β-Aryl Eliminations from Rh(I) Iminyl Complexes
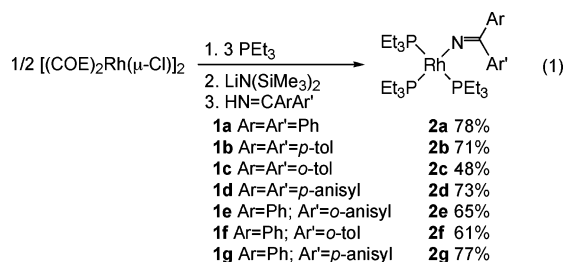
Pinjing Zhao and John F. Hartwig*

Department of Chemistry, Yale University, PO Box 208107 New Haven, Connecticut 06520-8107

Received June 22, 2005; E-mail: john.hartwig@yale.edu

β-Hydrogen elimination is a classic organometallic reaction of late transition metal complexes. However, analogous reactions that cleave carbon−carbon bonds are much less common.[1] A few examples of such β-carbon elimination reactions from late transition metal complexes have been reported, but these reactions are more common for early transition metal complexes. Directly observed β-carbon elimination from late transition metal alkoxides,[2] amides, and related compounds with nondative metal−heteroatom bonds are particularly rare, although several catalytic processes have been suggested to occur by β-carbon eliminations from transition metal alkoxides.[3,4] We report the direct observation of β-aryl elimination from the iminyl ligand of an isolated rhodium(I) iminyl complex. This reaction generates a discrete rhodium(I) aryl complex and a free aromatic nitrile.

Rhodium iminyl complexes were prepared by the sequence in eq 1. $[(COE)_2Rh(\mu\text{-}Cl)]_2$ was treated with 6 equiv of PEt_3, followed

Figure 1. ORTEP diagram of **2a**. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Rh−N = 2.039(2), Rh−P(2) = 2.268(1), Rh−P(1) = 2.304(1), Rh−P(3) = 2.321(1), Rh−N−C(19) = 130.6(2), N−C(19)−C(20) = 126.2(2), N−C(19)−C(26) = 117.8(2).

Complex			rhodium product	nitrile product
2a	Ar=Ph	30 min at 85 °C	**3a** 68% (68%)[a]	**4a** 88% (31%)
2b	p-tol	30 min at 85 °C	**3b** 63% (55%)	**4b** 74% (46%)
2c	o-tol	50 min at 40 °C	**3c** 95% (71%)	**4c** 71% (67%)
2d	p-anisyl	30 min at 85 °C	**3d** 60% (53%)	**4d** 48% (34%)

[a]Yields in parentheses are for reactions conducted in C_6D_6.

by 2 equiv of $LiN(SiMe_3)_2$ and 2 equiv of diarylimines **1a−g**. This procedure formed the silylamine and the rhodium iminyl complexes in 48−78% isolated yields. These complexes were all formed in moderate to high chemical yields; the isolated yields reflect the solubility of the compounds more than the chemical yield of the reaction sequence. The imine precursors **1a−g** are either commercially available or were formed by addition of the appropriate Grignard reagent to a nitrile, followed by careful protonation of the resulting anion.

Complexes **2a−g** were characterized by spectroscopic methods and elemental analysis, and the structure of **2a** was determined by X-ray diffraction (Figure 1). In the solid state, **2a** adopts a square-planar geometry. The sum of the angles around the Rh center was found to be 360°. The Rh−N−C19 angle is bent (130.6°), and this angle suggests weak N→Rh π donation. Related square-planar iminyl complexes also have bent M−N−C angles.[5a] The Rh−N distance (2.04 Å) is comparable to that of another bent Rh iminyl complex (2.02 Å),[5b] slightly shorter than that of a Rh amide (2.11 Å),[5c] and slightly longer than that in a linear Re iminyl complex (1.90 Å).[5d]

Symmetrical iminyl complexes **2a−d** underwent β-aryl elimination reactions to afford the corresponding rhodium aryl complexes **3a−d** in 60−95% yields and benzonitrile derivatives **4a−d** in 48−88% yields (eq 2). In benzene, the rhodium complexes were formed in somewhat lower 53−71% yields, and the nitriles were also formed in similarly lower 31−67% yields. Reaction of the rhodium
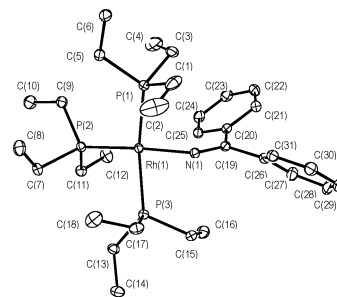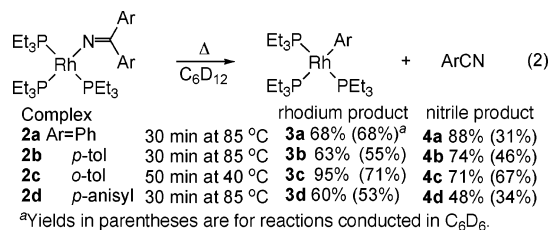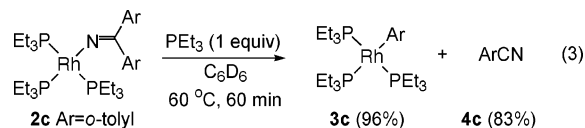
aryl product with solvent is likely to have complicated reactions in benzene solvent.[6,7] However, the reaction of the o-tolyl iminyl complex **2c** in the presence of added PEt_3 in benzene formed the rhodium aryl complex and free nitrile in excellent 96% and 83% yields, respectively (eq 3). The rates were slower in the presence of the added ligand, however (vide infra).


The reactions of compounds **2b−2d** were conducted to begin to assess the electronic and steric effects on the reaction. The more electron-rich p-tolyl and p-anisyl derivatives **2b** and **2d** reacted with similar rates and in similar yields to the parent iminyl complex **2a**. In contrast, the o-tolyl complex **2c** underwent β-aryl elimination at much lower temperatures and in higher yields than the phenyl, p-tolyl, or p-anisyl derivatives. This increase in reactivity could result from a starting iminyl complex that is less stable with o-tolyl groups because of the steric hindrance in the imine conformation that creates overlap of the aryl π-system with the C=N bond. The steric hindrance is less severe in the rhodium product that contains an aryl group that lies perpendicular to the square coordination plane.[8]

Trends in the migratory aptitudes of the aryl groups were determined by conducting the reactions with the unsymmetrically substituted iminyl complexes **2e−2g** and determining the ratios of the rhodium aryl complexes and nitrile products by a combination

Scheme 1
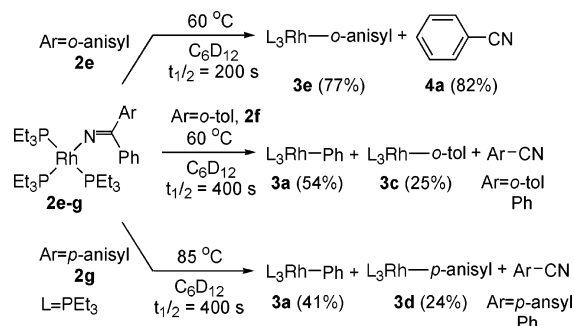
Scheme 2
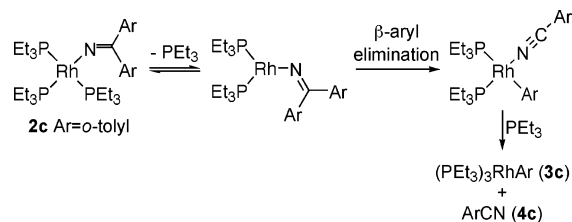
of NMR and GC methods with internal standards.[9] These reactions are summarized in Scheme 1. Complexes **2e**–**2g** were prepared by the method in eq 1 in 61–77% yields.

Most striking, *o*-anisyl phenyl iminyl complex **2e** underwent exclusive migration of the *o*-anisyl group at 60 °C, with a half-life of roughly 200 s in C_6D_{12} to afford 77% yield of $(PEt_3)_3Rh(o$-anisyl) (**3e**) and 82% yield of benzonitrile (**4a**). At the same temperature, *o*-tolyl phenyl iminyl complex **2f** underwent competitive migration of the two aryl groups. This reaction occurred with a half-life of roughly 400 s in C_6D_{12} to afford $(PEt_3)_3RhPh$ (**3a**) and $(PEt_3)_3RhP(o$-tolyl) (**3c**) in a roughly 2:1 ratio (79% overall yield), slightly favoring phenyl migration. Thus, steric effects alone do not control the relative rates for migration of the aryl groups. Likewise, a simple electronic effect cannot account for the faster migration of the *o*-anisyl complex. The phenyl *p*-anisyl iminyl complex **2g** underwent competitive migration of the two aryl groups to form a roughly 2:1 ratio of rhodium aryl products **3a** and **3d** (65% overall yield) in favor of complex **3a** that results from migration of the less electron-donating phenyl group. Thus, the reactions of unsymmetrical iminyl complexes **2e**–**2g** reveal the unexpected relative migratory aptitudes: *o*-anisyl ≫ phenyl > *p*-anisyl ≈ *o*-tolyl. Studies to understand the origin of these migratory aptitudes are ongoing. [10]

The mechanism of the clean *β*-aryl elimination from iminyl complex **2c** with added PEt_3 was investigated by kinetic methods. Reaction rate constants were measured by ^{1}H NMR spectroscopy at 60 °C with an initial concentration of **2c** of 0.020 M. Reactions were conducted while varying the concentration of PEt_3 from 0.020 to 0.40 M. A clear exponential decay of **2c** indicated that the reaction was first-order in rhodium. A plot of $1/k_{obsd}$ vs $[PEt_3]$ (Figure S2 in Supporting Information) showed that the reaction was inverse first-order in added PEt_3. The rate constants, as well as reaction conversions, were unaffected by added *o*-tolunitrile (see Supporting Information). These results are most consistent with a pathway that occurs by reversible dissociation of PEt_3 to form a 14-electron intermediate (Scheme 2), which undergoes *β*-aryl elimination,[11] presumably to form a nitrile-ligated, rhodium aryl complex. Subsequent displacement of the nitrile by PEt_3 would afford tris-triethylphosphine complex **3c**. This mechanism is analogous to the mechanisms of *β*-hydrogen eliminations from d[8] square-planar alkyl complexes[12] and the mechanisms for *β*-hydrogen

eliminations from isolated, isoelectronic iridium(I) amido and alkoxo complexes.[13]

In summary, we have prepared a family of rhodium iminyl complexes, all of which undergo C–C bond cleavage to form rhodium aryl complexes and free aromatic nitriles. Such *β*-eliminations that cleave C–C bonds in ligands bound to a transition metal through a metal–nitrogen bond have little precedent, but kinetic studies are most consistent with eliminations through a type of 14-electron intermediate that is analogous to intermediates that undergo more precedented *β*-hydrogen eliminations. Studies to probe the thermodynamics, potential reversibility, and origins of the relative rates of migration, as well as the potential of this reaction in catalytic transformations, are underway.

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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(9) The rhodium aryl complexes **3a**–**e** were prepared independently by the reaction of $(PEt_3)_3RhCl$ with the corresponding aryllithium or Grignard reagents in 55–77% isolated yields (see Supporting Information).

(10) During the review of this manuscript, we obtained X-ray structural data on complex **3e** that shows the absence of a Rh–O bonding interaction. Details will be reported in future publications.

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