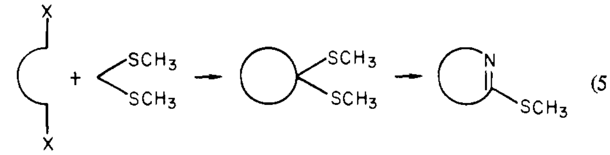
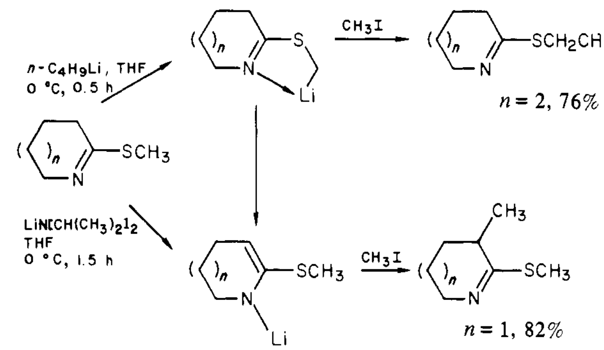
reactivity of the "super carbonyl" group, the thionium ion, was unmasked by the thiophilic electrophile. This unprecedented degree of control of reactivity can simplify synthetic design. In addition, the availability of thioketals by direct alkylation methods (see eq 5) enhances the utility of this new rearrangement.



(5)

In addition to imino thioethers serving as activated forms of an amide in terms of susceptibility to nucleophilic attack, we note an interesting behavior toward metalation, as summarized in eq 6, which allows them to be used as nucleophiles. Kinetic metalation occurs at the S–CH$_3$ group and allows elaboration of the *S*-alkyl group. Alternatively, thermodynamic metalation occurs at the methylene group α to the imine function to give a metalated enamine. Implications of these reactions toward elaboration of alkaloids is an exciting prospect.



(6)

Acknowledgment. We thank the NSF for their generous support of this work. We also express appreciation to NATO and the CNRS for making it possible for M.V. to be a visiting scientist in Madison.

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Synthesis of 2,2′-Bis(diphenylphosphino)-1,1′-binaphthyl (BINAP), an Atropisomeric Chiral Bis(triaryl)phosphine, and Its Use in the Rhodium(I)-Catalyzed Asymmetric Hydrogenation of α-(Acylamino)acrylic Acids

Sir.

Synthesis of well-designed phosphine ligands is crucial to develop efficient asymmetric catalysis by chiral transition-metal complexes.[1] We have prepared 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (**1**, hereafter abbreviated to BINAP), a new axially dissymmetric *bis(triaryl)phosphine.*[2]

As outlined in Scheme I, racemic BINAP was first synthesized and then the optical resolution was achieved by using the chiral Pd(II) complex **4**[3] through fractional recrystallization of the diastereomers of **5**.[4–6] This method allows the ready preparation of both enantiomers of a new type of diphosphine, BINAP, in an optically pure state.

The molecular structure of [Rh((+)-binap)(norbornadiene)]ClO$_4$ has been determined by the X-ray crystal structure analysis.[7] The absolute configuration of the dextrorotatory diphosphine ligand was found to be *R*. Perspective drawing of the complex is shown in Figure 1. The rhodium(I) atom has nearly square planar coordination and is surrounded by two phosphorus atoms and two C=C bonds of norbornadiene. The seven-membered chelate ring is fixed to the λ-skew-boat conformation, and this dissymmetry determines the orientation of the four phenyl rings on the phosphorus atoms. These phenyl rings are arrayed in an alternating edge-face manner as was observed for the Rh(I) complex of 1,2-bis[(*o*-methoxyphenyl)phenylphosphino]ethane.[8] The two double bonds of norbornadiene are not perpendicular to the P(1)–Rh–P(2) plane but are tilted 14.6° and 16.1° from the normal to this plane. The angle between the least-squares planes through the two naphthyl groups is 74.3°.

With optically pure BINAP in hand, we have examined the asymmetric hydrogenation of α-(acylamino)acrylic acid derivatives catalyzed by its Rh(I) complexes. When a solution of [Rh((*S*)-binap)(norbornadiene)]ClO$_4$ [(*S*)-**6**] in methanol was exposed to atmospheric pressure of hydrogen at room temperature, exactly 2.0 mol of hydrogen per Rh atom was taken up to give norbornane and two Rh complexes, (*S*)-**7a** and (*S*)-**8** (~9:1 ratio) (Scheme II).[9] The major, methanol-soluble complex (*S*)-**7a**, isolated as deep red prisms, loses methanol in vacuo at room temperature to produce an air-sensitive complex (*S*)-**7b**,[9] which reverts to (*S*)-**7a** in methanol solution. The minor Rh complex (*S*)-**8** is methanol insoluble and has been isolated as a brown crystalline solid.[10]

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(1) (a) Kagan, H. B.; Dang, T.-P. *J. Am. Chem. Soc.* **1972**, *94*, 6429–6433. (b) Hayashi, T.; Yamamoto, K.; Kumada, M. *Tetrahedron Lett.* **1974**, 4405–4408. (c) Achiwa, K. *J. Am. Chem. Soc.* **1976**, *98*, 8265–8266. (d) Vineyard, B. D.; Knowles, W. S.; Sabacky, M. J.; Bachman, G. L.; Weinkauff, D. J. *Ibid.* **1977**, *99*, 5946–5952. (e) Fryzuk, M. D.; Bosnich, B. *Ibid.* **1977**, *99*, 6262–6267. (f) Ojima, I.; Yoda, N. *Tetrahedron Lett.* **1980**, 1051–1054. Diphosphinites and aminophosphines derived from optically active diamines are also known to be effective ligands for Rh(I)-catalyzed asymmetric hydrogenations: (g) Tanaka, M.; Ogata, I. *J. Chem. Soc., Chem. Commun.* **1975**, 735. (h) Hanaki, K.; Kashiwabara, K.; Fujita, J. *Chem. Lett.* **1978**, 489–490.

(2) Some atropisomeric diphosphines and diphosphinites have been synthesized and used for metal-catalyzed asymmetric hydrogenations, but results are not always satisfactory: 2,2′-bis[(diphenylphosphino)methyl]-1,1′-binaphthyl [Tamao, K.; Yamamoto, H.; Matsumoto, H.; Miyake, N.; Hayashi, T.; Kumada, M. *Tetrahedron Lett.* **1977**, 1389–1392]; 2,2′-bis(diphenylphosphinoxy)-1,1′-binaphthyl [Grubbs, R. H.; DeVries, R. A. *Tetrahedron Lett.* **1977**, 1879–1880]. Quite recently an efficient asymmetric hydrogenation using 2,2′-bis[(diphenylphosphin)amino]-1,1′-binaphthyl as chiral ligand has been reported [Miyano, S.; Nawa, M.; Hashimoto, H. *Chem. Lett.* **1980**, 729–730].

(3) Otsuka, S.; Nakamura, A.; Kano, T.; Tani, K. *J. Am. Chem. Soc.* **1971**, *93*, 4301–4303. Tani, K.; Brown, L. D.; Ahmed, J.; Ibers, J. A.; Yokota, M.; Nakamura, A.; Otsuka, S. *Ibid.* **1977**, *99*, 7876–7886.

(4) Recently resolution of *o*-phenylenebis(methylphenylphosphine) has been attained by the similar procedure: Roberts, N. K.; Wild, S. B. *J. Am. Chem. Soc.* **1979**, *101*, 6254–6260.

(5) The stereospecific synthesis of **1** starting from chiral 2,2′-diamino-1,1′-binaphthyl was difficult.

(6) The Pd(II) complex of (*R*)-**1** [(*R*)-**5**]: mp 157–158 °C dec (from dichloromethane–ethyl acetate–benzene), $[\alpha]^{22}{}_D$ +381° (*c* 0.16, acetonitrile); (*S*)-**5**: mp 161 °C dec (from dichloromethane–ether), $[\alpha]^{22}{}_D$ −361° (*c* 0.14, acetonitrile); (*R*)-(+)-**1**: mp 240–241 °C, $[\alpha]^{25}{}_D$ +229° (*c* 0.32, benzene); (*S*)-(−)-1: mp 241–242 °C, $[\alpha]^{25}{}_D$ −229° (*c* 0.31, benzene).

(7) The crystals are dark-red micalike plates. Intensities of the reflections were measured on a diffractometer with Cu Kα radiation up to $2\theta = 120°$. The crystallographic data are $[RhP_2C_{51}H_{40}]ClO_4$, $M_r = 917.179$, orthorhombic, $P2_12_12_1$, $Z = 4$, $a = 11.104$ (1), $b = 35.238$ (2), $c = 10.892$ (1) Å, $U = 4261.6$ (3) Å^3, $D_x = 1.430$ g cm^{-3}, μ(Cu Kα) = 49.81 cm^{-1}. The structure was solved by routine application of the heavy-atom method and refined by block-diagonal least-squares calculations including hydrogen atoms. The final R and R_w values were 0.032 and 0.041, respectively, for all the 3249 observed independent reflections. The absolute configuration of the binaphthyl group in this complex was determined to be *R* by measuring further 1106 hkl reflections within the range of $2\theta \leq 70°$ and by comparison of the observed intensity relations between the hkl and $h\bar{k}l$ reflections with the calculated relations. The details of the results will be reported elsewhere.

(8) (a) Knowles, W. S.; Sabacky, M. J.; Vineyard, B. D. *Adv. Chem. Ser.* **1974**, *No. 132*, 274–282. (b) Knowles, W. S.; Vineyard, B. D.; Sabacky, M. J.; Stults, B. R. In "Fundamental Research in Homogeneous Catalysis"; Tsutsui, M., Ed; Plenum Press: New York, 1979; Vol. 3, pp 537–548.

(9) ^{1}H NMR of (*S*)-**7a** (CD_2Cl_2 containing tetramethylsilane): δ 7.50 (m) and 6.82 (m) (BINAP), 3.42 (s, CH_3OH); ^{31}P NMR of (*S*)-**7a** (CD_3OD solution, 5% H_3PO_4 in CD_3OD as external standard): δ 53.1 (d, $J_{Rh-P} = 206$ Hz). The ^{1}H NMR spectrum of (*S*)-**7b** in CD_2Cl_2 resembles closely that of (*S*)-**7a** but lacks the methanol signal.

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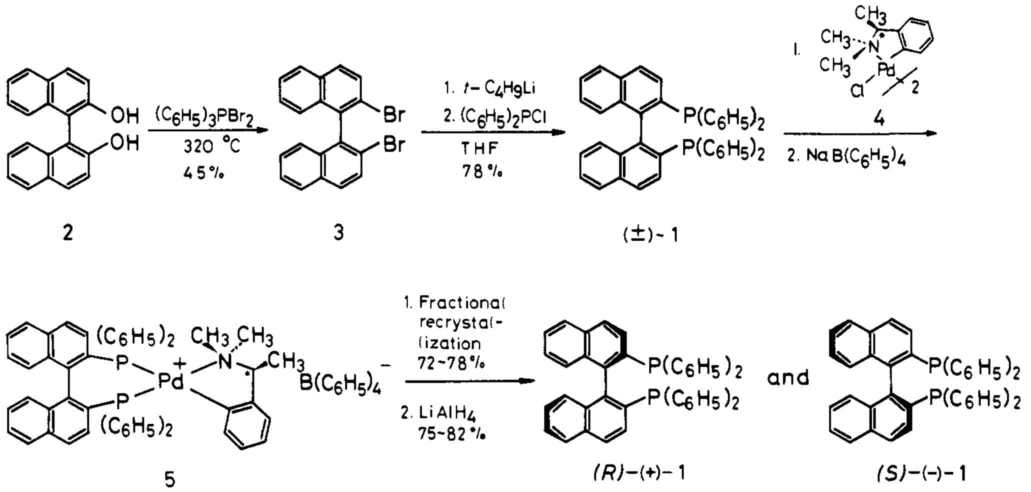
Scheme I



Scheme II

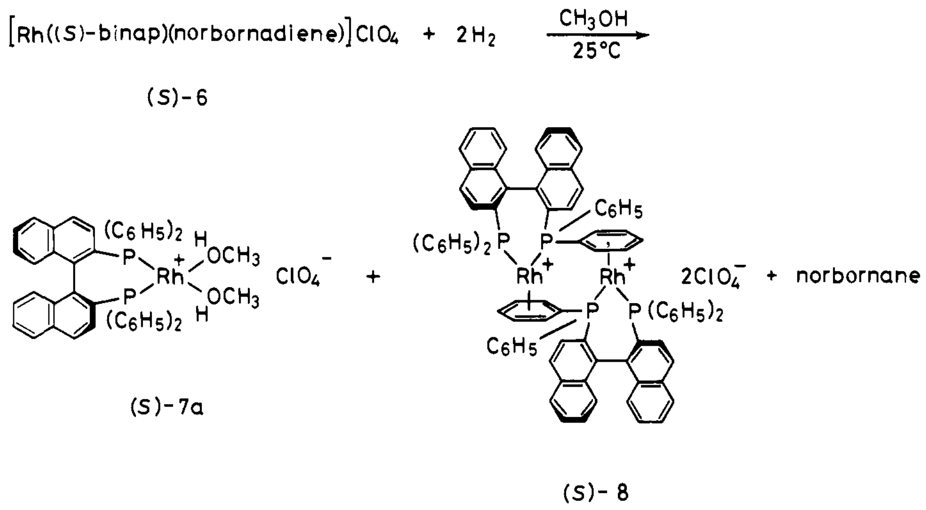
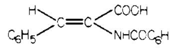
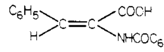
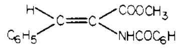
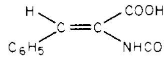
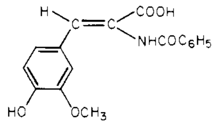
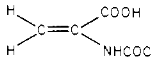


Table I. Asymmetric Hydrogenation of α-(Acylamino)acrylic Acids Catalyzed by the Rh-BINAP Complex[a]

substrate	catalyst	product	absolute confign	% yield	optical purity, % ee[b]
	(S)-7b (R)-7b	N-benzoylphenylalanine	R S	96 97	96 100
	(S)-7a	N-benzoylphenylalanine	S	93	87[c]
	(S)-7b (R)-7a	N-benzoylphenylalanine methyl ester	R S	98 97	93 92
	(S)-7a	N-acetylphenylalanine	R	99	84
	(S)-7b	N-benzoyl-3-(4-hydroxy-3-methoxyphenyl)alanine	R	97	79
	(S)-7b	N-benzoylalanine	R	97	98

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[a] The reaction was generally run with 0.5-1.0 mmol of substrate in 20-30 mL ethanol (or THF for configurationally labile E substrates) at room temperature for 48 h under an initial hydrogen pressure of 3-4 atm. [b] Optical yields were calculated with respect to the following values of the optically pure compounds: N-benzoyl-(R)-phenylalanine, $[\alpha]^{21}_D$ +41.8° (c 1, CH_3OH) (authentic sample, prepared); N-benzoyl-(S)-phenylalanine, $[\alpha]^{21}_D$ -41.4° (c 1, CH_3OH) (authentic sample, prepared); N-benzoyl-(S)-phenylalanine methyl ester, $[\alpha]^{25}_D$ -45.3° (c 1, C_2H_5OH) (Sinou, D.; Kagan, H. B. *J. Organomet. Chem.* 1976, *114*, 325); N-acetyl-(R)-phenylalanine, $[\alpha]^{20}_D$ -42.1° (c 1, CH_3OH) (authentic sample, prepared); N-benzoyl-3-(4-hydroxy-3-methoxyphenyl)-(S)-alanine, $[\alpha]^{25}_D$ -28.5° (c 1, CH_3OH) (Knowles, W. S., private communication); N-benzoyl-(S)-alanine, $[\alpha]^{21}_D$ +26.7° (c 1, 0.1N NaOH) (authentic sample, prepared). [c] Hydrogenation was carried out in THF.

The BINAP-incorporated Rh complex **7a** as well as the methanol-free complex **7b** serves as an excellent catalyst for the asymmetric hydrogenation of prochiral α-(acylamino)acrylic acids or esters. Some examples are given in Table I. Since both

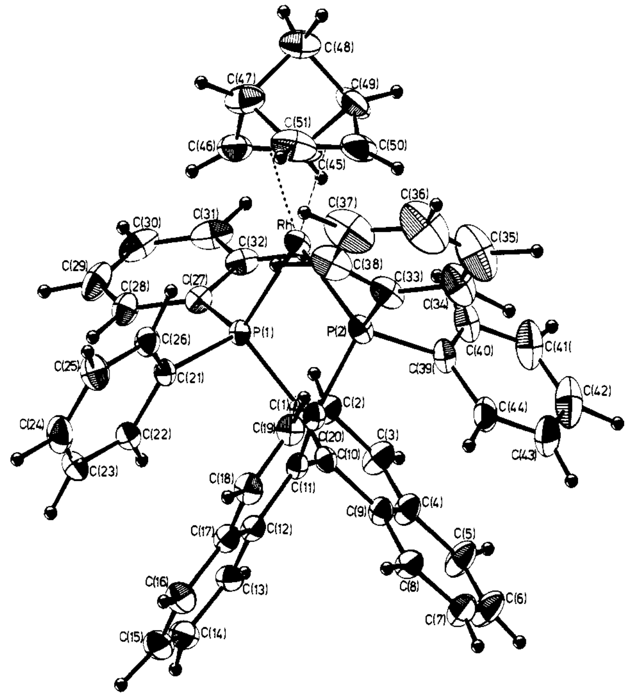

Figure 1. Moleculr structure of $[Rh((R)\text{-}(+)_{589}\text{-binap})(\text{norbornadiene})]^+$. Selected interatomic distances (Å): Rh–P(1), 2.305 (1); Rh–P(2), 2.321 (1); P(1)–C(1), 1.836 (5); P(2)–C(20), 1.844 (5); P(1)–C(21), 1.814 (5); P(1)–C(27), 1.828 (5); P(2)–C(33), 1.831 (6); P(2)–C(39), 1.810 (6); C(10)–C(11), 1.508 (7); Rh···H(C26), 2.79 (5); Rh···H(C40), 2.85 (5); Rh···H(C32), 3.61 (6); Rh···H(C38), 3.44 (5). Selected bond angles (deg): P(1)–Rh–P(2), 91.82 (5); Rh–P(1)–C(1), 113.60 (16); Rh–P(2)–C(20), 117.88 (16); P(1)–C(1)–C(10), 122.99 (35); P(2)–C(20)–C(11), 120.84 (36); C(1)–C(10)–C(11), 123.72 (44); C(20)–C(11)–C(10), 123.25 (42).

(*R*)-(+)- and (*S*)-(−)-BINAP ligands are accessible, one can obtain both enantiomers of hydrogenation products by choosing handedness of the ligand chirality. The optical yield of the reduction of the (*E*)-α-(benzamido)cinnamic acid was among the highest ever reported.[12] Usually, lower concentration of the substrate resulted in higher optical yield. For instance, the hydrogenation using a 0.013 M ethanolic solution of (*Z*)-α-(benzamido)cinnamic acid and the catalyst (*R*)-**7b** (0.7 mol%) gave the optically pure product, whereas the reaction with the 0.15 M solution of the olefinic substrate afforded the hydrogenation product in only 62% ee. In the hydrogenation of (*Z*)-α-(benzamido)cinnamic acid, higher initial hydrogen pressure resulted in lower optical yield (96–100% at 1 atm vs. 71% at 50 atm). The original Rh complex **6** or the methanol-insoluble species **8**, though containing chiral BINAP ligand(s), has proved to be poor as an asymmetric catalyst; attempted hydrogenation of (*Z*)-α-(benzamido)cinnamic acid with these catalysts under the standard conditions gave the amino acid derivative in 38 and 26% ee, respectively.

The present catalytic hydrogenation aided with a chiral BINAP ligand appears to be initiated by coordination of an olefinic substrate to Rh atom rather than rhodium hydride formation. ^{31}P NMR study[13] indeed indicates that the asymmetric reduction is proceeding mainly by the unsaturate mechanism, first postulated by Halpern.[11,14,15] The spectrum of a 0.006 M solution (low concentration usually employed in the highly asymmetric hydrogenation) of the chiral Rh complex (*S*)-**7b** in methanol with a 12 molar excess of methyl (*Z*)-α-(benzamido)cinnamate at −50 °C exhibited a sharp, rhodium-coupled AB quartet at δ 32.4 (J_{Rh-P} = 168 Hz, J_{P-P} = 42 Hz) and 21.0 (J_{Rh-P} = 162 Hz) due to the tetracoordinate Rh(I) complex containing the bidentate diphosphine, (*S*)-BINAP, and the olefinic substrate (chelate coordination via C=C and oxygen of amide carbonyl).[15] Here the occurrence of a single set of eight-line signals (within the limits of NMR detection) demonstrates that only one of two possible diastereomers exists in the solution. This indicates that the BINAP-coordinated Rh(I) complex has a very high ability of enantioface differentiation, although this might not necessarily be the criterion for the efficiency of the asymmetric reaction.[15b] Finally it should be pointed out that under some particular conditions Rh(I) complexes containing two olefinic substrates may participate in the catalytic hydrogenation. When the isolated 1:2 complex[16] of (*S*)-**7b** and (*Z*)-α-(benzamido)cinnamic acid was allowed to stir under hydrogen atmosphere in methanol containing 4.4 molar excess of the olefinic substrate, *N*-benzoyl-(*R*)-phenylalanine was formed in only 71% ee. Such a phenomenon is consistent with the marked concentration effect on the optical yields in the hydrogenations.

Thus the catalytic hydrogenation system contains a variety of catalysts and coordination complexes which behave differently in asymmetric reactions. In order to achieve a high optical yield, therefore, efforts are to be exerted to control the conditions so that a selected species leading to high stereoselectivity is created.

Acknowledgment. We thank Professor S. Otsuka and Dr. K. Tani for valuable suggestions regarding the optical resolution procedure. We also thank Dr. W. S. Knowles of Monsanto Co. for informing us of the value of optical rotation of pure *N*-benzoyl-3-(4-hydroxy-3-methoxyphenyl)-(*S*)-alanine.

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(10) ^1H NMR (CD_2Cl_2) of (*S*)-**8**: δ 7.48 (m, 14.5 H), 6.90 (m, 12 H), 6.55 (m, 7 H), 6.05 (m, 5 H). Among the four multiplet signal groups, the high-field signal centered at δ 6.05 could be assigned to the phenyl group of the BINAP ligand interacted with the second Rh atom through π-arene coordination.[11]

(11) Halpern, J.; Riley, D. P.; Chan, A. S. C.; Pluth, J. J. *J. Am. Chem. Soc.* **1977**, *99*, 8055–8057.

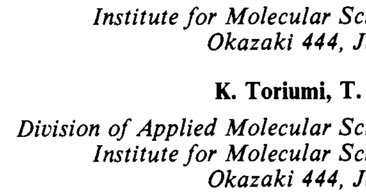
(12) (a) Detellier, C.; Gelbard, G.; Kagan, H. B. *J. Am. Chem. Soc.* **1978**, *100*, 7556–7561. (b) Koenig, K. E.; Knowles, W. S. *Ibid.* **1978**, *100*, 7561–7564.

(13) ^{31}P NMR studies on the mechanism of asymmetric hydrogenation catalyzed by chiral diphosphine-Rh(I) complexes: (a) Brown, J. M.; Chaloner, P. A. *J. Am. Chem. Soc.* **1980**, *102*, 3040–3048. (b) Brown, J. M.; Chaloner, P. A. *J. Chem. Soc., Chem. Commun.* **1980**, 344–346 and references cited therein.

(14) Chan, A. S. C.; Halpern, J. *J. Am. Chem. Soc.* **1980**, *102*, 838–840.

(15) (a) Chan, A. S. C.; Pluth, J. J.; Halpern, J. *Inorg. Chim. Acta*, **1979**, *37*, L477–L479. (b) Chan, A. S. C.; Pluth, J. J.; Halpern, J. *J. Am. Chem. Soc.* **1980**, *102*, 5952–5954.

(16) A 0.06 M solution of (*S*)-**7b** in methanol containing 20-fold excess of (*Z*)-α-(benzamido)cinnamic acid (a high-concentration mixture) at 20 °C gave another type of Rh complex. The isolated complex is unstable in solution. The ^1H NMR analysis and the stoichiometry of hydrogenation suggest the value between 2.1–2.2 for [olefin]/[Rh]. ^{31}P NMR spectrum exhibited a doublet centered at δ 50.0 (J_{Rh-P} = 165 Hz) and a *singlet* at δ 41.8 with equal intensity. These facts are in agreement with the rapidly equilibrating 1:2 coordination complex **9**.



9a 9b

(17) To whom correspondence on X-ray chrystallography should be made.

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