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COMMUNICATIONS

Published on Web 02/21/2006

Direct Observation of β-Aryl Eliminations from Rh(I) Alkoxides

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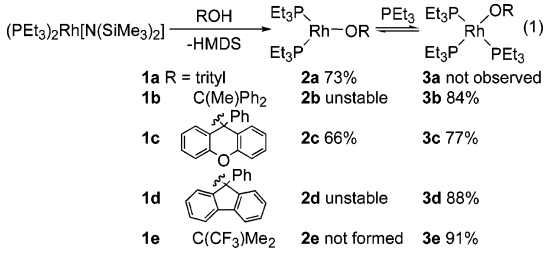
β-Hydrogen elimination from late transition-metal alkoxo and amido complexes is involved in many catalytic processes. The analogous β-hydrocarbyl eliminations from metal alkoxides were also suggested to occur in several catalytic processes.[1−5] In contrast to β-hydrogen eliminations from alkoxides, which have been observed from isolated alkoxo complexes in several cases,[6] few β-hydrocarbyl eliminations from isolated alkoxo complexes have been documented.[7,8] We report β-aryl eliminations from a series of isolated rhodium(I) alkoxides to generate ketones and a rhodium(I) aryl complex. One alkoxo complex of this series is coordinatively unsaturated and allows a direct measurement of the rate of β-phenyl elimination. The structure of the precursor to the elimination contains a metal−aryl interaction that is likely to lie on the reaction coordinate for C−C bond cleavage.

Triethylphosphine-ligated rhodium alkoxides were prepared by the sequence in eq 1. Reaction of the Rh(I) silylamido precursor $\{(PEt_3)_2Rh[N(SiMe_3)_2]\}$[9] with tertiary alcohols **1a**−**e** readily occurred at room temperature to eliminate $HN(SiMe_3)_2$ and form rhodium alkoxo complexes.[10,11]

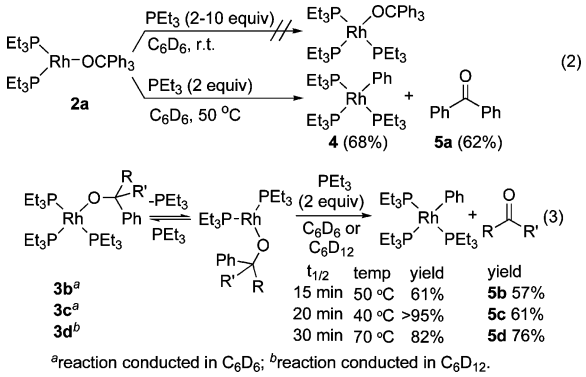


Reactions of the silylamide with alcohols led to both bisphosphine and trisphosphine complexes. Reaction of the silylamide with 1 equiv of trityl alcohol (**1a**) and 9-phenyl-9-xanthenol (**1c**) formed the bisphosphine complexes **2a** and **2c**. These alkoxide complexes were stable enough to isolate and were obtained in analytically pure form in 73 and 66% yields. Complex **2a** remained as the bisphosphine species in the presence of added PEt_3 at room temperature. In contrast, complex **2c** coordinated added PEt_3 and formed the trisphosphine-ligated rhodium alkoxide **3c**, which was isolated in good yield.

The addition of 1,1-diphenylethanol (**1b**) and 9-phenyl-9-fluorenol (**1d**) to the silylamide formed the bisphosphine complexes **2b** and **2d**, but these complexes were too unstable to isolate (see Supporting Information for spectral data). However, addition of these alcohols and addition of trifluoro-*tert*-butyl alcohol (**1e**) to the silylamido complex in the presence of 2−5 equiv of added PEt_3 formed more stable trisphosphine complexes **3b**, **3d** and **3e**, which were isolated as solids in good yields. Upon dissolution in the absence of added PEt_3, **3b**−**3e** spontaneously dissociated PEt_3 to create an equilibrium mixture of the bisphosphine and trisphosphine complexes that slightly favored the trisphosphine complex.

Complexes **2a** and **2c** were characterized by spectroscopic methods and elemental analysis. Complexes **3b**−**3e** were characterized by spectroscopic methods in solutions that contained added PEt_3 (∼5 equiv) to suppress ligand dissociation. Complexes **3c** and **3d** were stable enough as crystalline solids to allow satisfactory elemental analysis to be obtained.

Heating of a mixture of **2a** and PEt_3 afforded $(PEt_3)_3RhPh$[8] (**4**) and benzophenone in good yields from β-phenyl elimination (eq 2).[12] In contrast, the combination of complex **2c** and added PEt_3 generated the trisphosphine complex **3c**. However, heating of **3c**, as well as complexes **3b** and **3d**, with 2−5 equiv of PEt_3 for 90 min to 3 h at 40−70 °C led to β-phenyl eliminations to give arylrhodium complex **4** and the corresponding ketones **5b**−**5d** (eq 3). No products from ring opening of the alkoxides in complexes **3c** or **3d** were observed.[13] Heating of trifluoro-*tert*-butoxide **3e** gave the free alcohol **1e** as the major organic product and several unidentified Rh species, as indicated by ^{31}P NMR spectroscopy. The contrast between the lack of β-methyl elimination from **3e** and the facile β-aryl elimination from complex **3b**, which contains both β-aryl and β-methyl groups, shows that β-aryl elimination from these rhodium complexes is much more favorable than β-methyl elimination.[5]



The β-phenyl eliminations from trisphosphine alkoxide complexes **3b**−**3d** were inhibited by PEt_3. The reactions in eq 3 were conducted with 2 and 10 equiv of added PEt_3, and the reaction in the presence of the higher concentration of added ligand was 2−3 times slower. In addition, the yields of products from β-aryl elimination were lower (27−50%) in the presence of added PEt_3.[14] Because the yields were lower in the presence of added PEt_3, quantitative rate data were not obtained. However, the inhibition of the reaction by added PEt_3 observed during qualitative experiments is consistent with a reaction pathway that occurs by dissociation of PEt_3 and rate-limiting β-phenyl elimination from the resulting bisphosphine rhodium complex.

Consistent with this assertion, quantitative kinetic studies showed that the rate of β-phenyl elimination from bisphosphine complex **2a** was unaffected by added PEt_3. Reaction rate constants were measured by ^1H NMR spectroscopy at 50 °C with an initial 0.014 M concentration of **2a**, concentrations of PEt_3 varying from 0.028 to 0.14 M, and no added benzophenone or 0.070 M added

10.1021/ja058550q CCC: $33.50

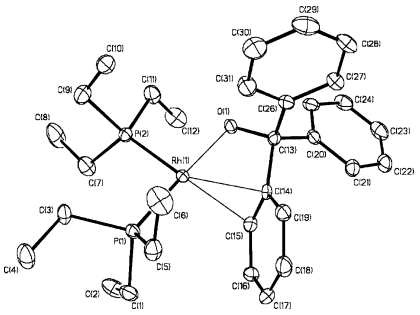
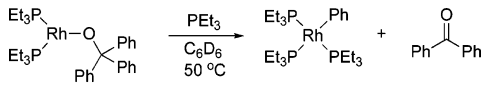


Figure 1. ORTEP diagram of $[Rh(PEt_3)_2(OCPh_3)]$ (**2a**). Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and bond angles (deg): Rh−O = 2.069(3), Rh−C(14) = 2.350(4), Rh−C(15) = 2.398(4), Rh−P(1) = 2.228(1), Rh−P(2) = 2.222(1), O−C(13) = 1.407(5), P(1)−Rh−P(2) = 97.21(5), O−Rh−P(2) = 88.05(9), Rh−O−C(13) = 101.4(2), O−C(13)−C(14) = 104.7(3), C(13)−C(20) = 1.528(6), C(13)−C(26) = 1.530(6), C(13)−C(14) = 1.552(6).

Scheme 1



2a (0.014 M) **4** **5a**

$[PEt_3]$ (M)	k_{obsd} (s^{-1})
0.028	0.00084
0.070	0.00093
0.140	0.00090
0.070*	0.00099 *(0.070 M of **5a** added)

benzophenone. A clear exponential decay of **2a** indicated that the reaction was first-order in rhodium (see Supporting Information). The rate constants for reactions with the different concentrations of PEt_3 or added benzophenone were indistinguishable (Scheme 1). These results support a mechanism in which irreversible β-phenyl elimination occurs from the bisphosphine-ligated Rh alkoxide. Further, these data reveal the rate constant for C−C bond cleavage in the absence of prior dissociation of ligand to generate the requisite open coordination site. This cleavage of the C−C bond occurs from an unstrained alkoxo complex with conventional phosphine ligands within 1 h at only 50 °C.

The solid-state structure of **2a** determined by X-ray diffraction (Figure 1) hints at the pathway for the β-aryl elimination. This structure consists of a pseudo-square planar rhodium center with two *cis*-oriented triethylphospine ligands and one triphenylmethoxy ligand that is bound through oxygen and the C(14)−C(15) carbons of an η^2-phenyl unit. The Rh−O distance is similar to those in previously isolated Rh(I) alkoxides,[15] and the Rh−C(14) and Rh−C(15) distances are longer than the $Rh-C_{olefin}$ distances of a Rh-(η^1:η^2-$CH_2CPh_2CH{=}CH_2$) complex (2.12 and 2.16 Å).[16,17] Most relevant to the reaction mechanism, the C−C bond between the alkyl carbon and the aryl group bound to rhodium is longer than the other C−C bonds between the sp^3 and ipso carbons. This structural feature suggests that this complex with an η^2-arene interaction lies on the β-elimination pathway.

The potential intermediacy of **2a** in the β-phenyl elimination draws parallels with the role of β-agostic complexes in β-hydrogen elimination.[18] Just as an interaction of the metal center with a β-hydrogen seems to precede β-hydrogen elimination, an interaction of the rhodium with the β-aryl group of the alkoxide **2a** seems to precede the β-aryl elimination event.[19] Simple lengthening of the C−C bond and shortening of the Rh−C bond to the ipso carbon in **2a** and its analogs would generate the initial arylrhodium ketone complex that would react with phosphine to displace the ketone and form the final arylrhodium product.

In summary, we have prepared a series of isolated rhodium(I) tertiary phenylmethoxide complexes that undergo mild β-phenyl eliminations. The bisphosphine complexes undergo elimination directly from the isolated species, and the trisphosphine complexes undergo elimination after dissociation of a phosphine. The need for an open coordination site for β-aryl elimination parallels the need for an open coordination site in classic β-hydride elimination pathways,[20] and the structure of a bisphosphine β-aryl alkoxide complex illustrates the interaction that is likely to precede C−C bond cleavage. Studies on the relative reactivities of different arylmethoxides and the potential reversibility of the elimination process are underway.

Acknowledgment. Financial support for this work was provided by the Department of Energy, Office of Basic Energy Sciences. We thank Boehringer Ingelheim for an unrestricted gift.

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

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(11) Treatment of the silylamido complex with less acidic alcohols, such as *t*-BuOH and $HOC(Me)_2Ph$, at 20−80 °C led to no reaction.

(12) Heating **2a** in the absence of ligand led to the formation of multiple products due to the instability of the 14-electron $[Rh(PEt_3)_2Ph]$ product.

(13) Both β-phenyl elimination and ring opening C−C cleavage have been reported in relevant Pd-catalyzed processes; see refs 5a−c.

(14) See Supporting Information for details. Complex **4** underwent slow aromatic C−H exchange with benzene as well as the aromatic ketone products. See ref 8 for an analogous observation.

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JA058550Q