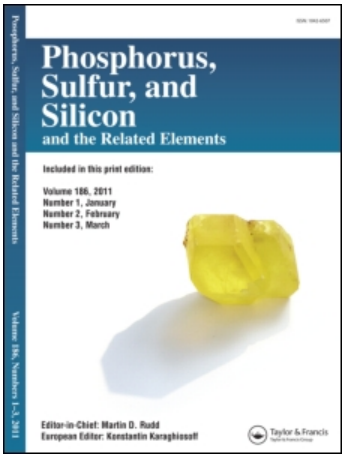

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Sterically Congested Bisphosphite Ligands for the Rhodium(I)-Catalyzed Hydrosilation of Ketones

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STERICALLY CONGESTED BISPHOSPHITE LIGANDS FOR THE RHODIUM(I)-CATALYZED HYDROSILATION OF KETONES

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Sterically congested bisphosphites were shown to be effective ligands for the Rh-catalyzed hydrosilation of ketones with diphenylsilane. The hydrosilation of 4-alkylcyclohexanones and (−)-menthone led to a significant proportion of the less stable (axial) alcohol, which suggests that these reactions are under kinetic, rather than thermodynamic, control.

Keywords: Diphenylsilane; hydrosilation; ketones; phosphite ligands; rhodium catalysis

INTRODUCTION

A fundamental principle in the design of ligands for stereoselective synthesis is the use of C_2 symmetry to reduce the possible number of isomeric transition states in a reaction.[1,2] In our investigations of chiral ferrocenyl ligands that do not possess C_2 symmetry yet provide high levels of enantio- and diastereoselectivity, we became interested in the concept of internal cooperativity of chirality,[3–19] or simply chiral cooperativity. The concept of chiral cooperativity as originally proposed by Pastor and Togni[3–8] is defined as cooperativity between the individual chirotopic elements within a ligand that promotes the appropriate steric and electronic interactions necessary to obtain high diastereo- or enantioselectivity for a particular reaction.[20–22] The ability of other secondary interactions to occur,[23] for example, hydrogen bonding, requires the appropriate chirotopic elements to energetically favor the desired

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interaction. In a much more general sense, the same principles apply to the design of achiral non-C_2-symmetric ligands for metal-catalyzed reactions to allow for high diastereo-, regio-, and chemoselectivity.[24] Our interest in the rational design of phosphite ligands for transition-metal-catalyzed reactions[25,26] led us to initiate studies to understand the fundamental factors required to achieve high reaction stereoselectivity in hydrosilation reactions[27–37] with this ligand class. Previous studies have shown that sterically hindered bisphosphite ligands posses larger bite angles than their unhindered analogs which can lead to unexpected metal-complex geometries.[38,39] Prior to the synthesis of enantiomerically pure bisphosphite ligands, our studies have focused on determining the stereoselectivity of the Rh(I)-catalyzed hydrosilation of ketones with the conformationally averaged achiral ligand **1**.

RESULTS AND DISCUSSION

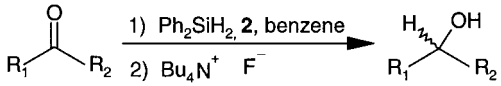
The sterically congested bisphosphite ligand **1** was prepared as reported previously.[25] The (acetylacetonato)Rh(I) bisphosphite complex **2** was prepared in situ by the reaction of one equivalent of acetylacetonato(dicarbonyl)rhodium(I) with one equivalent of bisphosphite **1** in benzene. The formation of **2** was supported by the observation of two doublet of doublets in the $^{31}P\{^1H\}$ NMR (benzene-d_6) spectrum at δ 136.0 (dd, $^2J_{PP}$ = 106 Hz, $^1J_{PRh}$ = 306 Hz) and δ 131.3 (dd, $^2J_{PP}$ = 106 Hz, $^1J_{PRh}$ = 299 Hz). Similarly the dimeric chlororhodium(I) bisphosphite complex **3** and a cationic Rh(I) bisphosphite tetrafluoborate complex **4** were prepared by the reaction of **1** with chloro(1,5-cycooctadiene)rhodium(I) dimer and bis(1,5-cycooctadiene)Rh(I) tetrafluoroborate, respectively.*,† Both the $^{31}P\{^1H\}$ NMR and ^1H NMR obtained support the in situ formation of the bisphosphite complexes **3** and **4**.

The hydrosilation of a series of ketones (entries 1–6 in Table I) with diphenylsilane catalyzed by 0.33 mole % of the Rh(I) complex **2** gave the corresponding silyl ethers. In all cases, 100% conversion of

*Dimeric chlororhodium(I) bisphosphite complex, $Rh_2Cl_2(\mathbf{1})_2$, (**3**): Under an inert atmosphere of nitrogen, chloro(1,5-cyclooctadiene)rhodium dimer (4.7 mg, 0.0095 mmol) and **1** (20.1 mg, 0.019 mmol) were added to 2 mL of benzene-d_6 and the resultant solution was stirred at room temperature for 72 h. $^{31}P\{^1H\}$ NMR (benzene-d_6, 121.47 MHz) δ 122.5 (dd, $^2J_{PP}$ = 45 Hz, $^1J_{PRh}$ = 317 Hz), 128.8 (dd, $^2J_{PP}$ = 45 Hz, $^1J_{PRh}$ = 311 Hz).

†Rhodium(I) bisphosphite tetrafluoroborate complex, $[(1,5\text{-COD})Rh(\mathbf{1})]^+ BF_4^-$, (**4**): Complex **4** was prepared by the method used to prepare compound **3** from bis(1,5-cycooctadiene)Rh(I) tetrafluoroborate hydrate (7.4 mg, 0.019 mmol) and **1** (19.2 mg, 0.018 mmol). $^{31}P\{^1H\}$ NMR (benzene-d_6, 121.47 MHz) δ 121.4 (dd, $^2J_{PP}$ = 26 Hz, $^1J_{PRh}$ = 253 Hz) 109.5 (dd, $^2J_{PP}$ = 26 Hz, $^1J_{PRh}$ = 264 Hz).

TABLE I Hydrosilation of Ketones with Diphenylsilane Catalyzed by Rh(I) Complex **2**

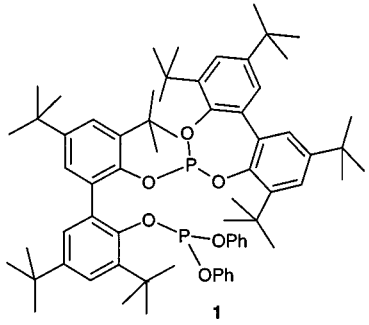


Entry	Substrate	Product[a]	Yield (isolated)	Isomer ratio[b]
1	2-heptanone	2-heptanol	85%	
2	acetophenone	1-phenethyl alcohol	75%	
3	2′-acetonaphthone	α-methyl-2-naphthalenemethanol	59%	
4	4-methylcyclohexanone	4-methylcyclohexanol	83%	46% cis/ 54% trans
5	4-*t*-butylcyclohexanone	4-*t*-butylcyclohexanol	87%	58% cis/ 42% trans
6	(−)-menthone	(−)-menthol/ (+)-neomenthol	76%	25% (1R, 2S, 5R)/75% (1S, 2S, 5R)

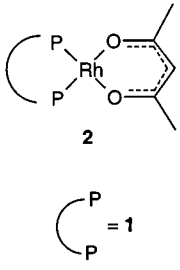
[a]After hydrolysis of the silyl ether with tetrabutylammonium fluoride.

[b]All reactions run in duplicate with isomer ratios (σ within ±3%) determined by integration of the appropriate peaks in the ^{1}H NMR spectrum prior to purification of the product.

starting ketone to silyl ether was observed. The corresponding alcohols were obtained in good overall isolated yields by treatment of the silyl ethers with tetrabutylammonium fluoride. The hydrosilation of both dialkyl and aryl alkyl ketones proceeded at room temperature in benzene solution (entries 1–3 in Table I).



STRUCTURE 1



STRUCTURE 2

A mixture of 46% *cis*- and 54% *trans*-methylcyclohexanol was obtained by hydrosilation of 4-methylcyclohexanone. The hydrosilation

of 4-methylcyclohexanone was complete within 1 h as measured by the disappearance of the starting ketone in the ^{1}H NMR spectrum of the reaction mixture. In a control experiment, the ratio of *cis*- to *trans*-4-methylcyclohexyl silyl ether in the reaction mixture monitored over a 24 h period was found to be constant. The cis : trans ratio of 4-methylcyclohexanols obtained is somewhat higher than the 39 : 61 cis : trans ratio reported by Ishiyama et al. using tris(triphenyphosphine)rhodium(I) chloride.[40] An explanation of the observed stereoselectivity in the hydrosilation of alkyl-substituted cyclohexanones based upon both stereoelectronic and steric effects has been advanced.[40,41]

The 58 : 42 cis : trans isomer ratio of *tert*-butylcyclohexanols obtained by hydrosilation of 4-*tert*-butylcyclohexanone catalyzed by **2** is nearly identical to the 57 : 43 cis : trans isomer ratio obtained by Semmelhack and Misra using tris(triphenylphosphine)rhodium(I) chloride.[42] In control experiments the product *cis*- and *trans*-methylcyclohexanols as well as *cis*- and *trans-tert*-butylcyclohexanols do not undergo equilibration when subjected individually to the reaction conditions. This experiment argues against possible equilibration of the product alcohols when subjected to the reaction conditions. Semmelhack has shown that the product silyl ethers do not equilibrate under tris(triphenyphosphine)-rhodium(I) chloride hydrosilation conditions.[42] In contrast to hydrosilation, metal hydride reduction of 4-methyl- and 4-*tert*-butylcyclohexanone leads predominantly to the trans (equatorial) alcohol.[43,44] Semmelhack has shown, however, that the observed stereoselectivity in the hydrosilation of a cyclic ketone is dependent upon the bulk of the alkylsilane.[42]

The hydrosilation of the terpene ketone, (−)-menthone, catalyzed by **2** favored the formation of the less stable alcohol. The 75 : 25 molar ratio of (+)-neomenthol/(−)-menthol (50% diastereomeric excess) is similar to that obtained by both Ojima et al.[41] and Ishiyama et al.[40] using tris(triphenyphosphine)-rhodium(I) chloride and diphenylsilane (see Table II). Under equilibrium conditions, (−)-menthol would be expected

TABLE II Stereoselectivities in the Reduction of (−)-menthone

Reducing agent	Solvent	% Less stable alcohol	Reference
$Ph_2SiH_2/(Ph_3)_3RhCl$	Neat	85	41
$Ph_2SiH_2/(Ph_3)_3RhCl$	Neat	75	40
Ph_2SiH_2/**2**	Benzene	75	(this work)
$LiAlH_4$	Ether	29	43

to be the predominant product.[44] The observation that hydrosilation reactions using diphenylsilane catalyzed by **2** yield significant amounts of the less stable product strongly suggests that these reactions are under kinetic, rather than thermodynamic, control.[45]

Work is currently in progress to synthesize new chiral bisphosphites for asymmetric hydrosilations and C—C bond forming reactions, and will be reported in due course.

EXPERIMENTAL

^{1}H NMR (300.08 MHz and 499.84 MHz respectively) spectra were taken on a Varian Model Gemini-300 or Unity-500 spectrometers. All ^{1}H chemical shifts are reported in ppm relative to tetramethylsilane, where a positive sign is downfield from the standard. ^{31}P NMR (202.33 and 121.47 MHz respectively) were obtained on a Varian Model Unity-500 or Gemini-300 spectrometers. All ^{31}P chemical shifts are reported in ppm relative to 85% phosphoric acid (external), where a positive sign is downfield from the standard. Significant ^{1}H NMR data are tabulated in the following order: multiplicity (m, multiplet; s, singlet; d, doublet; t, triplet; dd, doublet of doublets; dq, doublet of quartets; dt, doublet of triplets; ddq, doublet of doublets of quartets), atom assignments, coupling constant in Hertz, and number of protons. Merck silica gel 60 (200–400 mesh) was used for column chromatography. Merck precoated (0.25 mm) silica gel F-254 plates were used for TLC. Reagents were purchased from commercial laboratory supply houses. Solvents were dried prior to use when necessary with appropriate drying agents.

General Hydrosilation Procedure

All manipulations were carried out in dried apparatus under an inert atmosphere of nitrogen. A solution of (acetylacetonato)dicarbonylrhodium(I) (4.4 mg, 0.017 mmol) and **1** (18.1 mg, 0.017 mmol) in C_6D_6 was stirred at ambient temperature for 10 min. To the resultant catalyst solution was added diphenylsilane (0.94 g, 5.1 mmol) and substrate (5.1 mmol). The reaction mixture was stirred at room temperature for 24 h. To the reaction mixture was added dropwise over 20 min, a 1 M solution of tetrabutylammonium fluoride in tetrahydrofuran (5.1 mL, 5.1 mmol). The volatiles were removed in vacuo and the residues were purified by either recrystallization or chromatography. The spectral properties of all the products were identical in every respect to authentic samples.

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