“Long-Range” Metal–Ligand Cooperation in H₂ 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 H₂/KOH results in H₂ splitting between the Ru center and C9 with concomitant deauration 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 deaurationed 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 deaurationization,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 H₂ activation,7 which is a key step in numerous catalytic processes.

Reaction of complex 1 with 5 bar H₂ for 48 h in the presence of 1 equiv of KOH in refluxing toluene leads to deaurationization of the central acridine ring, forming complex 2 (Scheme 1).8 The ¹H NMR spectrum of 2 in benzene-d₆ exhibits a singlet at 74.73 ppm, and the ³¹P{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 appearace 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 CH₂ signal at 36.48 ppm in the ¹³C DEPT-135 NMR spectrum of 2 confirmed deaurationization as a result of H₂ splitting. A similar reaction with D₂ 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 CDH group of the middle acridine ring (C9).9 These observations confirmed the deaurationization as a result of D₂ splitting. The deaurationization 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 H₂ is conceptually different from that of the previously reported pyridine-based PNP complexes,2,3b which react with H₂ to give trans-dihydride complexes involving methylene “arm” deprotonation and deaurationization 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, the most likely reaction mechanism for the reaction of 1 with H₂ (shown in Scheme 2) involves bending of the acridine unit of Ru(0) intermediate A (obtained by deprotonation of 1 by KOH) with pinching together of the phosphine arms, resulting in seesaw-shaped complex B. H₂ 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 ΔG₂₉ₘ = 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. 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, failed. Another route to a “long-range” interaction between the acridine C9 position and the metal center. Its reaction with H₂/KOH results in H₂ 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 NH₃ results in transfer of the hydride from the Ru center 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.

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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.

References


(8) $\text{H}_2$ splitting over the methylacridinium salt was reported in modeling studies of hydrogenase enzyme activity using Cp*(dpmm)RuH. Tetramethylpiperidine was employed as the hydride acceptor. See: Hembre, R. T.; McQueen, S. *J. Am. Chem. Soc.* **1994**, *116*, 2141.

(9) H/D exchange into the alkylphosphine groups was also observed. See the Supporting Information.


(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 I with bases in the absence of $\text{H}_2$ 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.