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Carbon−Oxygen Bond Formation between a Terminal Alkoxo Ligand and a Coordinated Olefin. Evidence for Olefin Insertion into a Rhodium Alkoxide

Pinjing Zhao, Christopher D. Incarvito, and John F. Hartwig*

Department of Chemistry, Yale University, P.O. Box 208107, New Haven, Connecticut 06520-8107

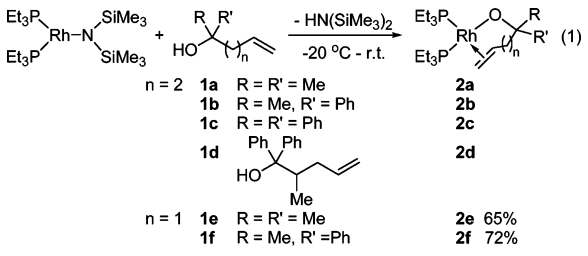
Received May 13, 2006; E-mail: john.hartwig@yale.edu

Migratory insertions of olefins into transition-metal alkyl complexes are well-known elementary organometallic reactions. Related migratory insertions of olefins into metal alkoxides have been proposed to occur during some catalytic processes,[1,2] but no well-characterized alkoxo complex has been shown to undergo insertion of an unactivated olefin.[3] Most often, characterized β-alkoxyalkyl complexes have been prepared by nucleophilic attack of an external alkoxide reagent onto a coordinated olefin.[4]

Few terminal alkoxide complexes with an olefin coligand have been prepared.[5] One recent example was studied because it would be expected to resist insertion and allow the observation of d^0 olefin complexes.[6] Here, we report the generation of a series of rhodium alkoxo complexes with olefin coligands that generate products from C−O bond formation. Kinetic studies, measurements of solvent effects, and stereochemistry of cyclization bear the hallmarks of a migratory insertion pathway.

Triethylphosphine-ligated rhodium alkoxides were prepared by the sequence in eq 1. Reaction of the Rh(I) silylamido precursor $\{(PEt_3)_2Rh[N(SiMe_3)_2]\}$[7] with enols **1a**−**f** readily occurred at room temperature or below to eliminate $HN(SiMe_3)_2$ and form the rhodium alkoxo complexes **2a**−**f**.[8] The alkoxo olefin complexes **2e** and **2f** generated from 4-hydroxy-1-alkenes were stable enough to isolate, were obtained as crystalline solids in 65 and 72% yields, and were fully characterized. The alkoxo olefin complexes **2a**−**d** derived from 5-hydroxy-1-alkenes were not stable at room temperature, but formed in quantitative yield at low temperature and were characterized in solution by NMR spectroscopic methods.

Coordination of the olefin in **2a**−**f** was evidenced by a set of resonances in the ^{1}H NMR spectrum that are located upfield of those of free olefins (see Supporting Information).[5,6] The complexes formed from chiral alcohols **1b**, **1d**, and **1f** generated diastereomeric mixtures of alkoxo olefin complexes **2b**, **2d**, and **2f**. Thus, the ^{31}P NMR spectra of **2a**, **2c**, and **2e** which were generated from achiral alcohols consisted of a pair of doublets of doublets from coupling between the two *cis*-oriented phosphines and the rhodium center, but the ^{31}P NMR spectra of **2b**, **2d**, and **2f** which were generated from the chiral alcohols consisted of two pairs of doublets of doublets corresponding to two diastereomers.



The structure of **2e** was determined by X-ray diffraction (Figure 1). In the solid state, **2e** adopts a square-planar geometry with two *cis*-oriented PEt_3 ligands and one chelating homoallylic alkoxide that is bound to rhodium through the oxygen atom and the terminal olefin unit, C(13,14). In comparison to the structures of related complexes, the Rh−O distance is similar to those in other Rh(I) alkoxides.[9] The Rh−C_{olefin} distances are shorter than the Rh−C distances of the η^2-phenyl interaction in $[(PEt_3)_2RhOCPh_3]$ (2.35 and 2.40 Å),[8] but are similar to the Rh−C_{olefin} distances of the alkyl olefin complex Rh(η^1:η^2-$CH_2CPh_2CH{=}CH_2$) (2.12 and 2.16 Å).[10]

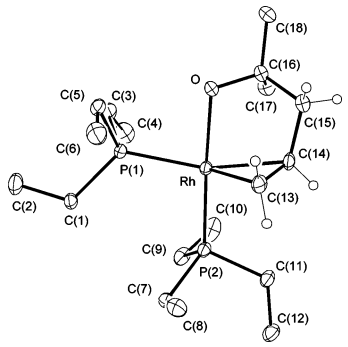
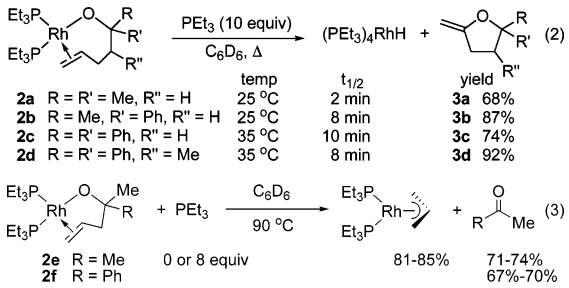


Figure 1. ORTEP diagram of $\{Rh(PEt_3)_2[\kappa^1{:}\eta^2\text{-}OCMe_2CH_2CH{=}CH_2]\}$ (**2e**). Most hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Rh−O = 2.052(1), Rh−C(13) = 2.135(2), Rh−C(14) = 2.201(2), Rh−P(1) = 2.291(1), Rh−P(2) = 2.230(1), O−C(16) = 1.407(3), P(1)−Rh−P(2) = 98.19(3), O−Rh−P(1) = 83.28(5), Rh−O−C(13) = 101.4(2), O−Rh−C(13) = 93.61(8), O−Rh−C(14) = 80.29(8).

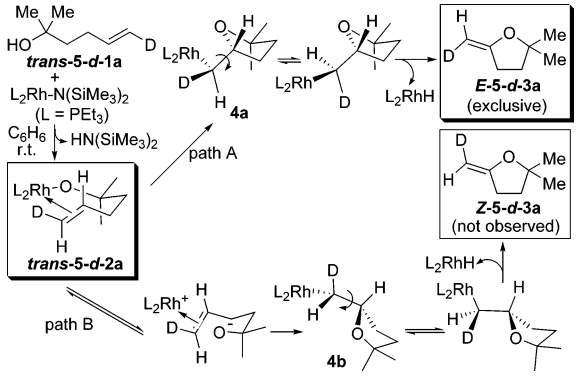
Complexes **2a**−**d** reacted in solution in the presence of added PEt_3 at ambient temperatures to afford 2,2-disubstituted-5-methylenetetrahydrofuran derivatives **3a**−**d** in 68−92% yields, as determined by ^{1}H NMR spectroscopy (eq 2). $[(PEt_3)_4RhH]$ was the only rhodium product detected by ^{31}P NMR spectroscopy.[11] The organic product was identified by comparison of the ^{1}H NMR spectra and GC retention times to those of an authentic sample prepared by intramolecular bromoetherification and subsequent dehydrobromination of the corresponding olefinic alcohol (see Supporting Information).



In contrast to the cyclization chemistry of complexes **2a**−**d**, complexes **2e** and **2f** underwent β-allyl elimination. Heating of **2e** and **2f** at 90 °C for 1−2 h formed $[(PEt_3)_2Rh(\eta^3\text{-allyl})]$[7] in 81−85% yields and acetone or acetophenone, respectively, in 67−74% yields (eq 3).[12]

10.1021/ja063347w CCC: $33.50

Scheme 1



Scheme 1 shows pathways for the C−O bond-forming process of compounds **2a**−**d** (illustrated for deuterium-labeled, dimethyl-substituted **2a**) involving migratory insertion (path A) or dissociation of alkoxide and backside attack on the olefin (path B).[13] These pathways were distinguished from each other and from alternative mechanisms by kinetic experiments that revealed whether the process was intramolecular or intermolecular, solvent effects that probed for charged intermediates, and stereochemical labeling experiments that distinguished between syn and anti addition across the olefin.

Rate constants for the reaction of diphenyl-substituted **2c** were measured by ^{1}H NMR spectroscopy at 35 °C with an initial 0.040 M concentration of **2c** and concentrations of PEt_3 varying from 0.12 to 1.20 M. A clear exponential decay of **2c** indicated that the reaction was first-order in rhodium (see Supporting Information). The rate constants for reactions conducted with these concentrations of added PEt_3 were indistinguishable and are consistent with the direct, unimolecular mechanisms of Scheme 1.

The solvent effects were inconsistent with the alkoxide dissociation step of path B to form a zwitterionic intermediate. The solvent effect was small, and the reaction was slightly faster in less polar solvents ($k_{THF-d_8} = 0.50 \times 10^{-3}$ s^{-1}, $k_{benzene-d_6} = 0.84 \times 10^{-3}$ s^{-1}, $k_{cyclohexane-d_{12}} = 1.44 \times 10^{-3}$ s^{-1}).

The stereochemical results were also inconsistent with the backside attack of alkoxide on the coordinated olefin in path B. Scheme 1 shows the predicted stereochemical outcome for reaction of the alkoxide derived from ***trans*-5-*d*-1a** by syn (path A) and anti (path B) addition of the rhodium and alkoxo units across the olefin, followed by β-hydrogen elimination through the usual syn coplanar transition state. Syn addition of the Rh−O bond across the olefin (path A) would afford diastereomer **4a**. Subsequent rotation about the C−C bond to create a syn coplanar transition state for β-hydrogen elimination would generate ***E*-5-*d*-3a**. Anti addition after dissociation of the alkoxide ligand (path B), followed by outer-sphere nucleophilic attack of the pendant alkoxide, would generate the opposite diastereomeric intermediate **4b**. Rotation about the C−C bond, followed by β-hydrogen elimination, would then form ***Z*-5-*d*-3a**.

Stereochemically defined, ^{2}H-labeled (45% deuterium) alcohol ***trans*-5-*d*-1a** was prepared as described in Supporting Information, and from this alcohol was generated the alkoxo olefin complex ***trans*-5-*d*-2a**. The stereoselectivity of the cyclization of ***trans*-5-*d*-2a** was studied by ^{1}H and ^{2}H NMR spectroscopy (Scheme 1). The ^{2}H NMR spectrum of the cyclization products contained a single resonance for a deuterium located trans to the oxygen, and the ^{1}H NMR spectrum contained a signal of appropriately decreased intensity corresponding to the hydrogen trans to the oxygen. The chemical shifts of the olefinic hydrogens were assigned by NOESY NMR spectroscopy. Thus, the kinetic data, solvent effects, and stereochemical results are consistent with an intramolecular process that occurs through neutral intermediates and syn addition of the metal and alkoxo units across the C−C double bond.[14,15] These data are consistent with the migratory insertion path A.

In summary, we report the preparation of a series of bis-(phosphine) rhodium(I) alkoxides containing an accompanying olefin ligand. The 5-hydroxy-1-alkene complexes undergo cyclizations to afford 5-methylenetetrahydrofurans and the corresponding Rh hydride as products. In contrast, the complexes of 4-hydroxy-1-alkene are more stable and undergo β-allyl elimination at elevated temperatures to afford a Rh allyl complex and the corresponding ketones. The intramolecularity, lack of evidence for ionic intermediates, and syn stereochemistry of the cyclizations are all characteristics of a migratory insertion mechanism. Future studies will focus on the scope of these reactions, extension into catalytic processes, and detection of the initial product from cyclization.

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Supporting Information Available: Experimental details and full structural characterization of **2e** (CIF and PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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