±0.01. [c] Errors are one standard deviation of the scatter in the data. [d] ΔH_{rxn} is calculated from q, Φ, and $E_{h\nu}$. See ref 13.

of η^1-**3** was 0.60 and was determined by competition with η^1-**1**.[11] These results are presented in Table I. Clearly, the size of the nascent ring has little influence on the quantum yield of the ring-closure process. This observation is consistent with initial CO dissociation leading to the solvated η^1 intermediate **7** followed by cyclization with rate constant k_c. The lack of participation of the pendant phosphine ligand in the CO loss step is supported by the similarity of the quantum yields in these ring closures to the quantum yield for intermolecular substitution of CO in $CpMn(CO)_2PPh_3$ by PPh_3.[7] Dobson et al.[12] have studied cyclizations of photochemically generated intermediates and have found these to occur with rate constants on the order of 10^6 s^{-1} in "coordinating" solvents such as chlorobenzene. In heptane solution, the intermediate should be poorly stabilized by the solvent and should cyclize even more rapidly, perhaps as fast as 10^9 s^{-1} (vide infra).

The overall cyclization reactions involve cleavage of a Mn–CO bond followed by formation of a new Mn–P bond. The heat of the ring-closure reactions, ΔH_{rxn}, is given by eq 1 where $\Delta H_{Mn\text{–}P}$ and $\Delta H_{Mn\text{–}CO}$ are the enthalpies of formation of the Mn–P and

$$\Delta H_{rxn} = \Delta H_{Mn\text{–}P} - \Delta H_{Mn\text{–}CO} \qquad (1)$$

Mn–CO bonds, respectively. The heat of the ring-closure reactions was determined by photoacoustic calorimetry.[13,14] The results are given in Table I. Consistent with the mechanism for cyclization, the photoacoustic data obtained upon photolysis of η^1-**1**, -**2**, and -**3** could each be precisely modeled by a single rapid decay that occurred within 1 ns of the irradiation pulse. This corresponds to a cyclization rate constant (k_c) on the order of 10^9 s^{-1} or faster, irrespective of the ring size, which is consistent with poor solvation of η^1-**7** by the heptane solvent. Since the Mn–CO bonds which are cleaved are essentially identical in **1**, **2**, and **3**, the differences between ΔH_{rxn} for the different systems can be attributed to the differences in the bond enthalpy of the new Mn–P bond.[15] The ring strain incurred upon closure of the ring will affect this bond enthalpy directly. The similarity of ΔH_{rxn} for the five- and six-membered rings suggests that neither ring is significantly strained while the slight endothermicity is in accord with the observation that Mn–CO bonds are slightly stronger than Mn–P bonds in the closely related $CpMn(CO)_2L$ system.[16] In contrast to the five- and six-membered rings, closure of the four-membered ring is significantly endothermic. Using the average ΔH_{rxn} for the five- and the six-membered rings as a reference point for unstrained rings, the more positive ΔH_{rxn} for the four-membered ring is indicative of a strain energy of nearly 12 kcal/mol.

In analogy to Marks' work on thoracyclobutanes[1] and the known data on heterocarbocycles where the substitution of a second-row element in the ring markedly decreases the ring strain,[17] a smaller first-row transition metal in the ring is expected to impart greater strain to the system in comparison to second- and third-row transition metals. In this context, our observed 12 kcal/mol strain can be compared to Hoff's result of 8 kcal/mol for the Mo-bisphosphine system.[4] The difference in the strain in these two systems can be attributed to the relative size of the Mn and Mo centers.[18] Recognizing that in both Hoff's systems and our systems two phosphorus atoms are contained in the ring, we expect the strain in metallacyclobutanes containing three ring carbons

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(10) Actinometry was performed as described by: (a) Nasielski, J.; Colas, A. *J. Organomet. Chem.* **1975**, *101*, 215–219. (b) Gauglitz, G.; Hubig, S. *J. Photochem.* **1981**, *15*, 255–257; **1985**, *30*, 121–125.

(11) Reliable data for the extinction coefficients were difficult to obtain for η^1-**3**, making the actinometry less reliable. The competition experiment was found to be less sensitive to trace impurities.

(12) (a) Dobson, G. R.; Mansour, S. E.; Halverson, D. E.; Erikson, E. S. *J. Am. Chem. Soc.* **1983**, *105*, 5505–5506. (b) Dobson, G. R.; Dobson, C. B.; Mansour, S. E. *Inorg. Chem.* **1985**, *24*, 2179–2184; *Inorg. Chim. Acta* **1985**, *100*, L7–L8. (c) Dobson, G. R.; Dobson, C. B.; Halverson, D. E.; Mansour, S. E. *J. Organomet. Chem.* **1983**, *253*, C27–C32. (d) Dobson, G. R.; Basson, S. S.; Dobson, C. B. *Inorg. Chim. Acta* **1985**, *105*, L17–L19. (e) Dobson, G. R.; Bernal, I.; Reisner, G. M.; Dobson, C. B.; Mansour, S. E. *J. Am. Chem. Soc.* **1985**, *107*, 525–532. (f) Wermer, P. H.; Dobson, C. B.; Dobson, G. R. *J. Organomet. Chem.* **1986**, *311*, C47–C50.

(13) Irradiation of a heptane solution of sample at 337.1 nm is performed with an N_2 laser with a pulse width of 1 ns. The absorbance of the sample and references is ~0.300 and it is matched to within 3%. With a collimated laser output of 20 μJ the compound under study typically absorbs ~10 μJ per laser pulse. The excited state species relax via chemical reaction and/or by loss of vibrational energy as heat to the solution generating a photoacoustic signal (see ref 14). The detected amplitude of the photoacoustic signal is proportional to the amount of heat released following photolysis of a sample solution. The fraction of the absorbed photochemical energy which is released as heat is expressed as $q = S_{sample}/S_{ref}$, where S_{sample} is the amplitude of the signal from the sample being examined and S_{ref} is the amplitude of the signal from a reference compound which releases all absorbed photochemical energy as heat. S_{sample} and S_{ref} are collected in separate experiments. The total amount of heat absorbed by an endothermic reaction is given by $(1 - q)E_{h\nu}$. The enthalpy of reaction (ΔH_{rxn}) is calculated by correcting for the quantum yield of the reaction Φ according to the equation $\Delta H_{rxn} = (1 - q)E_{h\nu}/\Phi$. Deconvolution of the data into "fast" and "slow" components did not significantly improve the quality of the fit to the data. See: (a) Klassen, J. K.; Selke, M.; Sorensen, A. A.; Yang, G. K. *J. Am. Chem. Soc.* **1990**, *112*, 1267. (b) Klassen, J. K.; Selke, M.; Sorensen, A. A.; Yang, G. K. *ACS Symposium Series*; American Chemical Society: Washington, DC, 1990; No. 428 and references therein.

(14) Radiative decay processes are not observed in any of these systems. Fluorescence in the IR is expected to be rapidly quenched in solution. Bray, R. G.; Seidler, P. F.; Gethner, J. S.; Woodin, R. L. *J. Am. Chem. Soc.* **1986**, *108*, 1312–1314.

(15) One referee suggested that the photolysis of η^1-**1** is endothermic by 12 kcal/mol as a consequence of formation of the corresponding solvent coordinated intermediate **7** which cyclizes very slowly due to potential strain in the four-membered ring. If this were true, then the photoacoustic data are only a measure of the endothermicity of the formation of **7** from **1**. This possibility is not consistent with the known thermochemical data in related systems. The Mn–CO bond in $CpMn(CO)_3$ is ~46 kcal/mol stronger than the Mn–heptane bond in $CpMn(CO)_2$heptane. This would imply that formation of **7** should be endothermic by approximately 45 kcal/mol. Since the observed reaction is considerably more exothermic, much more energy needs to be recovered as heat on a very rapid time scale than is available by binding solely to heptane. The only mechanism for this to occur is to replace the bound solvent molecule by a phosphine ligand. Reaction of intermediate **7** with the free phosphine portion of η^1-**1** in an intermolecular fashion to yield dinuclear species can be ruled out with the following observation. With concentrations of the starting η^1-**1** complex of 0.5 mmol and with the expected bimolecular rate constant for reaction of intermediate **7** with phosphine (~10^7 L/(mol·s), the rate of reaction of **7** with η^1-**1** is expected to 5 × 10^3 s^{-1}. This is several orders of magnitude slower than known cyclizations (ref 12) and is much too slow to contribute to the photoacoustic signal. Thus, the only possible reaction that could be observed on the nanosecond time scale of the photoacoustic experiment that is sufficiently exothermic to account for the observed signals is rapid displacement of heptane from intermediate **7** to yield the cyclized products. See ref 13a,b for supporting data.

(16) Although Mn–L bond enthalpies in $CpMn(CO)(PR_3)L$ are not known, reported Mn–L bond enthalpies in $CpMn(CO)_2L$ indicate that displacement of CO from $CpMn(CO)_3$ by $P(n\text{-}Bu)_3$ to form $CpMn(CO)_2P(n\text{-}Bu)_3$ would be *endothermic* by ~4 kcal/mol. This is in agreement with the values of ΔH_{rxn} reported for the cyclizations of **2** and **3** and is consistent with little strain in the 5- and 6-membered rings. M. Selke, D. M. Hester, G. K. Yang, unpublished results. See also ref 13a,b.

(17) Benson, S. *Thermochemical Kinetics*; Wiley: New York, 1976.

(18) The $CpMn(CO)_2L$ system is clearly a pseudooctahedral system with CO–Mn–L and CO–Mn–CO bond angles of 90–92°; see: Barbeau, C.; Dichmann, K. S.; Ricard, L. *Can. J. Chem.* **1973**, *51*, 3027–3031. On this basis, comparison to square planar and octahedral systems seems reasonable. However, all of the four-membered-ring systems discussed in refs 1–4 and in this paper exhibit some degree of distortion from the ideal X–M–X bond angle. The relationship between the amount of distortion of the X–M–X bond angle from the ideal and the strain energy in the ring is a complex issue. At the present time, distorted X–M–X bonds can at best be used as a qualitative indication of strain. See refs 1–4 and also: (a) Ibers, J. A.; DiCosimo, R.; Whitesides, G. M. *Organometallics* **1982**, *1*, 13–20. (b) Bruno, J. W.; Smith, G. M.; Marks, T. J.; Fair, C. K.; Schultz, A. J.; Williams, J. M. *J. Am. Chem. Soc.* **1986**, *108*, 40–56 and references therein. (c) Bruno, J. W.; Marks, T. J.; Day, V. W. *Ibid.* **1982**, *104*, 7357–7360. (d) Fild, M.; Handke, W. *Z. Naturforsch.* **1980**, *35b*, 838–842. (e) Cheung, K. K.; Lai, T. F.; Mok, K. S. *J. Chem. Soc., A* **1971**, 1644–1647.

to be even greater. It is difficult to quantitatively predict the net effect that changing the size of the atoms in the ring will have on the strain, yet it is evident that four-membered rings containing a first-row transition-metal center have a significant amount of strain.

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Highly Enantioselective Epoxidation Catalysts Derived from 1,2-Diaminocyclohexane[†]

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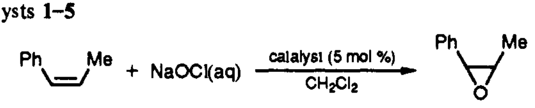
Enantioselective epoxidation of simple olefins constitutes a challenging and important synthetic problem, and chiral salen-based complexes have recently emerged as promising catalysts for these reactions.[1] Readily available Mn(III) complexes such as **1** catalyze alkene epoxidation by bleach (NaOCl) in good yield and with higher selectivity than any other reported synthetic catalysts. However, while ee's above 70% are obtained in the epoxidation of a variety of cis olefins by **1** and related catalysts, selectivities of genuine synthetic value are not generally attainable with such 1,2-diaryldiamine-derived systems. We describe herein a new, highly enantioselective epoxidation catalyst **5** (>90% ee for several substrates, Table I), which was developed through a logical sequence of ligand modifications.

Side-on perpendicular approach of the alkene to the metal–oxo bond of a high valent intermediate has been invoked to account for both the sense and degree of enantioselectivity displayed by chiral salen and porphyrin complexes with cis olefins.[1a,2] In this context, two structural features of **1** are crucial to its selectivity: (1) the presence of bulky groups to prevent substrate approach away from the diimine bridge (approach c, Figure 1a) and (2) the dissymmetry of the diimine bridge, which disfavors attack from the side syn to the phenyl group (approach b), but leaves accessible approach anti to the phenyl group (approach a). Approach d is presumably disfavored due to the steric bulk of the diimine bridge. The enantioselectivity in the epoxidation of every cis olefin we have examined can be explained within this general model.

Axially locked substituents on the diimine bridge might lead to more effective differentiation of approaches a and b, and with this in mind we prepared catalysts from *trans*-1,2-diamino-1,2-dimethylcyclohexane.[3] Disappointingly, the corresponding salen derivative **2** exhibited only moderate enantioselectivity in the epoxidation of *cis*-β-methylstyrene (Table I, entry 2). More surprisingly, the sense of asymmetric induction proved to be the opposite of that predicted from approach a in Figure 1b. This result suggested that **2**, which is less hindered than **1** in the vicinity of the diimine bridge, might undergo competitive attack from approach d.

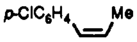
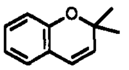
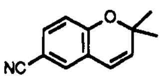
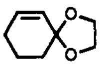
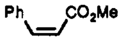
Table I. Asymmetric Epoxidation of *cis*-β-Methylstyrene with Catalysts **1–5**



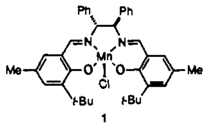
entry	catalyst	yield,[a] %	ee, %	epoxide confign
1	(*R*,*R*)-**1**	88	84	1*R*,2*S*-(+)
2	(*S*,*S*)-**2**	54	49	1*S*,2*R*-(−)
3	(*S*,*S*)-**3**	87	80	1*S*,2*R*-(−)
4	(*S*,*S*)-**4**	56	55	1*S*,2*R*-(−)
5	(*S*,*S*)-**5**	81	92	1*S*,2*R*-(−)

[a] Determined by GC by integration against an internal quantitative standard.

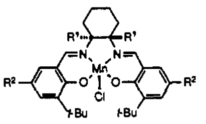
Table II. Asymmetric Epoxidation of Representative Olefins by Catalyst **5**[a]

entry	olefin	epoxide yield,[b] %	ee,[c] %	equiv of **5** required for complete reactn
1		84	92	0.04
2		67	92	0.04
3		72	98	0.02
4		96	97	0.03
5		63	94	0.15
6[d]		65[e]	89	0.10

[a] Reactions were run at 4 °C according to the general procedure outlined in ref 4. [b] Isolated yields based on olefin unless otherwise indicated. [c] Determined by analysis of the isolated epoxides by ^1H NMR in the presence of Eu(hfc)$_3$ and by capillary GC using a commercial chiral column (J & W Scientific Cyclodex-B column, 30 m × 0.25 mm i.d., 0.25-μm film). All reactions were run in duplicate with both enantiomers of **5**, and ee values were reproducible to ±2%. [d] Reaction carried out in the presence of 0.4 equiv of 4-phenylpyridine *N*-oxide. [e] Yield determined by GC.



1



2: $R^1 = Me$, $R^2 = Me$
3: $R^1 = H$, $R^2 = Me$
4: $R^1 = Me$, $R^2 = t\text{-}Bu$
5: $R^1 = H$, $R^2 = t\text{-}Bu$

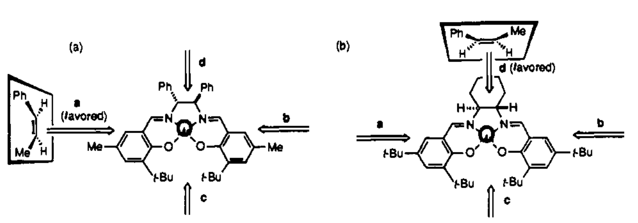


Figure 1.

This was supported by the observation that **3**, which is less hindered yet, also afforded the unexpected enantiomer of *cis*-β-methylstyrene and with a higher ee than **2** (entry 3). Introduction of a second set of *tert*-butyl groups para to the salen oxygens as in **5** resulted in a further improvement in catalyst selectivity, presumably by strongly disfavoring all side-on olefin approaches with the exception of approach d. Face selectivity within the latter approach may be attributed to the larger substituent on the substrate being directed away from the axial hydrogen on the bridge.

As illustrated in Table II, catalyst **5** displays high enantioselectivity with a variety of cis-disubstituted alkenes.[4] Several

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[†] This paper is dedicated with deep respect to Professor K. Barry Sharpless on the occasion of his 50th birthday.

(1) (a) Zhang, W.; Loebach, J. L.; Wilson, S. R.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1990**, *112*, 2801. (b) Zhang, W.; Jacobsen, E. N. *J. Org. Chem.* **1991**, *56*, 2296. See also: Irie, R.; Noda, K.; Ito, Y.; Katsuki, T. *Tetrahedron Lett.* **1991**, *32*, 1055.

(2) (a) Groves, J. T.; Myers, R. S. *J. Am. Chem. Soc.* **1983**, *105*, 5791. (b) Groves, J. T.; Viski, P. *J. Org. Chem.* **1990**, *55*, 3628.

(3) Zhang, W.; Jacobsen, E. N. *Tetrahedron Lett.* **1991**, *32*, 1711.

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