

¹⁰³Rh Shielding and the Stereoselectivity of H₂ Addition to Diastereomeric Olefin Complexes†

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The mechanistic understanding of rhodium-catalyzed asymmetric hydrogenation of prochiral enamide substrates is impressive.¹ Both Halpern and Brown have amply demonstrated that dihydrogen (H₂) reacts faster with the thermodynamically disfavored (minor) diastereomeric catalyst–substrate adduct than with the favored (major) one, but the reason why remains unclear. Current rationalizations (based on molecular mechanics calculations)² suggest that steric interactions alone control *both* the thermodynamic diastereomeric ratio of enamide complexes and their relative reactivities with H₂. Here we use ¹⁰³Rh NMR chemical shifts to demonstrate an electronic difference at rhodium between such diastereomers, and we suggest that the crucial H₂ addition step may be electronically controlled.

¹⁰³Rh chemical shifts were measured on a Bruker AM-400-WB spectrometer using 2D (³¹P, ¹⁰³Rh)-{¹H} reverse correlation techniques.³ The pulse sequence used features a two-fold coherence transfer and indirectly detects relatively insensitive ¹⁰³Rh nuclei via more sensitive J-coupled ³¹P nuclei.⁴ The significant gain in sensitivity compared to direct ¹⁰³Rh measurement allows the observation of both diastereomers for SS-dipamp and SS-chiraphos enamide complexes.⁵

All enamides and complexes were prepared as previously reported,⁶ except for the *tert*-butyl ester 2.⁷ All samples (0.1 M in methanol-*d*₄) were measured at 300 K in 5-mm tubes sealed under vacuum. Results are collected in Table I. All δ(¹⁰³Rh)

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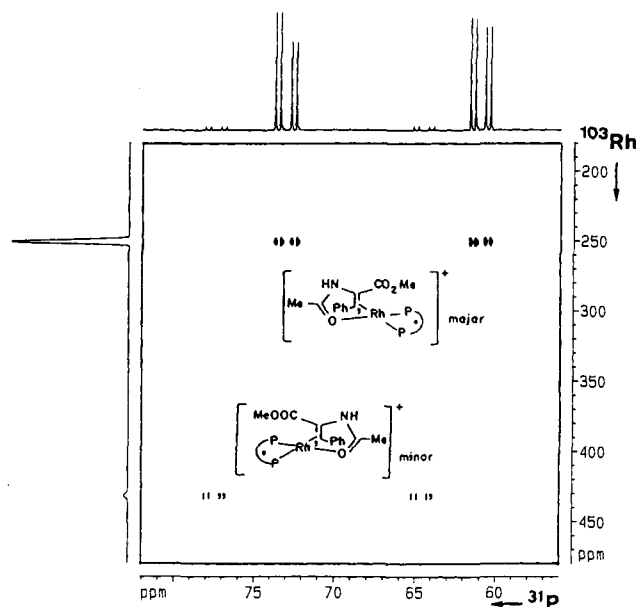
(1) Reviews: (a) Halpern, J. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic Press: New York, 1985; Vol. 5, pp 41–69. (b) Brown, J. M. In *Homogeneous Catalysis with Metal-Phosphine Complexes*; Pignolet, L. H., Ed.; Plenum: New York, 1983; pp 137–165.(2) (a) Bosnich, B. *Pure Appl. Chem.* 1990, 62, 1131. (b) Bogdan, P. L.; Irwin, J. J.; Bosnich, B. *Organometallics* 1989, 8, 1450. (c) Brown, J. M.; Evans, P. L. *Tetrahedron* 1988, 44, 4905. (d) More recent work casts doubt on the conclusions of these previous studies and on the assumed involvement of intermediate dihydride species: Giovannetti, J. S.; Kelly, C. M.; Landis, C. R. *J. Am. Chem. Soc.*, 1993, 115, 4040.(3) (a) Benn, R.; Brenneke, H.; Frings, A.; Lehmkuhl, H.; Mehler, G.; Rufinska, A.; Wildt, T. *J. Am. Chem. Soc.* 1988, 110, 5661. (b) Benn, R.; Brevard, C. J. *Am. Chem. Soc.* 1986, 108, 5622. (c) Ernsting, J. M.; Elsevier, C. J.; de Lange, W. G. J.; Timmer, K. *Magn. Reson. Chem.* 1991, 29, S118. (d) Elsevier, C. J.; Ernsting, J. M.; de Lange, W. G. *J. Chem. Soc., Chem. Commun.* 1989, 585.(4) $\pi/2(^{31}\text{P}) - 1/[4J(^{103}\text{Rh}, ^{31}\text{P})] - \pi(^{31}\text{P}), \pi(^{103}\text{Rh}) - 1/[4J(^{103}\text{Rh}, ^{31}\text{P})] - \pi/2(^{31}\text{P}), \pi/2(^{103}\text{Rh}) - t_1/2 - \pi(^{31}\text{P}) - t_1/2 - \pi/2(^{103}\text{Rh}), \pi/2(^{31}\text{P})$. ¹H decoupling is applied throughout. Nanz, D., Ph. D. Dissertation, University of Zurich, 1993.(5) Previous workers had reported that the minor diastereomer for SS-chiraphos is not observable by ³¹P NMR (ref 1). We attribute this to significant line broadening.(6) Bircher, H.; Bender, B. R.; von Philipsborn, W. *Magn. Reson. Chem.* 1993, 31, 293. The (Z)-enamides 5 and 6 were prepared using the appropriate para-substituted benzaldehydes.(7) Isobutene (10 mL) was condensed at –78 °C into a suspension of α-acetaminocinnamic acid (205 mg, 1.0 mmol) in 3 mL of CH₂Cl₂. After addition of 3 drops of concentrated H₂SO₄, the flask was sealed and the mixture was stirred at room temperature until the solution was clear (5 days). After the isobutene was vented, saturated aqueous NaHCO₃ (5 mL) was added, and the aqueous layer was extracted twice with CH₂Cl₂. The combined organic layers were washed with brine, dried (Na₂SO₄), and concentrated by rotary evaporation. Recrystallization from hexane/ether yielded colorless crystals of *tert*-butyl (Z)-α-N-acetylcinnamate (201 mg, 77%), mp 142–144 °C.(8) An absolute frequency standard introduced by Kidd et al. at 0 ppm corresponds to 3.16 MHz in a field where TMS protons resonate at 100 MHz. Kidd, R. G.; Goodfellow, R. J. In *NMR and the Periodic Table*; Harris, R. K., Mann, B. E., Eds.; Academic Press: London, 1978.

Figure 1. 2D (³¹P, ¹⁰³Rh)-{¹H}-Correlation spectrum for [(methyl (Z)-α-N-acetamidocinnamate)Rh(SS-chiraphos)]⁺. The spectrum was acquired with an 8-kHz spectral window in F₁ using 512 (word) × 1K data points in F₁ and F₂, respectively. The appropriate ³¹P window and J(Rh-P) were determined from 1D ³¹P-{¹H} spectra (see supplementary material). 64 FID were collected in each of the 512 traces in F₁. Prior to Fourier transformation, the data in t₁ were zero-filled and weighted with a shifted sine-squared function.

values are reported relative to $\Xi(^{103}\text{Rh}) = 3.16$ MHz.⁸ Figure 1 shows a spectrum of the chiraphos complex of 1 (measured in CD₂Cl₂).⁹

For achiral diphos complexes, a change in the enamide carboxylate functional group from methyl to *tert*-butyl to H has little effect on δ(¹⁰³Rh) (cf. entries 1, 2, and 3). Likewise, changing the amide functional group from *N*-acetyl to *N*-benzoyl has only a modest effect on δ(¹⁰³Rh) (cf. 3 and 4), suggesting that such steric perturbations have little effect on the rhodium. Substitution at the para position on the phenyl ring attached to the β-carbon of the enamide substrate markedly affects δ(¹⁰³Rh). An electron-donating group (*p*-OH) shields the rhodium nucleus (cf. 4 and 5), while an electron withdrawing group (*p*-NO₂) deshields the rhodium nucleus (cf. 4 and 6). These trends for the achiral diphos complexes hold for the diastereomeric SS-chiraphos and SS-dipamp complexes.

δ(¹⁰³Rh) of each major diastereomer appears at lower frequency (more shielded) than δ(¹⁰³Rh) of the corresponding minor diastereomer for the SS-chiraphos and SS-dipamp complexes, reflecting a consistent electronic difference at rhodium between the major and minor diastereomers. This trend may be understood via the paramagnetic shielding term, σ_p.¹⁰ The observed ¹⁰³Rh shielding variations are determined by, inter alia, the size of the metal valence orbitals, ⟨*r*⁻³⟩, and this factor decreases (*r* increases) for the major diastereomer because of better overlap between ligand and metal-based valence orbitals.^{3c,d} Because of the negative sign of σ_p, this implies a shift to lower frequency.

Several theoretical studies have discussed how ligand electronic factors control the regio- and stereoselectivity of H₂ addition to model d⁸ square-planar complexes.¹¹ The electronic barrier for H₂ addition to such complexes is a two-orbital, four-electron

(9) δ(¹⁰³Rh) values measured in CD₂Cl₂ and CD₃OD do not differ significantly (2–3 ppm).(10) (a) Mason, *Chem. Rev.* 1987, 87, 1299. (b) Kidd, R. G. *Annual Reports on NMR Spectroscopy*; Webb, G. A., Ed.; Academic Press: London, 1991; Vol. 23, pp 85–140.(11) Sargent, A. L.; Hall, M. B.; Guest, M. F. *J. Am. Chem. Soc.* 1992, 114, 517 and references to earlier work therein.

Table I. ^{103}Rh Chemical Shift Data for [(enamide)Rh(L-L)]ClO₄ Complexes (all $\delta(^{103}\text{Rh})$ values are ± 1 ppm)

	Enamide	diphos ^a	SS-chiraphos ^b	SS-dipamp ^c
1		+340	minor: +428 major: +250	minor: +727 major: +630
2		+304	minor: +274 major: +241	minor: +850 major: +560
3		+315	minor: +401 major: +241	minor: +675 major: +590
4		+310	minor: +369 major: +233	minor: +677 major: +569
5		+271	minor: +346 major: +212	minor: +538 major: +491
6		+495	minor: +584 major: +339	minor: +1032 major: +785

^a Diphos: 1,2-bis(diphenylphosphino)ethane. ^b SS-Chiraphos: (2*S*,3*S*)-bis(diphenylphosphino)butane. ^c SS-Dipamp: *S,S*-(1,2-bis(phenyl-*o*-anisoyl)phosphino)ethane.



Figure 2. Possible modes of H₂ addition to *cis*-diphosphino Rh(I) complexes containing donor/acceptor ligands. Left, disfavored approach; right, favored approach.

repulsion between a filled, metal-based, d_{z²}-like molecular orbital and the incoming filled H₂ σ -molecular orbital. The enamide complexes here are electronically similar to the model complexes studied theoretically, in that H₂ may add coplanar to P–Rh and a π -donor ligand (D), the conjugated amide carbonyl, or coplanar to P–Rh and a donor/acceptor ligand (A), the olefin (Figure 2).

By analogy to ref 11, addition parallel to the metal–oxygen bond will destabilize a five-coordinate transition state while H₂ addition parallel to the metal–olefin axis should be favored. Such kinetic stereospecificity has already been demonstrated for H₂ addition to a closely related [(*RR*-dipamp)Ir(olefin-amide)]⁺ analog.¹² Electron-withdrawing groups attached to the olefin should also enhance H₂ addition in the plane containing the rhodium and olefin, and it has been observed that electron-donating groups (attached to the β -carbon of enamide substrates)¹³ decrease reactivity, while electron-withdrawing groups (attached to the α -carbon of enol acetates)¹⁴ increase the overall rate and in some cases the enantiomeric excesses¹⁵ in catalytic asymmetric hydrogenation.

Based on the large rhodium shielding differences, we suggest that the major diastereomer in each diastereomeric pair is both

(12) Brown, J. M.; Maddox, P. J. *J. Chem. Soc., Chem. Commun.* 1987, 1278.

(13) Oliver, J. D.; Riley, D. P. *Organometallics* 1983, 2, 1032.

(14) (a) Koenig, K. E.; Bachman, G. L.; Vineyard, B. D. *J. Org. Chem.* 1980, 45, 2362. (b) Vineyard, B. D.; Knowles, W. S.; Sabacky, M. J. *J. Mol. Catal.* 1983, 19, 159.

(15) The enantiomeric excesses observed for a given substrate depend critically on the major/minor diastereomer interconversion and not just on the intrinsic reactivities of the major/minor diastereomers toward H₂. Landis, C. R.; Halpern, J. *J. Am. Chem. Soc.* 1987, 109, 1746.

magnetically more shielded and less reactive toward H₂ relative to its corresponding minor diastereomer because the substrate (enamide) ligand of the major diastereomer acts as a better electron donor (via both its amide carbonyl electrons and its olefin π -electrons), which augments the key two-orbital, four-electron repulsion. In other words, the increased shielding of the transition metal appears to indicate stronger bonding of the substrate, which in turn renders the metal less reactive toward adding another ligand.¹⁶

In conclusion, transition metal chemical shifts provide unique insight into the electronic environment surrounding the metal in organometallic complexes.¹⁷ In favorable cases, direct correlations between chemical shifts and reactivity are possible, as was already demonstrated for rhodium,^{18a} cobalt,^{18b} and manganese complexes.^{18c}

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Supplementary Material Available: Tables of ³¹P chemical shifts and *J*(RhP) and *J*(PP) values (3 pages). Ordering information is given on any current masthead page.

(16) Öhrström and co-workers have used analogous reasoning to explain rates of associative olefin exchange for Rh(I) square-planar complexes: Akermark, B.; Glaser, J.; Öhrström, L.; Zetterberg, K. *Organometallics* 1991, 10, 733.

(17) ³¹P chemical shifts for the complexes studied here (see supplementary material) do not show a clear-cut trend with respect to reactivity for all three phosphine ligands. Furthermore, the effects of the aromatic substituents (enamides 4–6) on $\delta(^{31}\text{P})$ are very small (<5 ppm).

(18) (a) Koller, M.; von Philipsborn, W. *Organometallics* 1992, 11, 467. (b) Bönemann, H.; Brijoux, W.; Brinkmann, R.; Meurers, W.; Mynott, R.; Egolf, T.; von Philipsborn, W. *J. Organomet. Chem.* 1984, 272, 231. (c) DeShong, P.; Sidler, D. R.; Rybczynski, P. J.; Olgivie, A. A.; von Philipsborn, W. *J. Org. Chem.* 1989, 54, 5432.