AD-A164 058 DIASTEREOSELECTION AND THE INFLUENCE OF CHIRAPHOS ON METAL-CENTERED CHIRA..(U) ROCHESTER UNIV NY DEPT OF CHEMISTRY A J KUNIN ET AL. 20 JAN 86 TR-9 1/1

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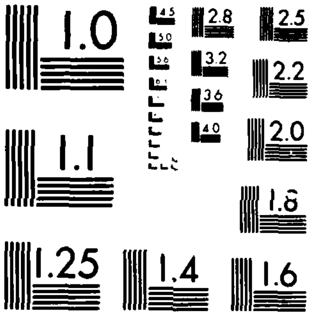

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Task No. NR 634-742

TECHNICAL REPORT NO. 9

Diastereoselection and the Influence of Chiraphos on Metal-Centered Chirality in Cis Oxidative Addition of Hydrogen and Triphenylsilane

by

Amanda J. Kunin, Ramy Farid, Curtis E. Johnson and Richard Eisenberg*

Prepared for Publication

in the

Journal of the American Chemical Society

University of Rochester
Department of Chemistry
Rochester, NY 14627

January 20, 1986

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		**READ INSTRUCTIONS BEFORE COMPLETING FORM**
1. REPORT NUMBER 9	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Diastereoselection and the Influence of Chiraphos on Metal-Centered Chirality in Cis Oxidative Addition of Hydrogen and Triphenylsilane		5. TYPE OF REPORT & PERIOD COVERED Interim Technical Report
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Amanda J. Kunin, Ramy Farid, Curtis E. Johnson and Richard Eisenberg		8. CONTRACT OR GRANT NUMBER(s) N00014-83-K-0154
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Chemistry University of Rochester Rochester, New York 14627		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR 634-742
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Department of the Navy Arlington, Virginia 22217		12. REPORT DATE January 20, 1986
		13. NUMBER OF PAGES 8
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

This document has been approved for public release and sale; its distribution is unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

Prepared for publication in Journal of the American Chemical Society

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Oxidative addition; Stereoselectivity; H_2 activation; silane; iridium; chirality

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The complex IrBr(CO)(chiraphos), chiraphos = 2S,2S-bis(diphenylphosphino)butane, has been prepared, and its oxidative addition reactions with H_2 and Ph_3SiH have been studied. The reaction with H_2 proceeds under kinetic control forming an initial pair of diastereomers in a 2:1 ratio followed by isomerization to a second, more stable pair of diastereomers which commence to form in a 2.4:1 ratio but exist at equilibrium in a 1.3:1 ratio. The kinetic differentiation observed for each pair of diastereomers results from the influence of chiraphos on the developing chirality at the metal center as the cis oxidative addition proceeds. A reaction coordinate diagram for the system is developed based on the observed kinetic and thermodynamic differentiations of the diastereomers. The oxidative addition of Ph_3SiH also takes place under kinetic control followed by isomerization. A 12:1 kinetic differentiation in the formation of the stable silyl hydride diastereomers occurs at 25° C due solely to the presence of chiraphos.

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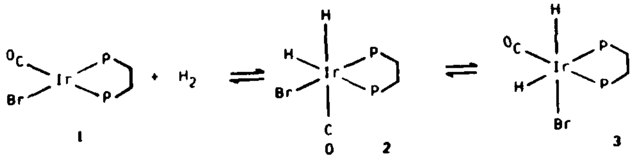
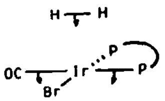
Abstract: The complex IrBr(CO)(chiraphos), chiraphos = 2S,3S-bis-(diphenylphosphino)butane, has been prepared, and its oxidative addition reactions with H_2 and Ph_3SiH have been studied. The reaction with H_2 proceeds under kinetic control forming an initial pair of diastereomers in a 2:1 ratio followed by isomerization to a second, more stable pair of diastereomers which commence to form in a 2.4:1 ratio but exist at equilibrium in a 1.3:1 ratio. The kinetic differentiation observed for each pair of diastereomers results from the influence of chiraphos on the developing chirality at the metal center as the cis oxidative addition proceeds. A reaction coordinate diagram for the system is developed based on the observed kinetic and thermodynamic differentiations of the diastereomers. The oxidative addition of Ph_3SiH also takes place under kinetic control followed by isomerization. A 12:1 kinetic differentiation in the formation of the stable silyl hydride diastereomers occurs at 25° C due solely to the presence of chiraphos.

In the stereoselective, kinetically controlled oxidative addition of H_2 to IrBr(CO)(dppe), 1, (dppe = bis(diphenylphosphino)ethane),[1] both the kinetic isomer 2 and the thermodynamic isomer 3 form as racemates resulting from H_2 approach to the metal center from above and below the Ir(I) square planar complex. This is illustrated for 2 as a and b with H_2 aligned parallel



1 2 3 (1)

to the P-Ir-CO axis of complex 1; formation of 3 proceeds similarly with H_2 parallel to P-Ir-X. In this communication, we describe studies in which the



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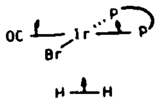


b

optically active diphosphine chiraphos, (2S,3S-bis(diphenylphosphino)butane),[2] is used in place of dppe leading to kinetic and thermodynamic differentiation of the racemic products of H_2 and Ph_3SiH oxidative addition. While the use of chiral diphosphines as catalysts for asymmetric hydrogenation has been widely investigated,[3,4] the present work represents the first study in which the effect of chiraphos on simple oxidative addition has been examined.

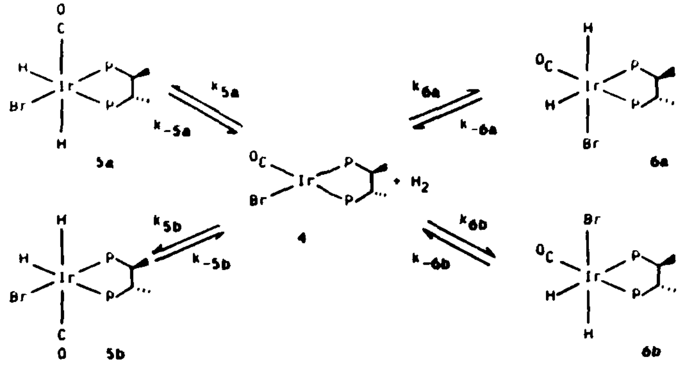
The complex IrBr(CO)(chiraphos), 4, prepared analogously to 1,[1a] reacts with H_2 in acetone similarly to eqn (1) forming first diastereomers 5a and 5b with >99.5 % stereoselectivity followed by slower formation of the more stable pair of diastereomers 6a and 6b. Figure 1 shows the hydride region of the ^1H NMR spectrum upon initial oxidative addition and subsequent isomerization, and NMR data for the diastereomers are summarized below.[5] At -25° C, the kinetic diastereomers 5 form in a 2.1:1 ratio which remains constant for extended periods of time, but on warming to room temperature, changes within 5 min to 1.2:1 as the thermodynamic diastereomers **6** start to grow in. The isomerization of **5** to **6** follows first order kinetics with a rate constant for the disappearance of **5a** at 35° C of 4.9×10^{-5} s^{-1}. During early stages of the isomerization the observed ratio of **6a**:**6b** is 2.4:1, while at equilibrium the ratio is 1.3:1 with diastereomers **6** comprising 85% of the total hydride species present. At equilibrium, the ratio of **6a**:**5a** is 7.2:1.

To establish that the initial ratio of 2.1:1 seen for **5** at -25° C corresponds to kinetic differentiation of the diastereomers, **5** was formed at low temperature followed by replacement of H_2 by D_2. After 1 hr at -25° C the amount and ratio of diastereomers of **5** showed no change, but upon warming to room temperature the hydride resonances rapidly diminished and disappeared within 1 hr, following first order kinetics with a rate constant of 3.3×10^{-3} s^{-1} for diastereomer **5a**.

The experiments outlined above show that in addition to the stereoselective, kinetically-controlled H_2 oxidative addition originally seen in eqn (1), diastereoselection for **5** and **6** occurs due solely to the influence of chiraphos on the developing chirality at the metal center as the cis oxidative addition proceeds. The kinetic differentiation expressed as $\Delta\Delta G^{\ddagger}$ for **5a**:**5b** and **6a**:**6b** is 0.40 and 0.50 kcal/mole, respectively. From the experiment under D_2, we see that reductive elimination of H_2 from **5** is rapid at room temperature, indicating that equilibrium between **5a** and **5b** is established prior to isomerization to **6**, and suggesting that the mechanism for isomerization involves reductive elimination to generate **4** followed by oxidative addition with H_2 parallel to P-Ir-X forming **6**. The proposed mechanism is shown as eqn (2).[6] From the initially observed ratio of >200:1 for **5**:**6** and eqn (3), we conclude that $\Delta\Delta G^{\ddagger}$ between the formation of **5a** and **6a** must be >3.1 kcal/mole. The thermodynamic differentiation between the diastereomers is obtained from the ratio of **5a**:**5b** as **6** starts to form, and the ratios **6a**:**6b** and **6a**:**5a** after equilibrium has been reached. A

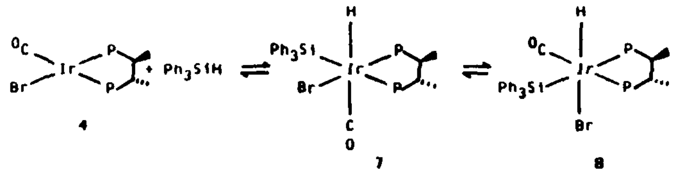
$$\frac{[5a + 5b]}{[6a + 6b]} = e^{-(\Delta G^{\ddagger}_{5a} - \Delta G^{\ddagger}_{6a})/RT} \frac{(1 + k_{5b}/k_{5a})}{(1 + k_{6b}/k_{6a})} \qquad (3)$$

reaction coordinate profile of the **4** + H_2 system summarizing all of these results is given in *Figure 2*.



(2)

The oxidative addition of Ph_3SiH to **4** also proceeds stereoselectively under kinetic control in agreement with recent observations for silane addition to complex **1**.[7] The reaction occurs as shown in eqn (4) with the initial formation of **7** (>99.5%) followed by isomerization to the more stable diastereomers **8**.[8] The kinetic differentiation for **8** is striking as evidenced by the ratio for **8a**:**8b** of 12:1 during early stages of the isomerization, corresponding to $\Delta\Delta G^{\ddagger}$ of 1.5 kcal/mole for the formation of the diastereomers. The eventual ratio of **8a**:**8b** at equilibrium is 1:1 indicating little thermodynamic differentiation between the diastereomers.



(4)

The isomerization of 7 to 8 most probably occurs by reductive elimination/oxidative addition similar to that shown in (2) since the reaction follows first order kinetics and reductive elimination of Ph_3SiH from 7 is rapid relative to isomerization. The latter was shown by preparing 7 at -20° C followed by the addition of 5 eq $MeCl_2SiH$ which acts as an efficient trap for 4 by its oxidative addition to form $IrHBr(SiMeCl_2)(CO)$(chiraphos). Further studies using these and other silanes will be reported separately.

The results described above show that kinetic and thermodynamic differentiation of metal centered chirality in simple cis oxidative additions by chiraphos is significant.[9] The results also provide a sensitive probe to the transition state structure in these systems through observed differences in the extent of kinetic and thermodynamic differentiation for the diastereomers in these cis oxidative additions. Based on these differences, it appears that for both H_2 and Ph_3SiH oxidative addition, the transition state in these reactions is not very product like.

Acknowledgements. We wish to thank the National Science Foundation (CHE 83-08064) and the Office of Naval Research for support of this work, and Johnson Matthey Co., Inc. for a generous loan of iridium salts.

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3. (a) Knowles, W. S.; Sabacky, M. J.; Vineyard, B. D. Adv. Chem. Ser. 1974, 132, 274. (b) Kagan, H. B. Pure Appl. Chem. 1975, 43, 401, and references therein. (c) Valentine, D. S.; Scott, J. W. Synthesis 1978, 329. (d) Bosnich, B.; Roberts, N. K. Adv. Chem. Ser. 1982, 196, 337. (e) Brown, J. M.; Chaloner, P. A.; Parker, D. Adv. Chem. Ser. 1982, 196, 355.

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5. ^1H NMR data for hydride resonances in d_6-acetone (J_{PH} in Hz). **5a**: -8.85 (dd; 144.7, 12.9), -9.25 (dd; 21.6, 16.7). **5b**: -9.02 (dd; 145.9, 12.9), -9.28 (~t; 20.8). **6a**: -8.71 (ddd; 127.1, 15.7, 4.3), -18.0 (mult). **6b**: -9.50 (ddd; 128.8, 16.7, 4.9), ~-18.1 (mult).
6. The assignment of metal-centered chirality for all of the diastereomers is based on an analysis of space-filling models of reactants and products for the oxidative addition reaction. These models, which are particularly informative for the silane oxidative addition, predict a kinetic preference for the Δ configuration in the formation of both 5 and 6, and little thermodynamic differentiation within each pair of diastereomers. These predictions must, of course, be confirmed by x-ray structural studies. A different analysis has been presented by Brown and Chaloner who propose that diastereoselection of H_2 oxidative addition to Rh(α-benzamidocinnamic acid)(chiraphos)$^+$, which was not observed directly, is determined by torsional strain in the Rh-chiraphos chelate ring. Brown, J. M.; Chaloner, P. A. in "Homogeneous Catalysis with Metal Phosphine Complexes", L. Pignolet, Ed., Plenum Publishing, New York, 1983, 161-2. However, the importance of electronic factors in determining the diastereoselection in the Rh(chiraphos) system has not been examined as it has for IrBr(CO)(dppe).[1]
7. Johnson, C. E.; Eisenberg, R. J. Am. Chem. Soc. 1985, 107, in press.

8. ^1H NMR data for hydride resonances in d_6-acetone (J_{PH} in Hz). **7a**: -7.93 (dd; 16.8, 12.6). **7b**: -8.49 (dd; 24.2, 13.7). **8a**: -16.04 (dd; 13.7, 7.4). **8b**: -16.34 (dd; 24.2, 5.3). Molecular models indicate that the configuration at the metal for diastereomer **8a** which is kinetically *preferred* over **8b** is Δ.

9. a. While diastereomeric cis dihydrides have been seen previously for $[IrH_2(dipamp)_2]BF_4$, the stereoselectivity of the oxidative addition was not reported. Brown, J. M.; Dayrit, F. M.; Lightowler, D. J. Chem. Soc., Chem. Commun. 1983, 414. b. For the oxidative addition of H_2 to $[Ir(cod)(diop)]$-(PF_6), only one set of hydride resonances was discernable. Presumably the diastereomers were not resolved. Crabtree, R. H.; Felkin, H.; Fillebeen-Khan, T.; Morris, G. E. J. Organomet. Chem. 1979, 168, 183.

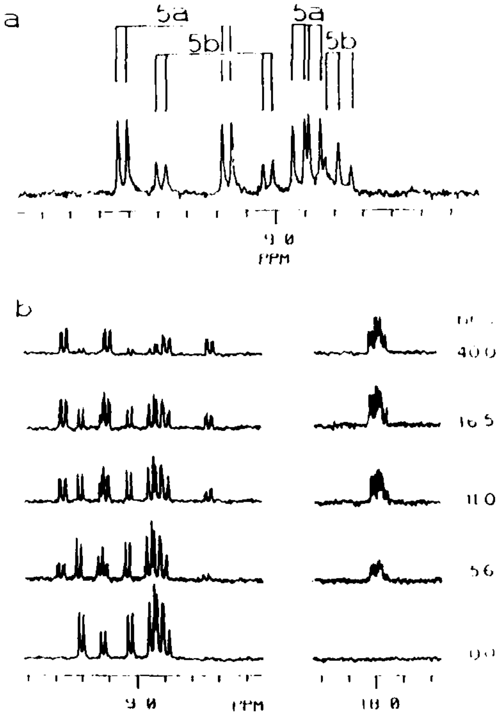

Figure 1. Hydride region of the ^1H NMR spectrum of IrBr(CO)(chiraphos), 4, plus H_2 in d_6-acetone: (a) expanded view at -25° C; (b) spectra taken over 40 hr period monitoring the conversion from diastereomers 5 to 6 at 25° C.

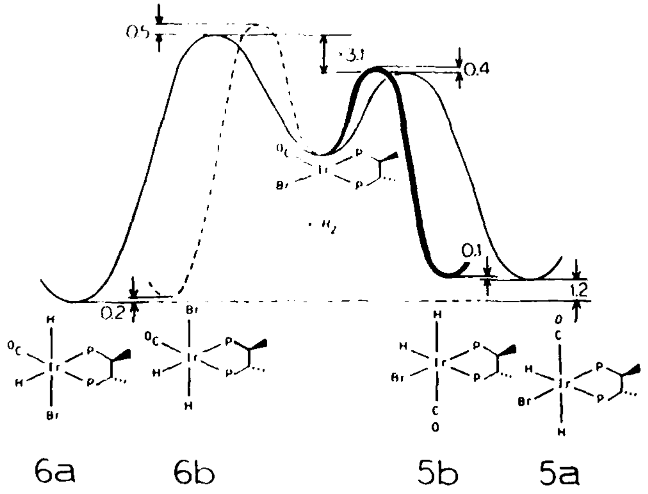

Figure 2. Reaction coordinate diagram for the system IrBr(CO)(chiraphos), 4, + H_2. Values of $\Delta\Delta G$ and $\Delta\Delta G^{\ddagger}$ are given in kcal/mole.

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