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Reactivity of a Parent Amidoruthenium Complex: A Transition Metal Amide of Exceptionally High Basicity

J. Robin Fulton, Marco W. Bouwkamp, and Robert G. Bergman*

Department of Chemistry, University of California Berkeley, California 94720

Complexes with late metal–oxygen and –nitrogen single bonds (metal alkoxides and amides) play important roles in biological systems and have been implicated as intermediates in a variety of industrially important catalytic reactions.^{1–3} When the metal–heteroatom bond reacts with carbon–hydrogen bonds of organic molecules, an important question concerns whether the transformation takes place via odd- or even-electron intermediates. For example, many late metal alkoxides undergo rapid overall even-electron RO[−] transfer reactions with electrophiles.^{4–8} In other cases, metal–oxygen bonds have been proposed to react by initial hydrogen atom abstraction, an odd-electron process.^{9–11}

Stimulated by this difference in behavior, we set out to determine the preferred mode of reactivity in the well-characterized parent hydroxo and amide complexes: *trans*-(DMPE)₂(H)-Ru(NH₂) (**1**) and *trans*-(DMPE)₂(H)Ru(OH) (**2**) (DMPE = 1,2-bis(dimethylphosphino)ethane).^{8,12} This study has uncovered only 2-electron behavior for both the OH and NH₂ metal-bound fragments, and has revealed that complex **1** bears a surprisingly basic amido ligand, a property that is expressed without dissociation of the NH₂ group from the ruthenium center.

In analogy to reactions reported by Stack and Mayer and their co-workers,^{9,11} our ruthenium amido and hydroxido complexes **1** and **2** cause the dehydrogenation of cyclohexadiene (1,4-CHD) and 9,10-dihydroanthracene (DHA) (eq 1). However, compounds **1** and **2** also catalyze the interconversion of 1,4- and 1,3-CHD more rapidly (*t*_{1/2} = <5 min) than dehydrogenation occurs.

The dehydrogenation and isomerization reactions could proceed by initial abstraction of a hydrogen atom (although the required oxidation state change is less favorable here than in the earlier-reported systems) or a proton, in addition to pathways that might involve interaction of the diene with the metal center. To explore this question, we extended the above reactions to a larger series of organic compounds having C–H bonds characterized by a wide range of bond dissociation energies and acidities.

Two interrelated modes of reactivity were observed with organic compounds containing relatively acidic C–H bonds (Scheme 1). The first includes the generation of a stable ion pair formed by overall proton transfer from carbon to ruthenium-bound nitrogen (e.g., **1** + fluorene → **4a** in THF or benzene).¹³ The second is overall displacement of the nitrogen fragment from

the Ru center (e.g., **1** + PhC≡CH → **5** in benzene;¹⁴ **1** + arylacetonitriles → **6a**, **6b** in benzene).¹³ We have evidence that proton transfer to form an ion pair is the initial step in these reactions as well. Monitoring the reaction of **1** with cyclobutanone by NMR at 25 °C in THF-*d*₈ reveals that ion pair **4b** is initially formed, and this is transformed more slowly into the stable substitution product **7**.¹³ It seems likely that the other displacement reactions proceed by analogous initial proton-transfer steps.

Surprisingly, amido complex **1** also reacts with exceedingly weakly acidic compounds, although these reactions are sufficiently endothermic that only H/D exchange is observed. One of the most striking reactions of **1** occurs upon its dissolution into toluene-*d*₈ (*pK*_a of toluene = 41,¹⁵ BDE = 89.8 kcal/mol¹⁶). Monitoring this reaction by ¹H and ²H {¹H}NMR spectroscopy showed full deuterium incorporation into both the N-bound positions and the DMPE ligand, concurrent with hydrogen incorporation into the benzylic position of toluene (Scheme 1). A similar, but much slower, exchange is observed with hydroxido complex **2**.

Consistent with this observation, complex **1** can be used to catalyze deuterium exchange between toluene-*d*₈ and carbon acids of similar or weaker acidities but widely varying bond dissociation energies (BDE's; listed in kcal/mol), including triphenylmethane (*pK*_a = 31.5 (THF),¹⁷ BDE = 81¹⁸), cycloheptatriene (*pK*_a = 38.8,¹⁵ BDE = 73¹⁹), ammonia (*pK*_a = 41,²⁰ BDE = 107.4¹⁹), dihydrogen (*pK*_a = 35,¹⁵ BDE = 104¹⁵), and even propene (*pK*_a = 43,¹⁵ BDE = 88.8¹⁶).²¹ No exchange is observed with benzene (*pK*_a = 43,¹⁵ BDE = 110.9)¹⁹ or THF (BDE = 95 (est),²² *pK*_a unknown), even at elevated temperatures.²³ No detectable amounts of radical coupling products are observed in any of these reactions.²⁴ Exchange is observed between **1** and the methyl hydrogens of toluene, but not between **1** and the benzylic hydrogens of *p*-toluidine, which is less acidic than toluene, but has a comparable bond dissociation energy.^{25,26} The fact that this selectivity exists, and that exchange occurs even with compounds having very high X–H bond energies (e.g., ammonia), provides strong evidence that amido complex **1** and hydroxido complex **2** abstract protons rather than hydrogen atoms from weak carbon (and other) acids.

In contrast to its behavior with stronger acids, no substitution of the ammonia ligand by the transiently generated anion is observed in any of the exchange reactions between **1** and very weak acids, such as toluene and propene.²⁷ Similarly, despite rapid H/D exchange between **1** and ND₃, *no labeled nitrogen is incorporated into amido complex 1 upon addition of ¹⁵NH₃ to a solution of 1 in THF-*d*₈, even after 1 month at room temperature.*^{28,29} A strongly hydrogen bonded complex [(DMPE)₂(H)Ru–NH₃ - -¹⁵NH₂], apparently incapable of interchanging the nitrogen groups, is presumably responsible for this intriguing behavior.

A quantitative assessment of the basicity of amido complex **1** is complicated by the influence of ion pairing in the calculation of proton-transfer equilibrium constants in nonpolar solvents.³⁰ However, we were able to obtain an approximate idea of the basicity of **1** and **2** by finding organic acids whose conjugate bases are of comparable proton-abstracting ability to **1** or **2**. In the case of hydroxido complex **2**, addition of fluorene (*pK*_a = 22.9 (THF),¹⁷ BDE = 80 kcal/mol¹⁸) in THF-*d*₈ led to an equilibrium mixture of fluorene, hydroxido complex **2**, and the cationic aquo complex/fluorenide ion pair **10a** as observed by ¹H NMR spectrometry (eq 2, *K*_{eq} = 6.4).

The much stronger base **1** completely deprotonates fluorene. For this system, triphenylmethane is required to establish a solution containing detectable equilibrium concentrations of Ph₃H, **1**, and the ammonia complex/triphenylmethide ion pair **4c**. This

proton-transfer equilibrium is rapid on the NMR time scale at room temperature, but at lower temperatures each species can be observed (eq 3). The equilibrium constant (K_{eq}) was measured at five different temperatures; a linear van't Hoff plot allowed us to calculate an extrapolated equilibrium constant of 3.6×10^{-1} at 25 °C.

If ion pairing effects are ignored, the basicity of hydroxido complex **2** is comparable to that of fluorenyl ($pK_a = 22.9$ in THF), and the basicity of amido complex **1** is comparable to that of triphenylmethide ($pK_a = 31.5$ in THF). However, this conclusion must be modified to the extent that the ions formed by proton transfer in THF tend to experience mutual stabilization due to their presence in a contact ion pair, a conclusion that is supported by preliminary UV/visible investigation of these systems.³⁰ Even though a realistic determination of the actual pK_a of the ruthenium ammonia complex awaits further study, it is clear that complex **1** exhibits an unusually high thermodynamic proton-abstraction propensity.

In summary, amido complex **1** can abstract hydrogen from a wide range of organic compounds, but in all cases that we have investigated, the hydrogen is removed as a proton rather than a hydrogen atom. By inference we believe the same to be true of hydroxido complex **2**, although we have collected less evidence to support this extension of our conclusions. We have preliminary indications that the corresponding iron complexes can be prepared, and it will be interesting to see if first-row M–X bonds exhibit a higher propensity to undergo one-electron reactions.

Most significantly, the NH_2 group in **1** exhibits a degree of basicity reminiscent of alkali metal amides, despite its undoubtedly strong bond with the ruthenium center, which remains intact through many reversible proton-transfer events. We assume the high basicity of the amido complex **1** is either due to a remarkably polarized Ru–N bond, resulting in a highly reactive π -orbital,³¹ or a strong filled/filled ($d\pi$ - $p\pi$) repulsion,⁶ a theory that has been invoked many times before but has never, to our knowledge, been exemplified so strongly as in amido complex **1**.

Supplementary Material

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27. The coordinated ammonia is never displaced by the benzyl anion to generate t-(DMPE)₂(H)Ru(CH₂Ph) (8), even at elevated temperatures. Treatment of t-(DMPE)₂(H)Ru(CH₂Ph) (8) with liquid ammonia does not result in the formation of amido complex 1 and toluene, establishing that the failure to observe 8 is not due to thermodynamic factors. We suggest that the exchange occurs via a strongly hydrogen-bonded complex or transition state, which has no low-energy route to the extrusion of ammonia and formation of the Ru–C bond.
28. In contrast to the behavior of (DMPE)₂(H)Ru(NHCOCF₃), see: Schaad DRL, Landis CRJ Am Chem Soc 1990;112:1628.
29. Labeled nitrogen is observed in the cis isomer, which is formed after 1 month at room temperature and is presumed to be the more thermodynamically stable isomer.
30. The λ_{max} of the UV–vis spectrum of 4a is 368 nm, consistent with a contact ion pair and not a solvent-separated ion pair; see: Smid, J. In Ions and Ion Pairs in Organic Reactions; Szwarc, M., Ed.; Wiley-Interscience: New York, 1972; Vol. 1, p 85.
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Scheme 1.