site in compounds such as **2** is built into the leaving group, this sort of strategy can in principle provide catalytic rate enhancement for the formation of amides by reaction of esters with widely varying acyl structures. Whether this generality will extend to structurally sensitive analogues of **2**, such as those required in peptide synthesis, ultimately depends on the mechanism of the reactions discussed above. Three types of mechanisms have been proposed for metal ion catalyzed acyl substitution processes;[9] all three have been postulated or demonstrated for several of the reactions studied in detail.[1-7] Mechanisms involving activation at the carbonyl oxygen or leaving-group oxygen of substrates such as **2** would likely lead to racemization of amino acid or peptide analogues of **2**.[18,19] On the other hand, a mechanism involving intracomplex transfer of a coordinated amine to the ester moiety should be less conducive to such racemization. With these considerations in mind, we are continuing study of **2**, as well as related compounds.

Acknowledgment. Support of this research by Research Corporation and the Furman University Research and Professional Growth Committee is gratefully acknowledged.

---

(18) A number of groups have described aminolyses of amino acid esters coordinated at Co(III) through the ester carbonyl oxygen. See, for example: Buckingham, D. A.; Dekkers, J.; Sargeson, A. M. *J. Am. Chem. Soc.* **1973**, *95*, 4173. Lability of the α hydrogens of such coordinated amino acid esters is a serious complication in their potential synthetic utility: Collman, J. T.; Kimura, E. *J. Am. Chem. Soc.* **1967**, *89*, 6096.

(19) Metal-ion catalysis of the enolization of 2-acetylpyridine is thought to involve coordination of the carbonyl oxygen of that substrate: Cox, B. G. *J. Am. Chem. Soc.* **1974**, *96*, 6823.

Homogeneous Asymmetric Catalysis: Structural Studies of Catalytic Intermediates Using Extended X-ray Absorption Fine Structure

B. Ray Stults,* Robert Mark Friedman,* Karl Koenig, and William Knowles

Corporate Research and Development Staff
Monsanto Company
Saint Louis, Missouri 63166

Robert B. Greegor and Farrel W. Lytle

Boeing Company
Seattle, Washington 98124

Received January 22, 1981
Revised Manuscript Received April 14, 1981

Optically active rhodium complexes function as very effective catalysts for the asymmetric hydrogenation of prochiral olefins such as α-acyl- or α-(benzoylamino)cimmamic acid.[1-7] In recent years, a number of cationic rhodium complexes with various phosphine ligands have been prepared, and, when employed as catalysts, they have been reported to yield products with enantiomeric excesses as high as 99%.[6c] Conjointly with studies of the catalytic chemistry of these systems, a number of groups have been investigating the mechanistic aspects of the asymmetric hydrogenation reactions.[2-8] Our most recent efforts have focused on the mechanism of asymmetric induction for systems of the general formulations $Rh(P-P)L^+X^-$[9] and $Rh(P)_2L^+X^-$[9] by using X-ray crystallography, ^{13}C and ^{31}P solution NMR spectroscopy, and solid-state ^{13}C NMR spectroscopy.[10] Our work combined with that of others has yielded the proposed mechanism for asymmetric hydrogenation[10a] shown in Figure 1. The present report describes our recent work using X-ray absorption spectroscopy and, in particular, the extended X-ray absorption fine structure (EXAFS) to investigate under simulated reaction conditions the various intermediate catalytic species depicted in Figure 1.

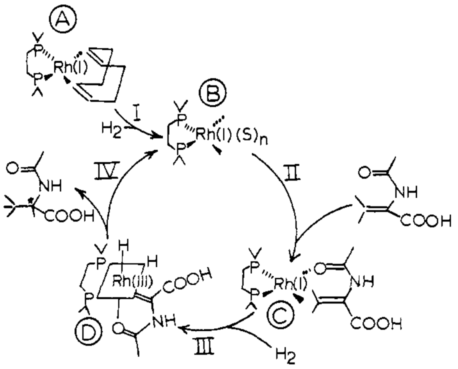


Figure 1. Proposed catalytic cycle for asymmetric hydrogenation.

Our interest in using EXAFS to study these homogeneous catalysts is twofold. First, we want to obtain structural information about the various intermediate species shown in Figure 1. EXAFS is a remarkable technique in its capability to provide this direct structural information on molecules in solution. This would allow us to compare the detailed crystallographic description of the material isolated in the solid state with the species actually present in its catalytically active phase, i.e., solution. Secondly, we want to evaluate the general potential of EXAFS for studying chemical reactions in solution. We are interested in determining the sensitivity of EXAFS to differing species in solution, present separately and concurrently, and the accuracy of the structural parameters derived from solution EXAFS. While there are numerous literature reports on EXAFS studies of heterogeneous catalysts[11] and reports on studies of single species in solution,[12] the present report describes the first attempts to study homogeneous catalysis, i.e., the identification of intermediate species

---

(1) (a) Morrison, J. D.; Mosher, H. S. "Asymmetric Organic Reactions"; Prentice Hall: Englewood Cliffs, NJ, 1971. (b) Morrison, J. D.; Mailer, W. F.; Neuberg, M. K. *Adv. Catal.* **1976**, *25*, 81. (c) Valentine, D., Jr.; Scott, J. W. *Synthesis* **1978**, 329.

(2) Vineyard, B. D.; Knowles, W. S.; Sabacky, M. J.; Bachman, G. K.; Weinkauff, D. J. *J. Am. Chem. Soc.* **1977**, *99*, 5946.

(3) Knowles, W. S.; Sabacky, M. J.; Vineyard, B. D.; Weinkauff, D. J. *J. Am. Chem. Soc.* **1975**, *97*, 2567.

(4) (a) Knowles, W. S.; Sabacky, M. J.; Vineyard, B. D. *J. Chem. Soc., Chem. Commun.* **1973**, 1912. (b) *Ann. N.Y. Acad. Sci.* **1973**, *214*, 119. *Adv. Chem. Ser.* **1974**, No. *132*, 274.

(5) (a) Kagan, H. B.; Dang, T. P. *J. Chem. Soc., Chem. Commun.*, **1971**, 481. (b) Kagan, H. B.; Dang, T. P. *J. Am. Chem. Soc.* **1972**, *44*, 6429. (c) Gelbard, G. H.; Kagan, H. B.; Stern, R. *Tetrahedron* **1976**, *32*, 233. (d) Kagan, H. B.; Langlois, N.; Dang, T. P. *J. Organomet. Chem.* **1975**, *90*, 353. (e) Sinou, D.; Kagan, H. B. *J. Organomet. Chem.* **1976**, *114*, 325.

(6) (a) Achiwa, K. *J. Am. Chem. Soc.* **1976**, *98*, 8625. (b) Florini, M.; Giongo, G. N.; Marcoti, F.; Marconi, W. *J. Mol. Catal.* **1975**, *1*, 451. (c) Fryzuk, N. D.; Bosrich, B. *J. Am. Chem. Soc.* **1977**, *99*, 6262. (d) Grubbs, R. H.; Devries, R. A. *Tetrahedron Lett.* **1977**, 1879.

(7) Tamao, K.; Yamamato, H.; Matsumoto, H.; Miyoke, N.; Hayachi, T.; Kumada, M. *Tetrahedron Lett.* **1977**, 1389.

(8) (a) Brown, J. M.; Chalonier, P. A. *Tetrahedron Lett.* **1978**, 1988. (b) Brown, J. M.; Chalonier, P. A.; Nicholson, D. N. *J. Chem. Soc., Chem. Commun.* **1978**, 646. (c) Halpern, J.; Riley, D. D.; Chan, A. S. C.; Pluth, J. J. *J. Am. Chem. Soc.* **1977**, *99*, 8055. (d) Halpern, J. *Trans Am. Crystallogr. Assoc.* **1978**, *14*, 59.

(9) Ligand abbreviations: P-P is diPAMP = (*R*,*R*)-1,2-ethanediylbis-[(*o*-methoxyphenyl)phenylphosphine], DIOP = (*R*,*R*)-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane, diPHOS = bis(1,2-diphenylphosphino)ethane, *cis*-ethylene = *cis*-bis(diphenylphosphino)ethylene; P is CAMP = (*R*)-*o*-anisylmethylcyclohexylphosphine; L = 1,5-cyclooctadiene or bicyclo[2.2.1]heptadiene.

(10) (a) Knowles, W. S.; Vineyard, B. D.; Sabacky, M. J.; Stults, B. R. *Fundam. Res. Homogeneous Catal.*, [*Proc. Int. Workshop*] **1979**, *3*, 537. (b) Stults, B. R. "EXAFS and Single-Crystal Studies of Asymmetric Homogeneous Catalysis"; American Chemical Society/Chemical Society of Japan Chemical Congress, Honolulu, HI, 1979.

(11) See, for example: (a) Via, G. H.; Sinfelt, J. H.; Lytle, F. W., *J. Chem. Phys.* **1979**, *71*, 690 and references cited therein. (b) Sandstrom, D. R.; Lytle, F. W. *Ann. Rev. Phys. Chem.* **1979**, 30.

(12) (a) Sandstrom, D. R.; Doden, H. W.; Lytle, F. W. *J. Chem. Phys.* **1977**, *67*, 473. (b) Eisenberger, P.; Kincaid, B. M. *Chem. Phys. Lett.* **1975**, *36*, 134. (c) Fontaine, A.; Lagarde, P.; Raoux, D.; Fontana, D.; Maisano, M. P.; Migliardo, G.; Wanderlingh, P. *Phys. Rev. Lett.* **1978**, *41*, 504. (d) Morrison, T. I.; Reis, A. H.; Knapp, G. S.; Fradin, F. Y.; Chen, H.; Kilppert, T. E. *J. Am. Chem. Soc.* **1978**, *100*, 3262.

0002-7863/81/1503-3235$01.25/0

Table I. Bond Distances from Least-Squares Fits to Rhodium Catalysts EXAFS Spectra

		av distances, Å		
			EXAFS	
compd[a]		single-crystal X-ray	solid state	soln
Rh(diPHOS)COD$^+$[e]	Rh–P[b]	2.28	2.29	2.33
	Rh–C	2.25	2.22	2.32
Rh(diPAMP)COD$^+$[e]	Rh–P[b]	2.27	2.28	2.28
	Rh–C	2.20	2.22	2.34
Rh(diPHOS)Ac[h,i]	Rh–P[c]	2.27	2.27	
	Rh–P	2.23	2.23	
	Rh–C	2.22	2.28	
	Rh–O	2.11	2.12	
Rh(diPAMP)Ac$^+$[i]	Rh–P[c]		2.29	
	Rh–P		2.26	
	Rh–C		2.28	
	Rh–O		2.01	
Rh(diPAMP)$_2$[g]	Rh–P[d]	2.31 (diPHOS)	2.30	2.29
Rh(AcAc)$_3$[f]	Rh–O[d]	1.99	2.03	2.07
Rh(DIOP)NBD$^+$[c]	Rh–P[b]	2.30	2.29	2.34
	Rh–C	2.22	2.19	2.36
Rh(CAMP)$_2$COD$^+$[e]	Rh–P[b]	2.35	2.32	2.34
	Rh–C	2.20	2.10	2.30
Rh(*cis*-ethylene)-COD$^+$[e]	Rh–P[b]	2.26	2.27	2.34
	Rh–C	2.26	2.26	2.30

[a] See ref 9 for ligand abbreviations. [b] Two unique atom fit. [c] Four unique atom fit. [d] One unique atom fit. [e] X-ray crystallographic results: this work. See ref 10a,b. [f] For X-ray crystallographic results, see: Morrow, J. K.; Parker, E. B. *Acta Crystallogr., Sect. B* 1973, *B29*, 1145. AcAc is the acetylacetonate anion. [g] For X-ray crystallographic results, see: Hall, M. C.; Kilbourn, B. T.; Taylor, K. A. *J. Chem. Soc. A* 1970, 2540. [h] See ref 14. [i] Ac is α-(acylamino)cinnamic acid.

prepared in situ under simulated reaction conditions.

Rhodium K-edge absorption data were recorded at the Stanford Synchrotron Radiation Laboratory. Data for both the solids and the solutions were recorded in the transmission mode by using standard procedures. The solution EXAFS data were obtained by using a special glass cell having a 5-cm path length between Mylar windows. The cell was designed to allow either H_2 or N_2 to be bubbled through the solution while it was being magnetically stirred. At the appropriate time (step II in Figure 1), solutions containing the substrate were added by syringe injection through a septum stopper. Solvents were degassed prior to addition of the catalyst, and an oxygen-free atmosphere was maintained throughout the reaction cycle. The data were processed using procedures outlined by Sandstrom.[11b,13] The values of the structural parameters reported in Table I for the first shell environments were obtained by least-squares fitting of the back-transformed, Fourier-filtered data. The input parameters used in the least-squares fitting were obtained from analysis of model crystalline compounds: $Rh[P(C_6H_5)_3]_3Cl$ (Wilkinson's catalyst), Rh(*cis*-ethylene)COD$^+BF_4^-$, and Rh_2O_3. The various amplitude and phase shift coefficients[13] for Rh, P, O, C, and Cl were laboriously varied until one uniform set of parameters for each atom type could be used to gain acceptable agreement with the crystallographic parameters for the collective group of model compounds. During the least-squares fitting for the unknown compounds, only the coordination number, N, interatomic distance, R, and pseudo Debye–Waller dampening factor, σ, were varied.

The results of these EXAFS studies can be described relative to three areas: (1) comparisions of the structural parameters derived from EXAFS with the parameters determined by X-ray crystallography, (2) comparisons of the structural parameters derived from solid-state and solution EXAFS, and (3) studies of the catalyst intermediates in solution. A comparison of the first shell coordination environments about the rhodium atoms as derived from X-ray crystallography, solid-state EXAFS, and solution EXAFS is given in Table I. The distances from the solid-state EXAFS studies are in good agreement with crystallographic results. The accuracy of the Rh–X distances are in the range ±0.02 Å. Single crystals of the compound Rh(diPAMP)Ac$^+$ were not obtained in spite of repeated attempts to grow them. However, on the basis of the solid-state EXAFS results, the coordination environment for Rh(diPHOS)Ac$^+$ and Rh(diPAMP)Ac$^+$ are viewed as being essentially the same. Generally good agreement was obtained between the solid-state and solution EXAFS data. The accuracy of the bond distances from the solution data is of the order ±0.07 Å. The lower accuracy of these values arises in part from the lack of data in the high k region, a probable consequence of vibrational dampening. In solution very little data is obtained above $k = 14$ Å^{-1}, whereas in the solid state the data extends beyond $k = 18$ Å^{-1}. A general increase in the Rh–P and Rh–C bond distances is seen on going from solids to their corresponding solutions. This might reflect relaxation of the crystal packing forces or a failure of our fitting parameters (which were derived from solid-state data) to adequately describe the solution EXAFS data or a combination of both effects.

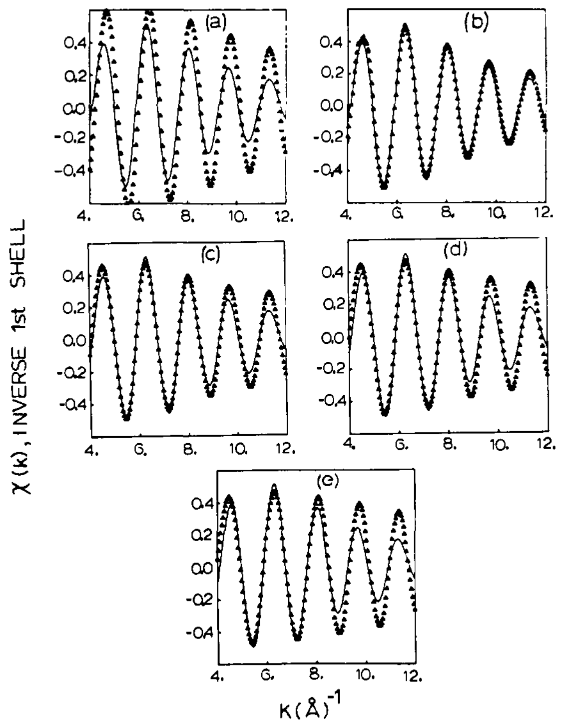


Figure 2. Solid curves: Fourier-filtered EXAFS spectrum for Rh(CAMP)$_2^+$ in methanol. Triangles: Two unique atom fits to the solid curves. All fits include contributions from two phosphorus atoms plus in (a) one oxygen atom, (b) two oxygen atoms, (c) three oxygen atoms, (d) four oxygen atoms, and (e) five oxygen atoms.

The primary focus of our work by using EXAFS was to determine the structural parameters for the catalyst intermediates under simulated reaction conditions. Limitations in available beam time at Stanford Synchrotron Radiation Laboratory precluded as complete an investigation of this area as we desired, but the initial measurements look very promising. We have determined the first shell coordination environment for species B (Figure 1) when the phosphine ligand is diPAMP or CAMP. The data were recorded after bubbling H_2 through the catalyst solution for approximately 30 min, followed by bubbling N_2 to remove the excess H_2. The first shell coordination environment about the rhodium atoms consists of two phosphorous atoms and two oxygen atoms presumably from coordinated solvent methanol. Figure 2 illustrates the comparison between the best fits for the back-transformed, Fourier-filtered experimental data with the calculated EXAFS data for different number of oxygen atoms bonded along with two phosphorus atoms to the rhodium. The solid lines are the experimental data, and the triangles are the calculated curves for the various numbers of oxygen atoms described in the figure

---

(13) Sandstrom, D. R. *J. Chem. Phys.* **1979**, *71*, 2381.

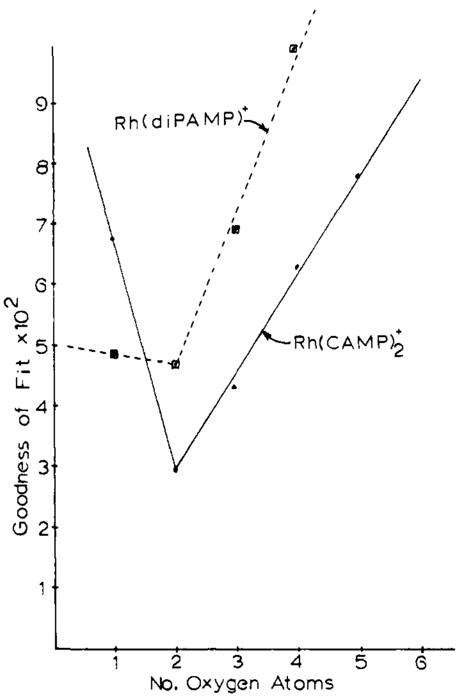
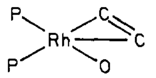


Figure 3. Plots of the goodness of fit from a two unique atom least-squares fit vs. the number of oxygen atoms in the fit. For all fits two phosphorus atom contributions were included.

caption. Plots showing the goodness of fit (derived from the data shown in Figure 2) vs. the number of oxygen atoms are presented in Figure 3. Both Figures 2 and 3 show that force fitting the data with different numbers of oxygen atoms resulted in the best fit when two oxygen atoms and two phosphorus are bonded to the rhodium.

Our final analysis used fixed integral values for the coordination numbers of the different ligands. Although an attempt to simultaneously vary N and σ resulted in similar results, these parameters may be highly correlated in the nonlinear least-squares procedure, and the effect of this coupling leaves undetermined the accuracy of the values acquired by general parameter variation.

The derived coordination distances for the Rh(diPAMP)$(CH_3OH)_2^+$ species are Rh–P = 2.34 and Rh–O = 2.34 Å, and for Rh(CAMP)$_2(CH_3OH)_2^+$ the distances are Rh–P = 2.35 and Rh–O = 2.36 Å. Data have been obtained and analyzed for species C in Figure 1 where the phosphorous ligand was diPAMP. When the substrate [α-(acylamino)cinnamic acid, Ac] was added to the methanol solvated species, Rh(diPAMP)$(CH_3OH)_2^+$, the following structural parameters were obtained: Rh–P$_1$ = 2.36, Rh–P$_2$ = 2.29, Rh–C = 2.26, and Rh–O = 1.86 Å. There are two distinct Rh–P distances, one being trans to an oxygen and one trans to the olefin. This square-planar arrangement is supported by the X-ray structural analysis of Halpern et al.[14] The coordination environment about the rhodium is



The Rh–C and Rh–P distances derived from the EXAFS data for the in situ prepared catalyst–substrate complex agree favorably with the values for the crystalline Rh(diPAMP)Ac$^+$ compound in Table I. The short Rh–O distance of 1.86 Å compared to 2.0 Å for the crystalline compounds is surprising and may not be valid. However, recent experimental observations[15] indicate differences between the crystalline Rh(diPAMP)Ac$^+$ and the in situ active catalytic species in solution. More EXAFS data for other rhodium–phosphine–substrate complexes is needed to verify the short Rh–O distance.

The sensitivity of EXAFS data to different species in solution is illustrated in the following experiment. When the catalyst substrate was added to the disolvated species, Rh(CAMP)$_2(CH_3OH)_2^+$ (CAMP is a monodentate ligand), no reasonable information pertaining to the catalyst–substrate complex was obtained. Attempts to fit the data as either the disolvated species or some reasonable catalyst–substrate complex resulted in diverging least-squares refinements. Numerous attempts to refine these data were unsuccessful. In hindsight, this was to be expected. From NMR experiments we now know that when the phosphine ligands are monodentate, as for CAMP, rapid isomerization occurs in solution. This isomerization is not possible for bidentate ligands such as diPAMP. At best we would expect a mixture of three or four different species in solution after the substance was added. The fact that we were unable to force fit this data is important in illustrating the sensitivity of EXAFS data to different species in solution.

In summary, our work with the asymmetric rhodium catalysts has shown EXAFS to be a valuable tool for studying homogeneous catalysis. We obtained good agreement between the structural parameters determined by EXAFS and X-ray crystallography. Our work demonstrates that useful information pertaining to the identity and structural parameters for solutions may be obtained from EXAFS. A word of caution to be stressed is that one needs to have very good model compounds whose structures are known in order to distinguish subtle differences between species by using EXAFS.

Our continued work in this area emphasizes obtaining data on other catalyst intermediates for complexes with several different phosphine ligand systems (Figure 1). Amelioration of the facilities at Stanford Synchrotron Radiation Laboratory through expansion and improvements hopefully will increase access for these data collection in the near future.

Acknowledgment. Some of the material incorporated in this work was developed at the Stanford Synchrotron Radiation Laboratory which is supported by the National Science Foundation (under Contract DMR-27489), in cooperation with SLAC and the Department of Energy.

---

[14] Chan, A. S. C.; Pluth, J. J.; Halpern, J. *Inorg. Chem. Acta.* **1979**, *37*, 477.

[15] (a) Chan, A. S. C.; Halpern, J. *J. Am. Chem. Soc.* **1980**, *102*, 839. (b) Chan, A. S. C.; Pluth, J. J.; Halpern, J. *Ibid.* **1980**, *102*, 5952.

Tetraanion of 1,1-Dimethyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene

Daniel H. O'Brien* and David L. Breeden

Department of Chemistry, Texas A&M University
College Station, Texas 77843

Received February 26, 1981

The alkali metal reduction of phenyl-substituted silacyclopentadienes **1** and **2** have been followed with electron spin resonance spectroscopy.[1] Monitoring the reactions with ultraviolet spectroscopy showed that further reduction leads to the disappearance of the anion radical spectrum and the appearance of a new UV spectrum attributed to the dianion. The presence of the dianion of **2** was also shown by aqueous quenching and the isolation of *cis*-dibenzylstilbene and poly(dimethylsiloxane).[2] The reduction of **2** showed the formation of another anionic species past the dianion stage, but this new species could not be identified from the UV evidence.[1] We report here the carbon-13 characterization of this species as the highly charged tetraanion $\mathbf{2}^{4-}$ (eq 1).

---

[1] Janzen, E. G.; Pickett, J. B.; Atwell, W. H. *J. Organomet. Chem.* **1967**, *10*, P6–P8.

[2] Balasubramanian, R.; George, M. V. *J. Organomet. Chem.* **1975**, *85*, 311–316.