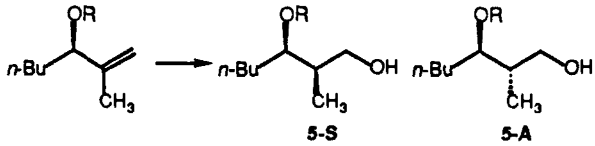
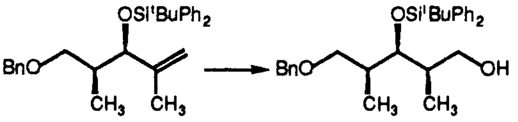
are employed, affording a >10:1 preference for **5-A** (eq 4).[10,11] *In contrast, the $Rh(PPh_3)_3Cl$-catalyzed hydroboration of 1,1-disubstituted allylic alcohol derivatives also takes place with high levels of stereoselectivity but in the complementary sense to that observed with dialkylboranes* with the major product being the syn diastereomer **5-S**. The related hydroboration illustrated in eq 5 illustrates the potential utility of these complementary reactions in the synthesis of polypropionate-derived natural products.[12] Although space limitations preclude the presentation of the analogous data for other catalysts, we have found the cationic catalyst, $[Rh(nbd)(diphos\text{-}4)]BF_4$, to be decidedly less regio- and diastereoselective than $Rh(PPh_3)_3Cl$. Collectively, these experiments suggest that the catalyzed and uncatalyzed reactions may well have different product-determining steps, and deuterium-labeling experiments to be described at a later date support this position.



(4)

5-S **5-A**

R	Conditions[11]	Yield,%	5-S	5-A
H	Uncatalyzed	80	8	92
	Catalyzed	77	75	25
Si^tBuMe_2	Uncatalyzed	94	11	89
	Catalyzed	80	96	4
Si^tBuPh_2	Uncatalyzed	92	14	86
	Catalyzed	96	97	3



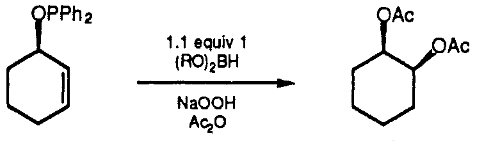
+ **6-A** (5)

6-S

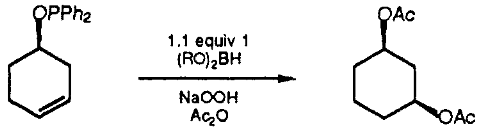
Conditions[11]	Yield,%	6-S	6-A
Uncatalyzed	82	14	86
Catalyzed	80	95	5

We have also addressed the notion that proximal functional groups might be employed to direct the stereochemical course of the hydroboration reaction. Because of the rapid reaction of catecholborane with alcohols to form borates, direction of the reaction by complexation of the hydroxy group to the catalyst is precluded. However, we have discovered that suitably disposed phosphinites[13] may effectively serve as directing groups in the metal-catalyzed hydroboration reaction (eq 6 and 7). Thus, in contrast to the aforementioned silyl ethers (eq 2), hydroboration of the illustrated allylic phosphinite selectively affords the syn 1,2-diol diastereomer **7-S**. Hydroboration of the analogous homoallylic phosphinite affords the syn 1,3-diol with high regio- and stereocontrol, whereas reaction of the corresponding silyl ether results in a statistical mixture of 1,3- and 1,4-diols.[14]

The previously described experiments illustrate the expanded scope which is provided by the rhodium-catalyzed hydroboration process. Additional studies regarding the metal-catalyzed hydroboration reaction continue in these laboratories.



diastereoselection >10 : 1 55% **7-S** (6)



diastereoselection >50 : 1 82% **8-S** (7)

Acknowledgment. This research was supported by the National Institutes of Health (GM33327-04). Fellowships from the American Cancer Society for a Postdoctoral Fellowship to AHH and the National Science Foundation Predoctoral fellowship to GCF are gratefully acknowledged. The NIH BRS Shared Instrumentation Grant Program 1 S10 RR01748-01A1 is also acknowledged for providing NMR facilities.

Supplementary Material Available: Detailed procedure for the catalyzed hydroboration reaction (3 pages). Ordering information is given on any current masthead page.

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(10) Still, W. C.; Barrish, J. C. *J. Am. Chem. Soc.* **1983**, *105*, 2487. For related work on vinyl ethers, see: McGarvey, G. J.; Bajwa, J. S. *Tetrahedron Lett.* **1985**, *26*, 6297.

(11) See the conditions defined in Table I for the catalyzed and uncatalyzed hydroboration reactions.

(12) A large number of 1,1-disubstituted allylic alcohols were examined, and all show similar levels and patterns of diastereoselection.

(13) For examples of phosphine-directed hydroformylation, see: Burke, S. D.; Cobb, J. E. *Tetrahedron Lett.* **1986**, *27*, 4237. Jackson, W. R.; Perlmutter, P.; Suh, G.-H. *J. Chem. Soc., Chem. Commun.* **1987**, 724.

(14) Stoichiometric quantities of catalyst are required for high yields, probably due to the instability of the uncomplexed phosphinite to catecholborane.

The Preparation and Structure of a Dinuclear η^2-H_2 Complex $(P\text{-}N)(\eta^2\text{-}H_2)Ru(\mu\text{-}Cl)_2(\mu\text{-}H)Ru(H)(PPh_3)_2$, $P\text{-}N = Fe(\eta\text{-}C_5H_3(CHMeNMe_2)P(i\text{-}Pr)_2\text{-}1,2)(\eta\text{-}C_5H_5)$

Cashman Hampton, William R. Cullen,* and
Brian R. James*

*Department of Chemistry, University of
British Columbia, Vancouver
British Columbia, Canada V6T 1Y6*

Jean-Pierre Charland[1]

*Division of Chemistry, National Research Council
Ottawa, Ontario, Canada K1A 0R6*

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A number of mononuclear complexes containing an η^2-dihydrogen ligand have been described recently,[2] and η^2-H_2 has been established in the two known solid-state structures.[3]

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(1) NRC publication no. 29296.

(2) (a) Kubas, G. J.; Ryan, R. R.; Swanson, B. I.; Vergamini, P. J.; Wasserman, H. J. *J. Am. Chem. Soc.* **1984**, *106*, 451. (b) Kubas, G. J.; Ryan, R. R.; Wroblewski, D. A. *J. Am. Chem. Soc.* **1986**, *108*, 1339. (c) Zilm, K. W.; Merrill, R. A.; Kummer, M. W.; Kubas, G. J. *J. Am. Chem. Soc.* **1986**, *108*, 7837. (d) Wasserman, H. J.; Kubas, G. J.; Ryan, R. R. *J. Am. Chem. Soc.* **1986**, *108*, 2294. (e) Kubas, G. J.; Unkefer, C. J.; Swanson, B. I.; Fukushima, E. *J. Am. Chem. Soc.* **1986**, *108*, 7000. (f) Vergamini, P. J.; Wasserman, H. J.; Koetzle, T.; Kubas, G. J., manuscript in preparation, quoted in ref 1e. (g) Kubas, G. J.; Ryan, R. R.; Unkefer, C. J. *J. Am. Chem. Soc.* **1987**, *109*, 8113. (h) Kubas, G. J. *Acc. Chem. Res.* **1988**, *21*, 120. (i) Crabtree, R. H.; Lavin, M.; Bonneviot, L. *J. Am. Chem. Soc.* **1986**, *108*, 4032. (j) Crabtree, R. H.; Hamilton, D. G. *J. Am. Chem. Soc.* **1986**, *108*, 3124. (k) Crabtree, R. H.; Lavin, M. *J. Chem. Soc., Chem. Commun.* **1985**, 1661. (l) Crabtree, R. H.; Lavin, M. *J. Chem. Soc., Chem. Commun.* **1985**, 794. (m) Crabtree, R. H., personal communication. (n) Morris, R. M.; Sawyer, J. F.; Shiralian, M.; Zubkowski, J. D. *J. Am. Chem. Soc.* **1985**, *107*, 5581. (o) Bautista, M. T.; Earl, K. A.; Morris, R. M.; Sella, A. *J. Am. Chem. Soc.* **1987**, *109*, 3780. (p) Bautista, M. T.; Earl, K. A.; Maltby, P. A.; Morris, R. H.; Sella, A. *J. Am. Chem. Soc.*, in press. (q) Morris, R. H.; Earl, K. A.; Luck, R. L.; Lazarowych, N. J.; Sella, A. *Inorg. Chem.* **1987**, *26*, 2674. (r) Arliguie, T.; Chaudret, B.; Morris, R. H.; Sella, A. *Inorg. Chem.* **1988**, *27*, 598. (s) Bautista, M. T.; Earl, K. A.; Morris, R. H. *Inorg. Chem.* **1988**, *27*, 1124. (t) Conroy-Lewis, F. M.; Simpson, S. J. *J. Chem. Soc., Chem. Commun.* **1987**, 1675. (u) Chinn, M. S.; Heinekey, D. M. *J. Am. Chem. Soc.* **1987**, *109*, 5865. (v) Bianchini, C.; Mealli, C.; Peruzzini, M.; Zanobini, F. *J. Am. Chem. Soc.* **1987**, *109*, 5548.

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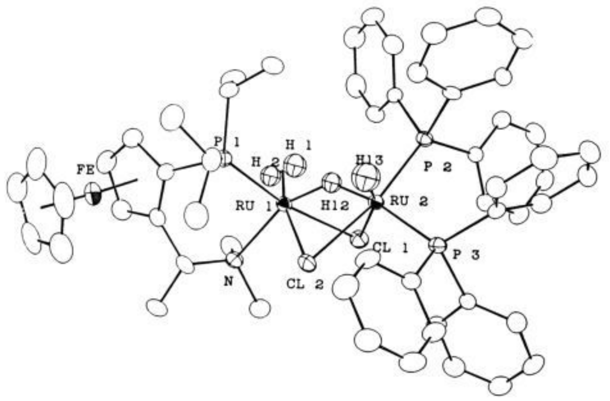

Figure 1. The molecular structure of **3**. Thermal elipsoids are drawn at the 50% probability level.

Three dinuclear ruthenium complexes have been described that contain this novel ligand: $(R_3P)_2(H)Ru(\eta\text{-}Cl)_2(\mu\text{-}H)Ru(\eta^2\text{-}H_2)(PR_3)_2$, R = Ph **1a**, *p*-tol **1b**,[5] $(R_3P)_2(H)Ru(\mu\text{-}H)_3Ru(\eta^2\text{-}H_2)(PR_3)_2$, R = C_6H_{11} **2**.[2r] We now report the synthesis and crystal structure (the first for a dinuclear species) of a related molecule $(P\text{-}N)(\eta^2\text{-}H_2)Ru(\mu\text{-}H)(\mu\text{-}Cl)_2Ru(H)(PPh_3)_2$, **3**, P-N = $Fe(\eta\text{-}C_5H_3(CHMeNMe_2)P(i\text{-}Pr)_2\text{-}1,2)(\eta\text{-}C_5H_5)$, that contains an $\eta^2\text{-}H_2$ ligand.

Complex **3** was prepared by treating $(P\text{-}N)Ru(PPh_3)Cl_2$[6] with hydrogen (1–4 atm).[7] The structure of **3** shown in Figure 1 clearly reveals the presence of the $\eta^2\text{-}H_2$ ligand.[8] The H–H bond distance is well established at 0.80 (6) Å which is similar to that found in the mononuclear complexes.[3] The H–H bond is parallel to the Ru(1)–Ru(2) direction and bisects roughly the P(1)–Ru(1)–N and H(12)–Ru(1)–Cl(1) angles. The $\eta^2\text{-}H_2$ ligand is symmetrically coordinated with Ru–H distances of 1.50 (4) and 1.47 (4) Å. The terminal Ru–H distance is 1.50 (4) Å. The μ-H bridge is unsymmetrical, with Ru(1)–H 1.71 (4) Å and H–Ru(2) 1.49 (4) Å. The heavy atom skeleton of **3** is very similar to that found for **1a**[5,9,10] and **1b**;[5,9] however, the location of the hydrogen atoms is established only in **3**.

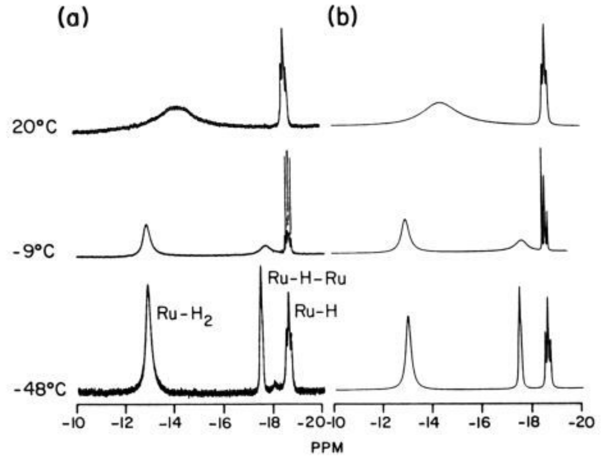

Figure 2. Observed and calculated variable temperature ^1H NMR spectra of **3** measured in CD_2Cl_2 at 300 MHz. The calculated *k* values for the fast exchange process are (s^{-1}) 2.7×10^3 (20°), 2.5×10^2 (−9°), and 5 (−48°).

The ^1H NMR spectrum of **3** shows some unique features, Figure 2. The terminal hydride on Ru(2) is coupled to the two cis phosphines over the temperature range 30° to −88 °C. Fast exchange is occurring between the $\eta^2\text{-}H_2$ and the μ-H at ambient temperature; separate signals are seen at −9 °C, and these sharpen on cooling but not to the extent of showing well-defined coupling. The simulated spectra in Figure 2[11] used the model of a BXYZ spin system exchanging rapidly with an A_2XYZ and slowly with a CXYZ, i.e., μ-H exchanging rapidly with $\eta^2\text{-}H_2$ and this system slowly exchanging with Ru(2)–H. In the dinuclear species **1** and **2**, exchange is faster and involves all hydrogen ligands. The T_1 values at −60 °C for the exchanging hydrogens, measured at 300 MHz, for **3** in CD_2Cl_2 are (ms) $\eta^2\text{-}H_2$ 13.8 (3), μ-H 182 (6), and Ru–H 251 (5),[12] which are in the expected ranges.[2i]

Complex **3** reacts with N_2, but the interaction is more complex than simple replacement of the $\eta^2\text{-}H_2$;[2q,r] **3** reacts also with 1-hexene (hexane is a stoichiometric product based on four available hydrogen atoms) and is a catalyst for the hydrogenation of hexene (30 °C, 1 atm); we are unaware of other examples where $\eta^2\text{-}H_2$ has been transferred to olefinic substrates.

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Supplementary Material Available: Tables of positional and thermal parameters and interatomic distances and angles (11 pages); table of calculated and observed structure factor amplitudes (51 pages). Ordering information is given on any current masthead page.

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(3) In $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_2)$ the H–H distance is 0.75 (16) Å (X-ray), 0.84 Å (neutron diffraction),[2a] 0.82 (1) Å (neutron diffraction).[2f] In $[Fe(H_2)H(dppe)_2]BF_4$, dppe = $Ph_2PCH_2CH_2PPh_2$, the H–H distance is 0.89 (11) Å (X-ray),[2n] 0.815 (20) Å (neutron diffraction of the BPh_4^- salt).[2p,4]

(4) Ricci, J. S.; Koetzle, T. F.; Bautista, M. T.; Hofstede, T.; Morris, R. H.; Sawyer, J. F., in preparation, quoted in ref 2p.

(5) Hampton, C.; Dekleva, T. W.; James, B. R.; Cullen, W. R. *Inorg. Chim. Acta* **1988**, *145*, 165.

(6) $(P\text{-}N)Ru(PPh_3)Cl_2$ was prepared from $(PPh_3)_3RuCl_2$ as described for a related complex. Rodgers, G. E.; Cullen, W. R.; James, B. R. *Can. J. Chem.* **1983**, *61*, 1314.

(7) All manipulations were carried out in a hydrogen atmosphere in an all-glass apparatus. The orange precipitate, **3**, obtained from a benzene/methanol solution (10:1 by volume), was recrystallized from CH_2Cl_2/hexane (39% yield from 334 mg starting complex). $(P\text{-}N)(H_2)Ru(\mu\text{-}H)(\mu\text{-}Cl)_2Ru(H)(PPh_3)_2$: IR ν(RuH) 2109, 2025 cm^{-1}; ^1H NMR (CD_2Cl_2, ambient temperature 300 MHz) δ −12 to −17 (br s $\eta^2\text{-}H^2$ and μ-H exchanging), −18.6 (dd, *J*(PH) 28, 32 Hz, Ru-H); $^{31}P\{H\}$ NMR (CD_2Cl_2, ambient temperature versus H_3PO_4) δ 78.8 (dd, *J*(PP) 25, 40 Hz), *P*Ph_3 trans to Cl), 77.2 (br s, *P*-N), 64.6 (dd, *J*(PP) 32, 40 Hz, *P*Ph_3 trans to μ-H). Anal. Calcd for $C_{56}H_{66}Cl_2FeNP_3Ru_2$: C, 57.29; H, 5.62; N, 1.19. Found: C, 57.37; H, 6.02; N, 1.39.

(8) (a) Orange crystals of **3**[7] were sealed in 0.2–0.3 mm glass capillaries under hydrogen. Data were collected on an automated Picker 4-circle diffractometer by using graphite-monochromatized Mo Kα radiation (λ = 0.71069 Å). Crystal data: $C_{56}H_{66}Cl_2FeNP_3Ru_2 \cdot 1.5C_6H_6$, fw = 1292.13, dimensions $0.15 \times 0.30 \times 0.45$ mm, triclinic, space group $P\bar{1}$, a = 10.433 (9) Å, b = 15.042 (9) Å, c = 21.012 (8) Å, α = 106.69 (4), β = 91.29 (6), γ = 106.64 (6)°, V = 3006.5 Å^3, u = 0.92 mm^{-1}, D_c = 1.427 g cm^{-3}, Z = 2; 8674 reflections collected in quadrants $\pm h,k,\pm l$ and $-h,-k,-l$ with $2\theta < 45°$. Symmetry-equivalent data averaged (R_{int} = 0.010) to give data set of 7895 reflections. Intensity data collected at room temperature and not corrected for absorption. Direct methods, least-squares, and Fourier solution (NRCVAX X-ray package[8b]). Hydrogen atoms located in ΔF map and successfully refined. Residuals R_f = 0.029 (R_w = 0.031), goodness-of-fit = 1.34, for 5460 observed ($I > 2.5\sigma(I)$) reflections. Some selected bond lengths (Å): Ru(1)–Ru(2) 2.811 (2), Ru(1)–Cl(1) 2.528 (2), Ru(1)–Cl(2) 2.435 (2), Ru(1)–P(1) 2.240 (2), Ru(1)–N 2.300 (4), Ru(1)–H(1) 1.50 (4), Ru(1)–H(2) 1.47 (4), Ru(1)–H(12) 1.71 (4), Ru(2)–Cl(1) 2.620 (2), Ru(2)–Cl(2) 2.453 (2), Ru(2)–P(2) 2.229 (2), Ru(2)–P(3) 2.249 (2), Ru(2)–H(12) 1.49 (4), and Ru(2)–H(13) 1.50(4); Ru(1)–H(12)–Ru(2) angle = 122 (3)°). (b) Gabe, E. J.; Lee, F. L.; LePage, Y. *Crystallographic Computing III*; Sheldrick, G., Kruger, C., Goddard, R., Eds.; Clarendon Press: Oxford, 1985; p 167.

(9) These compounds were first described with the $\eta^2\text{-}H_2$ represented as classical dihydrides. Dekleva, T. W.; Thorburn, I. S.; James, B. R. *Inorg. Chim. Acta* **1985**, *100*, 49.

(10) Robinson, B. H.; Simpson, J., personal communication.

(11) The program DNR4 (Quantum Chemistry Program Exchange No. 466) was used for the simulations. T_2 values were allowed to decrease with decreasing temperature, and allowance was made for the temperature dependence of the chemical shift of μ-H.

(12) T_1 measurements were made with the inversion recovery method over the range 20 °C to −88 °C. At −48 °C the T_1 of μ-H begins to average with the T_1 of $\eta^2\text{-}H_2$. A spin saturation transfer study at −48 °C did not reveal any spin transfer. At −9 °C, irradiating the $\eta^2\text{-}H_2$ saturates the μ-H resonance, and at this temperature the two T_1's are completely averaged. V-shaped plots of ln T_1 versus $1/T$ are not obtained in these dinuclear exchanging systems, so any H–H distance calculated from these data would be questionable.[2m,o]