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

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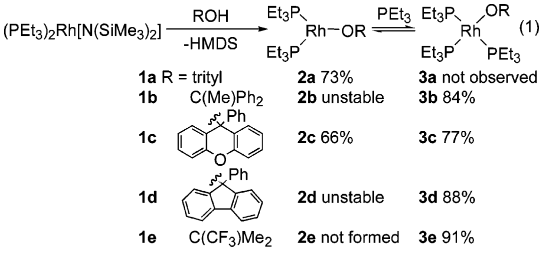
β-Hydrogen elimination from late transition-metal alkoxo and amido complexes is involved in many catalytic processes. The analogous β-hydrocarbyl eliminations from metal alkoxides were also suggested to occur in several catalytic processes.[1−5] In contrast to β-hydrogen eliminations from alkoxides, 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]

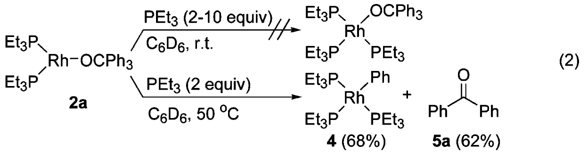


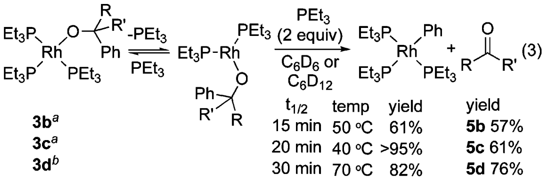
Reactions of the silylamide with alcohols led to both bisphosphine and trisphosphine complexes. Reaction of the silylamide with 1 equiv of trityl alcohol (**1a**) and 9-phenyl-9-xanthenol (**1c**) formed the bisphosphine complexes **2a** and **2c**. These alkoxide complexes were stable enough to isolate 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]





[a] reaction conducted in C_6D_6; [b] reaction conducted in C_6D_{12}.

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

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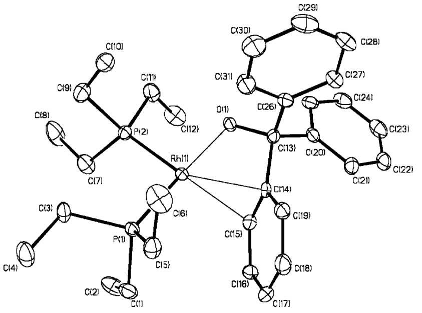
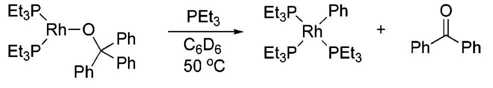


Figure 1. ORTEP diagram of $[Rh(PEt_3)_2(OCPh_3)]$ (**2a**). Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and bond angles (deg): Rh−O = 2.069(3), Rh−C(14) = 2.350(4), Rh−C(15) = 2.398(4), Rh−P(1) = 2.228(1), Rh−P(2) = 2.222(1), O−C(13) = 1.407(5), P(1)−Rh−P(2) = 97.21(5), O−Rh−P(2) = 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 $Rh(\eta^1:\eta^2-CH_2CPh_2CH{=}CH_2)$ 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.

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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.

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