J|A|C|S COMMUNICATIONS

Published on Web 10/06/2010

"Long-Range" Metal−Ligand Cooperation in H_2 Activation and Ammonia-Promoted Hydride Transfer with a Ruthenium−Acridine Pincer Complex

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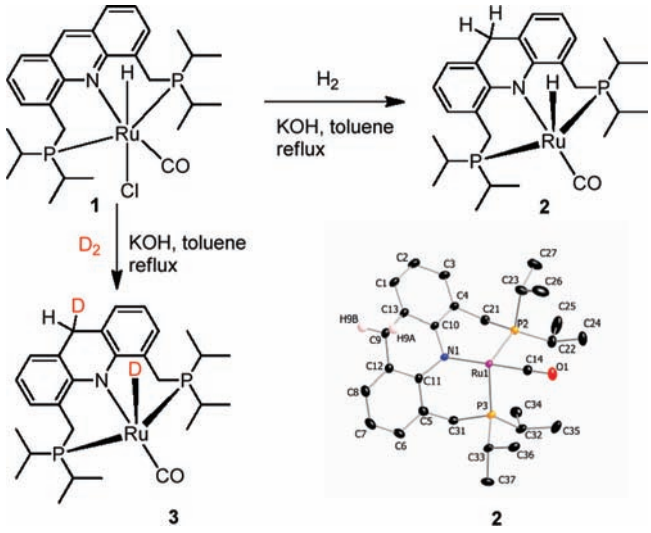
Abstract: The acridine-based pincer complex **1** exhibits an unprecedented mode of metal−ligand cooperation involving a "long-range" interaction between the distal acridine C9 position and the metal center. Reaction of **1** with H_2/KOH results in H_2 splitting between the Ru center and C9 with concomitant dearomatization of the acridine moiety. DFT calculations show that this process involves the formation of a Ru dihydride intermediate bearing a bent acridine ligand in which C9 is in close proximity to a hydride ligand followed by through-space hydride transfer. Ammonia induces transfer of a hydride from the Ru center of **1** to C9 of the flexible acridine pincer ligand, forming an unusual dearomatized *fac*-acridine PNP complex.

Bond activation based on cooperation between metals and ligands plays an important role in chemical and biological catalysis.[1] We recently discovered a new mode of metal−ligand cooperation based on pyridine-type pincer complexes that involves deprotonation of the pincer "arm" with concomitant ligand dearomatization,[2] which has led to new catalytic processes.[3] We now present another novel mode of metal−ligand cooperation involving an acridine-based pincer system.

We previously reported the acridine-based ruthenium pincer complex (A-PNP)RuHCl(CO) (**1**), which catalyzes the conversion of primary alcohols to acetals under neutral conditions and to esters in the presence of a base.[4] Complex **1** also catalyzes the reaction of alcohols with ammonia to yield primary amines selectively.[5] The crystal structure of **1** exhibits a very long Ru−N bond [2.479(2) Å], suggesting the possibility of hemilability. This, in conjunction with the known susceptibility of the acridine C9 to nucleophilic attack,[6] suggested to us the possibility of a unique, "long-range" mode of metal−ligand cooperativity. We initially examined this possibility for H_2 activation,[7] which is a key step in numerous catalytic processes.

Reaction of complex **1** with 5 bar H_2 for 48 h in the presence of 1 equiv of KOH in refluxing toluene leads to dearomatization of the central acridine ring, forming complex **2** (Scheme 1).[8] The $^{31}P\{^1H\}$ NMR spectrum of **2** in benzene-d_6 exhibits a singlet at 74.73 ppm, and the ^1H NMR spectrum has a triplet at −21.09 ppm for Ru−H, an upfield shift of 5 ppm from complex **1**, suggesting the absence of the *trans*-chloride ligand. The appearance of two new doublets at 3.24 and 3.41 ppm with geminal coupling constants in the ^1H NMR spectrum and the formation of a new CH_2 signal at 36.48 ppm in the ^{13}C DEPT-135 NMR

Scheme 1. Reactions of **1** with H_2 and D_2; ORTEP Drawing of **2**, with the Following Selected Bond Lengths (Å) and Angles (deg): Ru(1)−N(1), 2.171(1); Ru(1)−C(14), 1.845(1); Ru(1)−P(3), 2.334(1); N(1)−C(11), 1.399 (2); C(11)−C(12), 1.408(2); C(9)−C(12), 1.504(2); P(2)−Ru(1)−P(3), 104.68(2); C(14)−Ru(1)−N(1), 177.96(4)



spectrum of **2** confirmed dearomatization as a result of H_2 splitting. A similar reaction with D_2 leads to **3**. The ^2H and ^1H NMR spectra of **3** indicate the presence of a major amount of Ru−D (broad singlet at −20.75 ppm) and a very minor amount of Ru−H (triplet at −20.84 ppm), respectively. The ^2H NMR spectrum also exhibits a broad multiplet corresponding to the C*D*H group of the middle acridine ring (C9).[9] These observations confirmed the dearomatization as a result of D_2 splitting. The dearomatization was unambiguously corroborated by single-crystal X-ray crystallography of **2** (Scheme 1). The Ru center exhibits a distorted trigonal-bipyramidal geometry with an axial, linear C−Ru−N arrangement and a P−Ru−P angle of 104.68°. The Ru−N bond (2.171 Å) is dramatically shorter (by 0.308 Å) than that in **1**.[4] The central acridine ring has a boat-type conformation, and the acridine moiety is tilted toward the Ru center with a C(11)−N(1)−C(10)−Ru(1) torsion angle of 145.16°.

The reactivity of **1** toward H_2 is conceptually different from that of the previously reported pyridine-based PNP complexes,[2,3b] which react with H_2 to give *trans*-dihydride complexes involving methylene "arm" deprotonation and dearomatization of the pyridine moiety.[10] The A-PNP ligand affords a flexible ligand framework, as it forms six-membered rings, whereas the standard pincer ligands form five-membered rings. One advantage of this flexibility is the

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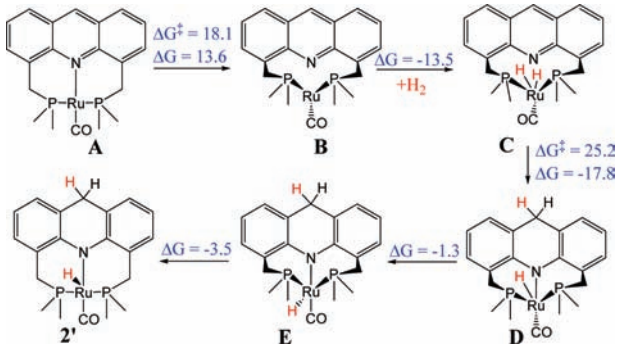
ability to form *mer* (i.e., **1**−**3**) and *fac* (i.e., **4**; see below) A-PNP complexes. On the basis of density functional theory (DFT) calculations,[11] the most likely reaction mechanism for the reaction of **1** with H_2 (shown in Scheme 2) involves bending of the acridine unit of Ru(0) intermediate **A** (obtained by deprotonation of **1** by KOH)[12] with pinching together of the phosphine arms, resulting in seesaw-shaped complex **B**. H_2 addition to this complex, which was shown to be a practically barrierless step, yields complex **C**, in which one of the two hydride ligands points directly toward the C9 position of the acridine ring. This distance (3.84 Å) is sufficiently short that the hydrogen atom can migrate through space from the metal to carbon. This transition state [**TS(C-D)**; Figure S1 in the Supporting Information] results in a barrier of $\Delta G^{\ddagger}_{298} = 18.1$ kcal/mol. In the case of the pyridine-based PNP complexes, hydrogen transfer to/from the methylene arm was found to be facilitated by water molecules likely present in the solvent.[2c] In this case, however, a solvent bridge is not required, nor is there sufficient room for one. In fact, all attempts to find a transition state for the water-assisted hydrogen transfer without prior acridine bending, akin to that found in the (PNP)Ir(Ph) system,[2c] failed. Another route involving initial hydrogen transfer to the acridine nitrogen followed by proton migration around the acridine ring system (Scheme S1 in the Supporting Information) was also considered, but the located intermediates and transition states were far too high in energy. A bimolecular reaction mechanism involving H_2 addition to **A** followed by transfer of one hydride to the C9 position of a second molecule of **A** was shown to be unlikely. The addition of H_2 to **A** was found to have a barrier of $\Delta G^{\ddagger}_{298} = 21.3$ kcal/mol [**TS(A-F)**; Scheme S1], which is significantly higher than the barriers in the route depicted in Scheme 2.

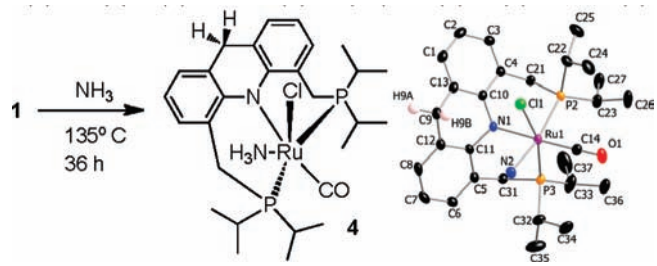
Scheme 2. Reaction Mechanism for the Reaction of **1**/KOH with H_2, As Determined Using DFT



Interestingly, dearomatization of the central acridine ring was also observed upon reaction of **1** with ammonia in toluene, leading to complex **4** (Scheme 3). The $^{31}P\{^1H\}$ NMR spectrum of complex **4** indicates the presence of two inequivalent P atoms, and ^1H NMR spectrum exhibits a broad singlet at 1.73 ppm for the coordinated NH_3 and no Ru−H signal. The $^{13}C\{^1H\}$ and ^{13}C DEPT NMR spectra show the presence of a C9 methylene group at 34.3 ppm, confirming the dearomatization of the acridine ring system by a long-range hydride migration. The structure of **4** was confirmed by single-crystal X-ray crystallography (Scheme 3) and shows the unusual *fac* configuration of the PNP ligand. Presumably, decoordination of the acridine nitrogen followed by NH_3 coordination places the bent acridine ring in a favorable position for hydride transfer to C9. This transformation is probably a key step in the selective reaction of primary alcohols with ammonia catalyzed by **1**.[5]

In summary, the acridine pincer complex **1** exhibits an unprecedented mode of metal−ligand cooperation that involves

Scheme 3. Reaction of **1** with Ammonia; ORTEP Drawing of **4** with the Following Selected Bond Lengths (Å) and Angles (deg): Ru(1)−N(1), 2.184(2); Ru(1)−C(14), 1.839(2); Ru(1)−P(3), 2.344(1); N(1)−C(11), 1.389(2); C(11)−C(12), 1.409(3); C(9)−C(12), 1.505(3); P(2)−Ru(1)−P(3), 103.44(2); C(14)−Ru(1)−N(1), 176.54(8)



a "long-range" interaction between the acridine C9 position and the metal center. Its reaction with H_2/KOH results in H_2 splitting between the Ru center and C9 with concomitant dearomatization of the A-PNP ligand. DFT calculations indicate that this process involves the formation of a Ru dihydride intermediate bearing a bent acridine ligand in which C9 is in close proximity to a hydride, which is followed by through-space hydride transfer. Reaction with NH_3 results in transfer of the hydride from the Ru center of **1** to C9, forming an unusual *fac* coordination of the dearomatized A-PNP ligand. We are currently studying the implications of this novel mode of metal−ligand cooperation for catalytic design.

Acknowledgment. This research was supported by the Israel Science Foundation, the European Research Council (ERC 246837), the Minerva Foundation, and the Bernice and Peter Cohn Catalysis Research Fund. D.M. holds the Israel Matz Professorial Chair of Organic Chemistry.

Supporting Information Available: Figure S1, Scheme S1, experimental procedures, X-ray data for complexes **2** and **4** (CIF), and full computational details and Cartesian coordinates for all calculated structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) All of the calculations were carried out using DFT at the PCM(toluene)-M06+d/SDB-cc-pVDZ//M06/SDD(d) level (see the Supporting Information for details and references). All energies are reported in kcal/mol and, unless stated otherwise, they are relative to **A**. A (′) is used to denote model complexes having Me−P in lieu of *i*-Pr−P.
(12) Attempts to isolate this unsaturated Ru(0) complex by treatment of complex **1** with bases in the absence of H_2 resulted in mixtures. Treatment of the related phosphinite pincer complex (PNP)Ru(H)(Cl)(CO) with a base was reported to result in the Ru(0) complex (PNP)Ru(CO). See: Salem, H.; Shimon, L. J. W.; Diskin-Posner, Y.; Leitus, G.; Ben-David, Y.; Milstein, D. *Organometallics* **2009**, *28*, 4791.

JA107770Y