Table I. Summary of Enthalpy Changes for Various Steps in the Thermodynamic Cycle Shown in Figure 3

step	$K^+(HMHCY)Na^-$, kJ mol^{-1}	$Cs^+(HMHCY)Na^-$, kJ mol^{-1}
1	6.0	5.6
2	5.9	5.9
3	-28.9	-31.0
4	-35.1	-35.1
5	-52.1	-54.6

from DSC measurements. We did not include the heat capacities for the various components as terms that contain them should nearly cancel out in the cycle. The results are given in Table I.

By examining the measured enthalpy of decomplexation at various temperatures and the entropies of melting of $K^+(HMHCY)Na^-$, HMHCY, and NaK, we can understand why the compound is stable to decomplexation at 225 K but decomplexes (slowly) at 300 K and above. Stability at 225 K with $\Delta H = +52.3$ kJ mol^{-1} for decomplexation implies $\Delta S < 232$ J mol^{-1} K^{-1} at this temperature. Slow decomplexation of the solid compound at 300 K with $\Delta H = +64$ kJ mol^{-1} implies $\Delta S > 213$ J mol^{-1} K^{-1} at this temperature. At 300 K, the products of decomposition are both liquids (NaK and HMHCY). Adding their entropies of crystallization (-22.6 and -21.8 J mol^{-1} K^{-1}, respectively) requires that $\Delta S > 169$ J mol^{-1} K^{-1} for the decomplexation process at 225 K. Thus, at the temperature of formation of the crystalline compound, 169 J mol^{-1} K^{-1} $< \Delta S <$ 232 J mol^{-1} K^{-1}. Decomplexation above the melting points of the products would occur for any value of ΔS between these limits.

Conclusions

HMHCY has proven to be a "robust" complexing agent not easily reduced by alkali-metal anions. That decomplexation occurs without decomposition indicates that the problems with long-term stability of the sodides arise from the small complexation constants of the two alkali-metal cations K^+ and Cs^+ with HMHCY and not from the reducibility of HMHCY.

Aside from the unique thermal properties, this compound has also provided the first evidence for contact ion-pair formation between an alkali-metal cation and an alkali-metal anion, a process that occurs without destroying the essential character of the ions.

The extraordinary stability of tertiary amine complexants should permit the synthesis of thermally stable alkalides and electrides, a property that has not been achieved with crown ethers and cryptands. A strategy for such syntheses would be to use tertiary amine complexants designed to yield more stable cationic complexes, such as bicyclic tertiary amines or aza crowns that are linked together to permit the formation of "hinged" sandwich complexes. Such studies are currently under way in our laboratory.[31]

Another noteworthy feature is the remarkable stability of solutions of these compounds in a solvent such as dimethyl ether. This provides an opportunity to study concentrated stable metal solutions. Such solutions may be useful for aprotic reductions.

Of special importance would be the ability to synthesize thermally stable electrides. The wide variety of optical, magnetic, and electron emission properties of electrides might make them useful in device applications if the problem of autocatalytic decomposition can be overcome. Initial studies of a lithium-based electride that employs a cyclic methylated polyaza complexant are very encouraging in this regard.[31]

Acknowledgment. This research was supported in part by National Science Foundation Solid-State Chemistry Grant No. DMR 87-14751. We are grateful to the Michigan State University Center for Fundamental Materials Research for providing funds for some of the equipment. We thank D. L. Ward for the crystal structures and L. E. Hill for the MAS-NMR measurements.

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Synthesis of η^1 Oxygen-Bound Rhodium Enolates. Applications to Catalytic Aldol Chemistry[1]

Greg A. Slough, Robert G. Bergman,* and Clayton H. Heathcock*

Contribution from the Department of Chemistry, University of California, Berkeley, California 94720. *Received June 20, 1988*

Abstract: Oxygen-bound rhodium enolate complexes are prepared by metathesis of carbonylbis(phosphine)rhodium(I) halides and potassium enolates, **3-6**. Rhodium enolates of acetophenone (**7**), propiophenone (**9**), ethyl mesityl ketone (**10**), and ethyl *tert*-butyl ketone (**11**) were prepared and fully characterized. Complex **11** condenses with benzaldehyde under a variety of conditions to produce isolable rhodium aldolate complex **12**. Cleavage of **12** with trimethylsilyl chloride yields aldol silyl ether and rhodium chloride. Similar treatment of **12** with an enol silane affords the aldol silyl ether and a rhodium enolate. A catalytic aldol reaction involving enol silanes, silylketene acetals, and benzaldehyde under rhodium catalysis is presented. Deuterium, phosphorus, and carbon NMR were used to demonstrate the intermediacy of rhodium enolates and aldolates in the aldol process and to elucidate the gross mechanistic features of the catalytic cycle.

Asymmetric induction in the synthesis of organic molecules is a topic of considerable current interest.[2] Significant progress has been made, particularly in oxidation and reduction reactions, where efficient catalytic processes are known that give high levels of asymmetric induction. Less progress has been made in achieving good levels of asymmetric induction in carbon-carbon bond-forming processes such as the aldol addition reaction. For this important reaction, several excellent enantioselective methods have been developed wherein the chiral auxiliary is used stoichiometrically,[3] and there is one report of good asymmetric induction involving a noncovalently bound chiral auxiliary.[4] However, there

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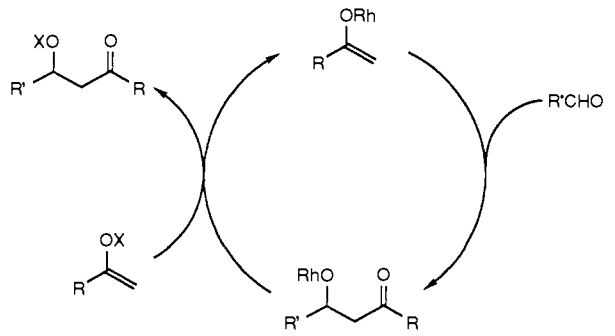
Table 1. Preparation of Rhodium Enolate Complexes (Equation 2)

complex	potassium enolate	product	potassium enolate geometry	rhodium enolate geometry	yield, %
1	**3**	**7**			91
2	**3**	**8**			93
1	**4**	**9**	*Z*	*Z*	49
1	**5**	**10**	1:1 *Z*/*E*	1:2 *Z*/*E*	97
1	**6**	**11**	*Z*	*Z*	96

Scheme I

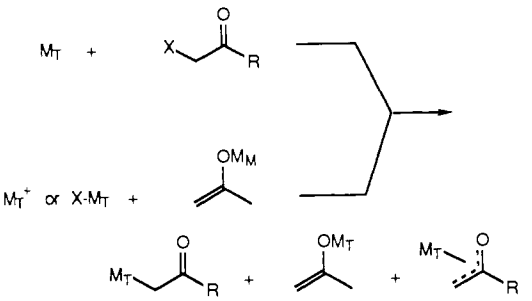


is to date only one example of a truly *catalytic* asymmetric aldol addition reaction, the Ito–Hayashi carbomethoxyisoxazoline synthesis.[5]

Over the past few years, the Heathcock group has spent a considerable amount of effort looking for effective chiral auxiliaries that could be used with lithium, magnesium, or zinc enolates to bring about good levels of asymmetric induction in aldol addition reactions. Although it is not appropriate here to recount all of this unfruitful research, representative examples of the types of systems investigated may be seen in a 1984 review of the stereochemistry of the aldol addition reaction.[6] Several years ago, the Bergman and Heathcock groups undertook a program aimed at the eventual use of transition-metal enolates as reagents for catalytic, asymmetric aldol addition reactions. We embarked upon this project in part because of the success that has been achieved in using transition-metal systems for asymmetric induction. Four notable examples of this strategy are Sharpless epoxidation,[7] homogeneous rhodium hydrogenation,[8] rhodium hydrosilylation of ketones,[9] and the aforementioned Ito–Hayashi chiral oxazoline synthesis.[5]

In prior publications, we have reported the discovery of photochemical aldol reactions with tungsten and molybdenum enolates.[10] In this paper, we report an investigation of the aldol chemistry of rhodium enolates, a study that has led to the discovery of a catalytic process with a turnover number of approximately 100.[11] This work lays the foundation for future exploration of the catalytic asymmetric aldol reaction involving rhodium enolates.

Preparation and Characterization of Rhodium Enolates. Two main methods have previously been used for the preparation of transition-metal enolates (eq 1). In the first, a metal anion is



(1)

used to displace halide ion from an α-bromo- or α-chlorocarbonyl compound.[10,12] Alternatively, a main-group enolate is utilized to displace halide from an electrophilic metal complex.[13] For early transition metals, the second approach is normally used and provides O-bound enolates. For middle and late transition metals, the first approach has been most commonly employed, leading to C-bound enolate complexes. In this paper, we show that trans substituted, square-planar rhodium halides provide convenient access to late-transition-metal O-bound enolates in nearly quantitative yield.[14]

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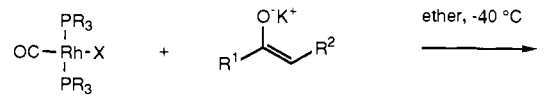
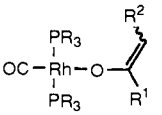
Treatment of a THF or diethyl ether solution of carbonylchlorobis(trimethylphosphine)rhodium(I)[15] (**1**) or carbonylfluorobis(triphenylphosphine)rhodium(I)[16] (**2**) at −40 °C with a solid potassium enolate results in the formation of potassium halide and rhodium enolate complexes **7**–**11** (eq 2; Table I). The enolate



1: R = Me, X = Cl
2: R = Ph, X = F

3: R^1 = Ph, R^2 = H
4: R^1 = Ph, R^2 = Me
5: R^1 = Mes, R^2 = Me
6: R^1 = *t*-Bu, R^2 = Me



(2)

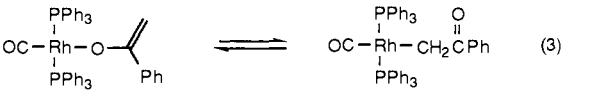
7: R = Me, R^1 = Ph, R^2 = H
8: R = Ph, R^1 = Ph, R^2 = H
9: R = Me, R^1 = Ph, R^2 = Me
10: R = Me, R^1 = Mes, R^2 = Me
11: R = Me, R^1 = *t*-Bu, R^2 = Me

complexes are isolated as analytically pure yellow powders, generally in yields of >90%, by concentration of the reaction mixture, dissolution of the residue in diethyl ether, filtration, and evaporation to dryness. The acetophenone and propiophenone enolates (**7**–**9**) crystallize from ether as fluffy yellow crystals.

Rhodium enolate complexes **7**–**10** prepared from aromatic ketones are air- and moisture-sensitive but are thermally stable at room temperature in the solid state. By contrast, the solid rhodium enolate **11** decomposes at room temperature over 2 h, forming ketone and unidentifiable organometallic products. When stored at −40 °C, this material is stable indefinitely. In polar solvents, the rhodium enolates decompose slowly at 25 °C, yielding ketone and a brown rhodium-containing residue. NMR analysis of the acetophenone produced in the decomposition of complex **7** in THF-d_8 indicates that proton abstraction from the phosphine ligand has occurred, since the methyl singlet at 2.51 ppm and the ortho protons at 7.97 ppm integrate in a ratio of 3:2. This decomposition mode is particularly acute in THF, where $t_{1/2}$ of complex **7** is ~50 min.

Analysis by IR, ^{1}H NMR, and ^{13}C NMR spectrometry indicates that the rhodium enolates **7**–**11** all exist as O-bound tautomeric forms. These complexes show no carbonyl infrared stretching absorption in the 1800–1600-cm^{-1} region, whereas the carbon-bound enolates of tungsten,[10a] molybdenum,[10a] rhenium,[10b,12d] manganese,[12d,g] and iron[12d,k] possess bands between 1700 and 1640 cm^{-1} for the organic carbonyl. Chemical shift data for the olefinic protons and carbons support the foregoing assignment. The vinyl methylene protons in complex **7** resonate as broad singlets at 4.40 and 4.62 ppm, while the methine protons for complexes **9**–**11** appear as quartets between 4.07 and 4.72 ppm. These chemical shifts are comparable to the methylene chemical shifts seen in zirconium,[17] titanium,[18] and tin[13h] O-bound enolates. In the carbon spectra, only one low-field resonance is observed. This signal, a double triplet at 193 ppm, is assigned to the phosphine-coupled metal carbonyl carbon and indicates a trans substituted complex.[19] The quaternary alkene carbons of the primary enolate complexes resonate at 80 ppm while those of the secondary systems appear at 78 ppm. These carbon shifts are only consistent with the hypothesis that the complexes are O-bound.

Although the spectral data strongly indicate O–metal bonding, the NMR data for complexes **8** and **10** show evidence for rapid equilibration with the corresponding carbon-bound isomer. In the ^{1}H NMR spectrum of complex **8**, the methylene protons appear as a broad singlet at 4.33 ppm. Upon cooling to 0 °C, this singlet splits into two signals, similar to the pattern seen in the spectrum of **7**. This behavior is consistent with a dynamic equilibrium between O-bound and C-bound forms (eq 3); from



(3)

the chemical shift difference of 64 Hz and the ^{1}H NMR coalescence temperature of about 25 °C, $\Delta G^{\ddagger}$ must be on the order of 10 kcal mol^{-1} for the isomerization. It seems likely that the interconversion of the methylene hydrogens takes place via a small amount of the O-bound enolate.

The *E*:*Z* isomer ratio in complex **10** also provides evidence for oxygen–carbon equilibration. Two different *E*:*Z* ratios of potassium enolate geometries (1:1 and 1:4)[20] react with chloride **1** to produce an identical 62:38 *E*:*Z* ratio of rhodium enolates **10** in 97% yield. The rhodium enolate ratios were determined by ^{1}H NMR, and geometric assignments were made on the basis of the products obtained by reaction of the enolates with trimethylsilyl chloride; (*E*)- and (*Z*)-enol silanes are produced in a ratio of 62:38 (^{1}H NMR and GLPC analysis). Control experiments demonstrated that no geometric isomerization of the potassium enolate occurred under the reaction conditions. The lack of correspondence of potassium and rhodium enolate geometries suggests that O-bound to C-bound isomerization occurs after metathesis.

Aldol Reactions or Rhodium Enolates. With an efficient route to O-bound rhodium enolate available, our attention focused on the development and generalization of a rhodium-catalyzed aldol reaction (see Scheme I). Four important features must be incorporated into this catalytic process: (1) the rhodium catalyst must be sufficiently nucleophilic to condense with aldehydes, (2) the rhodium aldolate complexes must be resistant to significant competing irreversible decomposition under the reaction conditions, (3) the rhodium–oxygen bond in the rhodium complexes must be reactive toward the organic enol derivatives, and (4) the enol source and the aldehyde must not condense without the catalyst.[21]

An investigation of these requirements reveals that an effective rhodium-based catalytic cycle exists in the reaction of enol silanes with aromatic aldehydes. Rhodium enolate complex **11** reacts with benzaldehyde at −20 °C in toluene over 5 days to produce *syn*-rhodium aldolate **12** in 79% yield (^{1}H NMR analysis) (eq 4). The yellow, crystalline aldolate complex was isolated in 31% yield by recrystallization from pentane at −40 °C. Compound **12** is extremely sensitive to air, moisture, and heat. Drying the crystals at room temperature under high vacuum leads to discoloration after 20 min. Prolonged standing at room temperature in a drybox leads to complete decomposition.

Because of the extended reaction time and tedious isolation procedure, a second synthetic route to complex **12** was devised. Treatment of a toluene solution of rhodium chloride **1** and benzaldehyde (1.0 equiv) with potassium enolate **6** at −40 °C resulted

(14) Drs. Thomas Tulip and Ken Feldman, Du Pont Central Research, were the first to make this observation. We thank Drs. Tulip and Feldman for sharing their preliminary studies with us.

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(17) ^{1}H NMR and ^{13}C NMR data for zirconium enolate hydride and iodide match closely: Moore, E. J.; Straus, D. A.; Armantrout, J.; Santarsiero, B. D.; Grubbs, R. H.; Bercaw, J. E. *J. Am. Chem. Soc.* **1983**, *105*, 2068. (b) Planalp, R. P.; Andersen, R. A. *Ibid.* **1983**, *105*, 7774.

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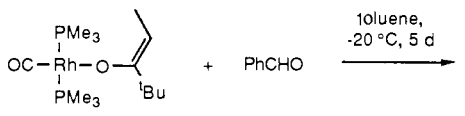
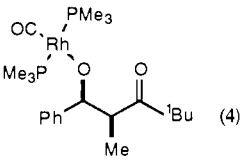
(19) All enolates show a Rh–CO infrared stretch at 1979–1960 cm^{-1}, analogous to that seen in $CO(PMe_3)_2RhCl$ (see ref 15), and a double triplet (193 ppm) in the ^{13}C NMR spectrum, due to equivalent coupling of the carbonyl carbon with the two phosphorus ligands.

(20) Potassium enolate geometries were measured by integration of the methine proton signals in the ^{1}H NMR spectra, 3.41 (*Z*) and 3.69 (*E*) ppm, respectively.

(21) Fluoride sources also function as catalysts in this reaction. For leading references, see: (a) Noyori, R.; Yokayama, K.; Sakata, J.; Kuwajima, I.; Nakamura, E.; Shimizu, M. *J. Am. Chem. Soc.* **1977**, *99*, 1265. (b) Nakamura, Shimizu, M.; Kuwajima, I.; Sakata, J.; Yokoyama, K.; Noyori, R. *J. Org. Chem.* **1983**, *48*, 932. (c) Noyori, R.; Nishida, I.; Sakata, J. *J. Am. Chem. Soc.* **1983**, *105*, 1598.



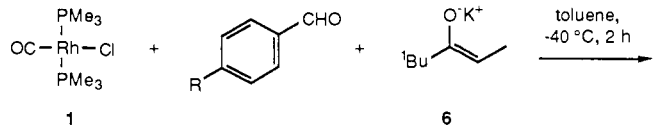
11



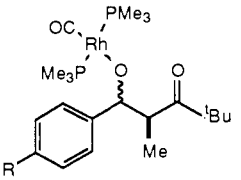
(4)

12

in a rapid reaction. After 2.0 h, NMR analysis of the crude mixture showed a mixture of *syn*-aldolate, *anti*-aldolate, and rhodium enolate in a ratio of 5.1:2.1:2.4. Crystallization of the crude product from pentane provided *syn*-aldolate **12** in 39% yield (eq 5). We believe that this reaction involves aldol addition of



1 6

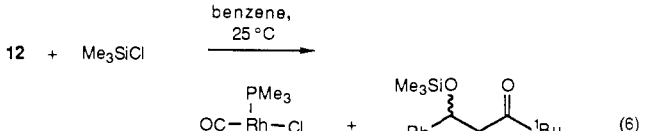


(5)

12: R = H
13: R = Me

potassium enolate **6** to benzaldehyde, giving a potassium aldolate, which reacts with rhodium chloride **1** to give the observed product. This synthetic method was also applied to tolualdehyde to obtain aldolate complex **13**.

In contrast to main-group aldolates,[22] the rhodium aldolates **12** and **13** have an open structure with only one rhodium–oxygen linkage. Infrared spectroscopy shows two carbonyl bands: a strong metal carbonyl stretch at 1950 cm^{-1}, which is characteristic of a 16-electron square-planar geometry, and a moderate band at 1699 cm^{-1}. The latter stretching frequency is comparable to that seen for ethyl *tert*-butyl ketone itself; a chelated carbonyl would be expected to have a significantly less energetic stretch.[23] Furthermore, low-temperature (−30 °C) ^{13}C NMR analysis of aldolate **12** shows a carbon resonance at 218.7 ppm, consistent with a nonchelated organic carbonyl.[24] Addition of trimethylsilyl chloride (1.08 equiv) to a benzene solution of purified *syn*-aldolate **12** causes Rh–O bond scission, leading to a 89:11 syn/anti mixture of silylated aldol and rhodium chloride **1** (eq 6).



(6)

1 14

The second requirement that must be satisfied in order to establish a viable catalytic cycle (Scheme I) is the smooth transfer of rhodium from the aldolate oxygen to an atom X of the enolate

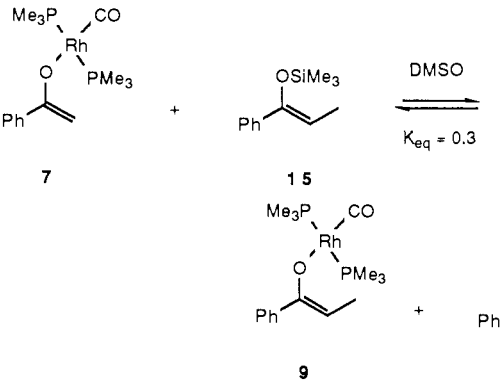
(22) The X-ray structure of a lithium aldolate shows a metal chelate: Willard, P. G.; Salvino, J. M. *Tetrahedron Lett.* **1985**, *26*, 3931.
(23) Chelated aluminum aldolate monomers have C=O stretches at 1640 and 1641 cm^{-1} for acetaldehyde and benzaldehyde adducts, respectively: Jeffery, E. A.; Meisters, A.; Mole, T. *J. Organomet. Chem.* **1974**, *74*, 373.
(24) The ester carbonyls in unchelated tungsten aldolates have infrared absorptions at 1735 cm^{-1}.[10c]

Table II. Rhodium-Catalyzed Aldol Reactions (Equation 12)

enol silane	catalyst	product[29]	yield, %	syn/ant[a]
16	**7**	**23**	29[b]	
15	**7**	**24**	70	78:22
21	**7**	**14**	83	86:14
22	7	**25**	90	50:50

[a] Determined by integration of the ^1H NMR signals of the benzylic protons. [b] Significant dehydration of the aldol to chalcone was observed.

precursor. To gain information on this point, we investigated the reactions of rhodium enolate and aldolate complexes with enol silanes. As shown in eq 7, reaction of an equimolar ratio of



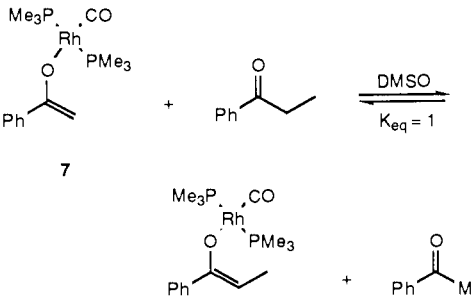
7 15 9 16

(7)

complex **7** and enol silane **15** in DMSO-d_6 resulted in rapid conversion to an equilibrium mixture containing **7** (35.6%), **9** (8.9%), **16** (35.6%), and **15** (8.9%). The same equilibrium ratio was obtained starting with rhodium enolate complex **9** and enol silane **16**.

In the course of the foregoing investigation, it was found that DMSO is the solvent of choice for equilibration and addition reactions of the rhodium enolates. A variety of other solvents, both polar (THF, CH_2Cl_2, and CH_3CN) and nonpolar (benzene, toluene), were found to be inferior. Mixtures of DMSO and less polar solvents were also found to be useful in some cases. For example, reactions were found to be exceedingly slow in benzene or toluene but too fast in pure DMSO for convenient monitoring by NMR spectrometry. A solvent mixture consisting of 1.0 vol of DMSO and 2.5 vol of benzene ("28% DMSO/benzene") moderates the reaction rates and was used in many of the mechanistic studies to be discussed later. The beneficial effect of DMSO on the rhodium enolate reactions does not appear to be due to ligation of the sulfoxide by the metal; addition of 2.0 equiv of DMSO to a benzene solution of enolate **7** shows no change in either the ^1H or ^{13}C NMR spectra. Furthermore, conductance measurements of a solution of enolate **7** in DMSO indicated no ionization, since only background conductivity was observed.

Rhodium enolates also show significant basicity toward protons. Enolate **7** reacts with propiophenone in DMSO-d_6 solution to give enolate **9** and acetophenone (eq 8); the equilibrium constant for this reaction is approximately 1, and NMR measurements indicate that enolates **7** and **9** comprise 90% of the original material used.

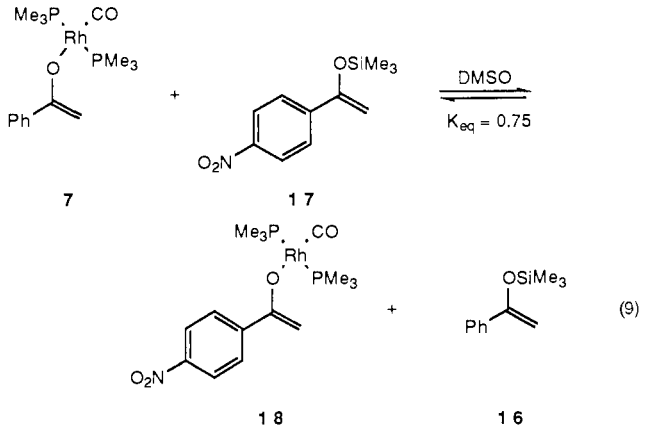


7

(8)

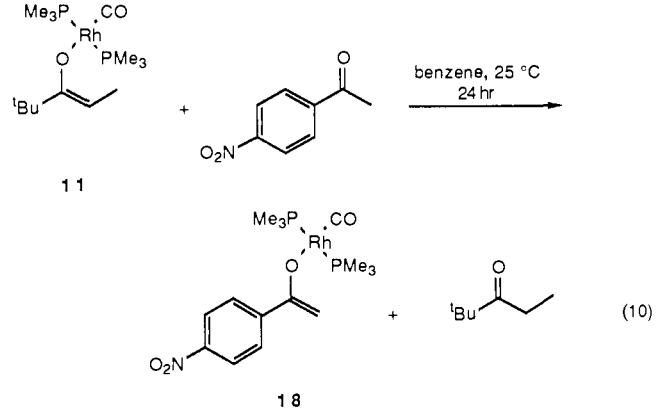
K_{eq} for the exchange reactions of rhodium enolates with enol silanes is only modestly effected by electron-withdrawing substituents. For example, K_{eq} for the reaction of complex **7** with

the enol silane of *p*-nitroacetophenone (**17**) is 0.75 (eq 9). On



(9)

the other hand, *p*-nitroacetophenone exchanges completely with the more basic ligand of enolate **11** in benzene to give the enolate complex **1**, and ethyl *tert*-butyl ketone in nearly quantitative yield (eq 10). The driving force for this conversion is probably because



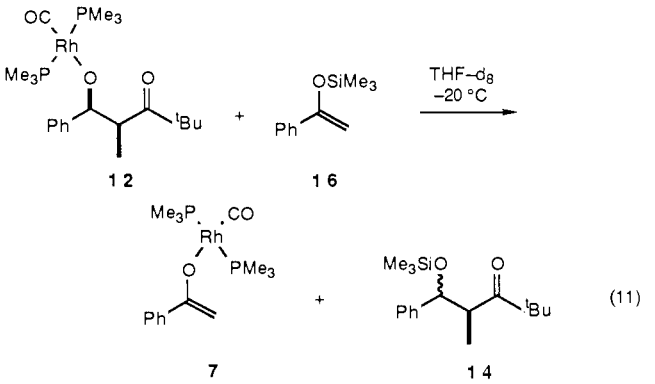
(10)

of (a) relief of steric compression between the *tert*-butyl group and the ligated rhodium center and (b) the greater thermodynamic acidity of an aryl methyl ketone relative to a *tert*-butyl ethyl ketone. This acid–base exchange process provides a synthetic route to rhodium enolates, which are otherwise inaccessible.[25]

The stability of rhodium enolates, as deduced from the foregoing experiments, is directly related to the acidity of the ketone from which it is derived. The relative thermodynamic acidities of pertinent ketones has been found to be *p*-nitroacetophenone > acetophenone > propiophenone > acetone.[26,27]

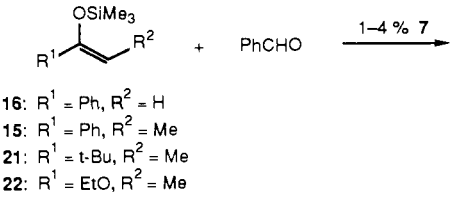
Cleavage of the rhodium–oxygen bond in the rhodium aldolate complexes can also be effected using enol silanes. As shown in eq 11, prolonged reaction of rhodium aldolate **12** with enol silane **16** in THF-d_8 at −20 °C results in 50% consumption of **12** (after 120 h), yielding complex **7** and a 2.3:1 mixture of syn and anti silylated aldols (**14**). At higher reaction temperatures complex mixtures resulted. The source of stereochemical loss in the cleavage is not understood. Analysis of the ^{1}H NMR spectrum of the reaction indicates no stereochemical deterioration of the rhodium aldolate during the course of the reaction.

The foregoing exchange results suggest the feasibility of a rhodium-catalyzed aldol reaction, a process that has now been realized. Addition of a small amount (1–4 mol %) of rhodium enolate complex **7** to a DMSO solution of an enol silane and



(11)

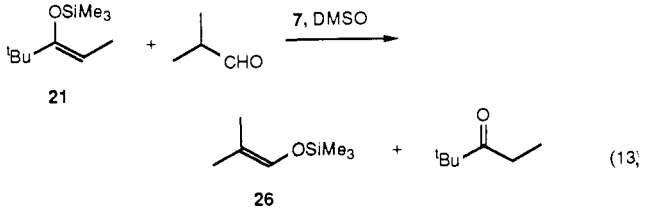
benzaldehyde causes the formation of the corresponding silylated aldol (eq 12); results for four enol silanes are summarized in Table



(12)

II. Appropriate control experiments have established the catalytic role of rhodium; benzaldehyde does not react with enol silanes under the reaction conditions. Catalyst turnover has been examined by varying the relative amount of rhodium enolate.[28] A turnover maximum of 100 is observed; lower rhodium concentrations result in only partial conversion to aldol products.

Enol silanes derived from methyl ketones yield mixtures of silylated aldol and the corresponding enone resulting from β-elimination. However, this side reaction is not observed with secondary enol silanes and ketene acetals. Propiophenone, ethyl *tert*-butyl ketone, and ethyl propionate give aldol products in excellent yields, with no evidence of β-elimination. Attempts to extend the generality of this catalysis to enolizable aldehydes have failed. Reaction of enol silane **16** with isobutyraldehyde under rhodium enolate catalysis results only in formation of the enol silane of the aldehyde (**26**) and ethyl *tert*-butyl ketone (eq 13). Similar results are obtained with hexanal.



(13)

The (*Z*)-rhodium enolates investigated in this study show syn selectivity, with the precise syn/anti ratio being dependent on reaction conditions. In nonpolar solvents, complex **11** reacts stoichiometrically with benzaldehyde at −20 °C to produce high syn/anti ratios of aldolate **12**. The same reaction in DMSO-d_6 at room temperature and 20% excess aldehyde affords aldolate

(25) Because of the nitro group, one cannot use conventional methods to prepare the lithium or potassium enolate of *p*-nitroacetophenone.

(26) (a) Bordwell, F. G.; Bares, J. E.; Bartmess, J. E.; McCollum, G. J.; Van Der Puy, M.; Vanier, N. R.; Matthews, W. S. *J. Org. Chem.* **1977**, *42*, 321. (b) Guthrie, J. P. *Can. J. Chem.* **1979**, *57*, 1177.

(27) The thermodynamic acidity of ethyl *tert*-butyl ketone is not known; however, it should be considerably less than that of acetone, both because of steric inhibition to solvation of the enolate and because of the inductive effect of the vinyl methyl substituent in the enolate.

(28) Rhodium enolate concentrations were studied between 0.6 and 4 mol % with enol silane **15** as substrate.

(29) Products after desilylation were identical in all regards with materials previously reported: Heathcock, C. H.; Buse, C. T.; Kleschick, W. A.; Pirrung, M. C.; Sohn, J. E.; Lampe, J. *J. Org. Chem.* **1980**, *45*, 1066.

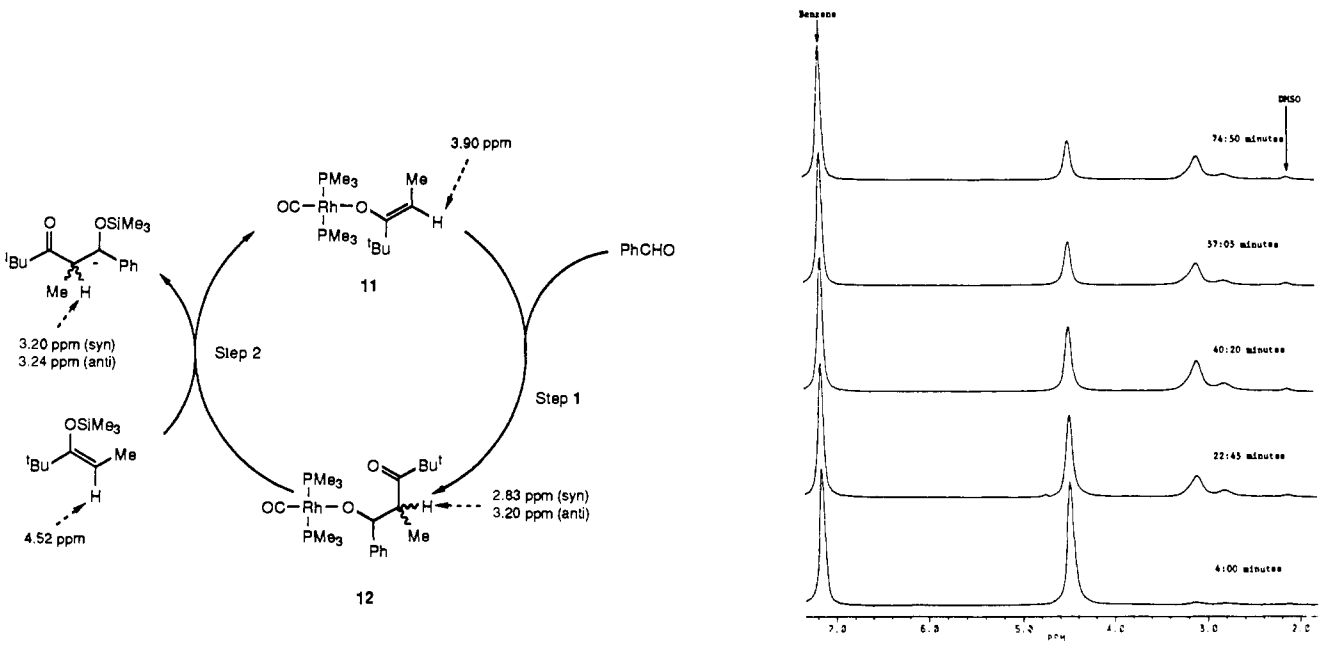


Figure 1. (Left) Schematic representation of the aldol catalytic cycle, along with important resonances involved in the cycle observable by ^{1}H NMR spectroscopy. (Right) Catalytic reaction monitored by ^{2}H NMR spectrometry, starting with enol silane **21**-d_1, benzaldehyde, and rhodium enolate **11**.

12 as a 2.1:1 syn/anti mixture, as measured by ^{1}H NMR and ^{31}P NMR spectrometry. Use of a large excess of benzaldehyde (50 equiv) also gives smooth conversion to aldolate **12** but as a 5:1 syn/anti mixture. In the catalytic reaction of enol silane **21** with benzaldehyde (eq 12), syn/anti ratios ranging from 8:1 to >20:1 have been observed, depending on the conditions of the reaction. With equimolar amounts of **21** and benzaldehyde, the stereoselectivity is independent of rhodium enolate concentration; an identical 92:8 ratio of *syn*- and *anti*-aldol silyl ethers was obtained with concentrations of catalyst **11** over the range 0.032–0.06 M. However, the stereoselectivity is moderately influenced by the relative concentrations of the two reactants; slightly higher ratios of benzaldehyde to enol silane result in enhanced syn/anti ratios.

Mechanism of the Catalytic Rhodium Enolate Aldol Reaction. The final aspect of our work concerns the existence and mechanistic role of each rhodium complex in the catalytic aldol reaction using isotopic labeling, deuterium, phosphorus, and carbon NMR spectrometry, and reaction kinetics. For these experiments, enol silane **21** with 97% deuterium enrichment at the vinyl position and benzaldehyde with 98.2% ^{13}C enrichment in the aldehyde carbon were prepared by standard protocols.[30,31]

In our first labeling experiment we followed deuterium incorporation into the rhodium complexes during the catalytic aldol process (Figure 1). A solvent mixture of benzene/DMSO (2.5:1, v/v) provided a reaction with suitable rates for convenient NMR monitoring. A solution 0.20 M in enol silane **21**-d_1, 0.30 M in benzaldehyde, and 0.04 M in rhodium enolate **11** was monitored by ^{2}H NMR spectrometry. Progress of the reaction was characterized by disappearance of the deuterium signal of the enol silane (4.52 ppm) and appearance of a deuterium signal at 3.20 ppm, the chemical shift of the methine position of the syn diastereomer of the silylated aldol product. Within the first 4 min of reaction (ca. 7% reaction), a deuterium signal was observed at 2.83 ppm, corresponding to the chemical shift of the syn diastereomer of the rhodium aldolate complex **12**. Unfortunately, the corresponding signal at 3.20 ppm for the anti diastereomer of **12** could not be observed, since it overlaps the 3.20 ppm signal of the silylated aldol product. The rhodium enolate **11** initially added to the reaction mixture is rapidly converted to **12**, whose concentration does not change during the remainder of the reaction. Thus, the aldol step is much faster than the trimethylsilyl transfer step, and consequently the rhodium is present primarily as the aldolate complex, rather than as the enolate complex, during the catalytic reaction. The foregoing experiment was repeated, initiating the catalytic cycle with rhodium aldolate **12**; identical results were obtained.

Phosphorus and carbon NMR provided more quantitative data on the distribution of the rhodium-containing intermediates during the course of the reaction. The ^{31}P NMR spectrum shows three phosphorus resonances: doublets (due to splitting by Rh, spin = $^1/_2$) at −11.42 and −12.67 ppm, corresponding to the syn and anti diastereomers of aldolate **12**, and a doublet at −10.19 ppm, corresponding to the rhodium enolate. The steady-state ratio of these signals showed that the aldolate/enolate ratio is about 10:1. The *syn*- and *anti*-aldolates were found to be present in a ratio of 68:32. It should be noted that the ^{31}P NMR spectrum of the catalytic mixture remains virtually unchanged over 2.1 h, which illustrates the robust nature of the catalytic rhodium intermediates.

The reaction was also monitored by ^{13}C NMR spectrometry using ^{13}C-labeled benzaldehyde. The ^{13}C NMR spectra show four principal resonances during the reaction. The ^{13}C-enriched benzylic carbons of the rhodium aldolates *syn*-**12** and *anti*-**12** appear as triplets (due to splitting by the two phosphine ligands) with J = 6.1 Hz at 85.80 and 86.83 ppm, respectively. The silylated aldols *syn*-**14** and *anti*-**14** appear as singlets at 77.24 and 78.60 ppm, respectively. The ^{13}C NMR experiments showed the *syn*- and *anti*-rhodium aldolates to be present in a steady-state ratio of about 2:1 throughout the course of the reaction, with starting benzaldehyde to enol silane ratios ranging from 1:3 to 4:1. In contrast, the ratio of syn and anti silylated aldols is approximately 10:1 under most conditions. However, when the reaction was carried out with a benzaldehyde/enol silane ratio of 4:1, the reaction was found to be significantly slower, and the ratio of syn and anti silylated aldols was found to be somewhat higher, being about 23:1 in the early stages of the reaction and falling to about 15:1 toward the end of the reaction.

The ^{13}C NMR experiments also revealed a transient sharp singlet (77.09 ppm), which disappeared as the reaction progressed. The chemical shift of this signal, and the fact that it is a singlet, suggests that it arises from a species having a carbinol carbon that is not associated with the rhodium. The structure of the species

(30) Ethyl *tert*-butyl ketone was deuteriated by stirring in D_2O (99% deuterium atom) at 80 °C with a catalytic amount of NaOH. The enol silane was prepared by a previously published method: Heathcock, C. H.; Davidsen, S. K.; Hug, K. T.; Flippin, L. A. *J. Org. Chem.* **1986**, *51*, 3027. The isotopic purity was determined by mass spectral analysis.

(31) Huan, Z.; Landgrebe, J. A.; Peterson, K. *J. Org. Chem.* **1983**, *48*, 4519.

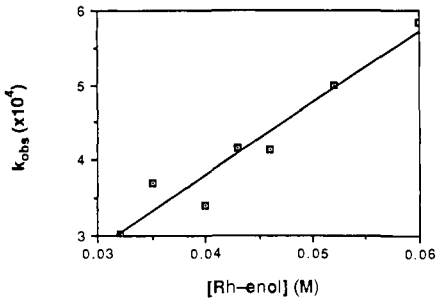


Figure 2. Variation of the pseudo-first-order rate constant for the catalytic aldol reaction caused by changes in the concentration of rhodium enolate catalyst.

giving rise to this signal is not known. Integration of the ^{13}C NMR spectra showed the ratio of the syn silylated aldol and the unknown species to be 3:1 after 15% reaction. At 50% reaction, the ratio was about 10:1, and, at 80% reaction, the ratio was in the range 20:1 to 60:1, depending on the initial ratio of benzaldehyde to enol silane.

The foregoing NMR experiments suggest a mechanism wherein condensation of the rhodium enolate with benzaldehyde is about 1 order of magnitude faster than the rate-determining transfer of the silyl group from the enol silane to the rhodium aldolate. We were able to provide at least partial support for this scheme from kinetic studies, although we have not been able to establish the rate law fully. Under standard preequilibrium conditions (i.e., 50 equiv of benzaldehyde), the rate of the catalytic reaction exhibited clean first-order dependence on the concentration of enol silane **16**. The magnitude of the measured rate constant k_{obs} was essentially independent of the concentration of the silane over a concentration range of 0.10–0.63 M, but some scatter in the data was observed (runs 1–6 in Table III; $k_{obs} = 4.01 \pm 0.4 \times 10^{-4}$ s^{-1} at 21.6 °C). With these data in hand, we next attempted to establish the order in rhodium catalyst. Unfortunately, technical problems frustrated our attempts to measure pseudo-first-order rate constants accurately over a very wide range of catalyst concentration. As shown in runs 7–12 of Table III and in the plot in Figure 2, within about a factor of 2.0 variation in [Rh], the reaction appeared to be first-order in this component. However, the overall change in k_{obs} measured over this range of concentration was not very different from the random variation observed in runs 1–6. Some reassurance that the 0.032–0.060 M variation in runs 7–12 may be meaningful is provided by the systematic variation in these values, as opposed to the apparently

Table III. Stereochemistry and Kinetics of Rhodium-Catalyzed Aldol Reaction

[Rh], M	enol silane **16**, M	[PhCHO], M	$10^4 k_{obs}$, s^{-1}	diastereomer ratio (syn/anti)
0.040	0.10	2.05	5.16	19.8:1
0.040	0.20	2.03	3.90	17.4:1
0.040	0.40	2.01	3.41	12.5:1
0.040	0.32	2.03	4.12	11.0:1
0.040	0.51	2.03	3.73	11.0:1
0.040	0.63	2.03	3.82	11.0:1
0.060	0.40	2.03	5.84	12.5:1
0.052	0.40	2.03	5.00	12.3:1
0.032	0.40	2.03	3.02	12.6:1
0.035	0.40	2.03	3.69	12.5:1
0.043	0.40	2.03	4.16	12.3:1
0.046	0.40	2.03	4.14	12.2:1

random scatter in the rate constants measured in the first six runs. In addition, one rate constant checked by ^1H NMR spectrometry (run 9) gave quite good agreement with the corresponding GLPC measurement ($k_{GLPC} = 3.02 \times 10^{-4}$ s^{-1}; $k_{NMR} = 3.20 \times 10^{-4}$ s^{-1}). Therefore, although we do not feel completely confident about the interpretation of the variable-rhodium runs, they seem to be at least suggestive that the reaction is first-order in the concentration of catalyst.

All of the data are consistent with the catalytic cycle summarized in Figure 3, wherein the rate-determining step is cleavage of the rhodium alkoxide **12** by enol silane with generation of rhodium enolate **11** and silylated aldol products. Figure 3 is, no doubt, over-simplified, as there are probably other intermediates. For example, the reaction of rhodium enolate **11** with benzaldehyde presumably requires a step in which coordination of the aldehyde to the metal center occurs. Similarly, transfer of the silyl group probably requires prior coordination of the enol silane double bond to the metal center. However, with the exception of the aforementioned unknown species giving rise to the ^{13}C NMR resonance of 77.09 ppm, no other intermediates are detected spectroscopically. Furthermore, as has already been stated, the singlet nature of this signal strongly suggests that the species giving rise to it is not associated with rhodium, so it may not be an intermediate at all but an initially produced side product that is subsequently destroyed.

The NMR experiments previously described revealed that the steady-state ratio of *syn*- and *anti*-rhodium aldolates during the catalytic aldol reaction is approximately 2:1. That this is the true equilibrium ratio of these stereoisomers was confirmed by dissolution of the *syn*-rhodium aldolate **12** in a benzene/DMSO

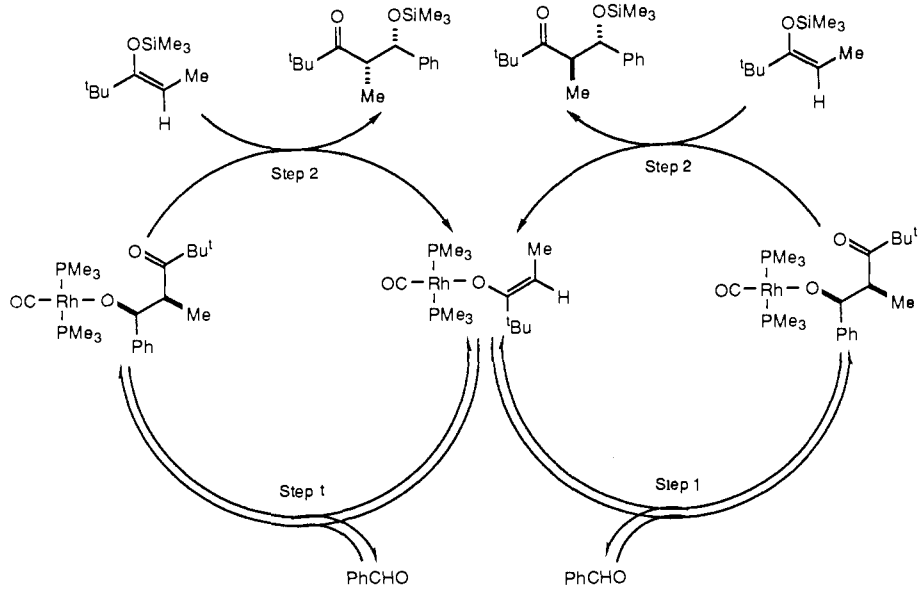
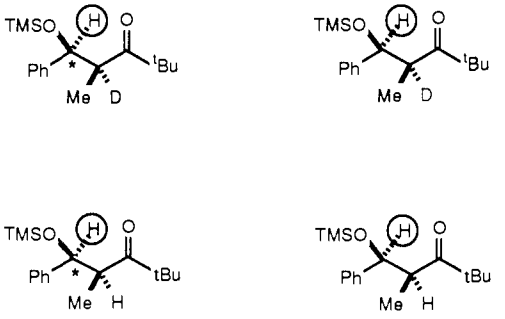
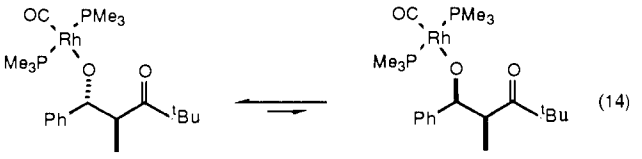


Figure 3. Proposed mechanism for the catalytic aldol reaction illustrating conversion of the rhodium enolate to the *syn*- and *anti*-TMS aldolate diastereomers.

Scheme II



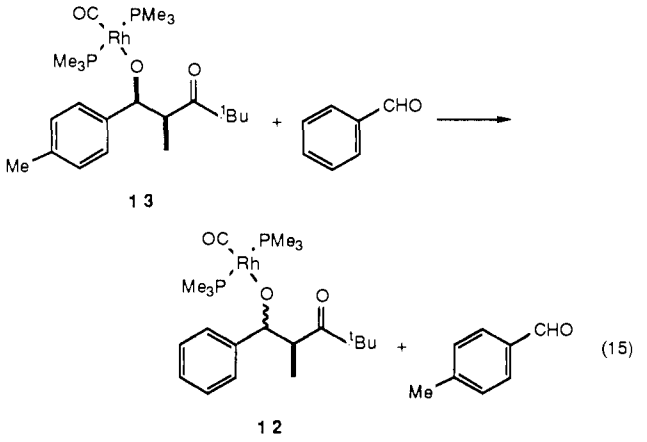
(2.5:1, v/v) solvent mixture, whereupon rapid equilibration (<5 min) to a 2.1:1 mixture of *syn*- and *anti*-aldolates was observed (eq 14). The same equilibrium ratio was obtained starting with a 1:4.5 mixture of syn and anti diastereomers of **12**.



(14)

anti-12 syn-12

We believe that the syn/anti equilibration results from reversibility of the aldol addition step. This was confirmed by demonstration that a mixture of the *p*-tolualdehyde aldolate complex **13** and benzaldehyde (2.0 equiv) is rapidly converted in 28% DMSO/benzene solution into a 70:30 mixture of aldolate complexes **12** and **13**; complex **12** was again formed as a 2:1 mixture of syn and anti diastereomers (eq 15).



(15)

12

The equilibration studies clearly indicate that the 2:1 ratio of syn and anti isomers of aldolate complex **12** is thermodynamic in nature and show that, under the steady-state conditions of the catalytic aldol process, the aldol addition step (step 1 in Figure 3) is fast and reversible. This reversibility indicates that a "Curtin–Hammett" situation[32] exists. The silylated aldol product ratio is significantly greater than 2:1 because, in step 2, the *syn*-rhodium aldolate reacts with the enol silane more rapidly than does the anti isomer.[33]

Curiously, the *syn*-aldolate in **12** is the thermodynamic isomer. This preference for the syn isomer contrasts with the situation in main-group aldolates, where kinetically derived *syn*-aldolates normally equilibrate to the anti diastereomers under thermodynamic conditions.[29,34] Perhaps this difference can be rationalized by consideration of a chelated versus a nonchelated aldolate structure. Chelated zinc and lithium ketolates[29] isomerize under

(32) Curtin, D. Y. *Rec. Chem. Prog.* **1954**, *15*, 111.
(33) The observed equilibrium ratio is consistent with the general electron-donating effect of a *p*-methyl group.
(34) House, H. O.; Crumrine, D. S.; Teranishi, A. Y.; Olmstead, H. D. *J. Am. Chem. Soc.* **1973**, *95*, 3310.

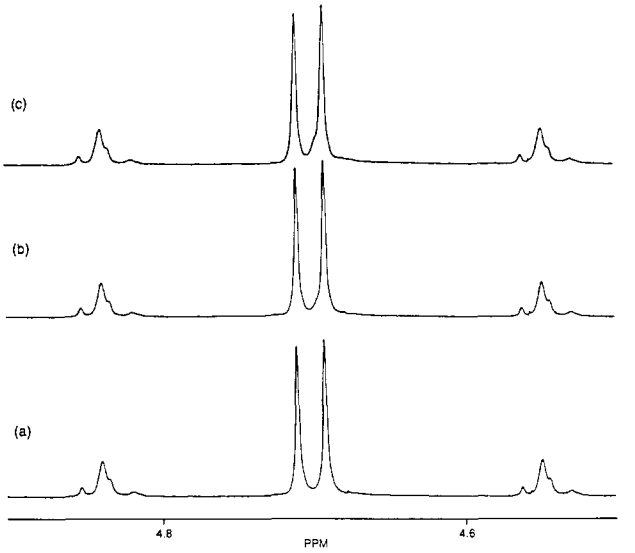


Figure 4. (a) Part of the ^{1}H NMR spectrum of the TMS aldol product recovered from the catalytic aldol reaction involving 1 equiv of rhodium catalyst **11**, 7.5 equiv of vinyl-deuteriated enol silane **21**-d_1, 7.5 equiv of benzaldehyde-^{13}C, and 7.5 equiv of unlabeled *syn*-TMS aldol (*syn*-**14**). (b) Sample shown in (a) spiked with 1.6% monodeuteriated TMS aldol. (b) Sample shown in (a) spiked with 4.0% monodeuteriated TMS aldol.

varying conditions to give predominantly anti diastereomers. The thermodynamic preference for the anti diastereomer may be understood in terms of the chelated conformations depicted in eq 16; there are more gauche interactions in the syn diastereomer than there are in the anti diastereomer.

(16)

syn anti

For the nonchelated aldolates (eq 17), the expected conformations of the syn and anti diastereomers are those with the fewest gauche interactions (two, in each case). It is, therefore, not

(17)

syn anti

surprising that there is not a pronounced preference for either diastereomer. Furthermore, because of the very large size of OM in the case of the rhodium aldolates, the gauche interactions of this group may be dominant. If this is the case, the gauche interaction of OM and the pivaloyl group in the anti diastereomer may be worse than that between OM and the planar phenyl group in the syn diastereomer.

In order to establish the irreversibility of step 2 in the catalytic reaction, we conducted a double isotope labeling crossover experiment. One equivalent of rhodium catalyst **11** was added to a solution of enol silane-d_1 (**21**-d_1, 7.5 equiv; 97% deuterium at the vinyl position), benzaldehyde-^{13}C (7.5 equiv; 98.2% carbonyl-^{13}C), and unlabeled *syn*-TMS aldol (*syn*-**14**, 7.5 equiv). After 1.0 h, termination of the reaction followed by chromatographic separation provided the TMS aldol in 74% yield. If step 2 of the catalysis is reversible or degenerate exchange between TMS aldol and rhodium aldolate **12** occurs during the reaction, then the four different isotopomers shown in Scheme II would be present. ^{1}H NMR analysis of these materials in the pure form demonstrated that the benzylic hydrogen in each compound exhibits a distinct, resolvable signal in the ^{1}H NMR spectrum. The doubly labeled

product shows a doublet at 4.69 ppm (J_{CH} = 145.0 Hz). The two monolabeled products show a singlet at 4.68 ppm and double doublet at 4.70 ppm (J_{HH} = 9.5 Hz; J_{HC} = 145.0 Hz), respectively. The unlabeled material exhibits a doublet at 4.69 ppm with J = 9.5 Hz.

The TMS aldol recovered from the double-labeling crossover experiment displayed three of these resonances, as shown in Figure 4: the doublet at 4.69 ppm for the unlabeled aldol, the doublet at 4.69 due to the doubly labeled adduct, and the double doublet attributable to the monolabeled product formed from protiated enolate **11** and benzaldehyde-^{13}C. The complete absence of the remaining singly (deuterium) labeled adduct indicated that no detectable crossover occurred during the catalytic reaction. In order to determine the limits of our ability to detect this fourth product, we added two successive aliquots of the potential crossover product, monodeuteriated (non-^{13}C-containing) TMS aldol, to the mixture isolated from the crossover experiment. As shown in Figure 4b, at 1.6% TMS aldol-d_1, a shoulder at 4.68 ppm became evident in the NMR spectrum. Adding more aldol-d_1 (4.0%; Figure 4c) increased the intensity of this signal. Interpreting this experiment conservatively, this sets a limit of <3% crossover in the aldol reaction. This experiment effectively demonstrates the irreversibility of step 2 in the catalytic cycle.

Summary

Oxygen-bound rhodium enolates are conveniently prepared by reaction of potassium enolates and rhodium halide derivatives. Several of these complexes have been fully characterized and are stable indefinitely at low temperatures. In DMSO solutions, these complexes react stoichiometrically with benzaldehyde to produce rhodium aldolate complexes. Enolizable aldehydes react as general acids, protonating the rhodium enolates, a property that seriously limits the scope of this rhodium aldol chemistry. Rhodium aldolates react with enol silanes and silyl ketone acetals giving the corresponding rhodium enolates and silylated aldol products. In favorable situations (e.g., nonenolizable aldehydes), a catalytic aldol cycle may be realized. A turnover number of approximately 100 has been observed. The gross features of the catalytic cycle have been elucidated and are summarized in Figure 3. It has been shown that step 1, the reaction of the rhodium enolate with the aldehyde, is fast and reversible. Step 2, reaction of the rhodium aldolate with the enol silane, is effectively irreversible under the reaction conditions investigated.

Prospects for a Catalytic, Asymmetric Aldol Process. Our observations on proton transfer between rhodium enolates and enolizable aldehydes reveal a serious limitation to the rhodium-catalyzed aldol process. Ketones are generally 7–8 kcal mol^{-1} more stable than isomeric aldehydes.[35] There is, therefore, a significant driving force for the reaction shown in eq 13, and it is unlikely that conditions can be found that will allow aldol reactions of enol silanes with enolizable aldehydes with this series of catalysts.

The mechanism summarized in Figure 3 has ramifications for the possible development of a catalytic, asymmetric aldol process based on rhodium enolates. Since step 1 is fast and reversible relative to step 2, the final diastereomer ratio depends only on the relative energies of the two diastereomeric transition states in step 2. This is, *it is the reaction of the rhodium aldolate with the enol silane that determines the final aldol stereochemistry.* The same situation would presumably exist if the rhodium were equipped with a chiral phosphine ligand; any asymmetric induction in the final aldol product would result not from stereodifferentiation in the aldol step but in the silyl-transfer step. It will, no doubt, be difficult to rationally design a system in which the diastereomeric silyl-transfer steps differ enough in energy (>3 kcal mol^{-1}) for effective asymmetric induction. Alternatively, one might find a set of rhodium ligands that would render step 1 irreversible. In that case, the stereochemistry of the final product would be established in the aldol step. Future work will be directed toward this goal.

Experimental Section

General Methods. All manipulations involving air-sensitive materials were performed under nitrogen by Schlenk or vacuum-line techniques[36] or in Vacuum Atmospheres 553-2 inert-atmosphere drybox equipment with a MO-40-1 inert gas purifier. Air-sensitive materials were exposed only to thoroughly dried and degassed solvents. Tetrahydrofuran (THF), diethyl ether, toluene, and benzene were distilled from sodium benzophenone under a nitrogen atmosphere. Pentane, dried over CaH_2, dimethyl sulfoxide (DMSO), dried over BaO, and ethanol, dried over magnesium turnings, were distilled under a nitrogen atmosphere. THF-d_8, toluene-d_8, and benzene-d_6 were dried over sodium benzophenone and then transferred under vacuum prior to use. DMSO-d_6 was dried over BaO and distilled at 19 mmHg prior to use. Acetophenone (Mallinckrodt), propiophenone (Aldrich), benzaldehyde (Mallinckrodt), isobutyraldehyde (Aldrich), hexanal (Aldrich), hexamethyldisilazane (Aldrich) were distilled prior to use. Trimethylphosphine (Strem) was dried over Na/K and added by vacuum-transfer techniques. Ethyl *tert*-butyl ketone,[37] mesityl ethyl ketone,[29] $(PPh_3)_3RhCl$,[38] $[(CO)_2RhCl]_2$,[39] $(PPh_3)_2(CO)RhF$,[16] and all enol silanes (**16**, **20**, **21**, **22**)[31] were prepared according to published procedures. ^1H NMR spectra were recorded at frequencies of 250, 300, or 500 MHz at the Berkeley NMR Facility and are reported in units of parts per million with residual protons in the solvent as an internal standard (benzene-d_6, 7.15; toluene-d_8, 2.09; DMSO-d_6, 2.49; THF-d_8, 3.58 ppm). Significant ^1H NMR data are tabulated in the following order: multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet), number of protons, and coupling constants in hertz. The ^2H NMR spectra (768 MHz) were recorded unlocked with a Bruker AM-500 spectrometer. The chemical shifts are relative to the 1% benzene-d_6 internal standard. The ^{31}P NMR and ^{13}C NMR spectra were recorded at frequencies of 121.5 and 125.8 MHz, respectively. The ^{13}C NMR spectra were referenced to solvent ^{13}C resonance (toluene-d_8, 20.4; benzene-d_6, 128.0 ppm). All ^{31}P NMR spectra were proton-decoupled and are reported in units of parts per million upfield from 85% H_3PO_4. Solution infrared spectra were recorded in 0.1-mm NaCl cells with a grating infrared spectrometer; data are reported as (solvent) reciprocal centimeter (intensity; s, strong; m, medium; w, weak) and are calibrated with polystyrene (1601 cm^{-1}). Fast atom bombardment mass spectra (FABMS) were recorded at the UCB Mass Spectrometry Facility with an AEI MS12 (low-resolution) mass spectrometer. Elemental analyses were performed by the Microanalytical Laboratory, operated by the Berkeley College of Chemistry. Melting points were obtained with a Thomas–Hoover capillary melting apparatus and are uncorrected. Flash column chromatography by the method of Still, Kahn, and Mitra was carried out with silica gel under nitrogen pressure.[40]

Carbonylbis(trimethylphosphine)rhodium(I) Chloride (1). The literature procedure was modified.[15] In a 50-mL round-bottomed flask, equipped with a stirring bar, was weighed μ-dichlorotetracarbonyldirhodium(I) (0.76 g, 1.96 mmol). Ethanol (10 mL) was added to the flask by vacuum-transfer techniques. The solution was degassed with two freeze/pump/thaw cycles. Gaseous trimethylphosphine (4.1 equiv) was measured by volume bulb technique (508.5 mL at 294.3 Torr) and then condensed into solution. Upon thawing, a bright yellow suspension resulted. The mixture was stirred at room temperature for 1.5 h and then was cooled to −40 °C to facilitate further crystallization. In a drybox, 906 mg of yellow sheets (73% yield) were collected by filtration. The solid was washed with pentane (10 mL) and dried at 0.080 mmHg for 12 h. The pure material had a melting point of 114 °C dec (lit.[15] mp 108 °C dec). IR (C_6H_6): 1965 (vs), 953 (m) cm^{-1}. ^1H NMR (C_6H_6): δ 1.45 (br s, 9 H). Anal. Calcd for $C_7H_{18}OP_2RhCl$: C, 26.39; H, 5.69. Found: C, 26.81; H, 5.69.

General Method for Preparation and Isolation of Potassium Enolates. A 100-mL three-necked round-bottomed flask equipped with a stirring bar and vacuum-line adapter was evacuated to 0.70 mmHg and backfilled with nitrogen twice. While under positive nitrogen pressure THF (10 mL) was added and the solvent was cooled to −78 °C (CO_2/acetone). Potassium hexamethyldisilazide[41] solution (8.1 mmol, in toluene) was

(35) The free energies of formation of propanal and acetone are −45.9 and −52.0 kcal mol^{-1}, respectively; comparable values for butanal and 2-butanone are −49.0 and −57.0 kcal mol^{-1}, respectively: Stull, D. R.; Westrum, E. F., Jr.; Sinke, G. C. *The Chemical Thermodynamics of Organic Compounds*; Wiley: New York, 1969; pp 649, 657.

(36) Shriver, D. F. *The Manipulation of Air Sensitive Compounds*; McGraw-Hill: New York, 1969.

(37) Obtained from the reaction of 2,2-dimethylpropanamide with excess ethylmagnesium bromide: Whitmore, F. C.; Noll, C. I.; Mennier, V. C. *J. Am. Chem. Soc.* **1939**, *61*, 683.

(38) Evans, D.; Obsorn, J. A.; Wilkinson, G. *Inorg. Synth.* **1966**, *8*, 214.

(39) McCleverty, J. A.; Wilkinson, G. *Inorg. Synth.* **1966**, *8*, 211.

(40) Still, W. C.; Kahn, M.; Mitra, A. *J. Am. Chem. Soc.* **1979**, *100*, 2923.

(41) Brown, C. A. *J. Am. Chem. Soc.* **1973**, *95*, 982.

added. After the solution was cooled for 0.4 h, neat ketone (8.3 mmol) was added dropwise over 0.1 h. The solution was stirred at −78 °C for 0.6 h. The solution was evacuated to 0.070 mmHg, and the cooling bath was removed. The mixture was concentrated to dryness under vacuum, yielding an off-white solid. In the drybox, a pentane suspension of the solid was filtered on a fine frit and the solid was washed successively with toluene (8 mL) and pentane (3 × 10 mL). The solid was dried at 0.70 mmHg for 12 h and used without further purification.

For acetophenone, the enolization was accomplished with KH at 0 °C. In a glovebox, an oven-dried 50-mL three-necked round-bottomed flask, equipped with a stirring bar, was charged with KH (331 mg, 8.1 mmol), previously freed from oil by washing three times with hexane and drying at 0.07 mmHg. On a vacuum manifold, the flask was purged with nitrogen. The KH was suspended in 10 mL of THF, and the suspension was cooled to 0 °C (ice water bath) over a period of 30 min. Neat acetophenone (996 mg, 8.3 mmol) was added dropwise over 12 min, and the mixture was stirred vigorously for 90 min. Solvent was removed at 0.07 mmHg, leaving an off-white solid. In the glovebox, a pentane suspension of the enolate was filtered on a fine frit. The solid was dried at 0.07 mmHg for 12 h and then used without further purification. The potassium enolates are stable for two months when stored at −40 °C under nitrogen. Prolonged storage results in coloration and decomposition.

Potassium Enolate of Acetophenone (3). Limited solubility precluded spectroscopic analysis.

(*Z*)-Potassium Enolate of Propiophenone (4). ^{1}H NMR (THF-d_8): δ 1.61 (d, 3, J = 6), 4.19 (q, 1, J = 6), 6.99 (m, 1), 7.07 (m, 2), 7.53 (d, 2, J = 7).

(*Z*)- and (*E*)-Potassium Enolates of Ethyl Mesityl Ketone (5). ^{1}H NMR (THF-d_8): [(*E*)-isomer] δ 1.16 (d, 3, J = 6), 2.15 (s, 6), 2.22 (s, 3), 3.41 (q, 1, J = 6); [(*Z*)-isomer] δ 1.40 (d, 3, J = 6), 2.15 (s, 6), 2.22 (s, 3), 3.69 (q, 1, J = 6). The *E*:*Z* isomer ratio was determined to be 1:1 by integration of signals at 1.16 and 1.40 ppm, respectively.

(*Z*)-Potassium Enolate of Ethyl *tert*-Butyl Ketone (6). ^{1}H NMR (THF-d_8): δ 1.00 (s, 9), 1.50 (d, 3, J = 6), 3.53 (q, 1, J = 6).

Preparation of Carbonyl(η^1-0-1-phenyl-1-oxyethyl)[bis(trimethylphosphine)]rhodium(1) (7). In a drybox, a solution of carbonylbis(trimethylphosphine)rhodium(1) chloride (102.1 mg, 0.32 mmol) in THF (8 mL) was prepared. The yellow solution was cooled to −40 °C over 0.5 h. Solid potassium enolate **3** (50.2 mg, 0.32 mmol) was added in one portion. The yellow suspension was stirred vigorously for 2 min and then recooled to −40 °C. After 1.0 h, nearly complete dissolution had occurred. After 6 h, the mixture was concentrated in vacuo to yield a yellow-brown oil. The oil was taken up in diethyl ether (10 mL) and filtered to remove precipitated KCl. The flask and frit were then rinsed twice with ether (3 mL). The volume of the filtrate was reduced to 1.5 mL, and the solution was cooled to −40 °C. The solvent was pipetted away from the yellow-tan flocculent needles. The needles were triturated with pentane (1 mL) at −40 °C, and again the solvent was pipetted away. The crystals were dried at 0.070 mmHg for 12 h. In this manner was obtained 117.4 mg (91%) of enolate complex **7** as yellow crystals. IR (C_7H_{16}): 1966 (s) cm^{-1}. ^{1}H NMR (500 MHz, toluene-d_8): δ 1.11 (br s, 18), 4.40 (br s, 1), 4.62 (br s, 1), 7.13 (m, 1), 7.26 (t, 2), 8.01 (d, 2). ^{13}C NMR (125.7 MHz, toluene-d_8, −30 °C): δ 15.13, 15.24, 15.36, 79.84, 125.96, 126.82, 127.69, 128.17, 129.09, 142.86, 166.82, 192.66 (dt, J = 17, 66). ^{31}P NMR (121.5 MHz, C_6D_6): δ −9.50 (d, J = 113). Anal. Calcd for $C_{15}H_{25}O_2P_2Rh$: C, 44.79; H, 6.26. Found: C, 44.52; H, 6.66.

Carbonyl(η^1-0-1-phenyl-1-oxyethenyl)[bis(triphenylphosphine)]rhodium(1) (8). The procedure used for the preparation of complex **7** was followed with carbonyl[bis(triphenylphosphine)]rhodium(1) fluoride (101.8 mg, 0.15 mmol) to obtain 107.6 mg (93%) of enolate complex **8** as yellow crystals. IR (toluene): 1970 (s) cm^{-1}. ^{1}H NMR (500 MHz, toluene-d_8): δ 4.33 (br s, 2), 7.00 (s, 18), 7.86 (s, 12). ^{13}C NMR (125.8 MHz, C_6H_6): δ 82.28, 126.03, 126.24, 126.80, 127.80, 128.44, 130.05, 133.75, 134.87, 143.50, 166.09, 191.31 (dt, J = 4, 17). Anal. Calcd for $C_{45}H_{37}O_2P_2Rh$: C, 69.77; H, 4.81; P, 7.65. Found: C, 69.47; H, 4.96; P, 7.48.

Carbonyl(η^1-0-1-phenyl-1-oxy-1-propenyl)[bis(trimethylphosphine)]rhodium(1) (9). The procedure used for the preparation of complex **7** was followed by using the (*Z*)-potassium enolate of propiophenone (**4**) to obtain 65.2 mg (49% yield) of enolate complex **9** as fluffy yellow crystals. IR (C_6H_6): 1948 (vs), 1606 (m), 954 (s) cm^{-1}. ^{1}H NMR (250 MHz, THF-d_8): δ 1.41 (br s, 18), 2.08 (d, 3, J = 6), 4.72 (q, 1, J = 6.7), 7.01 (m, 1), 7.11 (t, 2), 7.65 (d, 2). ^{13}C NMR (125.7 MHz, C_6H_6): δ 13.49, 15.21 (t, J = 13.8), 87.86, 125.44, 126.05, 128.19, 128.29, 128.76, 144.87, 161.48, 192.26 (dt, J = 18, 66). Anal. Calcd for $C_{16}H_{27}O_2PRh$: C, 46.17; H, 6.54. Found: C, 46.11; H, 6.62.

(*Z*)- and (*E*)-Carbonyl[η^1-0-1-(2,4,6-trimethylphenyl)-1-oxy-1-propenyl][bis(trimethylphosphine)]rhodium(1) (10). The procedure used for the preparation of complex **7** was followed except that a mixture of the (*Z*)- and (*E*)-enolates of ethyl mesityl ketone was used and the reaction was conducted in diethyl ether (8 mL). After complete dissolution, the mixture was diluted with pentane (8 mL) and recooled to −40 °C for 1 h. The suspension was filtered and the filtrate concentrated to dryness, yielding an analytically pure, yellow powder. The isolated yield of enolate complex **10** was 77.1 mg (97%), obtained as an inseparable 2:1 *E*/*Z* mixture. IR (C_5H_{12}): 1970 (vs), 1610 (m), 1240 (s), 952 (s) cm^{-1}. Anal. Calcd for $C_{19}H_{33}O_2P_2Rh$: C, 49.59; H, 7.25. Found: C, 49.20; H, 7.48.

***Z* isomer**: ^{1}H NMR (250 MHz, toluene-d_8): δ 1.16 (br s, 18), 2.22 (s, 6), 2.39 (d, 3, J = 5), 2.50 (s, 3), 4.07 (q, 1, J = 5), 6.85 (s, 2). ^{13}C NMR (125.8 MHz, toluene-d_8, −22 °C): δ 13.38, 14.77, 14.89, 15.04, 15.15, 15.26, 20.81, 21.04, 21.75, 87.79, 127.87, 133.90, 134.90, 143.56, 162.31, 192.06 (dt, J = 18, 66).

***E* isomer**: ^{1}H NMR (250 MHz, toluene-d_8): δ 1.22 (br s, 18), 1.63 (d, 3, J = 6), 2.50 (s, 6), 2.55 (s, 3), 4.74 (q, 1, J = 6), 7.00 (s, 2). ^{13}C NMR (125.8 MHz, toluene-d_8, −22 °C): δ 13.32, 15.49, 15.60, 15.71, 20.81, 21.04, 21.75, 91.23, 128.09, 134.37, 135.11, 139.82, 161.22, 192.06 (dt, J = 18, 66).

Cleavage of enolate **10** with trimethylsilyl chloride provided the corresponding enol silanes; the following procedure was employed. In a drybox, enolate **10** (10.5 mg, 0.023 mmol) was weighed into a 5-mm NMR tube and dissolved in 0.5 mL of toluene-d_8. On a vacuum line the yellow solution was degassed three times by the freeze/pump/thaw procedure. Trimethylsilyl chloride (0.024 mmol, 1.05 equiv) was measured by the volume bulb technique (25.47 mL at 17.52 Torr) and condensed into the NMR tube. The tube was sealed and the solution warmed to room temperature. After 18 min, no starting enolate remained. The ^{1}H NMR spectrum of the solution showed the vinylic protons for the (*E*)- and (*Z*)-enol silanes (5.10 and 4.62 ppm, respectively) in a ratio of 2:1. The NMR tube was opened in the drybox, and an aliquot was removed for capillary GLPC analysis. This analysis (oven temperature 175 °C, 25 M 5% phenylmethylsilicone) showed the product to be a 68:32 mixture of (*E*)- and (*Z*)-enol silanes, with the latter eluting more rapidly. To check for the possibility of *E*,*Z* equilibration under the reaction conditions, the foregoing reaction was repeated and 2.7 mg (0.012 mmol) of pure (*Z*)-enol silane was added. The ^{1}H NMR spectrum showed the *E*:*Z* ratio to be 1:1 after 12 min and 10 h.

(*Z*)-Carbonyl(η^1-0-4,4-dimethyl-1-oxy-2-pentene)[bis(trimethylphosphine)]rhodium(1) (11). The procedure used in the preparation of complex **10** was followed, giving 66 mg (96%) of enolate complex **11** as a yellow-orange solid. IR (C_6H_6): 1951 (vs), 1619 (m), 960 (s), cm^{-1}. ^{1}H NMR (250 MHz, toluene-d_8): δ 1.10 (br s, 18), 1.35 (s, 9), 2.37 (d, 3, J = 6.5), 4.14 (q, 1, J = 6.5). ^{13}C NMR (50 MHz, toluene-d_8): δ 14.28, 14.59, 14.87, 15.15, 15.46, 30.33, 38.83, 77.94, 137.23, 169.78, 192.50 (dt, J = 19, 71). Anal. Calcd for $C_{14}H_{31}O_2P_2Rh$: C, 42.43; H, 7.88. Found: C, 42.05; H, 8.06.

Preparation of Carbonyl[bis(trimethylphosphine)]rhodium Aldolate 12. Method A. In a drybox, a solution of rhodium enolate **11** (68 mg, 0.17 mmol) in toluene-d_8 (0.5 mL) was prepared. The solution was transferred into a 5-mm NMR tube and cooled to −40 °C. Benzaldehyde (17.5 μL, 0.17 mmol) was added by syringe. The solution was degassed once with a freeze/pump/thaw cycle, and the tube was flame-sealed. After 120 h at −20 °C, NMR analysis showed that 79% of the enolate had been converted to the rhodium aldolate complex. In the drybox, the solution was concentrated in vacuo to a brown oil. This material was dissolved in pentane (1 mL), and the solution was cooled to −40 °C. After 48 h, yellow crystals were isolated by filtration. The crystals were triturated with pentane (0.5 mL) at −40 °C overnight. The solvent was removed by pipet, and the crystals were dried in vacuo. The crystals were thermally sensitive and began to darken after 0.3 h at room temperature. Subsequent experiments showed that the best method for drying is to keep the moist crystals in an open vial at −40 °C for 1 week. Isolated in this manner was 26.4 mg (31%) of aldolate complex **12**. IR (C_5H_{12}): 1968 (m sh), 1950 (vs), 1698 (m) cm^{-1}. ^{1}H NMR (250 MHz, toluene-d_8): δ 0.80 (s, 9), 1.17 (br s, 18), 1.62 (d, 3, J = 6.7), 2.99 (m, 1), 4.99 (br d, 1, J = 8.2), 7.00–7.17 (m, 3), 7.51 (d, 2, J = 7.2). ^{13}C NMR (75.4 MHz, toluene-d_8): δ 15.69, 15.87, 16.06, 18.43, 25.98, 44.87, 53.89, 86.91 (br s), 125.37, 127.53, 127.87, 128.20, 152.28, 218.68. ^{31}P NMR (121.5 MHz, toluene-d_8): δ −14.28 (d, J = 131). FABMS: m/z 474 (M − 28, 61). This rhodium aldolate is extremely sensitive, and satisfactory elemental analysis could not be achieved.

Method B. In a 25-mL round-bottomed flask was prepared a solution of carbonyl[bis(trimethylphosphine)]rhodium(1) chloride (64.6 mg, 0.20 mmol) and benzaldehyde (21.5 mg, 0.20 mmol) in toluene (2 mL). The yellow solution was cooled in a drybox freezer to −40 °C over 0.8 h, and 30.9 mg (0.20 mmol) of the solid (*Z*)-potassium enolate of ethyl *tert*-butyl ketone (**6**) was added in one portion. The suspension was stirred vigorously for 2 min and then was replaced in the freezer at −40 °C. After 1 h, the suspension was removed, vigorously stirred for 1 min, and

then replaced in the freezer. After 2 h a bright yellow solution remained, and the mixture was concentrated to dryness in vacuo. The yellow residue, somewhat thermally sensitive, was taken up in pentane (7 mL) and filtered. The precipitate was rinsed twice with pentane (2 mL). The volume of the filtrate was reduced to 1.5 mL and cooled to −40 °C to effect crystallization. After 40 h, yellow crystals formed. The solvent was removed by pipet, and the crystals were triturated with pentane (0.5 mL) at −40 °C for 3 h. The solvent was removed, and the yellow crystals were slowly dried. Isolated in this manner was 39 mg (39%) of enolate complex, identical spectrally with the material prepared by method A.

Carbonyl[bis(trimethylphosphine)]rhodium Aldolate 13. Method B was used with *p*-tolualdehyde for the preparation of the aldolate complex; 29 mg (28%) was isolated. IR (C_5H_{12}): 1967 (m), 1950 (vs), 1699 (m) cm^{-1}. ^1H NMR (C_6H_6): δ 0.86 (s, 9), 1.18 (dt, 18, J = 1.0, 3.1), 1.68 (d, 3, J = 6.7), 2.17 (s, 3), 3.06 (m, 1, J = 6.7, 8.0), 5.05 (br d, 1, J = 8.0), 7.07 (d, 2, J = 7.8), 7.50 (d, 2, J = 7.8). ^{13}C NMR (125.8 MHz, toluene-d_8, −22 °C): δ 15.46, 15.57, 15.68, 17.73, 22.49, 25.75, 44.31, 53.36, 85.70 (t, J = 6), 127.41, 128.05, 134.68, 149.07, 191.98 (dt, J = 19, 63), 218.12. Because of its extreme sensitivity, we were not able to obtain a satisfactory elemental analysis for compound **13**.

General Procedure for Rhodium Enolate Catalyzed Aldol Reactions. In a drybox, a solution of enol silane (or silyl ketene acetal) (typically 0.29 mmol) and benzaldehyde (0.34 mmol) in DMSO (0.5 mL) was prepared in a 5-mL pear-shaped flask. To the magnetically stirred solution was added solid rhodium complex **7** (0.011 mmol). The yellow-tan solution was stirred at room temperature for 0.5 h. The remainder of the procedure was conducted in a fume hood. The reaction mixture was poured into pentane (15 mL) and extracted with saturated brine (10 mL). The aqueous layer was rinsed three times with pentane (8 mL). The combined organics were dried over Na_2SO_4 and concentrated to dryness with a rotary evaporator. The residual oil was purified by column chromatography on Woelm B, activity 1, basic alumina and characterized as described below for the individual products.

(3*RS*)-1,3-Diphenyl-3-[(trimethylsilyl)oxy]propan-1-one. Chromatography was conducted with hexane; yield 25 mg (29%) of a colorless oil. IR (CCl_4): 2990 (m), 1700 (s), 1262 (s) cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ −0.01 (s, 9), 3.02 (dd, 1, J = 3.8, 15.8), 3.56 (dd, 1, J = 8.8, 15.8), 5.37 (dd, 1, J = 3.8, 8.8), 7.25–7.6 (m, 8), 7.95 (d, 2). Desilylation with a catalytic amount of 5% citric acid in methanol yielded the free aldol, whose IR and ^1H NMR spectra were identical with those reported by House.[34] In addition, 32.6 mg (54%) of chalcone was also isolated by chromatography as a higher R_f material. This compound was identified by comparison with an authentic sample by capillary GLPC coinjection.

(2*RS*,3*RS*)-1,3-Diphenyl-2-methyl-3-[(trimethylsilyl)oxy]propan-1-one. Chromatography was conducted with 50:1 hexane/EtOAc to obtain 63.3 mg (70%) of a 3.1:1 syn/anti mixture of silylated aldols as a yellow oil. IR (CCl_4): 1688 (s), 1224 (vs) cm^{-1}. ^1H NMR ($CDCl_3$): (syn isomer) δ −0.01 (s, 9), 1.29 (d, 3, J = 6.7), 3.79 (m, 1), 4.98 (d, 1, J = 6.4), 7.1–7.55 (m, 8), 7.73 (d, 2); (anti isomer) δ −0.20 (s, 9), 0.86 (d, 3) 3.79 (m, 1), 4.86 (d, 1, J = 7.2), 7.1–7.55 (m, 8), 8.05 (d, 2). Anal. Calcd for $C_{19}H_{24}O_2Si$: C, 73.03; H, 7.74. Found: C, 73.16; H, 7.72. The syn/anti ratio was determined by integration of the 4.98 and 4.86 ppm methine signals.

(1*RS*,2*RS*)-2,4,4-Trimethyl-1-[(trimethylsilyl)oxy]-1-phenylpentan-3-one. Chromatography was conducted with hexane to obtain 70.3 mg (83%) of a 6.1:1 syn/anti mixture of diastereomers as a colorless oil. IR (CCl_4): 2985 (s), 1710 (s), 905 (s) cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): (syn isomer) δ −0.02 (s, 9), 0.63 (s, 9), 1.20 (d, 3, J = 9.5), 3.19 (dq, 1, J = 6.7, 9.5), 4.64 (d, 1, J = 6.7), 7.15–7.26 (m, 5); (anti isomer) δ −0.16 (s, 9), 0.63 (d, 3), 1.14 (s, 9), 3.19 (m, 1), 4.62 (d, 1, J = 3.8). Anal. Calcd for $C_{17}H_{28}O_2Si$: C, 69.81; H, 9.64. Found: C, 69.90; H, 9.73. The diastereomer ratio was determined to be 86:14 by integration of the ^1H NMR signals at 4.64 and 4.62 ppm. This ratio was confirmed by capillary GLPC analysis.

Ethyl (2*SR*,3*SR*)-2-Methyl-3-[(trimethylsilyl)oxy]-3-phenylpropanoate. The aldol product was isolated by flash chromatography on silica using 6:1 hexane/EtOAc. Isolated 74.4 mg of a 1:1 syn/anti mixture of diastereomers (90% yield, pale yellow oil). IR (CCl_4): 1745 (vs) cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): (syn isomer) δ −0.04 (s, 9), 1.05 (d, 3, J = 7.1), 1.10 (t, 3, J = 7.0), 2.63 (m, 1), 3.94 (m, 2), 4.90 (d, 1, J = 6.3), 7.25 (m, 5); (anti isomer) δ −0.10 (s, 9), 0.81 (d, 3, J = 7.1), 1.26 (t, 3, J = 7.1), 2.65 (m, 1), 4.14 (m, 2), 4.62 (d, 1, J = 7.1), 7.25 (m, 5). Anal. Calcd for $C_{15}H_{24}O_3Si$: C, 64.24; H, 8.62. Found: C, 64.28; H, 8.78. The diastereomer ratio was determined by integration of the 4.90 and 4.62 ppm signals.

General Procedure for Enol Silane Exchange. Preparation of the reaction mixture was conducted in a drybox under nitrogen atmosphere. A solution of enol silane (0.023 mmol) in DMSO-d_6 (0.5 mL) was prepared in an oven-dried vial. To the vigorously stirred solution was added solid rhodium enolate complex (0.023 mmol). Upon complete dissolution, the solution was transferred to 5-mm NMR tube and analyzed by ^1H NMR spectrometry. The ratios of rhodium enolate complexes and enol silane were determined by integration of the appropriate methine and methylene proton signals. The ratios were monitored over a period of 1.0 h until no further change occurred.

General Procedure for Rhodium Enolate Exchange with Enolizable Ketones. The procedure for enol silane exchange was followed except that ketone was used instead of enol silane. The product ratios were measured by ^1H NMR integration.

Catalytic Study by ^2H NMR Technique. Sample preparations were performed in a drybox under nitrogen atmosphere. A solution of deuteriated (*Z*)-4,4-dimethyl-3-[(trimethylsilyl)oxy]-2-pentene (0.10 mmol), benzaldehyde (0.15 mmol), and benzene-d_6 (5 μL) in a 2.5:1.0 stock solution of benzene and DMSO (0.5 mL, prepared by mixing benzene (5.0 mL) and DMSO (2.0 mL)) was prepared and transferred into a 5-mm NMR tube. The solution was frozen at −40 °C for 4.0 h. Solid rhodium complex **11** was placed on top of the frozen solution, and the mixture was degassed twice by freeze/pump/thaw cycles. The NMR tube was flame-sealed. The mixture was thawed, thoroughly mixed, and immediately placed into the NMR probe. The ^2H NMR spectra were recorded every 10 min for 2.0 h.

General Procedure for the Use of [^{13}C]Benzaldehyde in Catalytic Studies. In a glovebox, a stock solution of [^{13}C]benzaldehyde (42.2 mg, 0.39 mmol)[32] and enol silane **16** (74.4 mg, 0.40 mmol) in 28% DMSO-d_6/C_6D_6 was prepared in a 1.00-mL volumetric flask. Half of the solution (0.5 mL) was placed in a 5-mm NMR tube, and the solution was frozen at −40 °C over 2.0 h. Solid rhodium enolate **11** (10.5 mg, 0.026 mmol) was layered on top of the frozen solution. On a vacuum line, the solution was degassed once (0.01 mmHg), and the tube was flame-sealed. Immediately after it thawed, the NMR tube was placed in the probe of a Bruker AM-500 NMR spectrometer. The course of the reaction was monitored by CMR spectrometry with the INVGATE pulse program. The diastereomer ratios were determined by CMR integration of the signals at 86.78 (t, *anti*-rhodium aldolate), 85.80 (t, *syn*-rhodium aldolate), 78.60 (*anti*-TMS aldol), and 77.25 (*syn*-TMS aldol), respectively.

Stoichiometric Reaction of Rhodium Aldolate 12 with Enol Silane 16. Sample preparation was performed in a drybox under a nitrogen atmosphere. A solution of rhodium aldolate (13.4 mg, 0.027 mmol) in THF-d_8 (0.5 mL) was prepared in an oven-dried 5-mm NMR tube. The solution was cooled to −40 °C over 0.7 h. To the cold solution was added enol silane **16** (5.3 mg, 0.028 mmol) by syringe. On a vacuum line, the solution was degassed with two freeze/pump/thaw cycles. The NMR tube was flame-sealed. After it thawed, the tube was stored at −20 °C. The reaction progress was monitored by ^1H NMR spectrometry. The broad doublet at 4.71 ppm due to the rhodium enolate gave way to a benzylic signal for the *syn*- and *anti*-TMS aldols at 4.66 ppm. The two methylene protons for the rhodium enolate **7** grew in at 4.07 and 3.91 ppm, respectively. After 5 days at −20 °C, approximately 40% of the rhodium enolate was consumed as determined by comparison of the ratio of the benzylic aldolate resonance at 4.71 ppm and the THF resonance to the initial ratio of the same signals.

Kinetic Study of Complex 11 with Benzaldehyde. All sample preparations were carried out in a drybox. A solvent mixture was prepared containing benzene (40.0 mL) and DMSO (16 mL). A stock solution of 0.201 M naphthalene was prepared by dissolving 1.028 g of naphthalene (freshly recrystallized) in 50.00 mL of the solvent mixture. Into an oven-dried 1.00-mL volumetric flask was weighed enol silane **16** (19.4–117.5 mg, 0.10–0.63 mmol) and benzaldehyde (214 mg, 2.03 mmol). These oils were diluted with the stock solution to a volume of 1.00 mL. After thorough mixing, a 0.5-mL aliquot was pipetted into an oven-dried 10-mL two-necked flask, which was equipped with a septum and a stirring bar. The reaction mixture was placed in a −40 °C freezer for 1.0 h. Solid rhodium enolate **11** (0.01–0.03 mmol) was layered onto the frozen mixture. The flask was fitted with a vacuum-line adapter and attached to a vacuum line. Under a nitrogen atmosphere, the mixture was thawed and equilibrated to 21.6 °C in a thermostated water bath. Aliquots were removed by syringe (0.15 μL) and analyzed by capillary GLPC over 2.0 h. The ratios of the integrated area of the enol silane and the internal standard were compared to a standard concentration curve to obtain the concentration of enol silane in each sample.

Double-Label Crossover Experiment. In a glovebox, an oven-dried 10-mL pear-shaped flask, equipped with a stirring bar, was charged with the silylated aldol from ethyl *tert*-butyl ketone and benzaldehyde (58.7 mg, 0.201 mmol), deuteriated enol silane **16** (37.5 mg, 0.201 mmol; 97% deuterium isotope dilution as determined by mass spectral analysis), and [^{13}C]benzaldehyde (21.5 mg, 0.201 mmol; 98.2% ^{13}C determined by mass spectral analysis). The oils were dissolved in a 28% DMSO-d_6/C_6D_6 solvent mixture (0.5 mL). Solid rhodium enolate **11** (10.5 mg, 0.027 mmol) was added in one portion to the stirring solution. Stirring was

continued at room temperature for 0.8 h at which time ^{1}H NMR analysis showed 87% consumption of enol silane. The reaction mixture was diluted with pentane (10 mL) and extracted with saturated brine (8 mL). The aqueous layer was washed twice with pentane (10 mL). The combined organic layers were dried over Na_2SO_4 (1.5 g), filtered, and concentrated in vacuo. The pale yellow oil was purified by passing the mixture through a 1-in. plug of grade III basic alumina with hexane as eluant. A colorless oil, 86 mg (74% yield), was isolated. Anal. Calcd for $C_{17}H_{28}O_2Si$: C, 69.81; H, 9.64. Found: C, 69.86; H, 9.61. The extent of crossover was determined by ^{1}H NMR analysis. A sample of recovered TMS aldol **14** (25.4 mg, 0.087 mmol) was dissolved in $CDCl_3$ (0.5 mL), and the spectrum was run on a Bruker AM-500 spectrometer. To the solution was added two successive aliquots (10 and 15 μL) of 0.14 M TMS aldol-d_1 (4.1 mg in 0.10 mL $CDCl_3$). The first aliquot corresponded to addition of 1.6% deuterium-labeled aldol, while after the second addition 4.0% was present. Within the limit of detections, a conservative estimate of <3% crossover occurred during catalysis.

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Registry No. 1, 22710-50-5; **2**, 22481-17-0; **3**, 59175-43-8; **4**, 95070-47-6; **5**, 117775-76-5; **6**, 78904-15-1; 7, 117800-21-2; **8**, 117800-22-3; **9**, 117800-23-4; (*E*)-**10**, 117800-24-5; (*Z*)-**10**, 117893-69-3; **11**, 117800-25-6; **12**, 117800-26-7; **13**, 117828-03-2; *syn*-**14**, 117775-79-8; *anti*-**14**, 117775-80-1; **15**, 66323-99-7; **16**, 13735-81-4; **16** (deuteriated), 117775-83-4; **21**, 61878-68-0; **22**, 73967-96-1; **23**, 117775-77-6; *syn*-**24**, 96816-44-3; *anti*-**24**, 96816-43-2; *syn*-**25**, 117775-78-7; *anti*-**25**, 117775-81-2; PhCOCH=CHPh, 94-41-7; μ-dichloro-tetracarbonyldirhodium(I), 14523-22-9; acetophenone, 98-86-2; propiophenone, 93-55-0; ethyl *tert*-butyl ketone, 564-04-5; ethyl mesityl ketone, 2040-15-5; (*E*)-1-mesityl-1-[(trimethylsilyl)oxy]-1-propene, 72658-15-2; (*Z*)-1-mesityl-1-[(trimethylsilyl)oxy]-1-propene, 72658-08-3; benzaldehyde, 100-52-7; *p*-tolualdehyde, 104-87-0; benzaldehyde-^{13}C, 10383-90-1; deuteriated (*Z*)-4,4-dimethyl-3-[(trimethylsilyl)oxy]-2-pentene, 117775-82-3.

Conversion of an Unsaturated Metallacycle into a Carbon-Rich *nido*-Metallacarborane. The BH Fragment as a Cluster Functional Group

Fung-E. Hong, Charles W. Eigenbrot, and Thomas P. Fehlner*

Contribution from the Department of Chemistry, University of Notre Dame, Notre Dame, Indiana 46556. *Received May 31, 1988*

Abstract: The reaction of the metallacycle $Cp(PPh_3)\overline{CoCPhCPhCPhCPh}$, **1**, with monoboranes containing at least one B–H bond provides a new route to the formation of a *nido*-metallacarborane, 3,4,5,6-tetraphenyl-1-(η^5-cyclopentadienyl)-3,4,5,6-tetracarba-1-cobalta-7-debor[D_{5h}-(151)-Δ^{10}*closo*]heptaborane(7), ($CpCoC_4Ph_4BH$) **2**, or, alternatively, a cobalt sandwich complex containing a borole ligand. Optimum yields of 30% are obtained by using a 10-fold excess of $BH_2Cl{\cdot}SMe_2$ as the source of B–H. The structure of **2** was determined by single-crystal X-ray diffraction methods, and the isomer isolated contains the cobalt atom in an apical position and the boron atom in a basal position. Crystals of **2** are orthorhombic with a = 14.956 (2) Å, b = 25.999 (2) Å, c = 12.933 (2) Å, V = 5028.8 Å^3, Z = 8, and space group *Pbca* (no. 61). The structure was solved by direct methods and refined to R = 0.037 and R_w = 0.040 for 3106 independent [$F_o \geq 2\sigma(F_o)$] reflections. The single B–H fragment in this heteroatom-rich cluster permits ready access to a variety of B-substituted compounds. The B–H bond is brominated under electrophilic conditions and alkylated with alkyllithium reagents. The B–Br bond is reduced with hydride, hydrolyzed to yield the B–OH derivative, and B-substituted with Grignard reagents. The B–OH functionality yields the B–OMe and B–$OSiMe_3$ derivatives. These reactions and the properties of **2** suggest that the boron atom can be usefully viewed as trivalent boron intramolecularly coordinated to the cobalt atom.

The use of heterocycles containing boron as ligands to transition metals is an established area of inorganic chemistry.[1-4] Compounds such as **2** (Figure 1) containing an η^5 borole ligand are already known.[1] This structure can also be viewed as a carbon-rich metallacarborane and, thus, is related to metallacarboranes containing a majority of boron atoms in the cage structure.[5] The usual synthetic approach to compounds like **2** is via the reaction of the free ligand or an appropriate precursor with a metal fragment source.[1-6] Likewise, for boron-rich compounds the approach is via the free carborane.[5] Alternatively there are a few examples of the insertion of an alkyne into a metallaborane.[7] A third route is the reaction of an organometallic complex with a source of borane. Insertion of boron in the ring of a π complex has led to borabenzene complexes.[1,3] This approach leads naturally to compounds containing isolated B–R fragments, i.e., carbon-rich metallacarboranes.

The utilization of the last route for the production of compounds containing B–H is unexplored.[8] A new route to these compounds would be interesting in a synthetic sense and would allow the reactions of a B–H fragment in a heteroatom cluster environment to be explored. Existing experimental information on a related

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